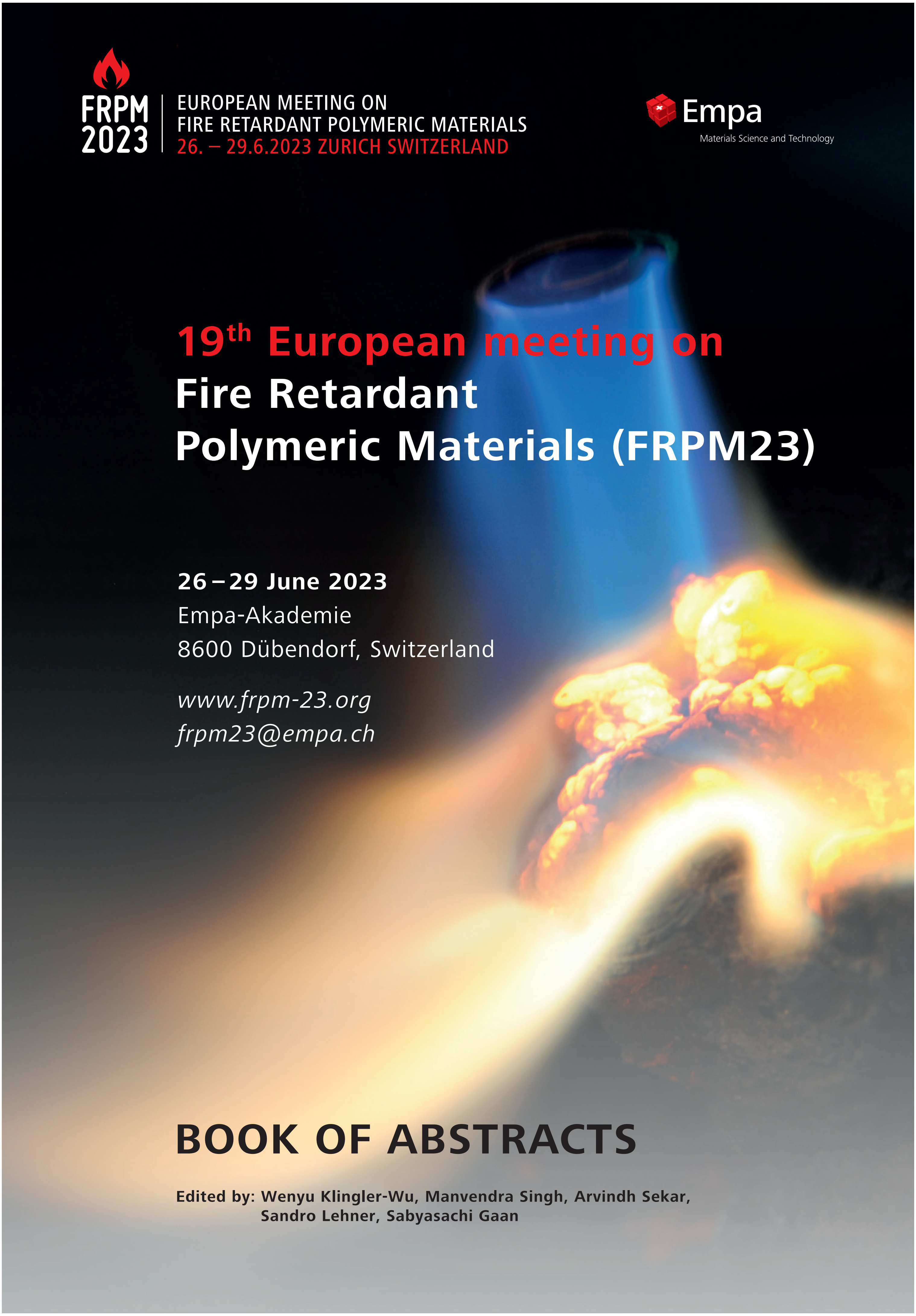

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BOOK OF ABSTRACTS

**Edited by: Wenyu Klingler-Wu, Manvendra Singh, Arvindh Sekar,
Sandro Lehner, Sabyasachi Gaan**

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PL1- EPOXY BASED VITRIMER MATERIALS AND COMPOSITES

F.G. Tournilhac

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Keywords: epoxy, composites, polyesters, rheology, processing, soft robotics

Abstract: Vitrimers, invented in 2011 by our group, are networks comprising exchangeable links. This characteristic makes it possible to modify the topology of the network while preserving its integrity at all times. This results in remarkable properties: vitrimers are both insoluble and processable; they flow like glass at high temperatures. This makes them recognized on a fundamental level, as a third and new class of polymeric materials, alongside thermoplastics and thermosets, and on a practical level as a new means of controlling and solving problems of implementation, chemical resistance and thermal resistance of materials and composites.

The chemistry of epoxies, already used in the pioneering work on vitrimers, is relevant in several fields where vitrimers could bring a technical advantage while preserving the possibility of recycling. This will be illustrated by several examples: i) formulation of epoxy-vitrimer matrices with high Tg,[1] ii) manufacture of composite parts with a vitrimer matrix and their assembly by autogeneous welding,[2] iii) crosslinking of an engineering thermoplastic polyester to improve thermal performance,[3] iv) the implementation of self-repairing biobased elastomers with rapid springback for soft robotics.[4]

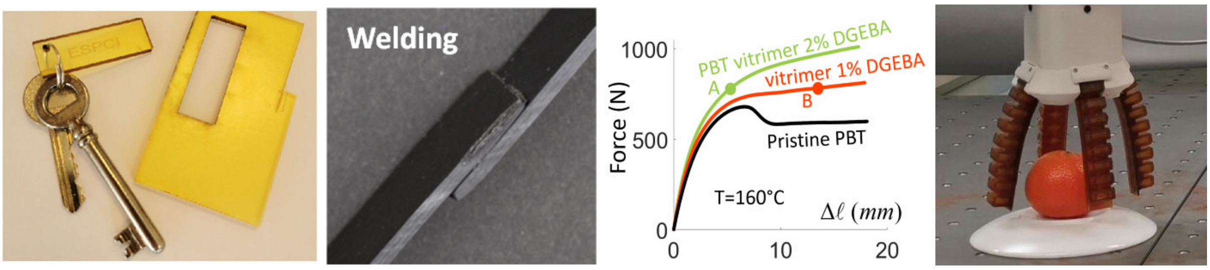

FIGURE 1. Examples of epoxy-vitrimer enbodiements as neat glassy material, as matrix for carbon-fiber reinforced composites, as engineering thermoplastics, as fast actuating elastomer.

Acknowledgements: Agence Nationale de la Recherche (ANR-18-CE06-0026-01), European Space Agency (ESA 4000128430/19/NL/KML/afm), European Union’s Horizon 2020 research and innovation program (Grant agreement No. 828818).

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K1- FULLY BIO-BASED VERSUS CARBON/GLASS EPOXY COMPOSITES: SCOPE AND LIMITATIONS IN FIRE AND PHYSICO-MECHANICAL PERFORMANCES

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Main message: Fire and mechanical performances of a fully bio-based flax/furan resin composite have been evaluated and compared with those of conventional carbon/glass fibre - reinforced structural composites. Fire retardant (FR) variants of flax/furan were obtained by adding FRs to the resin with or without FR treated flax fabrics. It was observed that to obtain optimized fire and mechanical properties, the use of a FR in the furan resin matrix is sufficient.

Keywords: Bio-based composites; flax fibre; furan; cone calorimetry; mechanical properties

Introduction

Owing to emerging environmental issues and new regulations on the recyclability of composites, in last two decades there has been a big surge in development of materials from renewable sources. Natural fibres, in particular cellulosic fibres, while theoretically having high elastic modulii, defects in their morphology and variation in crop to crop result in low strength compared to other commonly used reinforcements. In pursuit of bio based thermoset resins, a number of polyester and epoxy resins derived from plant oils such as soybean and castor oils have been developed. These resins however still need synthetic chemical crosslinking agents (i.e. isocyanates, amines), and hence are in fact only partially bio-based materials. Alternatively, to achieve fully bio based composites, poly(furfuryl alcohol) (PFA, derived from sugarcane bagasse) based resins, also known as furan resins, are of interest. This work reports the development and performances of flax/furan composites and their fire retardant variants and compares them with conventional composites used in structural applications.

Experimental

Prepregs of the control and fire retardant flax/furan were produced from untreated or FR treated flax woven fabrics and the control or FR containing furan resin. FR treatment of flax fabric (Composites Evolution, UK) involved pad-dry treatment with an aqueous solution of guanylurea methylphosphonate (Thor Chemicals, UK) to obtain 1.5% phosphorus on the fabric. FRs added to the furan resin (TransFurans Chemicals BVBA) included ammonium polyphosphate and melamine polyphosphate (Budenheim) at 10 and 20 wt% levels. Composites were prepared by stacking six layers of the prepregs between two PTFE sheets, pressing the whole assembly between two aluminium plates at 140^{o}C under 20 kg/cm^{2} pressure for 40 min using a hydraulic upstroking press (Moore ltd.), and then cooling down to ambient temperature under pressure.

Results and Discussion

The fire performance of flax/furan composite in terms of cone calorimetric results was comparable to those of other high performance composites (see Table 1), time-to-ignition (TT) being higher and peak heat release (PHRR) lower than even carbon/epoxy composites. The flammability though was higher than that of glass/furan composites, which can be due to the flammability of flax fibres. The mechanical, in particular tensile performance of flax/furan was though lower than those of other synthetic fibre composites (see Table 1).

TABLE 1. Fire and mechanical properties of flax/furan versus glass/carbon fibre composites

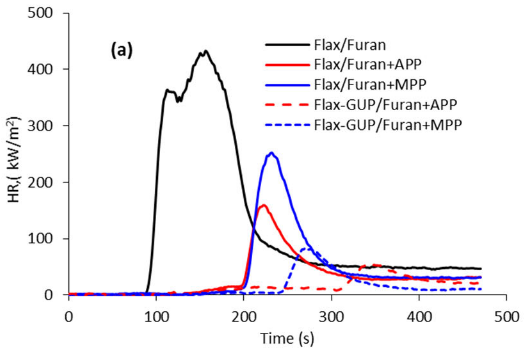
Composites	Fibre/resin composition (wt%/wt%)	Thickness (mm)	Cone calorimetric results at 50 kW/m^2				Mechanical performance	
			TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	TSR (L)	Flexural mod. (GPa)	Tensile mod. (GPa)
Flax/Furan	50/50		98	364	53	173	9.4	6.3
Carbon/EP-H [1]	67/33	3.0	64	224	19	1404	43.2	85.1
Glass/EP-H [2]	55/45	2.0	42	385	22	908	21.0	24.8
Glass/EP-L	50/50	2.8	44	456	38	1508	15.4	15.8
Glass/UP	40/60	3.0	33	440	42	1568	12.7	16.9
Glass/Phenolic [3]	40/60	4.5	164	110	25	336	10.4	13.5
Glass/Furan [4]	42/58	4.0	191	174	17	22	9.0	7.7
Flax/EP-L [5]	45/55	4.4	35	616	96	3038	10.0	8.8

Note: EP-H and EP-L represent high (tri- and tetra-) and low (bi-) functional epoxies respectively

In order to compensate for the flammability of flax fibres, composites prepared from resins with FRs with and without FR treated flax fabrics (Table 2) were tested and selected cone and tensile/flexural results are presented in Figure 1. While composites with FRs on both components provided excellent results, FR treatment of flax affected the mechanical properties of the composites. These results and other important aspects such as environmental impact and life cycle analysis of flax/furan versus other composites will be discussed more fully at FRPM 2023.

TABLE 2. Sample composition

	Sample	P content (%)
1	Flax/Furan	-
2	Flax/Furan+10%APP	1.5
3	Flax/Furan+20%MPP	0.65
4	Flax-GUP(1.5%P) /Furan+10%APP	2.25
5	Flax-GUP(1.5%P) /Furan+20%MPP	1.4



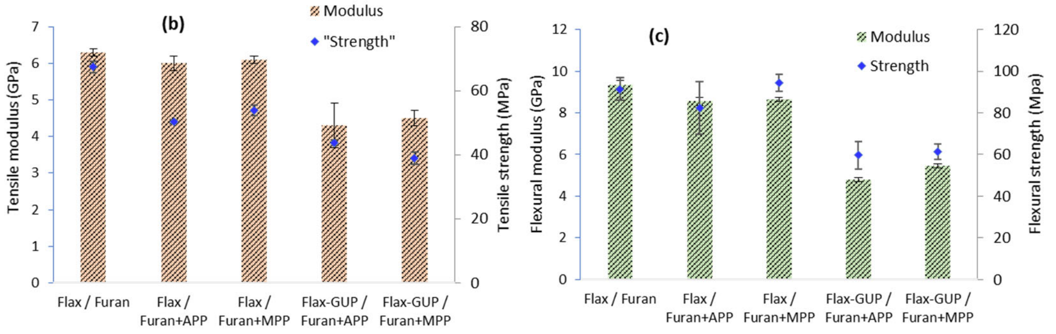


FIGURE 1. Fire: (a) HRR vesus time in cone calorimetry at 50 kW/m^2; and mechanical: (b) tensile and (c) flexural performances of composites

Acknowledgement: This research was funded by Innovate UK (formerly Technology Strategy Board), grant number TSB Project No 100982

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O1- Increasing Sustainability and Performance Requirements – what is the future for Phosphorus-based Flame Retardants?

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Main message: On the one hand, the regulatory environment for chemicals in general and flame retardants in particular is becoming more and more challenging with political programs like the European Chemicals' Strategy for Sustainability. On the other hand, material performance requirements from new applications like electro-mobility or miniaturization in electronics make it more difficult to achieve both flammability and other material requirements. This paper will elaborate how industry is addressing these challenges and why the future for phosphorus-based flame retardants (PFRs) looks bright.

Keywords: sustainability, flame retardants, phosphorus, CSS, environment

Introduction

Flame retardants have gained the attention of environmental researchers and regulatory agencies over the last decades because of wide-spread findings in the environment and biota. This mainly concerned brominated flame retardants, some of which have been restricted and phased out by now. However, phosphate ester-based FRs have also been found in the environment and indoors. Europe has been leading in regulating chemicals including flame retardants through laws like REACH, RoHS, WEEE and EcoDesign Regulations. In 2020, the European Commission announced the Chemicals' Strategy for Sustainability as part of the European Green Deal [1]. This policy program will revise existing regulation e.g. REACH and introduce new concepts like Generic Risk Assessments or Essential Use exemptions. The aim is to further restrict and reduce problematic chemicals whilst also promoting safer and more benign products. For flame retardants this means challenges on top of increasing technical performance requirements like those seen e.g. in electro-mobility where in addition to low flammability also excellent mechanical and electrical properties are necessary.

Results and Discussion

The flame retardants' industry has reacted to these regulatory initiatives and constraints by own programs to demonstrate the safety of flame retardants (and other products). For example, already in 2012 Clariant launched the Portfolio Value Program (PVP, updated in 2022) which is a screening tool to anticipate regulation, customer needs and stakeholder expectations in key sustainability areas and across the product life cycle [2]. It uses 39 criteria spanning water consumption, climate impact, bio-economy, circularity, safety, social value creation, product performance as well as zero waste and pollution.

In addition to these in-house assessments, independent third-party evaluations were carried out with GreenScreen™, the TCO Accepted Substances List and the ChemForward SAFER program. Clariant also participated in research large collaborative projects which assessed the environmental impact of flame retardants and potential alternatives to problematic substances. All these studies concluded that products like ammonium polyphosphate or dialkylphosphinates have excellent environmental and health profiles.

Since 2022, Clariant participates in a case study of the Joint Research Centre of the European Commission (JRC) on testing the criteria for "safe and sustainable-by-design" chemicals [3] (see Fig. 1).

First results show that the suggested methodology from JRC is very comprehensive and may need some simplifications to make it workable as a screening tool for new products in the development phase.

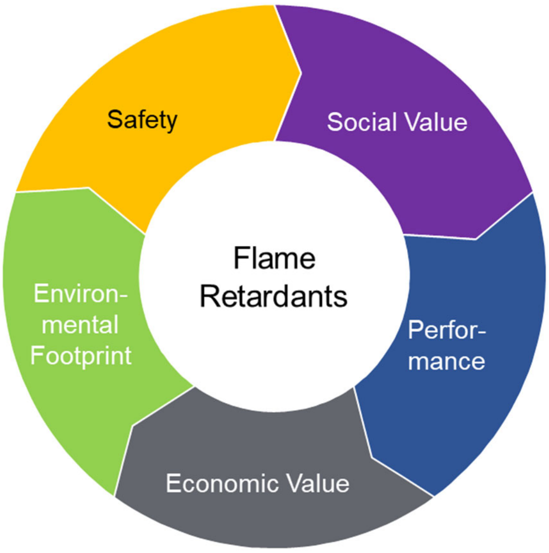

FIGURE 1. The Elements of Safe and Sustainable-by-Design for Flame Retardants.

Currently, a lot of focus is put on the carbon footprint of chemicals and materials. Phosphorus-based FRs have the inherent disadvantage that the extraction of phosphorus from phosphate rock is very energy intensive. Here, only a shift to renewable energy for this early production step can help. Using renewable carbon sources for the carbon content in PFRs (which is often >50%) can also reduce the carbon footprint. Clariant offers phosphinates with renewable carbon based on a certified mass balance approach.

In addition to all these sustainability aspects and demands, flame retardants need to perform. The materials they protect need to achieve not only stringent flammability tests but also other material requirements like mechanical and electrical properties or resistance against chemicals. Flammability performance is a necessary, but not a sufficient criterion for commercial success: ever thinner parts pose challenges as well as electric properties like comparative tracking index in E-mobility. Phosphorus chemistry offers great versatility so that PFRs can be tailored to fit the target polymer or textile. Both additive and polymeric / polymer-bound flame retardants are possible based on phosphorus and the range of PFRs with good environmental and health profiles suggests that they will have a great future.

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PL2- DEVELOPMENT OF BIOBASED AND NANOSCALE FLAME RETARDANTS

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Abstract

Polymers and polymer composites are widely and increasingly used in various industries and our everyday life. Many of these polymer materials are, however, highly flammable, which pose increased fire risk to people's lives and our society. The flammability of polymers and polymer composites is a serious issue and severely limits their applications. Adding flame retardants (FR) has been approved as an effective strategy to address the fire issues associated with these flammable polymers and composites. There are several very efficient FRs being developed, including halogen-based, phosphorus-containing, intumescent, and inorganic FRs. The new environmental and regulation requirements push us go to the approaches of biobased and nanoscale to make FRs greener and more efficient.

For the biobased FRs, we have worked on phytic acid based FRs, lignin based FRs and cellulose based FRs. Those biobased FRs have shown good flame retardancy but need further improvement in efficiency. They can be combined with traditional FRs in applications. For nanoscale FRs, we have worked on carbon nanotube, graphene and MXene FRs. Nanoscale FRs can significantly reduce heat release rate, and even smoke and toxic gases release. Once they are combined with traditional FRs, they can significantly reduce the amount of FR required and achieve the good LOI value and UL-94 rating. Some of our work has been presented in our paper "flame retardant polymeric nanocomposites through the combination of nanomaterials and conventional flame retardants", published in Progress in Materials Science 114 (2020) 100687.

K2- ALIPHATIC SILICA-EPOXY SYSTEMS CONTAINING DOPO-BASED FLAME RETARDANTS, BIO-WASTES, AND OTHER SYNERGISTS

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Main message: Most industrial applications require polymer-based materials showing excellent fire performances to satisfy stringent requirements. No-dripping and self-extinguishing hybrid silica-epoxy composites can be prepared by combining tailored sol-gel synthesis strategies with DOPO-based flame retardants, bio-wastes, and other synergists. This approach allows for achieving V-0 rating in UL-94 vertical flame spread tests, even using a sustainable route, aliphatic amine as hardener, and low P loadings.

Keywords: epoxy-silica nanocomposites, phosphorus flame retardant, in-situ sol-gel silica, aliphatic hardener, fire behavior.

Introduction

The industry demand, the rising pollution, and the depletion of phosphorus are moving the scientific community towards the development of flame retardant (FR) aliphatic epoxy composites characterized by low P contents and more sustainable additives [1]. The in-situ generation of inorganic phases has been explored in combination with DOPO-based FRs, bio-wastes, and other synergists to prepare no-dripping and self-extinguishing aliphatic epoxy composites, even keeping P at very low loadings (1, 2 wt.%) [2].

Experimental

High-Resolution Transmission Electron Microscopy analysis was performed by using a TEM/STEM JEOL JEM 2200 fs microscope working at 200 kV. Cone calorimetry (CC) tests were carried out by means of Noselab ATS Instr. (Monza, Italy) operating with an irradiative heat flux of 35 kW/m^2 (ISO 5660 standard) on 100 × 100 × 3 mm^3. Finally, the flammability of all epoxy-based composites was evaluated by UL-94 vertical burning tests according to IEC 60695-11-10 on 13 × 125 × 3 mm^3 samples.

Results and Discussion

The reaction between DGEBA (Bisphenol A diglycidyl ether)-based resin and APTES (3-aminopropyltriethoxysilane) allows for producing hybrid organic-inorganic epoxy moieties (silanized epoxy). The hybrid moieties can condensate with TEOS (tetraethyl orthosilicate), a silica precursor, to form an in-situ SiO_2 phase through sol-gel reactions (Figure 1). Microscopy analysis revealed that the SiO_2 phase was composed of nanoparticles showing a well-ordered multi-lamellar shape, intimately embedded in a hybrid co-continuous network [2, 3]. The application of this methodology for the preparation of silica-epoxy nanocomposites provides fully condensed aliphatic nanocomposites exhibiting high transparency, no-dripping phenomena during the UL-94 vertical flame spread tests, and a strong decrease (~50%) in the peak of the heat release rate (pkHRR) in CC tests with only 2 wt.% of silica loading [3]. By replacing TEOS with magnesium ethoxide, it is possible to generate in-situ $Mg(OH)_2$ nanoparticles in a hybrid epoxy network. These nanoparticles can act as flame retardant (FR) to obtain epoxy nanocomposites with improved fire behavior, even with low (i.e., 5 wt.%) filler loadings [4].

Flammability and CC tests performed on epoxy systems containing in-situ $Mg(OH)_2$ nanoparticles allowed for preventing dripping phenomena and a significant decrease (~37%) in pkHRR.

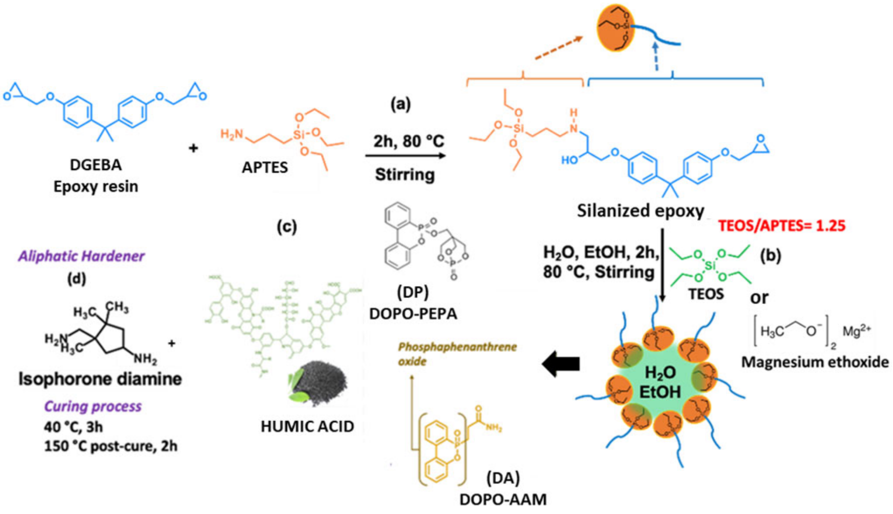

FIGURE 1. Synthesis route of no-dripping self-extinguishing aliphatic epoxy composites.

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is one of the most used reactive FRs for epoxy systems, though its use negatively affects the glass transition temperature of the final products. Therefore, the scientific community has developed several DOPO derivatives (e.g. 6H-dibenz[c,e][1,2]oxaphosphorin,6-[(1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl)methoxy]-,6-oxide (DP) and with 3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)propenamide (DA)) to overcome this limitation. Bifulco et al. incorporated DA/DP into silica-epoxy nanocomposites together with melamine (Figure 1). Despite the use of an aliphatic hardener (isophorone diamine) and low contents (2 wt.%) of P, the silica-epoxy nanocomposites exhibited UL-94 V-0 rating without any dripping and a strong decrease (up to 80%) in the pkHRR, with respect to the pristine resin [2]. A more waste-to-wealth approach concerns the use of bio-waste humic acids as FR, which can be well dispersed into an APTES-modified epoxy matrix (Figure 1). The addition of humic acids, ammonium polyphosphate (APP) and urea in this hybrid epoxy matrix guaranteed no-dripping self-extinguishing capability, lower (up to 23%) total smoke release, and a remarkable decrease in pkHRR (up to 52%) compared to pristine epoxy, even with only 1 wt.% of P loading [5].

Acknowledgement: This research received no external funding.

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O2- Next Generation of Radical Generators

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Main message: In this presentation we introduce the next generation of multifunctional radical generators based on phosphorous substituted sulfenamides. The prepared multifunctional flame retardants exhibited very high FR efficacy alone, i.e. they provided a UL-94 V2 rating in PP by themselves. Moreover, radical generators based on different silylamines and siloxyamines are introduced which together with a conventional phosphorous flame retardant, AFLAMMIT® PCO 900, give a UL-94 V0 rating in PP, LLPE and epoxy resins.

Keywords: Radical generator, Multifunctional flame retardant, Sulfenamide, Silylamine, Siloxyamine

Introduction

Today the concept of circular economy plays a vital role for industrial production of all goods. It must be underlined that plastic additives are intentionally added into the polymer and therefore we need to rethink and thoroughly assess what type of additives can be introduced without an ecological risk. To this aim, conscientious producers of FR products have made major efforts to find alternative FR solutions with better overall environmental profiles and higher efficacies at already low loadings of < 5%.

Experimental

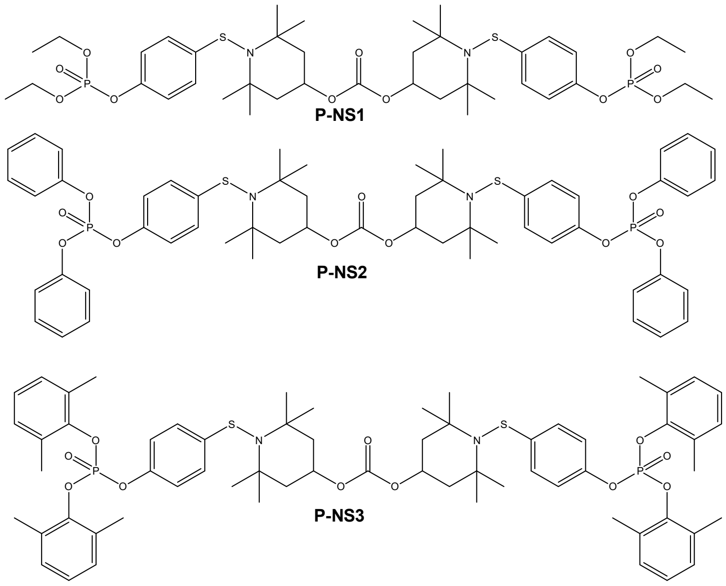
A series of innovative flame retardants containing phosphorous substituted sulfenamides (P-SN), silylamine (N-Si) and siloxyamine (N-O-Si) have been synthesized, as shown in Figure 1. The flame retardant efficacy in various polymeric materials were evaluated according to UL-94 V fire standard.

Results and Discussion

To the best of our knowledge the multifunctional sulfenamides are the first halogen free radical generators that can provide a UL94-V2 rating as standalone flame retardant at 4 wt% loading in PP, as shown in Table 1.

In contrast, the synthesized silylamine and siloxyamine flame retardants did not pass any UL-94V rating by themselves. However, a strong synergistic effect was observed when the phosphorous flame retardant was combined with either N-Si or N-O-Si containing compounds, since none of the flame retardants could independently provide a V-0 rating in the UL94-V test in PP, LLDPE and epoxy resins even at similar loadings.

a) Multifunctional phosphorous substituted sulfenamide based FR



b) N-Si based FR c) N-O-Si based FR

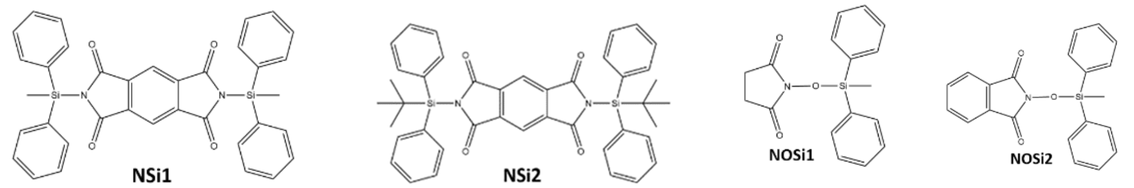


FIGURE 1. Chemical structures of synthesized radical generators.

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TABLE 1. Selected properties of flame retarded polymeric samples

Sample	Polymer	Radical Generator [wt%]	Aflammit PCO 900 [wt%]	UL 94V rating
1	PP	P-NS2 [4wt%]	-	V-2 rating
2	PP	P-NS3 [4wt%]	-	V-2 rating
3	PP	NSi1[2 wt%]	[10 wt%]	V-0 rating
4	PP	NOSi2 [2 wt%]	[10 wt%]	V-0 rating
5	LLDPE	NSi1 [2 wt%]	[15 wt%]	V-0 rating
6	Epoxy	NS1 [2 wt%]	[2.5 wt%]	V-0 rating

Acknowledgement: The authors gratefully acknowledge funding from Songwon and BYK/Altana for the development of sulfenamides[1] and silylamines/siloxyamines[2], respectively.

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O3- NOVEL PHOSPHORUS-CONTAINING FLAME RETARDANTS BASED ON CELLULOSE AND SUGAR ALCOHOLS

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Main message: Novel biobased flame retardants were synthesized from cellulose and phosphorus derivatives of sugar alcohols by a sustainable and efficient procedure: Cellulose was esterified using a mixture containing acrylic anhydride to give cellulose acrylate followed by *Phospha-Michael-Addition* [1]. For this purpose, phosphorylated anhydroerythrite (***PAHE***) was found to be particularly suitable. The flame retardants are white solids which were successfully tested in polypropylene (PP) and biobased polyamide.

Keywords: biobased flame retardant, cellulose, sugar alcohol, polypropylene, polyamide

Introduction

Forward-looking development of flame-retardant additives is targeted on the use of renewable sources, sustainable fabrication and innocuousness. However, low thermal stability and other serious shortcomings still limit the application of biobased flame retardants. To overcome these disadvantages, a class of thermal stable and efficient biobased flame-retardants was designed by exploitation the unique structure of cellulose. A derivative of erythrite was chosen as phosphorus-containing unit.

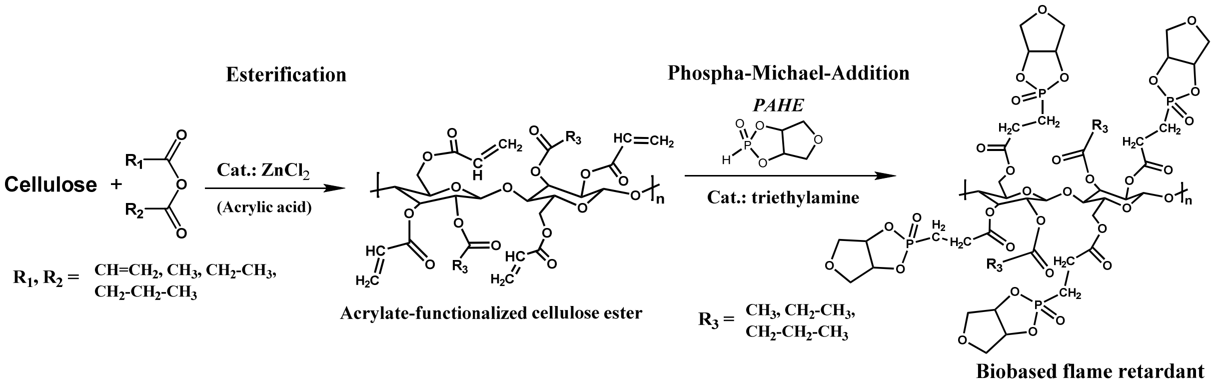
Experimental

The cellulose used in this work was purchased as 100 % bio-cotton from a drugstore (DM, ebelin) as well as the erythrite Xucker®; *Ultramid® Flex F29* was provided from *BASF SE,* PP with melt flow index (230°C) of 35 g/10 min (*PP 519A*) and 12 g/10 min (PPH 7069) were provided from *Sabic* and Total; and PP Copolymer *(Moplen RP 320M)* with melt flow index (230 °C) of 8,5 g/10 min from *Lyondell Basell*.
Nuclear magnetic resonance spectroscopy (NMR) measurements were performed on a BRUKER Avance 300 MHz. Thermal analysis was performed with a TG analysis from Mettler Toledo.
The flame retardants were incorporated into PP and *Ultramid® Flex F29* using a twin-screw lab extruder *Three Tec 12 mm* at 180 and 220°C, respectively. UL 94 test bars (1.6 mm) were manufactured by injection molding using a *Haake Minijet Pro*. UL 94-V test and B2 test were carried out according to DIN EN 60695-11-10 and DIN 4102, respectively.

Results and Discussion

Synthesis of novel flame retardants: An efficient and sustainable sequence to synthesize novel phosphorus-containing cellulose esters [1] have been developed (see scheme 1).
The first one of the two-step procedure includes the esterification to give acrylate-functionalized cellulose. Cellulose esters bearing acrylate groups are already reported in the literature but known methods to synthesize them required the use of toxic reagents and solvents and very laborious product isolation was necessary [2]. That is why, they could not be adapted for synthesis in large scale so far. The novel esterification approach does not need the use of toxic and/or chlorine-containing reagents and substances to dispose are not formed. It is performed using a reaction mixture consisting of acrylic anhydride, acrylic acid as well as propionic anhydride and/or butyric anhydride. That means the esterification is conducted in a quite similar manner like the industrial production of cellulose triacetate. The cellulose esters obtained this way bear acrylate groups as well as a moderate part of

propionic and/or butyric groups (17-30 % of ester groups). The latter are necessary to improve the solubility.



SCHEME 1. Two-step synthesis of a biobased flame retardant based on cellulose and erythrite.

The second step of the synthesis sequence – *Phospha-Michael-Addition* – includes the reaction of P-containing sugar alcohol derivates with the acrylate groups of the cellulose esters, whereby carbon-phosphorus-bonds are formed. Tetrahydrofuro[3,4-*d*][1,3,2]dioxaphosphole 2-oxide (phosphorylated anhydroerythrite; ***PAHE***) was successfully applied for this purpose. It is a literature-reported compound easily accessible from erythrite [3]. Erythrite is becoming a low-priced substance produced in large quantities from biobased sources (sugars). Novel flame retardants (***PAHE***-functionalized cellulose esters) were obtained in high yield (with different amount of ***PAHE*** groups). These macromolecular substances could be isolated as white powders. Investigations by NMR spectroscopy confirmed high purity of these novel flame-retardants. Ongoing work aim at suchlike substances based on wood or straw cellulose and optimization of their structural patterns including trials to synthesize phosphorus-containing derivatives from other sugar alcohols (e. g. xylite).

Thermal and flame-retardant properties: Fortunately, investigations of thermal stability by TGA revealed high onset temperature of decomposition (2% mass loss) of about 290°C.
The novel flame retardants were incorporated into PP and the biobased polyamide *Ultramid® Flex F29* – alone and in combination with synergists. The PP-test bars and foils were transparent and colorless. Investigations of the burning behavior of these specimens yielded promising results [4]. The foils passed the B2 test according to DIN 4102 already at low loading; UL 94 V0 rating was achieved at a loading of 18 wt-% in *Ultramid® Flex F29* (thickness of samples: 1.6 mm).

Acknowledgement: This work was supported by Bundesministerium für Bildung und Forschung (031B0719) and Fachagentur Nachwachsende Rohstoffe e.V. (220NR032), Germany.

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K3- SUSTAINABILITY FINDING ITS WAY INTO FLAME RETARDANCY: FOOD FOR THOUGHT BETWEEN FAKE FICTION AND FUTURE

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Main message: Sustainability, or in other words, exploiting environmental conservation for the economic welfare and prosperity for all, would revolutionise the plastics industry were it to become predominant practice as a linear, fossil-fuel–based economy is switched to a carbon circular economy. Food for though is given by dint of a critical overview of the current trends in sustainable flame-retardant polymeric materials.

Keywords: Renewable, biocomposite, sustainable, circular economy, natural.

Introduction

Transforming the plastics industry into a carbon circular economy over the next 30 years requires an immediate revolution entailing the development of cutting-edge materials and the planning of future industrial production plants. Hence, the innovative field of flame-retardant polymeric materials should lend its strength to drive this challenge. Visionary solutions are proposed to inspire us, while the implementation of economically feasible concepts can take us forward into the future.

Experimental

The synthesis, processing, polymer analysis, thermal analysis, and investigation of fire behaviour from our own research are performed according to the state of the art, mostly in accordance with the pertinent ISO standards. Indeed, some of our equipment is part of the accredited lab; for the other methods we fulfil equivalent quality standards in terms of maintenance, calibration, participation in round robins, etc. Work steps such as the synthesis or preparation of new materials are usually outsourced or done with partners that have the relevant core competence. The talk also presents examples from other groups whose experimental is described in the corresponding scientific papers.

Results and Discussion

An overview of current trends towards producing sustainable, flame-retardant polymeric materials is presented, using examples from the literature and by sketching our own projects performed in recent years. [1-5] The examples are structured along a common theme leading from the use of old and new natural materials with some intrinsic flame retardancy, via flame-retardant biopolymers and biocomposites, to using renewable sources for flame retardants with the objective of exploiting natural sources available as industrial waste streams. Natural flame retardants and adjuvants are highlighted, although the status of most may be assessed as merely motivating our vision. Nevertheless, there are natural material streams finding their way into polymer mass production as fillers, adjuvants, polymers, or renewable educt sources. Natural substances originating from industrial waste streams open the door to sustainable solutions, because they are often available at low cost and avoid competition for land with farming or virgin forests. Aside from this main topic, remarks will address the recycling of flame-retarded polymeric materials; vitrimers are mentioned as a potential material for recyclable thermosets. At the end of the day, only convincing property profiles will prevail both for exploiting renewable sources and circular design, including cost effectiveness, sufficient availability, consistent quality, processibility, mechanical properties, and flame retardancy. However, sustainability must not be merely tolerated as an additional demand, but should instead be recognized as a solution, because sustainability aspires to ensure our economic welfare now and in the future.

Acknowledgement:
The examples shown from own project were supported by funding grants: BMBF WTZ: 01DN16040, DFG Scha 730/19-1, VW-Stiftung: Experiment No: 97437, DFG Scha 730/20-1, BMBF KMU Innovativ 031B1289B.

Thanks to A. Battig, R. Bhatia, Y.Y. Chan, S. Çiftci, S.F. Falkenhagen, E. Gallo, K.I. Garfias González, F.R. Gleuwitz, S. Rabe, D. Rockel, G. Sánchez Olivares, and F.D. Sypaseuth (all BAM) for their contributions and D. Acierno (University of Naples Federico II, Italy), A. Greiner (University Bayreuth, Germany), Y. Hu (USTC, Hefei, China), R. Klein (LBF, Darmstadt, Germany) C. Ma (USTC, Hefei, China), J.C. Markwart (MPI Mainz, Germany), R. Pérez-Chávez (CIATEC León, México), P. Russo (University of Naples Federico II, Italy), G. Sánchez Olivares (CIATEC León, México) F.R. Wurm (MPI Mainz, Germany), F. Zhou (USTC, Hefei, China) for their co-operation and support.

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O4- FLY ASH AS ENGINEERING FILLER IN FLAME RETARDANT SYSTEMS FOR BIOPOLYESTERS

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Main message:

Fly ash is a waste byproduct issued from thermal power plants which has not been used fully regarding its potential as a vital resource of engineering materials, in particular as component of flame retardant systems. So, it has been shown that surface treated fly ash can replace a fraction of phosphorous FRs in PBS and PBAT, leading to synergistic effects. Investigations about the FR mechanisms involved highlight the role of new crystalline phases able to retain phosphorus in the residues.

Keywords: Fly ash, waste byproduct, biopolyesters, flame retardancy.

Introduction

Around 750 MT of fly ash are generated each year in the world, leading to serious concerns about their disposal. Depending on their specifications, fly ash can be used as functional fillers in polymers (1,2). The present study aims to assess a specific fly ash produced by Holcim company, possibly surface treated with silanes or titanates (3), to substitute a fraction of P/N based FRs. The objective is to reduce the environmental impact of flame retardant biopolyesters such as PLA, PBS and PBAT and blends (4).

Experimental

Formulations and specimens were prepared using a twin-screw extruder and injection moulding. Fly ash was combined with ammonium polyphosphate (APP) and melamine polyphosphate (MPP). The global loading of components was kept at 25wt%. 3-aminopropyl triethoxysilane, 3-glycidyloxypropyl trimethoxysilane and isopropyl tri[di(octyl)phosphato] titanate were used as coupling agents. Fire behavior was assessed using PCFC, TGA, cone calorimeter and UL94V test. The microstructure of the combustion residues after cone calorimeter tests was investigated using SEM and X-microanalysis. In order to assess the formation of new compounds resulting from possible interaction between flame retardants and fly ash, X-ray diffraction of cone calorimeter residues was performed.

Results and Discussion

From TGA and PCFC analyses, strong interactions occur between ammonium polyphosphate and PBS and PBAT during thermal degradation, whereas the interaction is limited with PLA. Consequently, the fire behavior of the initial composites as well as the microstructure of residues after degradation of compositions containing APP (or APP+MPP) and fly ash are different.

Cone calorimeter tests (Table 1) highlight synergistic effects on fire parameters (peak of HRR and MARHE) for mixed compositions in PBS and PBAT, particularly when fly ash are surface-treated with titanate.

For PBS and PBAT, the mechanisms of fire retardancy involve the formation of new crystalline structures ($Al(PO_3)_3$ and $Al_3(NH_4)H_{14}(PO_4)_8{\cdot}4H_2O$) identified by X-Rays diffraction and appearing as windroses on SEM micrographs (Fig.1). The use of X-microanalysis indicates that most part of the initial phosphorous remains in the residue. Consequently, two fire mechanisms (reaction of polymers with APP and formation of alumino-phosphates or phosphites) can work together to improve the fire retardancy of biopolyesters.

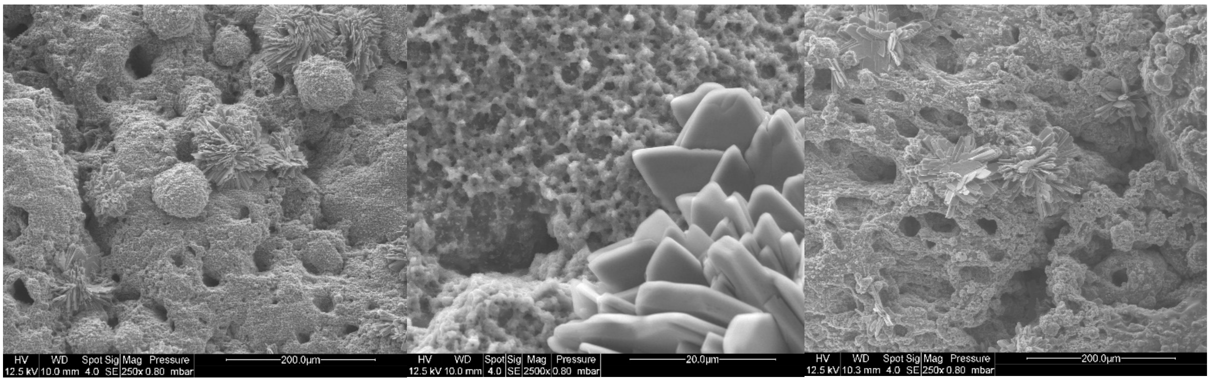

FIGURE 1. SEM pictures of PBAT cone calorimeter residues containing fly ash and APP ((left: upper side (X250), center: upper side (X2500), right: cross section (X250 or X2500)).

TABLE 1. Cone calorimeter and UL94V results of flame retarded PBS samples (irradiation of 50kW/m^2)

Formulation	**UL94V**	**pHRR (kW/m^2)**	**THR (MJ/m^2)**	**MARHE (kW/m^2)**	**Residue (%)**
PBS	nc	698	103	314	8
APP25	V-2	524	92	241	22
APP18.75/P6.25	V-2	483	97	225	21
APP12.5/P12.5	V-2	450	98	281	21
APP16.67/MPP8.33	V-2	419	92	246	20
APP12.5/MP6.25/P6.25	V-0	383	98	225	19
APP12.5/MP6.25/P6.25T	V-0	338	98	213	19

P: SuperPozz fly ash, T: titanate-treated

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O5- FLAME RETARDANTS: A CHANGING LANDSCAPE

James Houlder, Richard Clay, and Stephen Blair.
Polymer Compounders Limited
Edwardson Road, Meadowfield, Durham
DH7 8RL, United Kingdom
https://polymer-compounders.com/en/

Main message:

Due to the growing health concerns regarding the toxicity of flame retardants in polymers around the world, Polymer Compounders Limited (PCL) investigated ways to develop safer alternatives. The Notoxicom® family of flame retardant materials have now been developed and we truly believe that these polymers are the world's lowest toxicity FR PC/ABS and FR PC/ASA materials that still meet UL94 V0 at 0.8 mm and that do not compromise on material properties.

Keywords: Self Extinguishing Polymer, halogen-free flame retardant, Low Toxicity Flame Retardant,

Introduction

The benefits of moving to halogen free flame retardants have long been recognised but now the most widely used non-halogen flame retardants and their synergists are coming under increasing scrutiny from bodies such as the ECHA due to their toxicity. By utilizing the excellent halogen free performance of polyphosphonate-co-carbonates it was found that an excellent balance of material properties and flame retardancy could be achieved.

Experimental

UL94 flammability testing on moulded test bars is commonly used to measure burning rate and characteristics. A V-0 rating carries the following requirements:

1. None of the five samples can have flaming combustion for more than 10 seconds after each of two 10 second flame applications.
2. The total flaming combustion time for the ten 10 second flame applications (5 samples, 2 applications each) of more than 50 seconds.
3. None of the five samples may burn with flaming or glowing combustion up to the holding clamp.
4. None of the five samples may drip flaming particles which ignite dry absorbent cotton located 305mm below the sample.
5. None of the five samples may have glowing combustion which persists for more than 30 seconds after the second removal of the flame.

UL94 20mm Vertical Burning testing of Notoxicom® PC/ASA grade S6000 at 0.8 mm thickness.

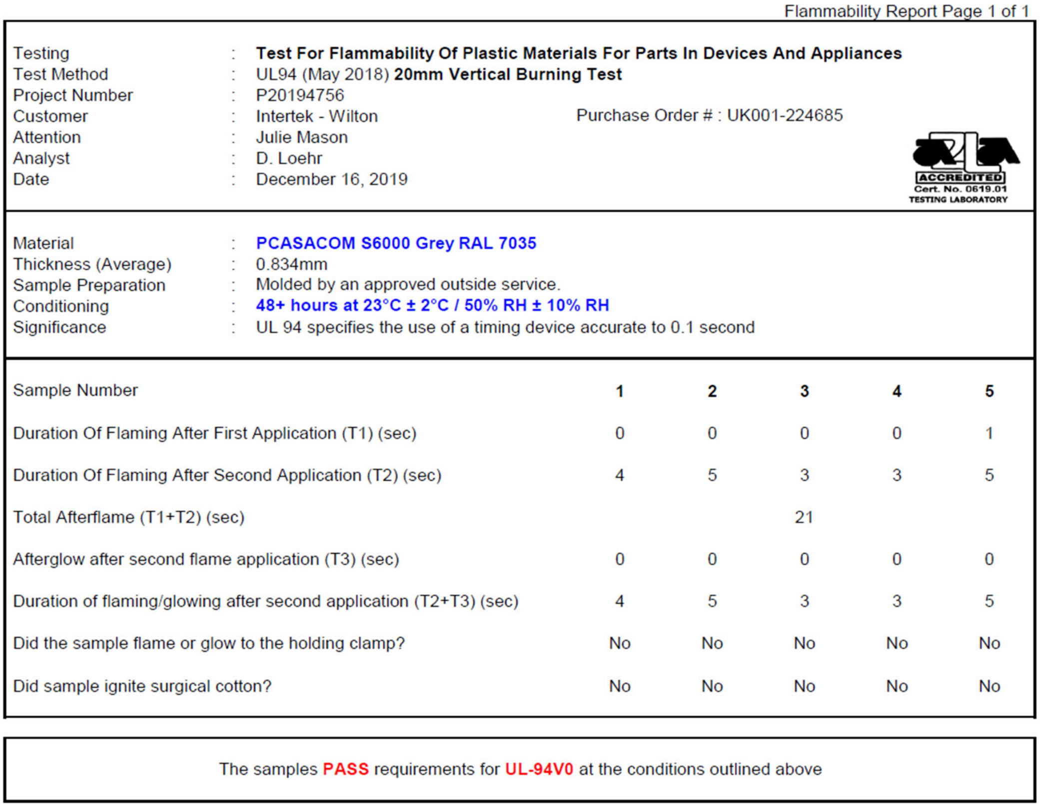
A bag of polymer granules was sent from Polymer Compounders to Intertek for injection moulding into UL94 test specimens.
The moulded test specimens were conditioned for at least 48 hours under standard laboratory conditions of 23 ± 2°C, 50 ± 10% relative humidity prior to testing.
One set of specimens were tested after ambient conditioning and another set was aged for 168 hours at 70 ± 2°C in accordance with UL94 (May 2018) at Intertek Pittsfield.

UL94 20mm Vertical Burning testing of Notoxicom® PC/ABS grade B6000 at 1.6mm and 0.8 mm thickness.

Further UL94 testing was also conducted on the Notoxicom® PC/ABS grade B6000.

Results and Discussion

UL94 20mm Vertical Burning testing of Notoxicom® PC/ASA grade S6000 at 0.8 mm thickness.



Flammability Report Page 1 of 1

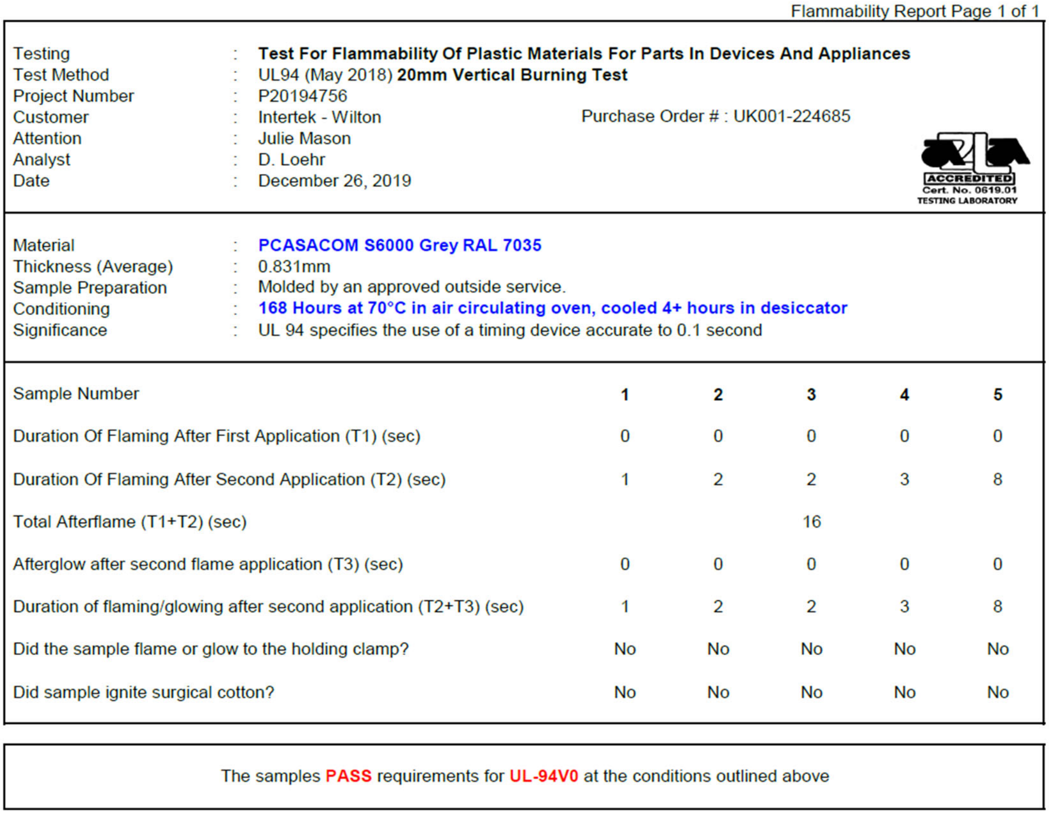
Testing : **Test For Flammability Of Plastic Materials For Parts In Devices And Appliances**
Test Method : UL94 (May 2018) **20mm Vertical Burning Test**
Project Number : P20194756
Customer : Intertek - Wilton Purchase Order # : UK001-224685
Attention : Julie Mason
Analyst : D. Loehr
Date : December 16, 2019

ACCREDITED
Cert. No. 0619.01
TESTING LABORATORY

Material : **PCASACOM S6000 Grey RAL 7035**
Thickness (Average) : 0.834mm
Sample Preparation : Molded by an approved outside service.
Conditioning : **48+ hours at 23°C ± 2°C / 50% RH ± 10% RH**
Significance : UL 94 specifies the use of a timing device accurate to 0.1 second

Sample Number	**1**	**2**	**3**	**4**	**5**
Duration Of Flaming After First Application (T1) (sec)	0	0	0	0	1
Duration Of Flaming After Second Application (T2) (sec)	4	5	3	3	5
Total Afterflame (T1+T2) (sec)			21		
Afterglow after second flame application (T3) (sec)	0	0	0	0	0
Duration of flaming/glowing after second application (T2+T3) (sec)	4	5	3	3	5
Did the sample flame or glow to the holding clamp?	No	No	No	No	No
Did sample ignite surgical cotton?	No	No	No	No	No

The samples **PASS** requirements for **UL-94V0** at the conditions outlined above



Flammability Report Page 1 of 1

Testing : **Test For Flammability Of Plastic Materials For Parts In Devices And Appliances**
Test Method : UL94 (May 2018) **20mm Vertical Burning Test**
Project Number : P20194756
Customer : Intertek - Wilton Purchase Order # : UK001-224685
Attention : Julie Mason
Analyst : D. Loehr
Date : December 26, 2019

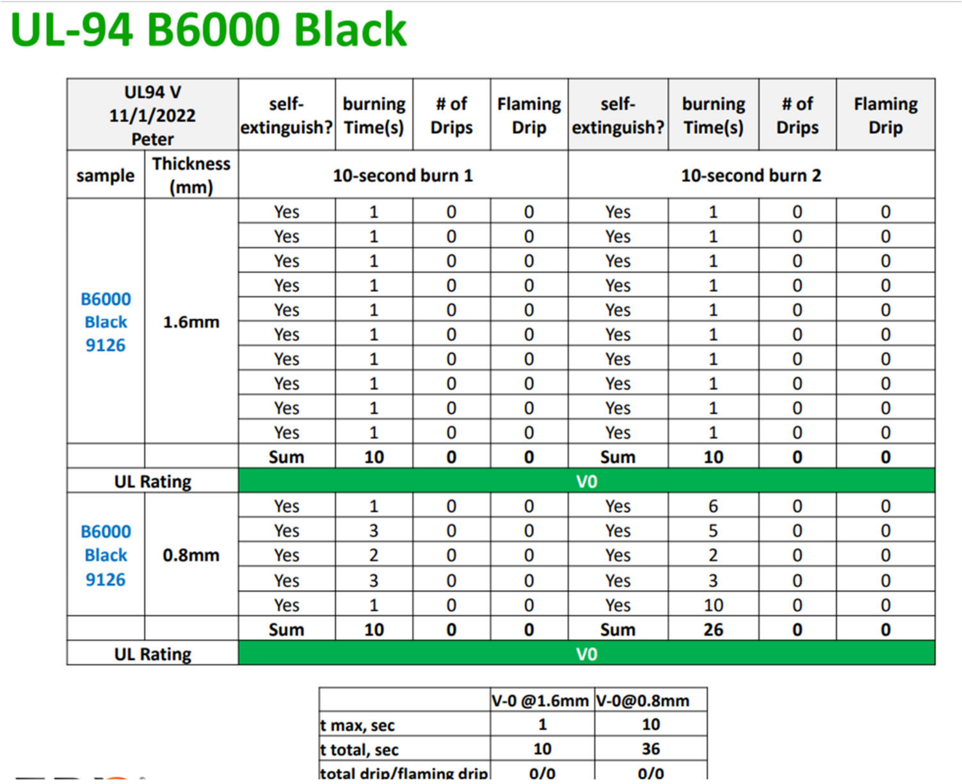
ACCREDITED
Cert. No. 0619.01
TESTING LABORATORY

Material : **PCASACOM S6000 Grey RAL 7035**
Thickness (Average) : 0.831mm
Sample Preparation : Molded by an approved outside service.
Conditioning : **168 Hours at 70°C in air circulating oven, cooled 4+ hours in desiccator**
Significance : UL 94 specifies the use of a timing device accurate to 0.1 second

Sample Number	**1**	**2**	**3**	**4**	**5**
Duration Of Flaming After First Application (T1) (sec)	0	0	0	0	0
Duration Of Flaming After Second Application (T2) (sec)	1	2	2	3	8
Total Afterflame (T1+T2) (sec)			16		
Afterglow after second flame application (T3) (sec)	0	0	0	0	0
Duration of flaming/glowing after second application (T2+T3) (sec)	1	2	2	3	8
Did the sample flame or glow to the holding clamp?	No	No	No	No	No
Did sample ignite surgical cotton?	No	No	No	No	No

The samples **PASS** requirements for **UL-94V0** at the conditions outlined above

UL94 20mm Vertical Burning testing of Notoxicom® PC/ABS grade B6000 at 1.6mm and 0.8 mm thickness.



UL-94 B6000 Black

UL94 V 11/1/2022 Peter		**self-extinguish?**	**burning Time(s)**	**# of Drips**	**Flaming Drip**	**self-extinguish?**	**burning Time(s)**	**# of Drips**	**Flaming Drip**
sample	**Thickness (mm)**	**10-second burn 1**				**10-second burn 2**			
B6000 Black 9126	**1.6mm**	Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Yes	1	0	0	Yes	1	0	0
		Sum	**10**	**0**	**0**	**Sum**	**10**	**0**	**0**
UL Rating		V0							
B6000 Black 9126	**0.8mm**	Yes	1	0	0	Yes	6	0	0
		Yes	3	0	0	Yes	5	0	0
		Yes	2	0	0	Yes	2	0	0
		Yes	3	0	0	Yes	3	0	0
		Yes	1	0	0	Yes	10	0	0
		Sum	**10**	**0**	**0**	**Sum**	**26**	**0**	**0**
UL Rating		V0							

	V-0 @1.6mm	**V-0@0.8mm**
t max, sec	**1**	**10**
t total, sec	**10**	**36**
total drip/flaming drip	**0/0**	**0/0**

The results demonstrate that a solid UL94 V0 rating can be achieved at thicknesses as low as 0.8mm for the Notoxicom® blends of polymers. Furthermore, because this flame retardant system comprises of large polymeric molecules, they are far less likely to migrate out of the host plastic and thus do not bioaccumulate making them far safer to use.

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O6- Flammability of thick but thermally thin materials including bio-based materials

<u>R. Sonnier</u>[a], L. Dumazert[a], A. Regazzi[b], L. Deborde[c], C. Lanos[c]

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Main message: A phenomenological model allows properly calculating the pHRR of various thermally thin materials, as foams, fabrics, fibers in bulk, fibers panels, biobased concretes but also some woods in cone calorimeter.

Keywords: Flammability, thermally thin behavior, cone calorimeter, prediction

The fire reaction of various types of flammable insulating materials is investigated using cone calorimeter. The influences of several parameters as sample density, sample mass, effective heat of combustion, heat flux or the presence of a grid on the heat release rate are discussed.
The thermally thin behavior of these lightweight materials exhibited during cone calorimeter tests is a consequence of their low effusivity. Only a thin top layer exposed to the heat flux contributes to the pHRR occurring just after ignition. The deeper part of samples remains at insufficient temperature to contribute to pHRR. The thickness of the top layer of the sample contributing to pHRR was estimated from experimental data conducted on bulk FR and FR-free hemp fibers. This top layer is believed to absorb directly the heat flux from the radiant cone. Its thickness was also evaluated with a numerical model.

A phenomenological model is then proposed to calculate the peak of heat release rate (pHRR) of such thermally thin materials. The model is based on the distinction of the contributions of the exposed top layer and the deeper layer to the combustion. The model was also applied to some limit cases like dense woods (for which the more pronounced heat transfer due to a non-negligible thermal conductivity is prevented by a char development) and as biobased concretes (for which the mineral fraction must be considered). A database gathering the results of more than 400 tests performed on fibers, bio-resources panels, bio-based concretes, fabrics and woods is used to validate the proposed model. Accuracy of the proposed model is discussed (Figure 1).

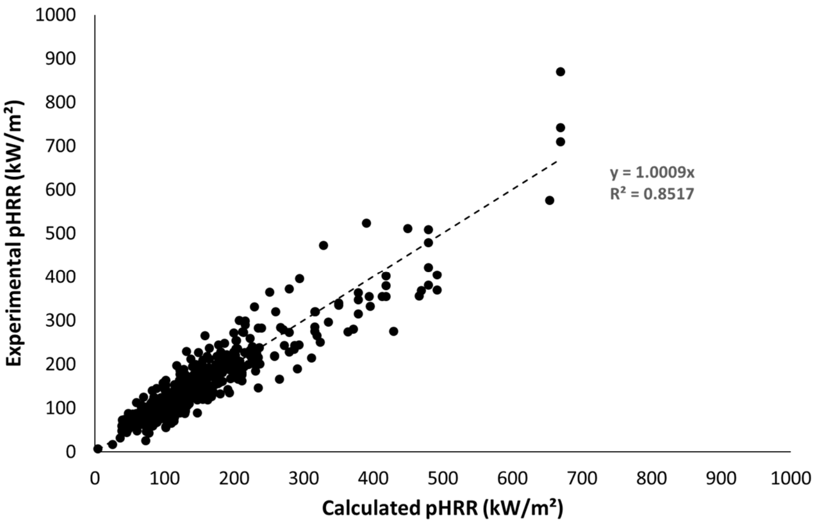

FIGURE 1 – Experimental versus calculated pHRR for all materials tested

S1- RING-OPENING POLYMERIZATION OF L-LACTIDE WITH PHOSPHORUS CONTAINING COMPOUNDS

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Sabyasachi Gaan,[b] **Gaëlle Fontaine** [a*]

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Main message:
Poly(lactic acid) (PLA) is a highly flammable aliphatic polyester of biological origin. In order to increase its fire resistance, phosphorus fragments have been directly incorporated into the PLA skeleton by ring-opening polymerization. This results in a better thermal stability of PLA. This strategy also prevents leaching or migration that occurs when additives are mixed.

Keywords: Poly(lactic acid), Phosphorus, Ring-opening polymerization, Fire retardancy

Introduction

Poly(lactic acid) (PLA) can be manufactured either by polycondensation of lactic acid or by the ring-opening polymerization (ROP) of L-lactide promoted by a metal based catalyst. [1] ROP can be conducted in bulk *i.e.* without solvent affording higher molecular weight polymers at low cost and in safer conditions than polycondensation. [1] It is this latter that be used to synthesize heat resistant PLA.

Experimental

The phosphorus fire retardant moieties were synthesized and characterized with NMR spectroscopy, mass spectrometry as well as with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis. Bulk polymerization were performed with $Sn(Oct)_2$ as the catalyst in glass reactors (sealed under inert atmosphere in a glove box) and heated in an oil batch for a given time and temperature. The obtained PLA were analyzed by TGA, DSC, nuclear magnetic resonance spectroscopy (NMR) and gel permeation chromatography (GPC).

Results and Discussion

Polymerization of (*L*)-lactide and the phosphorus compounds were conducted at different temperatures and various amount of Tin catalyst. The formation PLA was highlighted by ^{1}H, ^{13}C and DOSY NMR analysis Molecular weights up to 20,000 g/mol have been obtained depending on the polymerization conditions. Moreover, TGA analysis results show an improved thermal stability of the Phosphorus containing PLA compared to neat PLA. All the results will be fully discussed during the talk.

Acknowledgement: This work is supported by the PLARE project (ANR-20-CE93-0004) funded by the Agence Nationale pour la Recherche (ANR) and Swiss National Science Foundation (SNF, Grant No. 200021L_196923). This project is in partnership with Empa, St. Gallen, Switzerland and ETHZ, Zürich, Switzerland.

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S2- Synthetic papers inspired by wasp nest material: Flame-retardancy mechanism investigations and their potential for sustainable flame retardant materials

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Main message:
Materials evolved by organisms adapted to fire-prone habitats are promising candidates for new environmentally friendly flame retardancy solutions. Initial studies of *Vespula germanica* nests, which are built of a paper-like composite of wood particles and protein-rich saliva, showed low flammability and a good structural integrity of the residual material. Therefore, we developed biomimetic papers based on the same design principle to investigate the flame retardancy mechanisms involved.

Keywords: sustainable flame retardancy, bioinspired, bio-based, proteins

Introduction

Evolution has brought forth a variety of organisms that survive wildfires, and not only plants but also animals have remarkable fire-adaptive properties [1]. Besides that, biomolecules are in the focus as flame retardant additives for polymers as well [2]. In these contexts, wasp nests built from chewed wood and protein-rich saliva are an interesting material. Since fire is a phenomenon in the wasp's ecosystem it is probable that they evolved flame retardant properties for their materials.

Experimental

Wasp nests were collected as reference material in the field after the wasps abandoned them. Biomimetic papers were produced using wood particles and commercial proteins to mimic the main component of the wasp saliva and optimized for fire resistance. Additionally, polypropylene based polymer composites were prepared by extrusion using the same constituents to test whether the results can be transferred to wood plastic composite-like materials.

All samples (biological and synthetic) were flame tested and investigated by thermo gravimetric analysis (TGA). The evolved gases where analyzed by a coupled Fourier transform infrared (FT-IR) spectrometer to classify the combustion behavior and find possible synergies. In addition, the samples and their burnt residues were structurally characterized and analyzed by light-microscopy as well as scanning electron microscopy.

Results and Discussion

Wasp paper of *Vespula germanica* nests in comparison with plain commercial multilayer pulp show some flame-retardant behavior and charring when flame tested. This behavior was confirmed by TGA measurements (fig. 1a, b), where the decomposition of the wasp nest paper starts earlier, but is significantly slower than the decomposition of the multilayer pulp. The wasp nest paper is also releasing more of non-combustive gases like H_2O and CO_2 in the beginning of the decomposition as can be seen in the FT-IR spectra (fig. 1c). It also produces more residual char than commercial multilayer pulp (fig 1a).

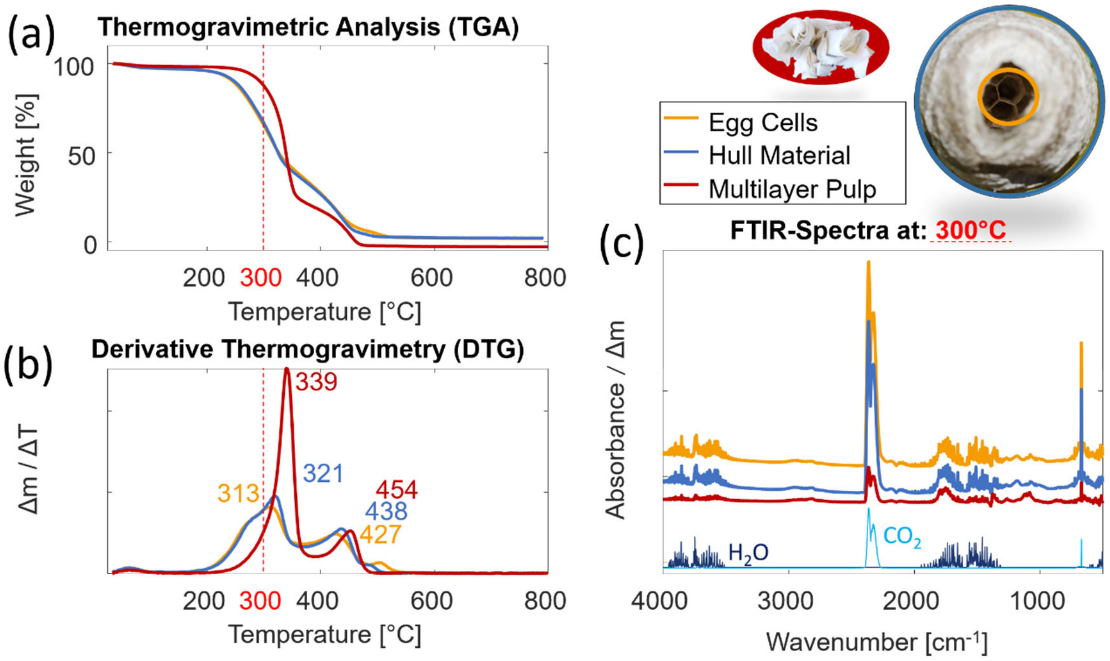

FIGURE 1. TGA and FT-IR analysis of wasp paper in comparison to multilayer pulp. (a) normalized TGA curves, (b) corresponding numerically derived DTG curve, with inserted peak temperatures (c) FT-IR spectra at 300°C normalized to the weight change Δm of the TGA, CO_2- and H_2O- spectra inserted at the bottom as references.

The release of non-combustive gases as well as charring are typical mechanisms used for flame protection of polymeric materials [2] and also for wood plastic composites (WPCs), where developing halogen-free flame retardants is still a challenge [3]. Therefore, we mimicked the wasp paper using industrial wood particles and commercial gluten, to systematically investigate the influence of quantity and distribution of proteins on the flame retardancy properties observed in the biological blueprint.

In conclusion, the wasp nest material inspired new, flame retarded wood-gluten paper-like composites, that are self-extinguishing in a horizontal flame test. The release of the nonflammable gases H_2O, CO_2 and NH_3 and indications for intumescent behavior make gluten a potential biological flame retardant with possible synergistic effects with wood. Further development might bring forth a sustainable flame retardant which is also applicable in WPCs.

Acknowledgement: This project is funded within the “FF-HAW Kooperation” program by the Ministry of Culture and Science NRW, Germany.

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PL-3 PROGRESS OF FLAME-RETARDANT TECHNOLOGIES TO ELECTROLYTES IN LITHIUM-ION BATTERY: STRATEGIES AND CHALLENGES

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Main message:
lithium-ion batteries (LIBs) represent vital technologies that have enabled the recent advances in electrically powered portable devices, electric vehicles, and internet of things (IoT) sensors. The recent surge in fire accidents and explosions originating LIBs in electric vehicles, mobile phones,etc., has become a serious issue threatening life and damaging properties. Amonst of all basic components of LIBs, electrolyte usually is an important but flammable. In this lecture, the latest flame-retardant progress on the electrolyte and some challenges faced will be summarized.

Keywords: Lithium ion battery; ectrolyte; fire safety; flame retardancy; Challenges

Introduction

The safety risks posed by electrolytes of lithium-ion batteries have drawn large-scale concern recently due to the increased reports of fires in electric vehicles. Efforts to address the fire safety of electrolytes have predominantly focused on the incorporation of flame retardant additives. However, some of these strategies generally lea to poor electrochemical properties when used in large quantities. Furthermore, how to properly evaluate flammability or flame retardancy of electrolytes are still challenging due to the lack of reliable characterization technology.

Experimental

i) An in-depth fire hazard and resistance diagnosis approach to liquid electrolytes[1]

A precise and reliable technique for diagnosing the fire resistance efficiency and hazards of flame retarded liquid electrolytes has been developed based on the cone calorimter. Following the encouraging results with dimethyl carbonate (DMC), which was selected as a model solvent since it is a common constituent of the liquid electrolytes, the cone calorimter was used for real-time fire behavior analysis of a standard carbonate liquid electrolyte sample, 1M $LiPF_6$ in Ethylene carbonate (EC)/Ethyl methyl carbonate (EMC) (named LE). Similarly, this experiment was carried out at a heat flux of 0 kW m^{-2}, i.e., without supplying any heat from the conical heater. 10 ml of the samples were transferred into the designed sample holder covered by an aluminum foil and then placed on the sample stage. The ignition was provided by an external lighter.

2) Development of flame-retardant liquid, gel-polymer and fully solid electrolytes to LIBs[2-5]

By using vairied flame retardant strategies, series of flame-retardant liquied, gel-polymer and fully solid electrolytes have been developed in the lab. Both of the flame retardancy and electrochemical performance of the coin cell were investigated. Some new mechanisms of performance were studied.

Results and Discussion

In this study, the sample was ignited instantly, and the gas analysis system continuously measured the oxygen consumption data. This approach allows for real-time analysis of key fire behavior parameters of the flame retarded electrolytes such as time to ignition, heat release rate, fire growth rate index, smoke toxicity index, carbon monoxide, and smoke produced. The main results from cone calorimter to the LE in were collected in Figure.1.

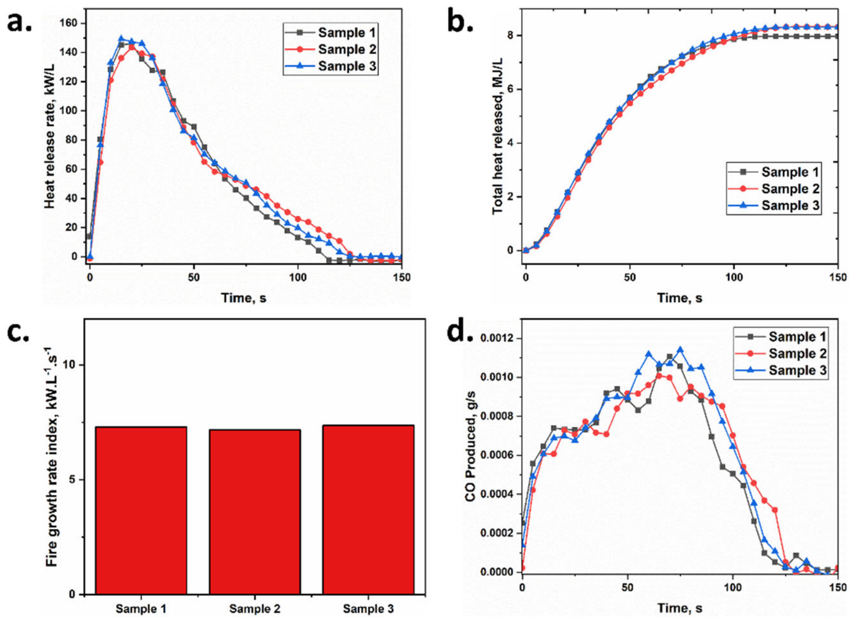

FIGURE 1. a.) Heat release profile b.) Total heat released profile c.) Fire growth rate index and d.) carbon monoxide production profile for 1M LiPF6 in EC/EMC, measured at a heat flux of 0 kW m^{-2} (all data measured are presented in triplicates). [1]

According to Figure 1, it can be observed that all the test parameters measured and computed, such as pHRR, THR, COP, and fire growth rate index (FIGRA), fire performance index (FPI), are accurate with high reproducibility. This study indicates that the modified cone calorimetry is a promising technology for diagnosing flame retarded liquid electrolyte fire resistance and hazard.

Acknowledgement: We acknowledge the financial support of this work by the IMDEA Materials STRUBAT Project, BIOFIRESAFE Project funded by Ministerio De Ciencia E Innovación (MINECO), Spain with the project number: PID2020-117274RB-I00BIOFIRESAFE and PEJ-2018 MINECO.

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K4- The Potential of Phosphorus-Containing Flame Retardants for Current Application

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Main message: Nowadays, phosphorus-containing compounds are important flame retardants that can exert their flame-retardant effect either in the gas phase (flame inhibition) or in the condensed phase (charring catalyst), depending on the chemical environment of the phosphorus. A number of molecular, salt and polymer flame retardants established on the market. By formulating gas-phase and condensed-phase active flame retardants or synergistic blends, optimized results can be achieved in terms of flame retardancy, material and processing parameters, and price.

Keywords: Phosphorus-containing flame retardants, synthesis efficiency, synergism, technical application.

Introduction

This presentation describes the potential of phosphorus-containing flame retardants for technical application based on efficient, green manufacturing processes of the flame retardants and on optimized material- and application-related flame retardancy. Technical flame retardant solutions, including those for engineering plastics, are explained and new promising concepts are presented, taking into account modern material developments, e.g., in sustainable electrification.

Results and Discussion

The combination of differently acting phosphorus-containing flame retardants in one polymer is able to produce excellent flame retardant efficacy. This was demonstrated by the example of these applications in glass fiber reinforced engineering plastics [1]. New potential flame retardant candidates and formulations and their advantages in terms of processing and material properties are now presented here. Flame retardants have become established which, in addition to their outstanding flame retardant properties, can also be produced advantageously by synthesis chemistry.

Other synergistic formulations in which phosphorus-containing compounds can be used as primary flame retardants or as synergist are summarized in Table 1. Selected current examples with technical significance or potential, such as the synergistic effect of radical generators in phosphorus-containing flame retardant mixtures [2] and ceramifiable flame retardant formulations [3,4] will be discussed.

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TABLE 1. Selected Examples of Flame-retardant Synergistic Formulation

Type of flame retardants	Examples	Synergists	Usual FR loading [%]
Inorganics	$Mg(OH)_2$, $Al(OH)_3$	Nanoclays, exp. graphite, P-C- and P-H-compounds	>60 (PP)
Silicon/Silica	Ceramifiable formulation	Phosphate	25 (EP)
Expandable graphite		Phosphorus compounds, polyols, APP/metal oxide	13 (EP)
Halogenated	Brominated compounds	Sb_2O_3, borates, radical generators, P compounds	25-35 (PP)
Phosphoric compounds (P-O)	Phosphate (polyphosphate, phosphoric ester)	Polyols, metal salts, triazine derivatives, P-C-compounds	20-30 (PP)
Phosphine oxide, Phosphinate, Phosphonate (P-C, P-H)	DOPO, DEPAL, methylphosphonate, Al-hypophosphite	Phosphate, phosphonate, radical generator	20-22 (PA)
Radical Generators	Disulfide, sulfenimide, NOR, oxyimide	Halogenenated and phosphorus compounds	1-15 (PP)

O7- COFFEE BIOWASTES AS SUSTAINABLE FLAME RETARDANTS FOR POLYMERS

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Main message: This work provides answer to the question "is it possible to use coffee biowastes (spent ground coffee) as biowastes to make polymers flame retardants?", which is "YES". We proved that with some modifications and assistance of conventional non-toxic flame retardants, it is possible to convert coffee biowastes into promising flame retardants for protection of highly flammable polymers.

Keywords: Biowaste; Flame retardant; Phytic acid; Flame retardancy; Sustainability

Introduction

Development of biobased and cost-effective flame retardants has attracted the attention of researchers to develop safe and sustainable materials [1]. Various types of biowastes such as oyster shell powder and eggshell have already been incorporated into polymers to control their flammability. Coffee wastes are among biowaste fillers, as of by-products of industry, as well as end-of-use wastes or spent ground coffee, which are recently known to be served for development of flame-retardant polymer biocomposites [2, 3]. It has been used as-collected/received in development of biocomposites, also with some modifications became promising precursors, e.g. extracted to yield porous activated carbon precursors [3] or hybridized with other biowastes like eggshell [4] for energy storage and waste treatment or adsorption. In a previous work, we used spent ground coffee and also reinforced it with non-biobased phosphorus to develop a sustainable biofiller for epoxy. We achieved acceptable flame retardancy as studied by UL-94 and micro calorimeter of combustion [5].

Experimental

In this work, the coffee biowaste was chemically modified with phytic acid and dimethyl phosphite molecules and then incorporated into epoxy and polylactic acid (PLA). PLA and epoxy composites containing different loading percentage of unmodified/modified coffee biowaste were investigated using thermogravimetric analysis (TGA), cone calorimetry, pyrolysis combustion flow calorimeter analysis (PCFC) and UL94 tests. Chemical structure of phytic acid-modified coffee and thermal decomposition behavior of biocomposites are investigated by Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA), respectively.

Results and Discussion

The chemical modification led to a significant increase in the char content up to 60% as detected by TGA. The results clearly showed the effectiveness of the modified coffee biowaste as flame retardant additive, as signaled by the decrease in peak of heat release rate pHRR in cone calorimetry microcalorimeter of combustion in epoxy and also in PLA.

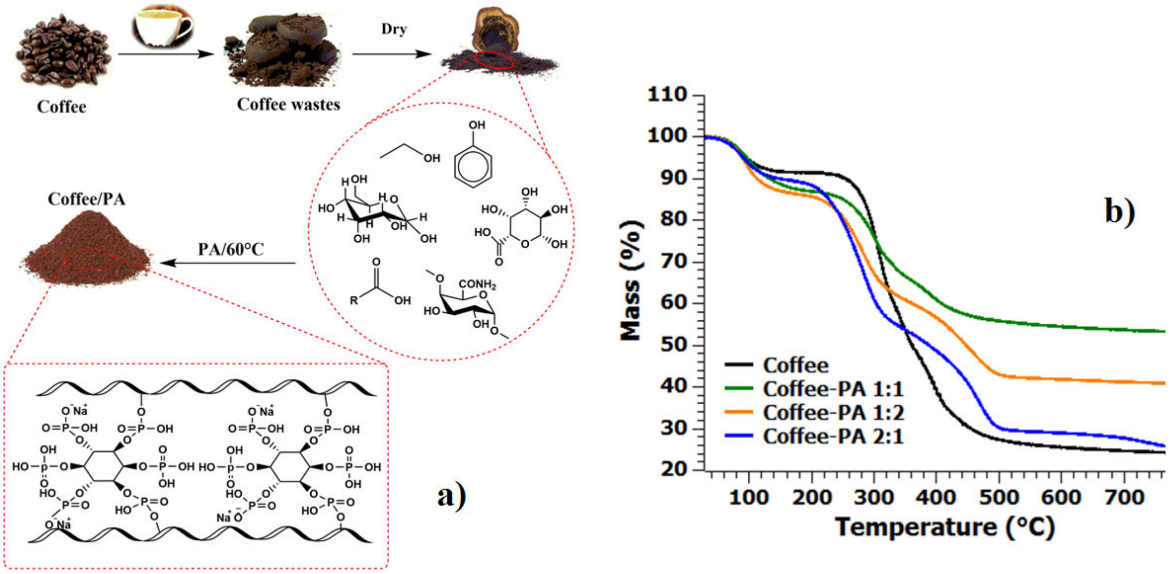

FIGURE 1. Scheme of chemical modification of coffee waste using phytic acid (a), thermogravimetric analysis (TGA) curves for coffee waste and modified coffee waste with different ratios of phytic acid (b).

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S3- Introduction of an Organic Flame Retardant with High Phosphorous Content in Unsaturated Polyester Resins

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Main message: The quest for an ideal, low cost halogen-free flame retardant (FR) for *Unsaturated Polyester Resins* (UPRs) has been an interesting topic of research since the past decade. It is quite challenging to find an FR which does not impact the mechanical and optical properties of the UPRs. In this study, an organo-phosphorous tri-alcohol (*P-3-ol*) compound with a high phosphorous weight percentage is chosen as an ideal template for investigation and the various chemical techniques to incorporate them in UPR thermosets are discussed, either as additives or intrinsically in the resins with chemical modifications. A brief outlook on the final flame-retardant behavior and other physico-mechanical properties are then elaborated.

Keywords: UPR, phosphorous FRs, thermosets, additives, intrinsic flame retardants

Introduction

UPRs have found extensive use in industrial and commercial moulding processes, with a significant interest in their use as the polymer matrix in composites with a plethora of applications ranging from furnitures to automobiles.[1] Incorporation of an appropriate FR in UPRs has been an ongoing research topic, as the advantages like transparency and tensile strengths of the cured thermosets is influenced by additive FRs. Besides, the flame retardance in such thermosets is also quite low due to the large amount of flammable organic material present.[2] In this work, *P-3-ol* (**Figure 1**) and its derivatives are used to enhance the flame retardance in UPRs, and an overall strategy to reduce flammability is investigated.

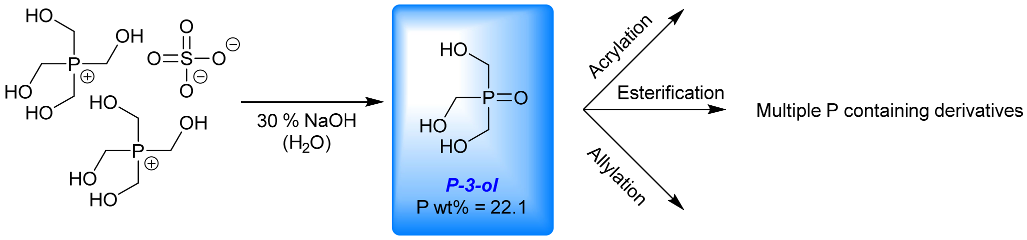

Figure 1: Reaction Scheme of obtaining P- FRs used in UPRs.

Experimental

All reagent grade chemicals were sourced from *Sigma-Aldrich* and *TCI, Europe.* The UPR (Gremopal 170.10) was provided by *Gremolith AG* (Bazenheid, Switzerland). ICP-OES, ^{1}H, ^{13}C and ^{31}P NMR were employed to characterize the organic compounds. A pyrolysis combustion flow calorimeter (PCFC, Fire Testing Technology Instrument, London, UK) was employed to determine pHRR, THR, and heat release capacity (HRC, $J^{-1}\cdot g\cdot K$), following the ASTM D7309 standard. Forced combustion tests (with a cone calorimeter, in accordance with the ISO 5660 standard) and flammability tests were used to analyse the fire behavior.

Results and Discussion

The results show that the use of *P-3-ol* and its derivatives do indeed reduce the flammability of the final cured thermosets. The extent of flame reduction, and other thermos-pyro analyses will be discussed in detail during the presentation.

Acknowledgments: This work is part of INPOL project funded by Innosuisse (Innovation project 58603.1 IP-ENG). The implementation partner in this project is *Gremolith AG*, who have graciously provided the essential reagents to synthesize UPRs.

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S4- POLYMERIZABLE SULFENAMIDE AS AN EFFECTIVE FLAM RETARDANT FOR POLYSTYRENE

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Main message: Herein, we report the successful copolymerization of a new sulfenamide monomer with styrene via suspension polymerization to give polystyrene with enhanced fire retardation. The prepared poly(styrene-co-sulfenamide) copolymer passed the DIN4102-B2 fire tests even at a low content of sulfenamide comonomer of ca. 2 wt%.

Keywords: Sulfenamide monomer, polystyrene, suspension polymerization, polymerizable flame retardant

Introduction

Despite a great deal of publicity in recent years regarding the concerns on the effects of halogenated flame retardants and leaching of different plastic additives to the environment, no viable commercial solution for flame retarded foamed polystyrene exists that would fully address these issues. This work aims to tackle this challenge via copolymerization of sulfenamide flame retardant with styrene.

Experimental

A series of styrene suspension copolymerizations were conducted in the presence of sulfenamide monomer as shown in Figure 1. Flame retardant efficacy was evaluated by the DIN4102-B2 fire test and the content of comonomer was determined by 1H NMR.

Results and Discussion

The results collected in Table 1 show that sulfenamide monomer can be successfully copolymerized with styrene to give polystyrene with enhanced flame retardancy. The obtained polystyrene beads containing FR-014 had a spherical shape and both the molecular weight and its distribution were similar to the reference polystyrene. Thus, the sulfenamide monomer did not have notable negative impact on the process of breakage and coalescence of monomer/polymer droplets nor on the kinetics of the suspension polymerization.

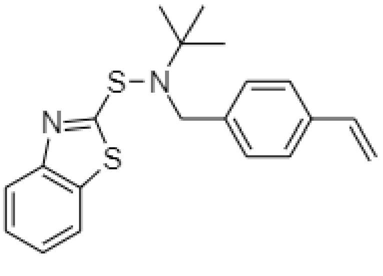

FIGURE 1. Chemical structure of polymerizable sulfenamide FR-014.

TABLE 1. Results of DIN 4201 fire test of polystyrene films and molecular weight information.

Sample	Polymer	Flame Retardant [wt%]	Mw/Mn [g/mol]	Fire Test DIN4102-B2 [Fail/Pass]
1	PS	-	83 000/42 000	Fail, burns completely
2	PS	1.5 wt% of FR-014	86 000/41 000	Pass
3	PS	2 wt% of FR-014	88 000/36 000	Pass
4	PS	2.5 wt% of FR-014	82 000/39 000	Pass

Acknowledgement: The authors would like to thank Doctoral Education Network in Materials Research (DNMR) for the financial support of this research.

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Special Talk - CHEMICALS STRATEGY FOR SUSTAINABILITY, TOWARDS ZERO POLLUTION

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Main message: In 2020, the European Commission published the 'Chemicals Strategy for Sustainability: Towards a Toxic-free Environment' as part of the European Green Deal. The main objectives of the Chemicals Strategy are to ensure better protection of human health and the environment from hazardous chemicals, to boost innovation for safe and sustainable chemicals and to enable the transition to chemicals that are safe and sustainable by design.

The chemicals strategy fully recognises the fundamental role of chemicals for human well-being and for the green and digital transition of European economy and society. At the same time, it acknowledges the need to address the health and environmental challenges caused by the most harmful chemicals. This includes for instance prohibiting the use of the most harmful chemicals in consumer products and ensuring that all chemicals are used more safely and sustainably. The strategy will also boost the investment and innovative capacity for production and use of chemicals that are safe and sustainable by design, and throughout their life cycle. By doing so the EU industry will remain a global frontrunner in the production and use of safe and sustainable chemicals.

The Chemicals Strategy aims to prioritise regulatory action on substances with specific hazardous properties. To facilitate this action, the Commission has prepared a roadmap to prioritise substances for (group) restrictions under REACH. The Roadmap identified the need for further regulatory management measures for flame-retardants as a group. The European Chemicals Agency prepared an overall strategy to regulate these substances.

During the presentation, the most important elements in the Chemicals Strategy and the flame retardant strategy will be presented.

Keywords: EU policy, REACH, restriction, group approach, substitution

PL4- PROGRAMMABLE DESIGN ON DEMAND: QUANTITATIVE CONTRIBUTION OF MOLECULAR MOTIFS IN FLAME-RETARDANT THERMOPLASTIC POLYMERS

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Main message: Adding flame retardants and/or copolymerizing specific flame-retardant groups into polymers are the main methods to achieve flame retardancy of polymers. However, due to the complex pyrolysis/combustion process of polymers, different flame-retardant structures exhibit different pyrolysis/combustion behaviors in different polymer materials and make different contributions to the flame-retardant properties. Here, based on an accurate understanding of the pyrolysis/combustion behavior of polymers from our homemade real-time and online polymer burning/combustion analysis apparatus (PBCA), we clarify the contribution of specific group structures to flame retardant performance and combustion behavior from the molecular level, further quantitatively analyze the flame retardancy contribution of different primitive structures and propose a predictive model for flame retardancy of thermoplastic polymers using the combining strategy of artificial intelligence and experimental big data. Thus, we illustrate the scientific principle of polymer materials to achieve flame retardant function, establish the structure and property gene library of flame retardant groups and materials, and give a new insight into the high-throughput development of high-performance flame-retardant functional polymer materials.

Keywords: flame retardance, quantitative contribution, real burning processes, thermoplastic polymer

Introduction

Thermoplastic polymers are an extremely important class of synthetic polymer materials. Because of their excellent comprehensive properties, they are widely used in many fields such as electronics, construction, transportation, aerospace, and textiles. However, most thermoplastic polymers are flammable materials, which will generate a lot of heat and toxic fumes when burned, which leads to their great fire safety hazards in practical applications, and also limits their use in some application fields where the fire safety is required.

Adding flame retardants and/or copolymerizing specific flame-retardant groups into thermoplastic polymers can endow materials with excellent flame-retardant properties. Flame retardants/flame retardant structural units mainly achieve flame retardancy through two modes of "gas phase flame retardation" and/or "condensed phase (solid phase) flame retardation" in thermoplastic polymers. However, due to the different structures of thermoplastic polymers, their pyrolysis/combustion behaviors show great differences, which makes the flame retardant effect of flame retardant groups in different materials uncertain. It is urgent to characterize the quantitative flame retardant contribution of flame retardant structures to achieve a more accurate and effective design and preparation of flame retardant materials.

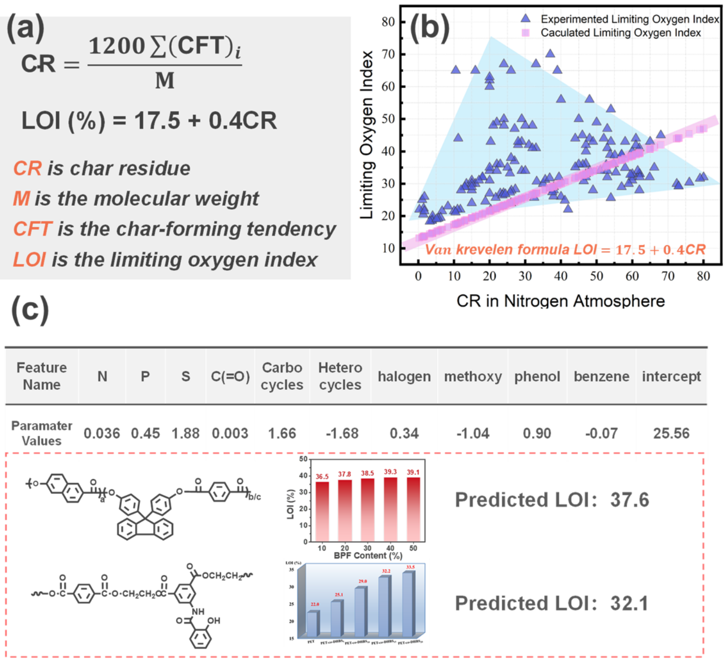
There are two main problems to be solved. On the one hand, there is no apparatus focusing on the real-time online analysis of the burning process, and the past research on flame-retardant mechanism was carried out under the unreal fire circumstance, so the previous work cannot effectively guide the design of the flame-retardant functionalization, even if it is completely ineffective. On the other hand, although previous studies have constructed a data set of polymer flame-retardant structure and flame-retardant properties, and built a model to predict the flame-retardant properties of materials, due to the lack of key parameters in the combustion chemistry and pyrolysis process. As a result, the flame retardant performance prediction model based on these descriptors is not accurate enough, and when the material system undergoes migration changes, the prediction is almost invalid.

Experimental

We first construct real-time and online polymer burning/combustion analysis apparatus (PBCA) to simultaneously analyze the flame retardant properties of polymers (heat release, smoke release, etc.) and the chemical structure of pyrolysis/combustion products; further based on these large amounts of data, analyze the contribution of polymer pyrolysis/combustion products to flame retardant properties. Then, based on collected flame retardance materials datasets, we construct the structure and flame retardance model by the machine learning algorithm.

Results and Discussion

Real-time and online polymer burning/combustion analysis apparatus (PBCA) can simultaneously obtain the heat release, smoke release, and fine chemical structure information of the combustion products of the material in real-time, and obtain the real combustion behavior and flame retardant performance data of the polymer. More information will be shown in the presentation. In the structure and flame retardance model aspect, the abstract exhibit parts results of our research. As shown in Figure 1, the Van Krevelan formula always gets the inaccurate LOI value in the novel thermoplastic polymers. We explore a multiple linear regression formula, which exhibits a more precise LOI value, and give the flame retardance contribution of different elements such as the N, P, S, or some motifs like the C=O, benzene, halogen, etc.



Feature Name	N	P	S	C(=O)	Carbo cycles	Hetero cycles	halogen	methoxy	phenol	benzene	intercept
Paramater Values	0.036	0.45	1.88	0.003	1.66	-1.68	0.34	-1.04	0.90	-0.07	25.56

FIGURE 1. a) The Van Krevelan formula. b) The experimental and the predicted LOI value based on the Van Krevelan formula. c) the multiple linear regression formula and the predicted LOI value of polymers.

Acknowledgement:
The National Science Foundation of China (51827803).

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O8- MODE OF ACTION OF ZN-DOPOx AND MELAMINE POLYPHOSPHATE AS FLAME RETARDANTS IN GLASS FIBER-REINFORCED POLYAMIDE 66

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Main message: The zinc salt of 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (Zn-DOPOx), melamine polyphosphate (MPP) and mixtures were studied in glass-fiber reinforced polyamide 66 towards flame retardancy. Strong interaction between Zn-DOPOx and MPP results in a more open char structure. Fuel dilution, less exothermic decomposition, and increased gas phase activity are responsible for improved flame retardancy in Zn-DOPOx/MPP (1/1).

Keywords: PA 66, phosphorus-containing flame retardant, metal phosphorus salt

Introduction

The flame retardant mode of action for metal salts of organophosphorus compounds (like aluminum diethylphosphinate) in glass fiber reinforced polyamide 66 is described very well. [1, 2] Unlike, other metal phosphinates and phosphonates, e.g. from DOPO or DOPOx, are mentioned in the patent literature, [3] but their mode of action is not well understood. In this study, this gap is bridged for the zinc salt of DOPOx, both alone and in synergistic mixtures with MPP.

Experimental

Zn-DOPOx (DOPO Zink Polymer S20) and MPP (Budit® 342) were purchased from Metadynea Austria and from Chemische Fabrik Budenheim, respectively. PA 66 (Ultramid® A3K) was provided by BASF, glass fibres (CS7928) by Lanxess, and calcium stearate (Ceasit AV) from Baerlocher. Compounds were made with a 27 mm twin screw extruder (Leistritz ZSE 27), specimens for fire testing were injection-molded (Arburg 320A). The flammability was evaluated using UL 94 V and cone calorimetry (both Dr. Ing. Georg Wazau Mess- und Prüfsysteme GmbH). Influence on char formation was analyzed by SEM (SM300, Topcon Corporation) and SEM EDX (JSM-7600F, Jeol, with the sensor X Max-80 mm2, Oxford Instruments) regarding the elements C, N, O, P and Zn. Thermal decomposition of Zn-DOPOx and MPP was studied by TGA and ATR-FTIR (Nexus 670, Thermo Fisher Scientific) with an ATR Golden Gate module. The release of gaseous decomposition products was investigated using TGA-DTA-FTIR.

Results and Discussion

Zn-DOPOx, MPP and mixture as flame retardants in PA 66GF were investigated towards the mode of action. Very short after-flame times and V-0 classification (0.8 mm) with total loading of 22 % were observed for Zn-DOPOx/MPP (1/1) in the UL-94 V test (PA-3, see Table 1). The synergistic effect for Zn-DOPOx/MPP (1/1) becomes obvious when comparing the higher afterflame times and burning melt dripping behaviour (0.8 mm) for MPP (PA-2) and the very poor fire extinguishing effect for Zn-DOPOx (PA-1). The latter was traced back to (i) an excessive thermal stability of Zn-DOPOx that prevents to act efficiently as flame retardant in PA66, (ii) an overall release of high amounts of combustible C-H fragments and (iii) the lack of a heat sink in the condensed phase. Nevertheless, a char promoting effect for Zn-DOPOx (PA-1) could be seen using SEM. For MPP (PA-2), the literature-known mode of action through fuel dilution and barrier formation could be confirmed. When the overall loading of flame retardants is 22%, the best flame retarding effect is observed for equal parts of weight in Zn-DOPOx/MPP (1/1) compared to mixtures with different ratios between Zn-DOPOx and MPP (2/1 in PA-4 or 1/2 in PA-5). TGA and ATR-FTIR analyses revealed a strong interaction between the components through a significant change in thermal stability and in the absorption patterns of TGA residues for Zn-DOPOx/MPP (1/1). A major change in decomposition was also observed for Zn-DOPOx/MPP (PA-3) compared to the sole use of Zn-DOPOx (PA-1) and MPP (PA-2) in PA66 GF using DTA-FTIR analysis. The intrinsic contribution to the thermal feedback through exothermic decomposition was reduced significantly in PA-3. Less C-H fragments were detected compared to PA-1 and PA-2. A high fraction of inert gases are released from PA-3 upon thermal decomposition diluting the fuel in the gas phase. At the same time, the pronounced endothermic process at about 370 – 400°C acts as a heat sink in the condensed phase. The latter can be attributed to the use of MPP as seen in PA-2. By using cone calorimetry, it was shown that in spite of the open char structure of PA-3, low heat release rates (HRR) are achieved similar to PA-2. In combination with the significantly higher CO release and smoke production of PA-3, it was concluded that radical quenching species are released through the interaction of the components in Zn-DOPOx/MPP (1/1). This is supported by the lowest phosphorus content in burnt UL-94 V specimen measured with SEM-EDX. Overall, this release of phosphorus species and the beneficial changes in thermal decomposition regarding less exothermic behavior and release of less C-H fragments with high portion of inert gases leads to the improvement in flame retardancy of the mixture Zn-DOPOx/MPP (1/1). An interesting topic for further studies would be the improvement of the char stability and morphology while using the observed improved gas phase activity for the combination of Zn DOPOx/MPP (1/1).

TABLE 1. Results of UL-94 V testing of formulations using Zn-DOPOx and MPP in PA66 GF.

Sample	Flame retardant		UL-94 V (0.8 mm)		UL-94 V (0.8 mm)	
	Zn-DOPOx [wt. %]	MPP [wt. %]	Total Afterflame [s]	Classification	Total Afterflame [s]	Classification
PA GF	-	-	> 300	n.c.	> 300	n.c.
PA-1	22	-	80.6	n.c.	182.3	n.c.
PA-2	-	22	15.6	V-2	52.7	V-1
PA-3	11	11	10.4	V-0	4.7	V-0
PA-4	14.7	7.3	38.6	V-2	5.5	V-0
PA-5	7.3	14.7	56.8	n.c.	7.9	V-0

Acknowledgement: The authors want to thank L. Brüggemann GmbH and Co. KG (Heilbronn, Germany) for the financial support for this research.

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O9- AN IN-SITU, NONINTRUSIVE INTERMEDIATES MONITORING METHOD FOR POLYMER COMBUSTION MECHANISM STUDY

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Main message:
The investigation of the flame retardant mechanism is extremely important. However, due to the lack of effective characterizations, many mysteries to the mechanism still remain. Particularly, "free radical inhibition", one of the most crucial flame-retardant mechanism in the gas phase, it is undeniable that the understanding of this process is still superficial due to the lack of effective ways to monitor the transient intermediate products (qualitatively or quantitatively) during combustion. Recently, we design and fabricate a special burner, and proposed an in-situ, nonintrusive intermediates monitoring method based on the chemiluminescence fingerprint of intermediates. Several typical combustion tests, including pure polymer and polymers containing flame retardants, have been made to prove the feasibility of this method. Particularly, by qualitative or semiquantitative monitoring of key radicals (OH, CH, C_2, H_2O, CO_2, and X, where X represents those important radicals that significantly affect combustion chain reactions, such as, Br_2, Cl_2, PO, PHO, etc.) in the combustion zone, this method can provide key evidence for the investigation of polymer combustion/flame retardant mechanisms.

Keywords:
Polymer combustion, Flame-retardant mechanism, Radical chain reaction.

Introduction

Synthetic polymers have changed our daily life deeply since the birth. But most polymers, always flammable, need to compound with flame retardants to meet the use criteria[1]. With the increasing drastic demands for safety, highly efficient flame retardants are urgently required. However, lacking the in-depth understanding of mechanisms makes the development of new flame retardants more like an experience-led guesswork followed by complex synthesis and characterization tests, which waste a lot of time and resources. Therefore, the investigation of flame retardant mechanisms, especially the gas phase flame retardant mechanisms still surrounded by tons of mysteries, is pivotal and urgent.

Generally, polymer combustion is a multi-phased, highly coupled process[2]. Extensive researches focus on those reactions in the condensed phase (gasification/pyrolysis). Pity that the corresponding results are often unreasonable since neglecting the open-flame-involved burning process.

Particularly, numerous literatures point out that "free radical inhibition" is one of the most crucial flame retardant mechanism in the gas phase[3]. Key radicals ·X are released during the pyrolysis of flame retardants. In this case, hydrogen and hydroxy radicals, the most important species for combustion chain, are replaced by these radicals (·X) or are rendered less active by radical recombination in the gas phase. Branching and chain reaction of the oxidation of hydrocarbons are therefore interrupted, leading to the slow-down or even stop of combustion. Although the above theory has been widely accepted, due to the lack of effective ways to monitor the transient intermediates, it is undeniable that the understanding of this process is still superficial.

Here, an in-situ, nonintrusive intermediates monitoring method based on the chemiluminescence fingerprint of intermediates is proposed and a special burner is designed and fabricated. By e monitoring of key radicals (OH, CH, C_2, Br_2, Cl_2, PHO, PO etc.) in the combustion zone, this method can provide direct evidence for the investigation of polymer combustion/flame retardant mechanisms.

Experimental

General purpose polypropylene, and Tetrabromobisphenol A are selected as substrate and additive. 10 wt% TBBA is melt compounded with PP using a torque rheometer at 100 rpm under 180 °C to obtain PP/TBBA composites. The pristine plastic and composites are cooled by liquid nitrogen, crushed in a pulverizer, and screened out uniform particles for subsequent tests. To minimize the effect of moisture content, all samples are dried at 50 °C for 12 h and stored in electrothermal driers before use.

Results and Discussion

Polypropylene (PP), one of the most commonly-used general plastics, is chosen for combustion tests. Figure 1a shows the digital images of flames at different sample temperatures. At the beginning of heating (the sample temperature < 300 °C), flame length and shape remain nearly constant. When heating to around 350 °C, the flame becomes oscillating, and the length rapidly increases, which is principally because large numbers of pyrolysis products are into the combustion zone, leading to a transition from laminar to turbulent flame. At the same time, characteristic emission bands for OH (308 nm, A2Σ+-x2Π), CH (431 nm, A2Δ-x2Π; 390 nm, B2Σ-x2Π), C2 (473 nm, 516 nm, 558-563 nm, A3Πg-x3Πu) and H2O (930 nm, Vibration-Rotation Bands)[4] are observed in the combustion zone (Figure 1b), which are generated from the hydrocarbon oxidation.

For PP/TBBA blends (TBBA represents tetrabromobisphenol A), as shown in Figure 1c, it shows two distinct flames during the combustion process. When heating to around 250 °C, the flame becomes oscillating, and the strong orange-red emission bands attributed to Br_2 (5500-10000 Å, A3Π-x1Σ, Figure 1d) occur in the combustion zone. This is ascribed to the combustion of bromine compounds from the pyrolysis of TBBA. As temperatures rises (above 400 °C), the flame length and the turbulence intension significantly increase, and the intensity of orange-red emission decreases, while the characteristic bands for OH, CH, C_2 and H_2O, and thermal radiation of soot particles are clearly observed.

In conclusion, an in-situ, non-contact intermediates monitoring method based on the chemiluminescence fingerprint of the free radicals is proposed, and a special burne is designed and fabricated for polymer combustion. Several typical combustion tests, including pure polymer and polymer composites, have been made to prove the feasibility of this method. Particularly, by qualitative or semiquantitative monitoring of key radicals (OH, CH, C_2, H_2O, CO_2, and X) in the combustion zone, this method can provide key evidence for the investigation of polymer combustion/flame retardant mechanisms.

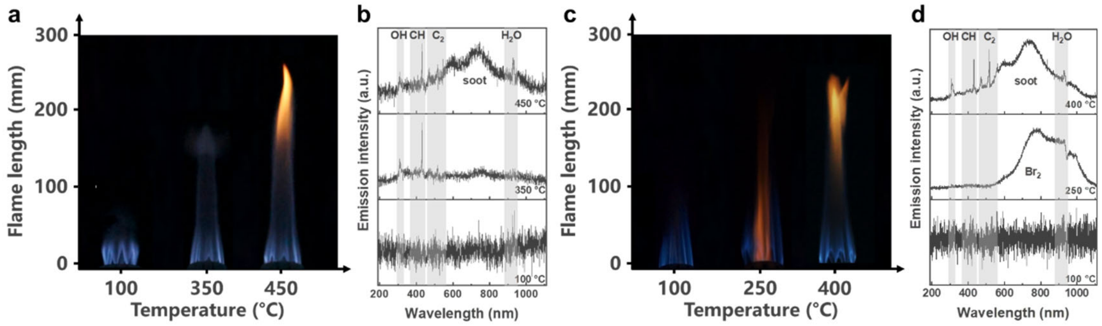

FIGURE 1. a) Digital images of PP combustion. b) Emission spectra of flames in PP combustion. c) Digital images of PP/TBBA combustion. d) Emission spectra of flames in PP/TBBA combustion.

Acknowledgement: The National Science Foundation of China (51827803).

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O10- NITROGEN and PHOSPHORUS CONTAINING SILANES as VERSTAIL FLAME RETRADANTS: NOT ONLY FOR TEXTILES

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Main message: In the last years novel flame retardants on the basis of commercially available amino-silanes where developed by us. The aminosilanes were modified with different phosphor groups and N- and P-conataing silanes (N-P-silanes) were obtained. These silanes are highly effective FRs for textiles, whereby a low add-on with a washing durability is obtained. The effectivity can also be transferred to composites materials, wood surfaces and extrusion applications.

Keywords: textile finishing, composite materials, N-P-silanes, FR mechanism, smoke suppression

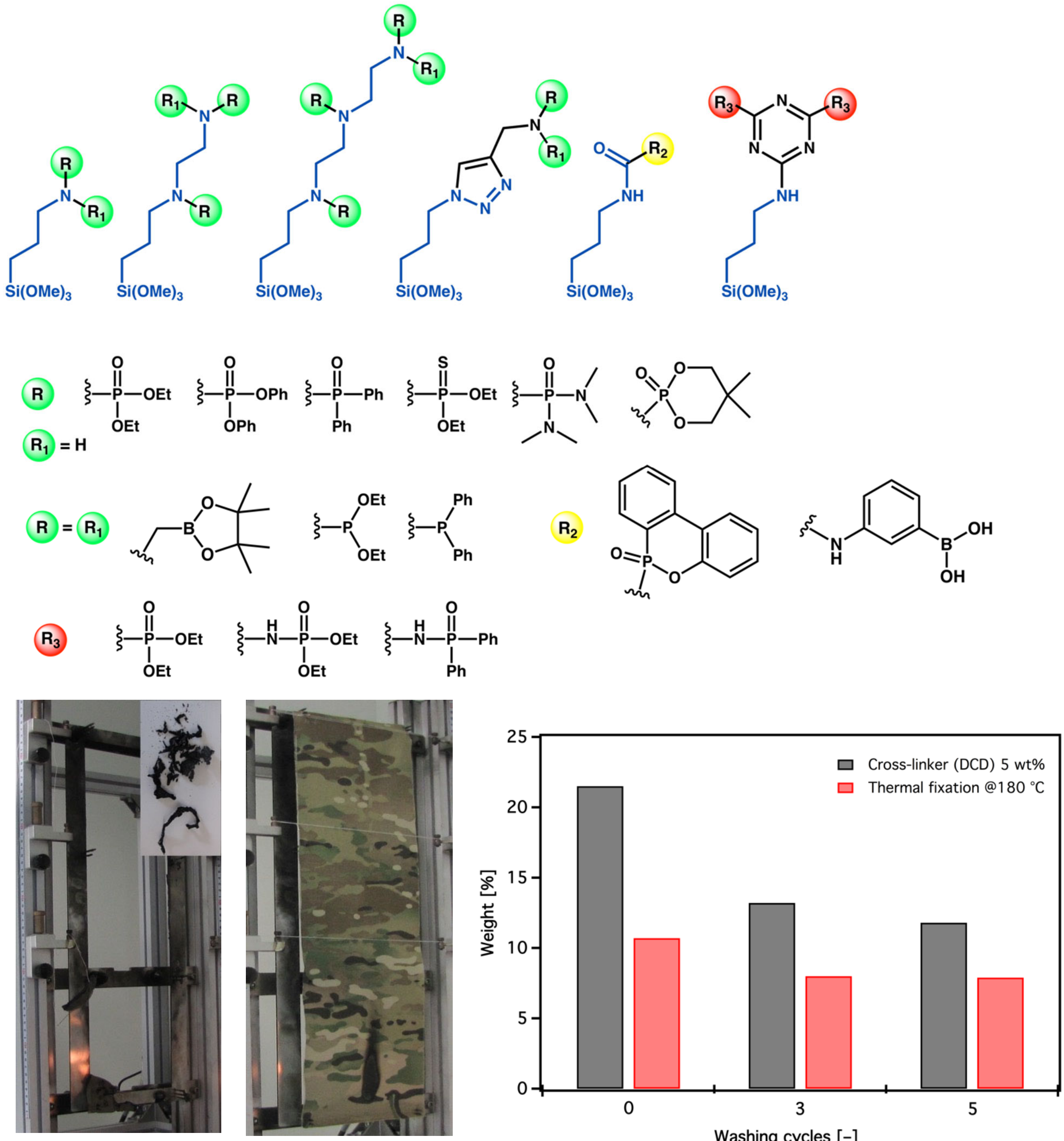
Introduction

N-P silanes can be synthesised on the basis of industrial available educts, whereby, one-to-two reaction-steps are needed and a yield between 80-95 % are obtained. On this basis, a wide library of versatile N-P-silane-based FRs are developed. Based on these FR library, cotton, polyamide, polyester and their blends were applied and their thermal behavior and durability were assessed. A combination of nitrogen and phosphorous-based flame retardants with boron-based silanes exhibit smoke suppressant properties also offer a green alternative to halogenated flame retardants for composite materials.

Results and Discussion

In this presentation an overview will be given about the currently flame retardants developed in our group and the main trends seen with respect to fire protection of materials, including fabrics, composites, wood and polymers. In **Figure 1** an overview of the different FR is given. Finished textiles passes different standardized test, e.g. for personal protective clothing (DIN EN 15025) or building materials with a rating (DIN 4102-B2) and show a high washing resistance. In **Figure 1** (below) a comparison of a FR-finished and native nylon-cotton (NYCO) fabric is given. In cooperation with abcr GmbH we could commercialize different N-P-silanes for textile finishing, for WPC applications or for the modification of glass fibers for polyamide in E&E applications.

The FRs in **Figure 1** (top) can have different functionalities for intumescence applications. A typical intumescence mixture consists of three components, an acid source, a gas source and a carbon donor. All these functionalities can be included into the silane. But these can be designed easily as acid and gas source. Different FR have been tested for wood coatings in intumescent mixtures, all of the FR acted with the desired function in the mixture.



native

FR-finished

FIGURE 1. top: different N-P-silane based FR and organo-boron based silanes; below left: NYCO native and finished with a N-P-silane FR, the native fabric burns totally down, then FR-finished is self-extinguished after removal of flame source; below right: washing resistance of the fabric finished with FR using dicyandiamide (DCD) or through thermal fixation of cotton fabrics.

Acknowledgement: The research was founded within the IGF-research program of the BMWK. Grant numbers: 19617 N, 21318 N and 21993 N and with the BMWK ZIM program. Grant number ZF4139703EB9.

S5- THERMAL STABILITY AND FIRE SAFETY BLACK PHOSPHORUS-BORON HYBRID NANOCOMPOSITES: MECHANISM OF PHOSPHORUS FIXATION EFFECTS AND CHARRING INSPIRED BY CELL WALL

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Main message: This research develops the nanocomposite of polycarbonate/black phosphorus–boron, PC/BP-B1.0 achieves better thermal stability and fire safety with a 57.16 °C increase in $T_{-1\%}$ and a 70.50% decrease in the heat release rate. The pyrolysis products of polycarbonate-based polymers (CO_2) and black phosphorus-based hybrids (cations of $[P_4]^+$, $[P_3]^+$, and $[P_2]^+$) in the gas phase are also analyzed. The work paves a general path for the nanocomposites with properties of thermal stability and fire safety.

Keywords: fire safety; phosphorus fixation effects; BP-B nanohybrid; thermal stability

Introduction

Flame retardancy of the condensed phase is a promising trend that meets human safety. Currently, the major challenge is to achieve the capture of flammable product fragments in fire and retain them in the condensed phase with a more stable form by PFRs. In this research, we propose and exemplify a novel strategy inspired by the structure of cell walls in plants. PFRs are self-assembled into a structure inspired by cell wall driven by the heat to capture combustible fragments into char.

Experimental

Through programmed ball milling, boron nanoflakes (B) are used as an agent to simultaneously exfoliate and hybrid the black phosphorous (BP) to obtain the BP-B nanohybrid (Figure 1b).

Results and Discussion

The emerging two-dimensional BP and B posse numerous attractive physicochemical properties, which are expected to simultaneously endow their composites with diverse functionality. Interestingly, by introducing BP-B into polycarbonate (PC), the HRR shows a progressive decrease as BP-B increased. Notably, only the introduction of 0.3 wt% BP-B achieves a PHRR reduction of 45.20% which is close to the loadings of 1.0 wt% BP and B alone. Meanwhile, PC/BP-B1.0 dramatically decreases the PHRR by 70.50%. Moreover, time to PHRR is delayed by 49.66%, from 145 s to 217 s. To evaluate the combined effects of reducing and delaying the HRR, the fire growth index (FGI, defined as the PHRR divided by time to the PHRR) is calculated. It declines sharply and is significantly lower than that of BP and B alone, which indicates that the hybridization of B on BP inhibits combustion and acceleration significantly. As a result, THRs of PC/BP-B0.5 and PC/BP-B1.0 are separately decreased by 29.46% and 36.03%. The introduction of 1 wt% B nanoflakes reduces the PHRR by 44.52%. These results strongly reveal that the hybridization strategy of B on BP can dramatically reduce thermal hazards on the basis of two components alone.

Smoke and toxic gases are key indicators to evaluate the effectiveness of this strategy. Interestingly, BP-B overcomes the shortcomings of BP, exhibiting a trend of a significant decrease in peak smoke release and peak CO release as the loadings increased. For 1.0 wt% BP-B loading, the peak smoke production (PSP), TSR, peak CO production (PCOP) and TCOP are separately reduced by 58.19%, 15.97%, 58.19% and 36.52%, accompanied by a significantly delayed time to PSP and PCOP of 28.22% and 45.07%, respectively. Moreover, the law of dramatic decrease for CO_2 change synchronizes with the HRR, which provides a natural inspiration for reducing the carbon emissions of fire. To reveal whether the hybridization of B to BP forms a structure inspired by the cell wall to capture and convert combustible fragments into char, Fig. 3e shows the real-time monitoring of the sample weight for nanocomposites. The final char increases progressively as BP-B loadings increased. For example, PC/BP-B0.5 achieves a char yield close to PC/BP1.0 (38.42 wt% vs. 39.35 wt%), in addition to PC/BP-B1.0 which increased the char yield by 79.39% to 45.69 wt%. These results demonstrate that the hybridization of B to BP significantly reverses the increasing tendency of BP (B) for non-thermal hazards via synergistic heat reduction. It also postpones and reduces the smoke and CO which is vital to allow trapped people to escape from fire, which may be caused by the outstanding effects of enhanced charring. To further observe the practical application of PC/BP-B, both LOI and UL-94 show progressively improved performance with increasing loadings. The BP-B loadings of 0.5 wt% and 1.0 wt% achieve a high LOI of 31.0% and 33.0%, and the corresponding UL-94 passes the V-0 rating. This is better than the 1.0 wt% loading of BP (30.5%, V-0 rating) and B (28.5%, V-1 rating) alone. This work further highlights the significant advantages of the application of B to modify PFRs.

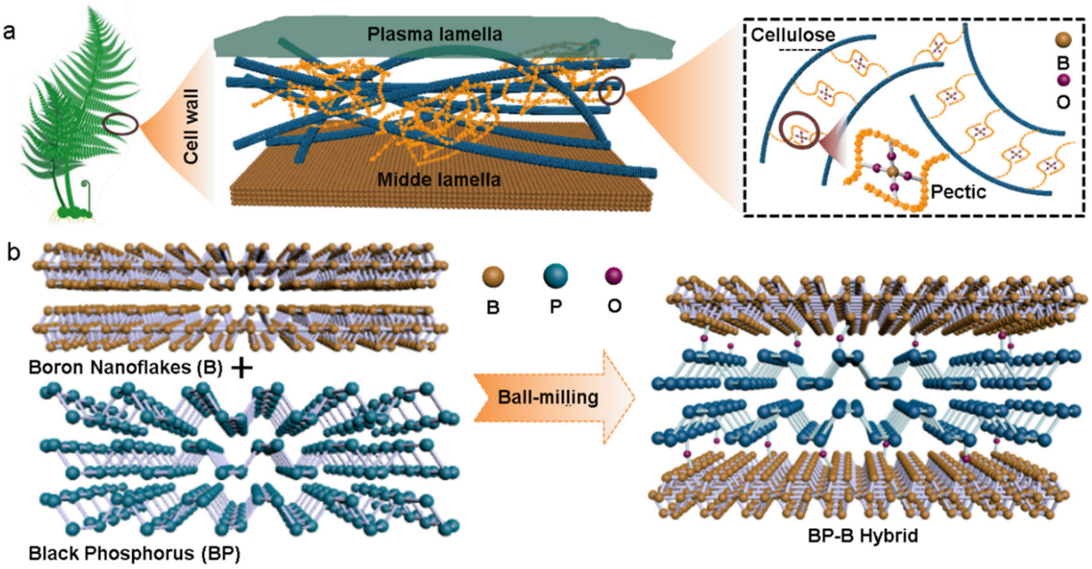

FIGURE 1. a) Schematic diagram of the self-assembled structure of cell wall for plants. b) Fabrication process of BP-B nanohybrid for bionic cell wall precursor.

This example attained a record performance in thermal stability and fire safety, which is attributed to the self-assembly of BP-B into a structure with BPO_4 serving as the node inspired by cell wall driven by the high-temperature oxidizing environment of combustion. The network is densely distributed with Lewis acid-base sites to capture organic free radicals or polymer fragments with low ionization potential generated by the pyrolysis of the matrix and fix them into char. In this process, we reveal the identifiable molecules of pyrolysis for PC (CO_2) and BP-based hybrid ($[P_4]^+$ et al.) and its mechanism for the first time, which inspires the design of PFRs. Specifically, we firstly use this strategy to design and demonstrate the regulation and fixation of phosphorus in the condensed phase, reducing phosphorus compounds released in a fire that leads to health and ecological risks. In total, this work systematically elucidates the mechanism of biomimetic-inspired nanocomposites to improve the thermal stability and fire safety of composites.

Acknowledgement: This work was financially supported by the National Natural Science Foundation of China (51991352, 51973203 and 22175167).

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PL5- WATER-BASED AND ENVIRONMENTALLY-BENIGN FLAME RETARDANT SURFACE TREATMENTS FOR POLYMERIC MATERIALS

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Main message: Flame retardants (FRs) mitigate the threat of fire from inherently flammable materials responsible for sustaining a high standard of living. Although bulk FRs have proven effective for many years, there is now increased interest in the use of surface treatments to localize flame retardant chemistry at the exterior of a material, where combustion occurs. Here we demonstrate very effective, environmentally-benign, water-based coatings that preserve desirable bulk properties and minimize the amount of FR needed. These coatings can be easily applied to wood, foam, and textiles via spray or dip coating.

Keywords: polyelectrolytes, renewable, self-extinguishing, nanocoatings, clays

Introduction

Our work in the fields of layer-by-layer (LbL) assembly and polyelectrolyte complexation has provided new water-based coating technologies for imparting effective flame retardancy to polymeric materials without using environmentally harmful chemistries [1-5]. These water-based coatings are very thin (typically < 500 nm thick) and conformal. The ability to place flame retardant chemistry exclusively at the surface prevents loss of beneficial bulk properties and reduces the amount of flame retardant required to achieve self-extinguishing behaviour.

Experimental

All water-based polyelectrolyte complex (PEC) and layer-by-layer assembled coatings are deposited by exposing a given substrate to the appropriate aqueous solutions containing the stated flame retardant ingredients. In general, a given foam or fabric is immersed in a given solution. Both procedures are very simple. Once dried in ambient conditions or in an oven, the samples are tested. The references provide more detail about these deposition and testing procedures [3-5].

Results and Discussion

A layer-by-layer (LbL) assembled 15 quadlayer (QL) coating, consisting of chitosan (CH), phytic acid (PA), and tannic acid (TA), was applied to a nylon-cotton (NYCO) blended textile [3]. Individually pairing TA or PA with CH is not self-extinguishing, but they work synergistically in the QL system to create an effective intumescent coating. This completely bio-sourced, water-based coating self-extinguishes in a vertical flame test (ASTM D6413) (Fig. 1(a)), with only 16.6% weight added to NYCO, yielding 91% post-burn residue and a 51% decrease in peak heat release rate.

Existing methods of depositing polyelectrolyte treatments on wood are extremely time consuming and difficult to scale. Here, a polyelectrolyte complex is formed by the photopolymerization of an anionic phosphate-containing methacrylate in solution with cationic polyethylenimine (Fig. 1(b)) [4]. The resulting polyelectrolyte complex is the first such photopolymerized flame retardant coating to be reported in the literature. This coating imparts greater mechanical strength to the plywood at high temperatures with just 1.6 wt% added. Additionally, the coating reduces the plywood's peak heat release rate in cone calorimetry testing and significantly decreases total smoke release. This scalable solution could enable more widespread adoption of polyelectrolyte-based technology and could make wood structures safer.

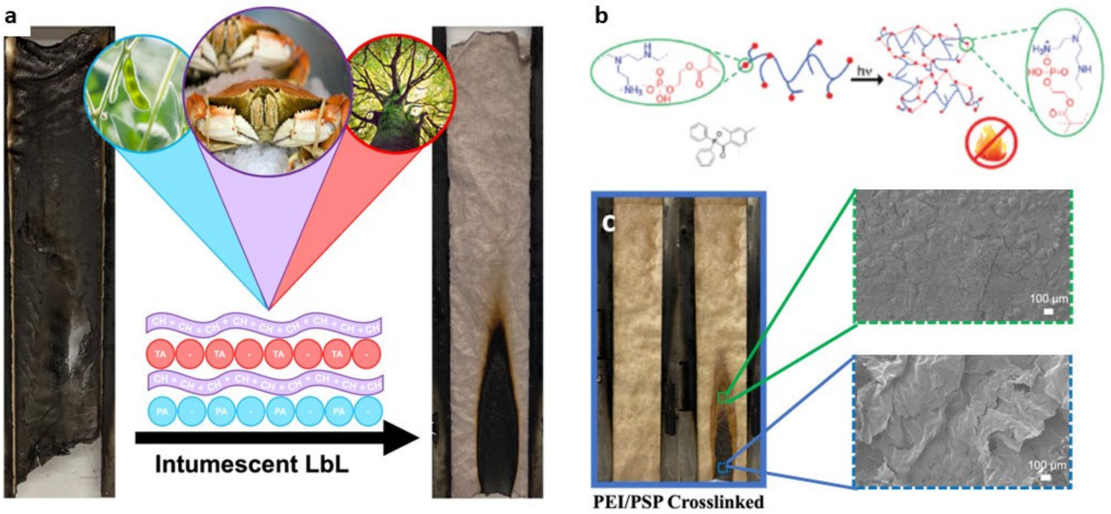

FIGURE 1. a) Images of NYCO, after vertical flame testing, without (left) and with a 15 QL coating of PA/CH/TA/CH [3]. b) Scheme showing polycation (PEI) and anionic monomer (HMP) utilized for UV-coating wood in this study [4]. A complex is formed when HMP is polymerized in the presence of UV light and a photoinitiator. c) Images before and after vertical flame testing of paper coated with a PEI/PSP coacervate [5]. Colored boxes in the photographs show where SEM images were taken.

Cellulosic paper (from wood fibers) is a highly flammable material that is used in corrugated carboard, packaging, printing, and construction. While there is significant work focused on depositing a flame retardant coating onto the individual wood pulp fibers, there are very few studies that apply flame retardant coatings to already-cast paper. In an effort to improve the flame retardant properties of paper, a polymer-dense coacervate composed of polyethylenimine (PEI) and poly(sodium phosphate) (PSP) was deposited in a single step and subsequently crosslinked with glutaraldehyde [5]. In a vertical flame test, the crosslinked PEI/PSP coacervate-coated paper achieves self-extinguishing behavior (Fig. 1(c)), and an average char length of 3.4 in, with only a 35% weight gain. Additionally, the crosslinked coating retains its flame retardant properties after water immersion and conditioning tests. This coacervate system is the first polymeric coating to be successfully deposited onto commercially available cellulosic paper for the purpose of flame retardancy.

Acknowledgement: N/A

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K6- FLAME RETARDANCY OF ENGINEERING POLYMERS USING IONIC LIQUIDS

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Main message: Ionic liquids used as synergists are likely to improve the flame retardancy of different engineering polymers through various mechanisms in the gas and condensed phase.

Keywords: Flame retardancy, ionic liquid, polyamide 11, thermoplastic acrylic resin

Introduction

Ionic liquids (ILs) have aroused the interest of the polymer community because they exhibit very specific features such as chemical stability, low volatility, thermal resistance and non-flammability. They can be used as solvent, plasticizer, lubricants or compatibilizer. In recent years, they have also retained attention for flame retardant (FR) applications due to the fact that, in addition to the before-mentioned properties, they can also bear heteroatoms with fireproofing activity, e.g. phosphorus, chlorine, nitrogen or sulphur.

ILs can be used as synergist of conventional FRs such as APP, melamine or nanoparticles [1,2], but also as unique FR additive [3]. Epoxy resins have been a prominent polymer for fireproofing applications, because ILs were initially used as crosslinkers in these thermosetting matrices [4]. Applications can also be found in thermoplastics such as polypropylene or polylactic acid which are particularly difficult to protect against fire [5]. This study aims at investigating the interest of ILs as flame retardant synergists into two engineering polymers, polyamide 11 and Elium thermoplastic resin.

Experimental

Polyamide 11 Rilsan®X1003 and Acrylic resin Elium® 188 O from Arkema were used as polymer matrices. Exolit® EP 150, OP1311 from Clariant, Melapur® MC25 from BASF and Luvogard® HF P70 from Lehvoss were used as conventional flame retardants. Different ammonium, imidazolium and phosphonium based ionic liquids were supplied by IoLiTec-Ionic Liquids Technologies GmbH and Solvionic. In the case of polyamide 11, matrix and additives were blended using an internal mixer at 250°C/60 rpm. Afterwards, specimens were obtained by injection molding. In the case of Elium, resin accelerator and additives were mixed in a beaker and then poured in a mould. After demoulding specimens were post-cured for 4h at 80°C. DSC, PCFC, cone calorimeter and UL94 tests were carried out to characterize the prepared samples.

Results and Discussion

In order to improve the fire behavior of polyamide 11, different phosphorous ionic liquids were associated with melamine cyanurate or OP1311 keeping a constant global FR content of 20 wt%. A first screening of fire performance was performed using PCFC. For all materials, a decrease of pHRR was observed at low IL content. Moreover, a decrease of the thermal stability was noted with increasing IL content, except for the phosphonium based IL where the thermal stability was almost unchanged. The most interesting formulations were submitted to the UL94 vertical flame test. Combination of melamine cyanurate with IL did not allowed to improve the fire rating of polyamide 11 compared to pure melamine cyanurate due to the presence of flaming droplets. On the opposite, the reaction to fire was enhanced when associating OP1311 with 1-ethyl-3-methylimidazolium dimethyl phosphate IL with the observation of non-flaming droplets that did not ignite cotton. In this latter case, it assumed that the presence of the phosphorous IL may induce two effects : a flame inhibition mechanism and a rheological change that favors the polymer flow.

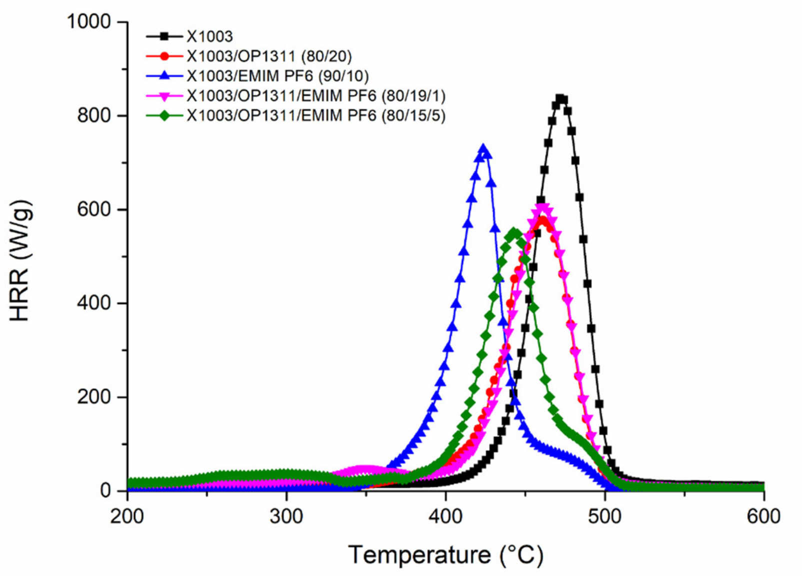

FIGURE 1. PCFC curves of polyamide 11 containing OP1311 and ILs

As regards the Elium acrylic resin, in a first stage, the influence of a phosphonium based IL was investigated as single additive. It was highlighted that the presence of IL affects both the glass transition and the burning behavior of Elium. In a second stage, different ILs were combined with Exolit EP 150 with the aim to obtain synergistic effects. Contrary to polyamide 11, it was evidenced by PCFC that the presence of IL tends to shift the main degradation step of Elium towards high temperature. Concerning the UL94 flame test, the best result was obtained once again with 1-ethyl-3-methylimidazolium dimethyl phosphate IL. The improvement of the fire behavior was mainly assigned to a gas phase mechanism.

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O11- PHOSPHATE-MODIFIED POLYURETHANE BINDER POLYMERS FOR TRANSPARENT, FIRE-RETARDANT WOOD COATINGS

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Main message: Fire-retardant wood coatings are often colored paints as high amounts of non-transparent fire-retardant agents are needed. To achieve transparency of the wood coatings and to obtain a high level of fire-retardancy, phosphorous polyols were chemically bonded to the polyurethane binder during the polymerization process. The resulting wood coatings passed the single-flame source test. Reaction-to-fire and other tests are currently under investigation and will be presented.

Keywords: wood coatings, phosphorous polyols, transparency, fire-retardancy

Introduction

Wood as building material is of high interest due to its sustainable origin. In addition, it provides a warm and homelike atmosphere if the natural appearance of wood is visible and not hidden by paints or plasters. However, fire-retardant agents often confer opacity or even non-transparency to the coating film. In addition, some salt-like agents are at risk to migrate to the surface and to wash or rub out over time [1]. In this study, phosphorous polyols were chemically bonded to the polyurethane binder to result in non-leachable, transparent, fire-retardant wood coatings.

Experimental

Polyurethane dispersions were prepared by a two-step process. At first, a polyester polyol based on phthalic anhydride, adipic acid, isosorbide and hexane diol was prepared by polycondensation, followed by a polyaddition reaction of the polyester polyol, a phosphorous polyol (Exolit® OP 550, provided by Clariant), dimethyl propionic acid and isophorone diisocyanate to obtain a polyurethane, which was dispersed in water and chain- extended by ethylene diamine. The amount of phosphorous polyol was varied between 5 wt-% and 15 wt-%.

The liquid dispersions were characterized to determine the influence of phosphorous polyol on viscosity, particle size and pH value. Coalescent agents were added to guarantee film formation at room temperature. Free-standing coating films were casted and mechanical properties were investigated via dynamic mechanical analysis. Transparency was measured by UV-vis spectroscopy. Thermo-analytical investigations included differential scanning calorimetry and thermo gravimetric analysis. The coatings were applied on spruce wood panels. To determine reaction-to-fire properties, the single-flame source test according to DIN EN 11 925-2 and cone calorimeter tests were performed.

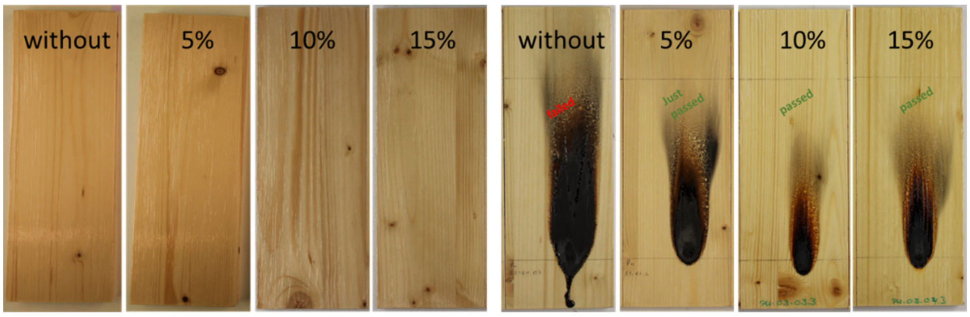
Results and Discussion

Four polyurethane dispersions with solid content of 35 wt-% were obtained. With increasing amount of phosphorous polyol, the viscosity increased and dispersions became more opaque. Casted coating binders formed colorless, transparent films. Table 1 shows the glass transition temperatures of binders measured by differential scanning calorimetry. The phosphorous polyol caused a softening effect and lowered the glass transition temperature from 17.8 °C to 8.8 °C.

TABLE 1. Glass transition temperatures of PU-based coatings measured by differential scanning calorimetry.

Sample	Glass transition temperature [°C]
reference	17.8
5 wt-% Exolit® OP 550	14.0
10 wt-% Exolit® OP 550	10.2
15 wt-% Exolit® OP 550	8.8

Figure 1 shows the results of the single-flame source test before and after flame treatment of coated spruce specimens. All samples passed the test with 15s flame treatment and self-extinguished when the flame was removed. When the flame treatment was extended to 30s, the reference coating without phosphorous polyol did not self-extinguish. Specimens with 5 wt-% phosphorous polyol self-extinguished, but just before the permitted time period of 30s expired. Specimens with 10 wt-% phosphorous polyol passed the test.



before flame treatment 30s flame treatment

FIGURE 1. Specimens with different amounts of phosphorous polyol before and after the single-flame source test (left: before, right: after 30s flame treatment).

Puyadena et al. investigated polyurethane/acrylate hybrid dispersions containing phosphorous monomers [2]. They were able to include 7.4% phosphorous polyol to the hybrid polymer system which resulted in transparent coating films. Using the cone calorimeter, they did not find a noticeable action of phosphorous as fire-retardant as the phosphorous content was too low and could not be increased using that synthesis strategy due to gelation. Compared to our study, the phosphorous content was similar to the specimens with 5 wt-% phosphorous polyol which just passed single flame test. The next step in our investigations will be to subject the transparent, fire-retarded wood coatings to cone calorimeter tests. Results will be presented at the conference.

Acknowledgement:
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O12- FLAME RETARDANT AND TRANSPARENT WOOD FOR BUILDING APPLICATION

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Main message: Transparent woods with promising flame retardance behavior and high transmittance were easily fabricated. Their micro-structures, fire safety properties, and optical properties were thoroughly characterized, which support their potential applications in fire-safety building as energy saving materials.

Keywords: Transparent wood, flame retardant, building

Introduction

Transparent wood (TW) is a wood-based material that can display high optical transmittance and clarity. It is made by selectively removing much of the lignin (i.e.; delignification, up to an ideal limiting concentration), then substituting it with a suitable, refractive index-matched polymer [1]. Recent studies indicate that TW has great potential to achieve energy-efficient buildings, replacing currently established materials, due to its high transmittance, excellent thermal insulation, low density and low cost [2,3]. We expect to incorporate TW into fire-safe building structures via flame retardant modification.

Experimental

Herein, we report on the formation of polycrystalline ZnO-coated TW. TW was fabricated by delignification, followed by infiltration of epoxy resin together with flame retardant thiol–ene polymer. Subsequently, a continuous, solid, pure-phase polycrystalline ZnO coating was obtained, via a silver-mediated seeding process using a sonochemical deposition method. This sonochemically coated transparent wood (CTW) was characterized in optical transmittance, mechanical property, and thermal insulation as well as high flame retardancy, to evaluate its potential application in fire-safe building structures.

Results and Discussion

This study investigated the coating of a transparent wood substrate. A natural balsa wood substrate (NW) was delignified (DW), then impregnated with an epoxy and thiol-ene polymer to form the transparent wood substrate (TW).

In Figure 1, highly aligned microchannels with the size of ~20-50 mm can be observed from the cross-sectional and top views of the original balsa NW. After delignification, the highly aligned microchannels are well preserved in the DW, while the cell walls become much thinner due to removal of lignin. For TW, the microchannels were fully filled with the epoxy resin and thiol-ene polymer without any gaps between epoxy and cell walls. Strong hydrogen bonding between the wood cellulose and epoxy / thiol-ene polymer is believed to stabilize the composite interfaces. Subsequently, a polycrystalline ZnO coating was applied to the TW, to fabricate the CTW.

The fire-retardant property of CTW was also characterized with vertical burning test and cone calorimeter test according to standard requirement, which support their potential applications in fire-safe building structures.

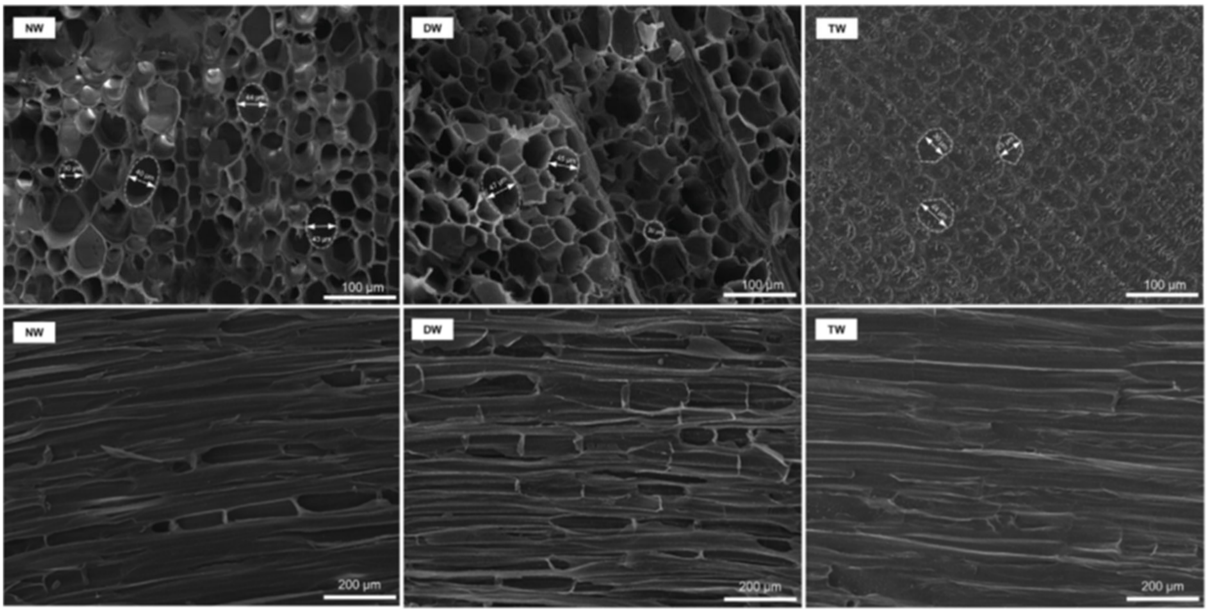

Figure 1. SEM images of NW, DW and TW from the top view and side view.

Acknowledgement: We thank the financial support from the Environment and Conservation Fund of Hong Kong (No. 2020-107).

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S6- Graphene oxide - modified Aramids as Early Fire Warning Sensors

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Main message: This work reports the construction of a graphene oxide (GO) based nanocoating on the surface of a functionalized fibrous aramid veil. On exposure to heat/fire, the GO reduces to graphene and becomes electrically conductive, triggering an alarm, for fire detection.

Keywords: Fire-warning, Graphene oxide, Nano-coatings, Sensors, Fire.

Introduction

A novel method for the accurate and prompt detection of a fire hazard is the use of graphene oxide (GO)-based fire sensors in polymers [1]. When a polymer containing GO is exposed to heat or fire, the decomposition of oxygen-containing functional groups such as carboxyl groups, epoxy groups, and hydroxyl groups of the polymers acts as a reducing agent for GO, transforming it into reduced graphene oxide (rGO). The electrical conductivity of GO is typically low, but rGO has a high electrical conductivity. By integrating electrodes within the polymer substrate (e.g., a textile structure), the change in electrical conductivity can be monitored for pre-ignition warning and in the case of fire, can trigger an alarm. Most of the previous work in this area has been on textiles, where GO, dispersed in a resin binder has been applied as a surface coating on the fabric. Because commonly used resin binders for textiles are flammable, emphasis has been on using additional flame retardants in the coating or using inherently flame retardant resins [2,3]. The majority of GO-based fire sensors have restricted detection ranges (a few cm). Khan (one of the authors of this abstract) et al. recently designed a large-scale sensor (>33 cm) by depositing GO, hexagonal boron nitride and poly(dimethylaminoethyl methacrylate) onto cotton woven fabric together with conductive ink that was parallel-patterned [4]. The designed sensor showed a short alarm time of <3 s in response to abnormal high temperature. The sensor coating being highly wash durable and self-extinguishing, has the potential to continue warning both during and after a fire. The pupose of this work is to build on this knowledge and develop systems which can be used in large strutures for pre-ignition warning. For this, an aramid fibrous veil has been chosen as a carrier for GO. Due to aramid's high thermal stability, this sensor system would not require additional flame retardant and the sensing feature is expected to be operational over an extended time.

Experimental

Preparation of fibrous GO- based composite fibrous veil:

GO was prepared from graphite powder by a modified Hummer's method [5].The prepared GO was dispersed in water through bath sonication for 60 min at 1 mg/mL concentration. Non-woven aramid fiber veil was immersed in the dispersion, soaked for 30 min, removed and then dried overnight. The process was repeated three times in order to increase GO adsorption. During the drying process, the water was evaporated and a tangled network of GO sheets was left behind on the substrate and was followed by UV treatment to partly reduce the GO on the surface in order to improve sensor sensitivity (Figure 1).

Preparation of aramid nano-fiber/GO composite film:

Aramid fiber (Kevlar 69) and KOH are dispersed in a solution of dimethyl sulfoxide (DMSO), which was magnetically stirred for 1 week at room temperature forming a dark red dispersion of aramid nanofibers. Another dispersion was prepared using GO and DMSO. The prepared aramid nanofiber dispersion was then added to the GO/DMSO dispersion, and it was stirred for 20 minutes. To protonate the aramid nanofibers, deionized water was gradually added to the mixture while stirring. At the end, suction filtration was used to form the film.

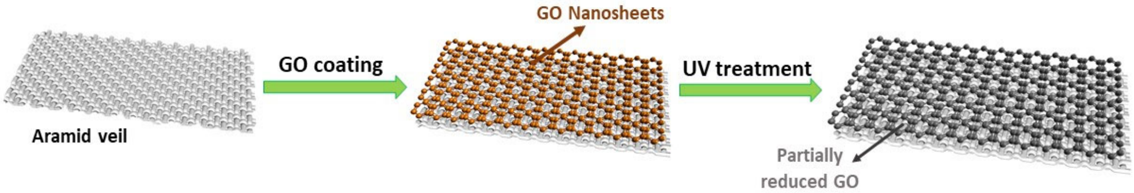

Figure 1. Schematic illustration of the fabrication procedure of GO-coated aramid veil.

Results and Discussion

Work is in progress in which prepared coating and film are being characterised by various analytical methods such as Fourier transform infrared spectrometry (FTIR), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Thermal stability will be tested by thermogravimetric analysis (TGA), micro combustion calorimetry (MCC), LOI, VFT and other burning tests. In order to characterise the sensing, the electrical conductivity of the composites will be measured before and after exposure to different heat fluxes for varying periods of time. A fire alarm system will also be developed using a simple electrical circuit as demonstrated in Figure 2. The ultimate aim of this work is to use these structures as surface layers on other polymeric substrates for early fire detection.

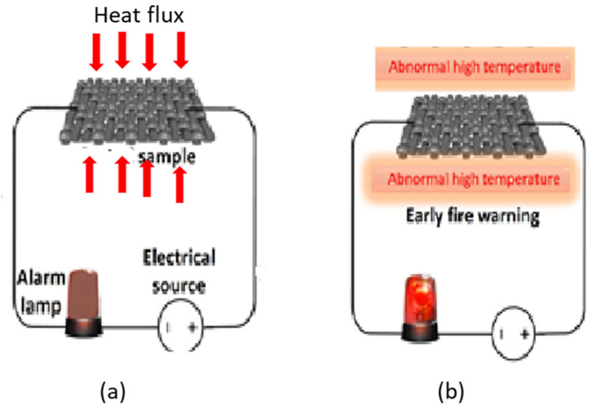

Figure 2. Construction of early fire warning sensors using GO-coated fabric aramid veil, (a) at normal temperature, (b) at high temperature

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PL6- MATERIALS IN EXTREME FIRE: DESIGN, EVALUATION AND CHARACTERIZATION

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Main message: Design of fire barrier for extreme condition including battery fire, hydrogen fire and fire in microgravity – Fire scenarios in extreme conditions at reduced scale.

Keywords: battery, hydrogen, microgravity, fire barrier, testing.

Introduction

There is not a commonly accepted definition of the concept of ‘extreme fire’. According to its common use the expression ‘extreme fire’ is a complex entity as it involves different realities and ways of looking. It contains at least three concepts [1]: (i) an idea of extension in the sense that ‘extreme fire behavior’ is very commonly associated to very large fires or fires that extend in large areas during extended periods of time; (ii) an idea of intensity in the sense that some properties of fire spread, namely its rate of spread or its rate of energy release acquire very large values; (iii) a third idea that is associated to ‘extreme fire behavior’ is related to rapid change in fire behavior conditions that is also linked to some degree of uncertainty in its prediction and danger. In this paper, we consider high heat flux fires (in 1G) and fire in microgravity (in 0G) as an extreme condition for fire-retarded material. Those fires fulfill well with the above definition of extreme fire. It is obvious for high heat flux fires but microgravity is still unconventional. In microgravity, radiation (net loss from the surface and gas phase) becomes comparatively more important than normal gravity, not because the radiative flux increases, but rather because of the absence of natural convection. It leads to unexpected behavior of the fire spread [2].

The paper aims at discussing the fire scenarios involving extreme fire and how to mimic them at the reduced scale with the appropriate online instrumentation. It considers: (i) fire of lithium-ion battery packs, (ii) hydrogen fire and (iii) fire behavior in microgravity. Fire protection to be developed are also investigated and commented.

Battery on fire

High energy density batteries, such as lithium-ion, provide an advantage in less mass and volume. Their high energy density provides a makeup of constituents with highly exothermic decay properties, and as a result fire and explosions can occur when they are abused or made with defects. In a package or in a closed container, the sudden battery failure (usually termed “runaway”) can rapidly produce a high release of energy, temperature and pressure in a container. This results in the entire battery pack being consumed in a fire or even exploding.

The prevention of thermal runaway (TR) in lithium-ion batteries is vital as the technology is pushed to its limit of power and energy delivery in applications such as electric vehicles, aircraft, grid-scale energy storage and aerial surveillance technology. The recommended SAE and ISO fire safety tests for lithium-ion batteries is simulated fuel fire. This scenario is considered in this paper using the description defined in GB T 31467.3 (1000° for 70s and then 1000°C or 800°C for 60s) with an instrumented bench-scale equipment.

Hydrogen fire

Hydrogen energy applications may require that systems be used at the large scale outside and even inside rooms or enclosures. The ignition of accidentally released hydrogen may result in a jet-fire.

Hydrogen release has shown to produce significantly more severe fire events than natural gas releases of the same mass flowrate. The higher exit velocities increase both the convective heat transfer and the erosive forces. Pure hydrogen releases give high convective heat fluxes, but the flame is less radiant. The erosive forces may be higher at short stand-off distances but will decrease more rapidly than in gaseous jet fires. To date, there is insufficient evidence to conclude whether passive fire protection (PFP) materials will respond differently, however there are numerous reasons for caution. Reduced scale bench equipped with IR instrumentation was developed to mimic hydrogen jet fire (heat fluxes as high as 500 kW/m² are involved). Different types of protection will be evaluated and presented in the talk. The associated mechanism will be also commented.

Fire in microgravity

Fire safety is a concern in space travel, particularly with the current plans of increasing the length of the manned space missions. The effect of microgravity on the fire behavior of polymers is a condition far away from that found on earth which is not very well understood. Flame spread is very much affected by external environmental conditions which may be very different in a spacecraft from on Earth, e.g. microgravity (absence of floatability forces), low-velocity flow, variable oxygen concentrations, and reduced pressures.

The motivation of this paper is to examine the fire retardancy of low density polyethylene (LDPE) using the concept of intumescence. The intumescent LDPE containing different systems were evaluated as thin cylindrical samples. All experiments at normal and micro-gravity were conducted on the Detection of *Ignition And Mitigation Onboard for Non-Damaged Spacecrafts* (DIAMONDS) rig [3]. Figure 1 shows that an intumescent behavior is observed in all conditions (1G and 0G). The shape and the expansion of the intumescent coating does not seem to be influenced by the gravity but the flame spread rate is higher in microgravity. This particular behavior will be fully commented in the talk.

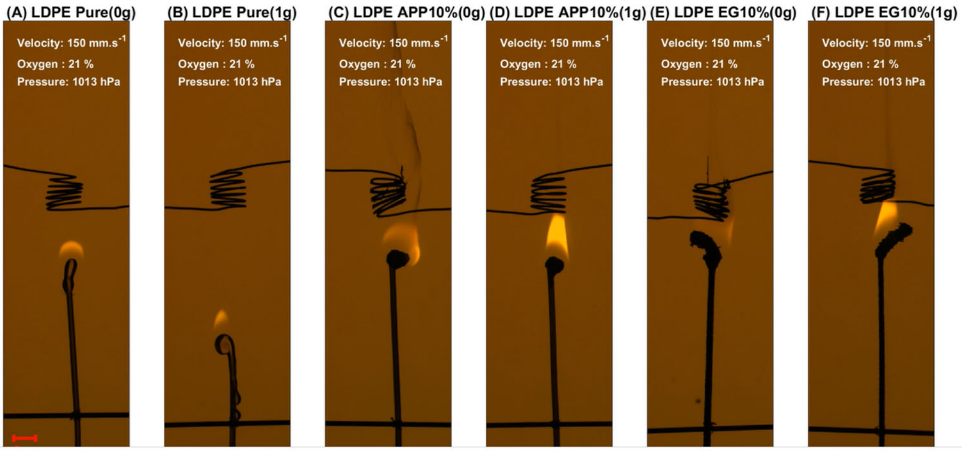

FIGURE 1. *Intumescent LDPE burning in the conditions of DIAMONS rig at normal and microgravity*

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K7- THERMAL ANALYSIS AND FLAMMABILITY

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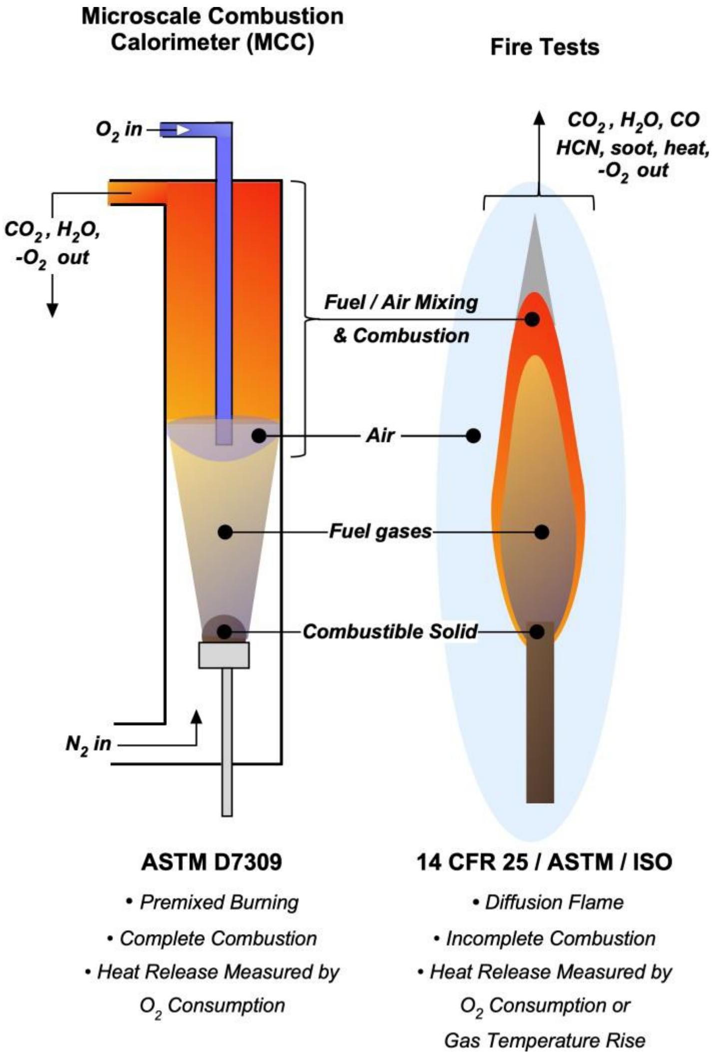
ABSTRACT

Flammability is the continuum level response of combustible solids to the thermal insult of fires or flames. Each molecule in a burning solid (test specimen) experiences a temperature history that can be simulated using a milligram sample in a thermal analyzer to study the rate and products of pyrolysis in the absence of heat and mass transfer limitations. The rate of pyrolysis is temperature-dependent via the Arrhenius form of the rate constant, $k = A\exp[-E/RT]$, where A is the frequency of molecular collisions resulting in volatile fuel species, and E is the energy barrier to that fuel generation process at temperature T, while R is the gas constant. These molecular-level kinetic parameters E and A are measured using thermal analysis, but depend as much on the test method as on the composition of the combustible solid. This ambiguity makes computational fluid dynamics (CFD) simulations of fire growth that rely on E and A uncertain.

From a flammability perspective, the products of thermal decomposition (pyrolysis) are important because the volatile species determine the amount of heat released by combustion and any solid residue is a barrier to heat and mass transfer at the burning surface. In this talk we discuss how thermal analysis in general, and pyrolysis-combustion flow calorimetry in particular, can be used to understand and predict the fire behavior of combustible solids (see figure).



O13- Effect of oxygen concentration on the fire behavior of Cross-Laminated Timber

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Main message: The effect of oxygen on the fire behavior of Cross-Laminated Timber (CLT) has never been studied and there is a lack of data on the gaseous emissions and the aerosols production of CLT in vitiated conditions. The reaction to fire of CLT is studied under several oxygen concentration (21, 18, 15 and 10% O_2) using a Controlled-Atmosphere Cone Calorimeter (CACC) at different heat fluxes. In addition to common Cone Calorimeter data, gas and aerosols production were investigated using a Fourier Transformed Infrared (FTIR) spectroscopy and an Electrical Low Pressure Impactor (ELPI). Decrease of oxygen concentration leads to incomplete or non-combustion which affects the gas and aerosols production that were fully analyzed.

Keywords: Cross-Laminated Timber, Controlled-Atmosphere Cone Calorimeter, oxygen concentration, gases, aerosols.

Introduction

Due to climate change, sustainable development is a major concern in all sectors of activity. Thus, recently, the construction industry has turned to the use of renewable and/or recycled building materials in order to develop energy-efficient buildings with a low carbon footprint. So, Cross-Laminated Timber (CLT) is widely used because of its structural properties, low weight and fast construction times. Like most organic materials, CLT can react under fire and lose its properties. In addition to the loss of structural properties, gases and aerosols emitted from fire reduce visibility and cause vision impairment, respiratory problems or death. In addition, under ventilated atmosphere increases the production of dangerous gases. Therefore, in order to ensure safety, CLT behavior under different fire scenario must be evaluated and understood.

The widely used standard cone calorimeter assesses the reaction to fire of materials under well-ventilated conditions but it does not enable to create reduced oxygen atmospheres. In the purpose of gases and aerosols evaluation under vitiated environment, a CACC was designed where a Fourier transformed Infrared Spectroscopy (FTIR) and an Electrical Low Pressure Impactor (ELPI) are coupled.

Experimental

The material used in this study is a commercial Cross-Laminated Timber (CLT) made from spruce. It is composed of two panels glued perpendicular to each other. The glue used is polyurethane based and it does not release formaldehyde. The sample dimensions are 100 x 100 x 40 mm^3. The specimens are conditioned at 23±2 °C and at a relative humidity of 50±5 % until the mass is constant, in order to reach a moisture of wood close to 11% as described in the standard EN 13238 [1].

Results and Discussion

The effect of the oxygen concentration (21, 18, 15 and 10 vol-% O_2) on the CLT was studied at two different heat fluxes, 50 and 20 kW/m², to simulate respectively well-ventilated fire and smoldering. The combustion is considered incomplete when the CO/CO_2 ratio is superior to 0.05 [3].

At 50kW/m², when the O_2 concentration is lower than 15 vol-% the sample does not ignite (Figure 1) and the decomposition rate is lowered. The peak of mass loss rate and times to ignition are not affected by oxygen depletion in flaming combustion. Moreover, the oxygen concentration does not affect the peaks of heat release rate values of flaming samples whereas it influences their steady state (Figure 1).

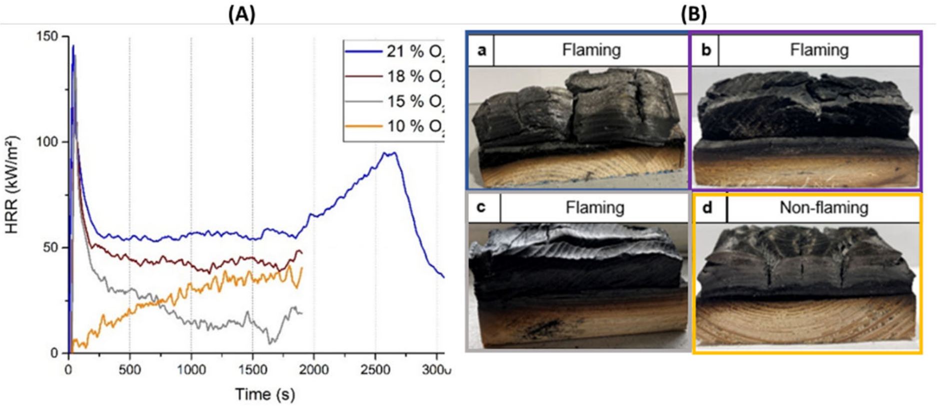

FIGURE 1. A) Effect of oxygen concentration on the HRR at 50kW/m², B) Sliced CLT after 32 min of test at 50 kW/m² at a. 21% O_2, b. 18% O_2, c. 15% O_2 and d. 10% O_2

Before ignition, the main compounds released are formaldehyde, methanol, formic acid, acetic acid and phenol compounds and after ignition, CO_2 and CO are mainly observed. For the non-flaming sample, additional gases such as acetaldehyde (C_2H_2O) and ethene (C_2H_4) are detected with a high production of CO and methane.

Regarding the aerosols, the flaming and non-flaming samples behave differently. At ignition, for the burning samples (21, 18 and 15 vol-% O_2), the distribution size is bimodal and centered on the modes 0.267 µm and 0.109 µm (Figure 2 (A)). This distribution changes during fire to a monomodal one centered on the mode 0.03 µm corresponding to a nucleation mode (Figure 2(B)). For the non-flaming specimen (10 vol-% O_2) the distribution is monomodal centered on the mode 0.03 µm all along the experiment.

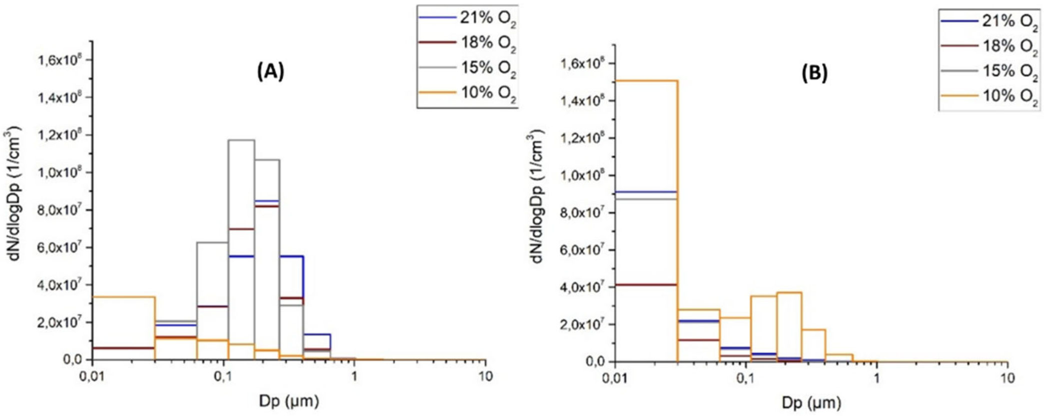

FIGURE 2. Distribution size of aerosols at 50 kW/m² at ignition (A) and at 1484s (B)

This approach is appropriate to examine the effect of the oxygen and the heat flux on the solid/gas phase phenomena occurring during thermal degradation of CLT. During the presentation, all the results obtained at 20 and 50 kw/m² under different oxygen concentration will be presented and fully discussed.

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O14- An analysis of the functional dependence of the rate of buoyancy-driven flame spread on a solid material to pyrolysis and combustion properties

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Main message: In this work, an extensive literature review is conducted to enable a numerical study that quantifies (a) the sensitivity of model-predicted fire growth rate to uncertainties in material thermophysical properties and (b) the functional dependence of fire growth rate in a full-scale, room corner fire scenario to these properties within their respective measured ranges. This work allows for the identification of the material properties that require future improvements in measurement and/or calibration accuracy and can help enable material development and product design by identifying some of the material properties that have the strongest impact on predicted fire growth rate.

Keywords: Flame Spread, Fire Modeling, Material Properties, Pyrolysis, Sensitivity Analysis

Introduction

In the early stages of a fire, upward, buoyancy-driven flame spread over combustible solids is frequently the dominant contributor to fire growth. Thus, an ability to accurately predict fire development is strongly linked to the accuracy of flame spread modeling, which requires knowledge of a wide range of material properties that serve as model inputs. In this study, the sensitivity of flame spread dynamics to variations in these properties was examined to determine which properties carry measurement uncertainties that translate into the largest errors in predicted flame spread behavior and to calculate the functional dependence of flame spread rate on these properties.

Experimental/Modeling

An extensive literature review was conducted to determine representative material properties of a well-balanced set of 26 materials including: ten non-charring synthetic polymers, ten charring synthetic polymers, and six wood-based products. This group represents the combustible polymeric solids most widely used in industrial, transportation, and construction applications [1,2]. Upward flame spread over this representative combustible solid was simulated in a vertical corner configuration (full-scale burning, 2.45 m tall samples) using two widely used computational tools – ThermaKin2Ds [3,4] and the Fire Dynamics Simulator (FDS) [5] – and predicted sensitivity of fire growth dynamics to variations in material properties was assessed. Simulations were repeated using increased and decreased material property values, which were varied, one at a time, both (a) to the upper and lower boundaries of the uncertainty quantification of each specific measurement and (b) across the full range of measured values (of 26 different materials) for each model input of interest.

Results and Discussion

Figure 1 shows time-resolved plots of heat release rate (HRR) calculated in ThermaKin2Ds and FDS simulations when material properties are each varied to within their respective uncertainty bounds. In this figure, the base case (i.e., all material properties defined as their average value) is plotted in black and select HRR profiles are highlighted to identify the cases showing the greatest sensitivity to variations in a given parameter value within its respective uncertainties. These parameters include (in order of highest sensitivity): reaction kinetics, $E_a/\ln(A)$ [red and magenta profiles]; virgin heat capacity, c_{virgin}, [blue and green profiles]; and heat of combustion, $H_{c,eff}$ [light blue and orange profiles].

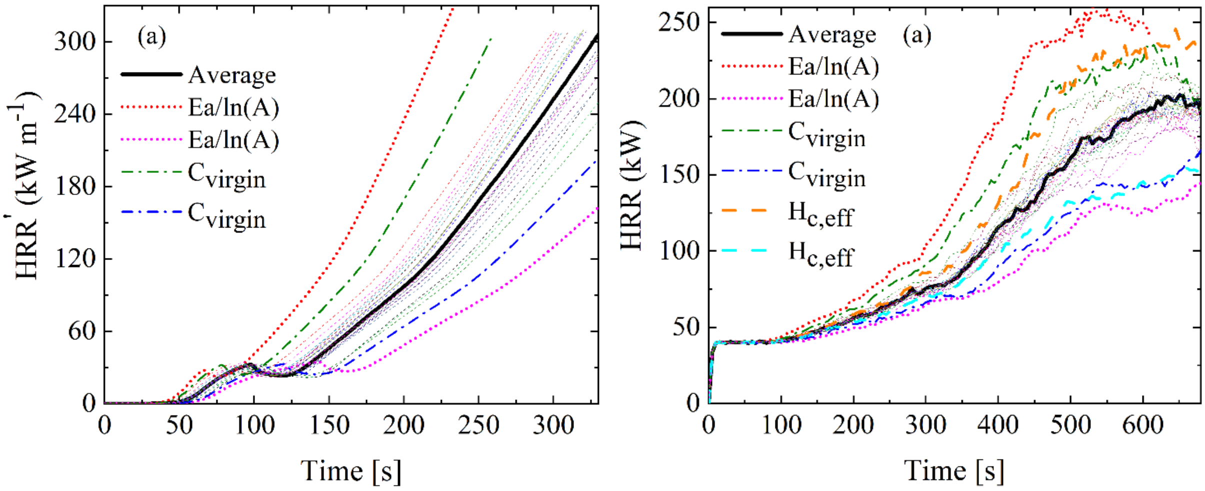

FIGURE 1. Time-resolved predictions of heat release rate in (a) ThermaKin2Ds and (b) FDS.

To deconvolute how much of the calculated change in model-predicted flame spread rate is attributed to the inherent sensitivity of model predictions to a given parameter (i.e., its functional dependence) versus the magnitude of variations in a property of interest, the following analysis was conducted. First, a condition number was calculated for each parameter to define the relative change in predicted fire growth rate given a relative change in a material property of interest (assessed around each material property's measured uncertainty). Next, relative changes in model-predicted flame spread rate were calculated across the full range of measured values for each model input of interest (defined based on the measured ranges for all 26 materials considered in this work). Flame spread rate was assumed to be dependent on each property as per the equation below.

$$\frac{\Delta\overline{V_p}}{\overline{V_p}_{avg}} = \prod\nolimits_{N_{properties}} \left(\frac{\Delta(property_i)}{property_i|_{avg}}\right)^{n_i}$$

Here $\overline{V_p}_{avg}$ is the flame spread calculated when all material properties are defined as their average values, $property_i|_{avg}$, and n_i is the functional dependence of $\overline{V_p}$ on each material property, *i*, of interest.

Acknowledgement:
This research was supported by the Opening Fund of State Key Laboratory of Coal Combustion (No. FSKLCCA2207), and the "CUG Scholar" Scientific Research Funds at China University of Geosciences (Wuhan) (Project No. 2020088).33

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K8- FROM FLAME RETARDANT POLYSTYRENE FOAMS TO INTRINSICALLY FLAME RETARDANT STYRENIC COPOLYMERS WITHOUT HALOGENS

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Main message:
A combination of organo-phosphorus flame retardants and organic disulfides proved to provide an efficient, completely halogen-free flame retardant solution for polystyrene foams [1] and impact-modified polystyrene (HIPS) [2]. Elucidation of the underlying flame retardant mechanisms enabled the design and synthesis of a novel set of intrinsically flame retardant styrenic copolymers without halogens in a flexible building-block approach using elemental sulfur and phosphorous (meth)acrylates as comonomers.

Keywords: Polystyrene foams, styrenic copolymers, halogen-free flame retardants, organo-phosphorus.

Introduction

Styrenic polymers are highly flammable materials with a strong demand for compatible, highly efficient, and preferably gas-phase active flame retardants. Recently, halogen-free flame retardant solutions on the basis of organic phosphates and phosphonates in combination with organic disulfides [1], sulfenamides [3], and oxyimides [4] have been described for use in polystyrene foams. Inspired by these findings, a series of phosphorus comonomers were synthesized for mass polymerization with styrene and sulfur, yielding styrenic terpolymers with good flame retardant properties.

Experimental

Synthesis of the comonomers was performed using standard techniques, while polymerization was undertaken in mass and in an inert gas atmosphere, without any solvents added.
All (co)polymers were either extruded and injection molded on a lab-scale, or foamed from polystyrene foils containing residual blowing agent using hot water vapor. The resulting test specimens (UL-94 V and DIN 4102 (B2)) were used to assess ignitibility and flame resistance. TGA as well as GPC, TGA-MS and EDX analyses were performed to elucidate the involved flame retardant mechanisms.

Results and Discussion

The flame retardant mechanism derived for a combination of organic phosphates and oligomeric organic disulfides in polystyrene foams, namely flame poisoning by thiyl or sulfur radicals in the gas phase, increased melt dripping, and barrier formation caused by phosphate formation on the surface of the foams, formed the basis for the synthesis of co-reactive (meth)acrylate phosphates and phosphonates, which were successfully copolymerized with styrene and elemental sulfur to form a novel set of color- and odorless, intrinsically flame retardant terpolymers with 1-5 wt.% P-comonomer and 0.5-1 wt.% S. Polymer properties like molecular weights, polydispersities, glass transition temperatures and decomposition temperatures (T_d) at 5% mass loss of selected products are given in Table 1.

The synthesized terpolymers were successfully processed with lab-scale extrusion and injection molding techniques, yielding a solid V-2 classification with short overall afterburning times and occasional burning melt dripping in the performed UL-94 flame tests (see Figure 1).

TABLE 1. Selected properties of the flame retardant styrenic terpolymers

Sample	M_n [kDa]	M_w [kDa]	Đ	T_g [°C]	T_d (5%) [°C]
CP-1	14.7	47.8	3.3	101.9	358
CP-2	32.0	62.0	1.9	90.3	405
CP-3	13.7	64.5	4.7	96.8	334
CP-4	12.1	51.0	4.2	93.5	325

Noticable are the high polydispersities combined with rather high thermal stabilities at acceptable T_gs.

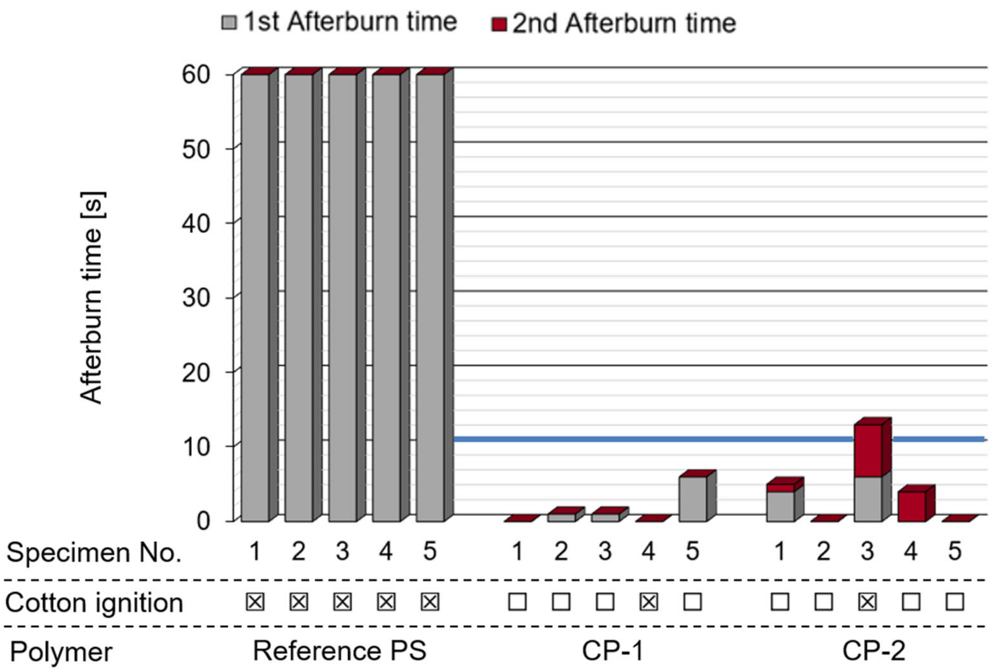

FIGURE 1. UL-94 V (1.6 mm) test results of copolymers CP-1 and CP-2 in comparison with non-flame retardant reference polystyrene.

The pleasingly short burning times give reason to hope for further optimization in terms of burning dripping. Furthermore, the clarification of the polymer-intrinsic flame retardant mechanism remains an exciting task.

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O15- Intrinsically flame-retardant long-chain aliphatic polyamide with high mechanical property

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Main message:
Long-chain polyamides bridge the gap between conventional polyolefins and short-chain polycondensates, but exhibit high flammability. In this work, we designed a novel reactive flame-retardant monomer PR, which brings high flame retardancy to typical long-chain polyamide PA 1010 without destroying its great mechanical property.

Keywords: Flame retardancy, Mechanical property, Long-Chain aliphatic polyamide

Introduction

Long-chain aliphatic polyamides are easily obtained from bio-based raw materials like plant oils, thus show potential in developing bio-based polymeric materials [1-3]. However, these polyamides are highly flammable, which severely restricted their applications. In this work, we designed and synthesized a novel nitrogen-based flame-retardant monomer PR, and copolymerized it into the molecular chain of typical long-chain aliphatic polyamide PA 1010. The obtained copolymer PA 1010-*co*-PR successfully passed the UL-94 V-0 rating, and achieved a high LOI value of 32.6%. At the same time, the mechanical property of PA 1010-*co*-PR was largely maintained. This work provided a novel strategy for improving the overall performance of long-chain aliphatic polyamide.

Experimental

PA 1010-*co*-PR was synthesized through conventional melt polymerization using sebacic acid, decamethylene diamine, and PR. The mixture was first heated at 240 °C with stirring at 120 rpm for 3 h, then the pressure of the mixture was gradually reduced by a vacuum pump, and the micromolecules and water generated during polymerization were removed. After 3 h reaction under high vacuum, the final product PA 1010-*co*-PR was obtained. The UL-94 vertical burning behavior and the limiting oxygen index (LOI) values of the samples were carried out according to the ASTM D3801-20a and ASTM D2863-19 standards.

Results and Discussion

The flame retardancy of PA 1010-*co*-PR was evaluated by the UL-94 vertical burning test and the limiting oxygen index (LOI) test. As shown in Figure 1, pure PA 1010 is easily ignited during the UL-94 test, and burned continuously while generating large amounts of melt drips, thus failed to pass the test. With the incorporation of PR, the burning time of PA 1010-*co*-PR significantly shorten, and the melt dripping phenomenon was inhibited. At a PR content of 6 mol%, PA 1010-*co*-PR_6 self-extinguished immediately after both ignitions, and successfully achieved a UL-94 V-0 rating. Pure PA 1010 possessed a low LOI of merely 21.0%, indicating its high ignitability and poor self-extinguishing performance. With the incorporation of PR, the LOI value of PA 1010-*co*-PR gradually increased with the increase of PR content. At a PR content of 2 mol%, PA 1010-*co*-PR_2 showed a largely increased LOI value of 25.0%, which further increased to 28.0% by increasing the PR content to 4 mol%. Surprisingly, PA 1010-*co*-PR_6 exhibited high LOI value of 32.6%, which was much higher than most reported literatures. The TG-IR and Py-GC/MS results revealed that PR mainly played free-radical-capturing effect, representing a typical gas-phase flame-retardant mechanism.

As proved by the DSC results, the rigid PR structure largely increased the glass transition temperature (T_g) of PA 1010-*co*-PR, while at the same time the melt-crystallization performance was largely maintained. Furthermore, PA 1010-*co*-PR exhibited high mechanical property, for which the tensile strength was basically unchanged with PR content of 2 and 4 mol%.

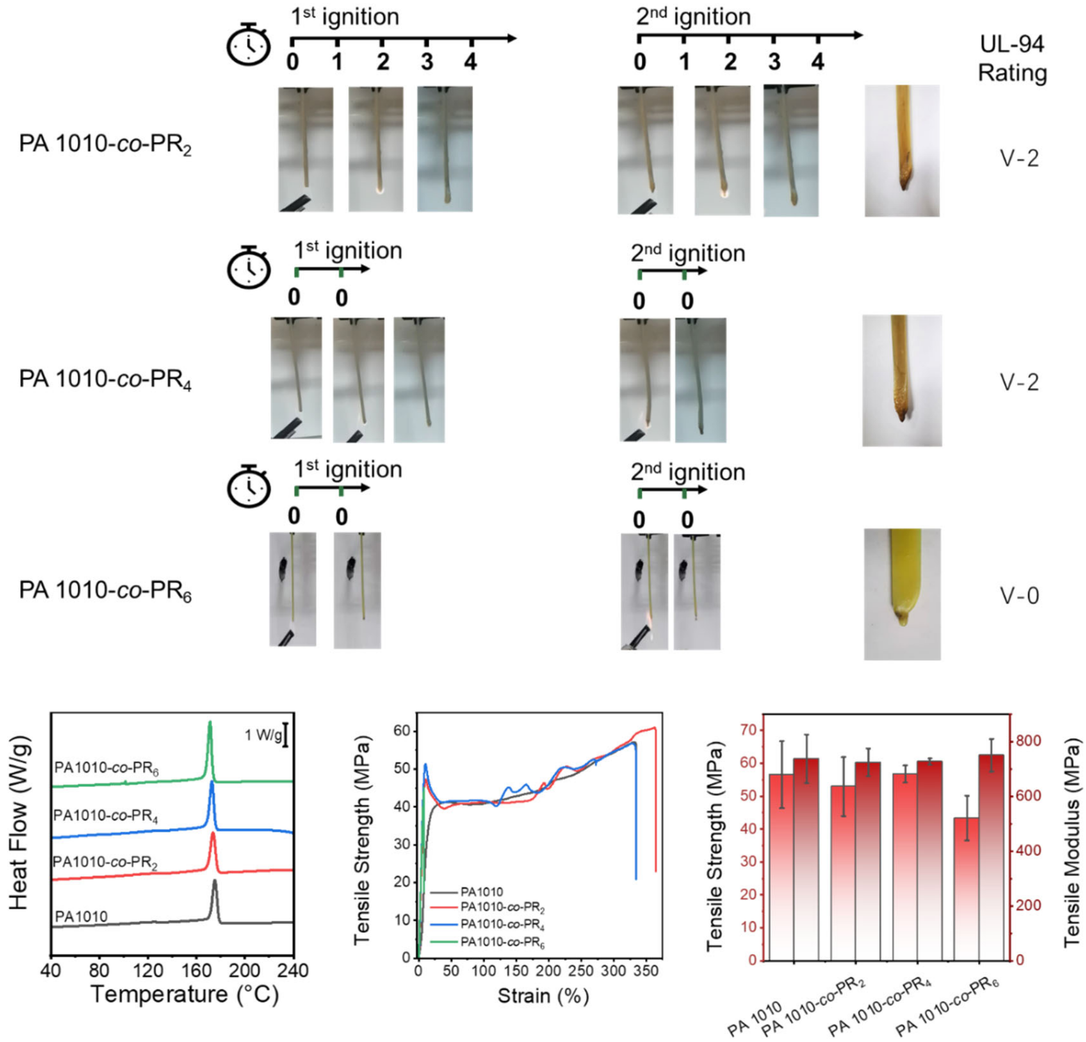

FIGURE 1. (a) Combustion process during UL-94 vertical burning test, (b) 1st cooling curves obtained from DSC test, (c) stress-strain curves, and (d) tensile strength and modulus of pure PA 1010 and PA 1010-*co*-PR.

Acknowledgement: This work was supported by the National Natural Science Foundation of China (52003167).

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S7- CARBON NANOHORNS AS A NOVEL SYNERGIST TO ACHIEVE EFFICIENT FLAME RETARDANT COTTON FABRIC – A CASE STUDY

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Main message: In this work, a novel fire-resistant cotton fabric by combining SWCNHs and ammonium polyphosphate was proposed. The effects of different concentrations of SWCNHs on the flame retardancy of fabric were investigated, and the mechanism of flame retardancy for SWCNHs was also discussed in detail. The unique combination of SWCNHs and ammonium polyphosphate endowed cotton fabric with prominent fire resistance. As we know, this novel, halogen-free carbon nano-synergist was proposed for the first time.

Keywords: SWCNHs, Synergistic effect, Flame retardancy, Fire behaviors Cotton fabric.

Introduction

The development of environmentally friendly flame retardants that can achieve high efficiency for textiles at low addition levels is of great significance to human life. Halogen flame retardants have long dominated in flame retardant applications. However, there are increasing calls to ban its use because of the threat they pose to human health and the environment. Herein, this work investigated the potential of a novel SWCNHs-based nanocoating for the flame retardancy of cotton fabrics.

Experimental

First, the cotton fabrics were mercerized with 10 wt% NaOH, then washed several times with distilled water, and finally placed in an oven at 80 ℃ for 2 h before use. In order to obtain 1 wt% of APP solution, 1 g of APP was added to 100 mL of deionized water and stirred evenly. After stirring, the pH value of the APP solution was adjusted to 10 with NaOH solution. Then SWCNHs (typical 'dahlia-like' CNHs with a diameter range of 30-80 nm) was added to the APP solution with 0.05 wt%, 0.1 wt%, 0.15 wt%, 0.2 wt% and 0.25 wt% concentration, respectively and sonicated for 15 min. 4 mL of the solution was sprayed on the cotton fabric, then the fabric was dried at 80 ℃ for 20 min.

Results and Discussion

The cone calorimeter (CONE) and TG technique were used to study the effect of CNHs on the combustion heat release, combustion properties of cotton fabric, and to understand the synergistic mechanism of CNHs during thermal degradation. The study showed that the addition of 0.15wt% CNHs further reduced the heat release rate (HRR) and total smoke production (TSP) (Figure 1(a, b)); To analyze the flame retardancy of Cotton, Cotton-APP, Cotton-SWCNHs, and Cotton-APP/SWCNHs (0.15), the vertical flammability and LOI tests were conducted. As presented in Figure 1(c, d), Cotton suggested high flammability with a LOI of 17.5 ± 0.5%, and the after-flame time and after-grow time of cotton fabric were 14 s and 17 s, respectively. Additionally, there was almost no residue observed after burning. In contrast, the flame retardancy of Cotton-APP and Cotton-APP/SWCNHs (0.15) were distinctly improved with both of them reaching UL94 V-0 level and self-extinguishing. Besides, their damage length dropped to 84 mm for Cotton-APP and 65 mm for Cotton-APP/SWCNHs (0.15) from 300 mm for Cotton, maintaining their original form except for partial carbonization. Moreover, the LOI values of Cotton-APP and Cotton-APP/SWCNHs (0.15) increased to 25 ± 0.7% and 27.5 ± 0.2%, respectively, increment by 1.6 times. The results demonstrated that the addition of CNHs could enhance the flame retardancy of cotton fabric.

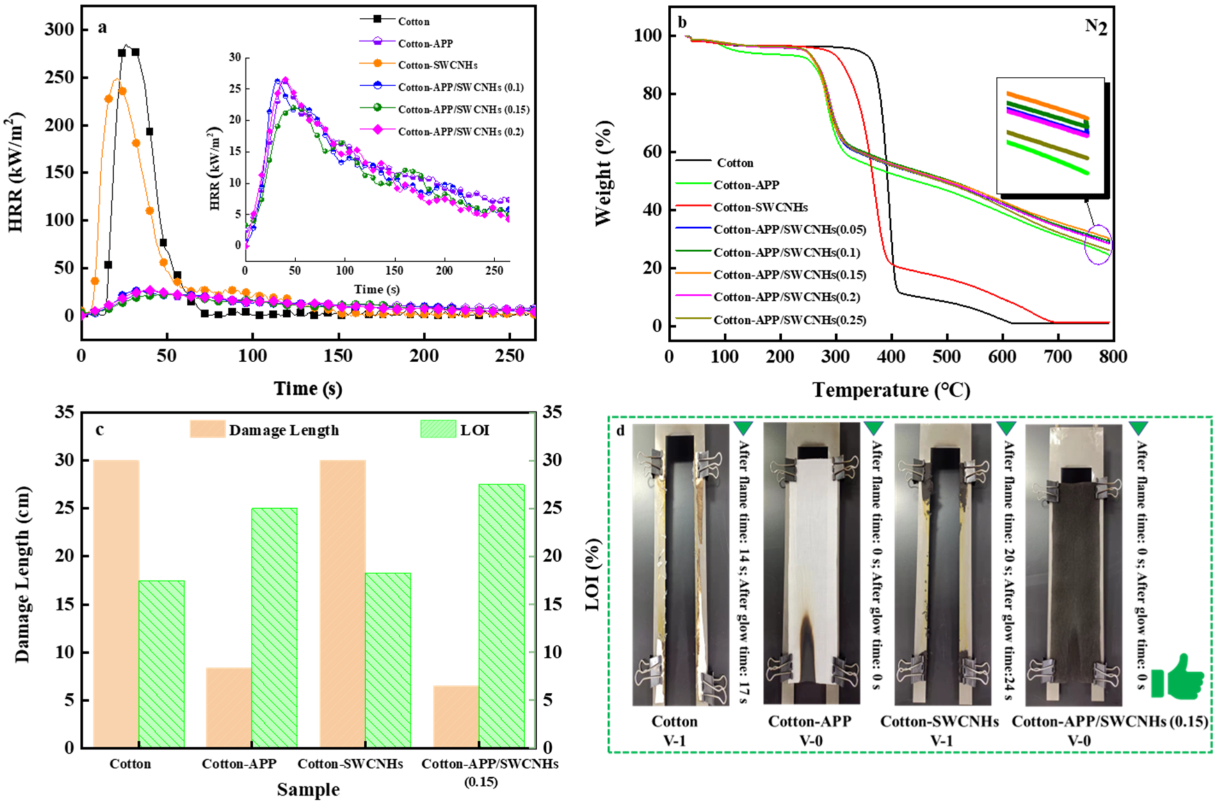

FIGURE 1. HRR (a) and TG (b) curves of Cotton, Cotton-APP, Cotton-SWCNHs, and Cotton-APP/SWCNHs (0.1-0.2); Flammability behavior and durability of Cotton, Cotton-APP, Cotton-SWCNHs, and Cotton-APP/SWCNHs (0.15). LOI values and damage length in the vertical burning test (c); Data of vertical burning test (d).

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K9- Synthesis and Application of Flame Retardant Organophosphine Compounds

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Main message: The flame retardant efficiency of flame retardants in polymers was influenced by exchanging the P-O bonds with P-C bonds. In our research, different organophosphine flame retardant oligomers were synthesized for unsaturated polyester (UPR), epoxy (EP), polyurethane (PU) and other polymer materials, effectively improving the flame retardancy of the polymer. Compared with the flame retardant with higher phosphorus oxidation state, the difference of flame retardancy and mechanism was analyzed.

Keywords: Flame retardant, Organophosphine compounds, Polymers, Properties, Mechanism.

Introduction

Because of their flammability, polymer materials are very easy to cause fire accidents, resulting in loss of life and property [1]. At the same time, as polymer materials appear in more application scenarios, higher requirements are put forward for flame retardants [2,3], such as efficiency, environmental friendliness, etc. Compared with phosphorus flame retardants with higher oxidation state such as phosphates, organophosphine compounds have higher phosphorus contents and higher activity in vapor phase [4,5].

Experimental

The linear and hyperbranched oligomer flame retardants were synthesized based on phosphorus containing monomers with different oxidation states. The effects of the structural differences of flame retardants on the flame retardancy and mechanism of UPR, EP and PU were systematically analyzed.

Results and Discussion

Dozens of oligomeric flame retardants were synthesized for flame retardant modification of UPR (FIGURE 1). Compared with flame retardants with highest +5 oxidation state (PO-S, POEG), organophosphine flame retardants (PCH_3-S, PB-S, PBEG) have higher flame retardant efficiency, and 15 wt% of PCH_3-S or PBEG make UPR reach UL-94 V-0. In contrast, although the composites with 20 wt% of PO-S or POEG had higher phosphorus contents, their UL-94 levels were still lower than the former. Therefore, compared with the highest oxidation state of phosphorus structures, the organophosphine oligomers were more suitable for improving the flame retardancy of UPR. The analysis of flame retardant mechanism showed that the flame retardancy of organophosphine oligomers was mainly in gaseous phase, supplemented by condensed mechanism.

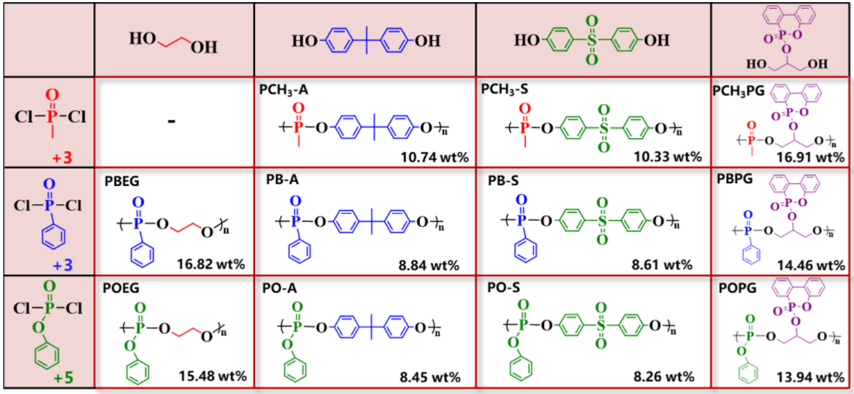
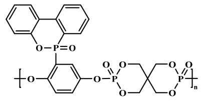
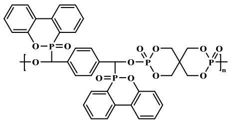
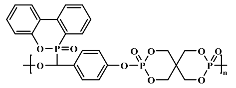


FIGURE 1. Monomer selection and flame retardant structure of flame retardant oligomers for UPR

Three poly(DOPO substituted phenyl dimethanol pentaerythritol diphosphonates) organophosphine compounds (PFR1, PFR2 and PDPDP) were prepared from the polycondensation of DOPO-based derivatives with pentaerythritol diphosphonate dichloride (SPDPC), which were applied for EP. Among them, PFR2 showed the highest thermal stability and flame retardant efficiency (TABLE 1). The $T_{5\%}$ of EP composites with 10 wt% of PFR2 was up to 311 ^{o}C. The LOI values increased from 21.5% for pure EP to 36.0 % and UL-94 V-0 materials were obtained with the 15 wt% of PFR2. In addition, the peak heat release rate (PHRR) was obviously reduced by 60.04%.

TABLE 1. Flame retardant structure of flame retardant oligomers for EP and their properties

Sample		$T_{5\%}$	UL-94	LOI	PHRR
EP/PFR1		291 (10 wt%)	-	30.2 (10 wt%)	-
EP/PFR2		311 (10 wt%)	V0 (15 wt%)	33 (10 wt%)	PHRR ↓ 60.04% (15 wt%)
EP/PDPDP		305 (10 wt%)	V0 (15 wt%)	31.5 (10 wt%)	PHRR ↓ 54.60% (15 wt%)

Additionally, hyperbranched organophosphine oligomers were used for the highly efficient flame retardant modification of PU. A novel organophosphine oligomer (POCHP) was synthesized from the polycondensation of phthalic anhydride and trihydroxymethylphosphine oxide (THPO) followed by the ring-opening reaction of the polycondensate and 1,2-epoxypropane. Then POCHP and/or expandable graphite (EG) were incorporated into rigid polyurethane foam (RPUF). A 12.8% improvement of compressive strength and slightly decreased density and thermal conductivity are achieved. And it reaches a LOI of 30.0% and UL-94 V-0 rating. The PHRR, THR and TSP of ERPUF50 are reduced by 71.1%, 52.2% and 71.1% via bi-phase flame retardant mechanisms.

Acknowledgement: The research was financially supported by the National Natural Science Foundation of China (No. 51991352, No. 51973203 and No. 51874266).

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O16- TOWARDS SIMULTANEOUS CHARACTERIZATION OF FLAMMABILITY AND FIRE TOXICITY OF SOLID FUELS BURNING AT CONTROLLED EQUIVALENCE RATIOS

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Main message: Past research has shown that heat release rates and yields of toxic products of combustion (including, but not limited to carbon monoxide, acid gases, solid particulate matter) are affected by the ventilation conditions of a fire. These conditions can be characterized by the global equivalence ratio, ϕ, defined as the ratio of the actual fuel/air ratio during combustion to the fuel/air ratio for a stoichiometric mixture. Real fires in enclosures typically transition from well-ventilated ($\phi<1$) during early stages to underventilated ($\phi>1$) at later stages and post-flashover. Bench scale tests for toxic yields, such as the Steady State Tube Furnace allow for the control of the equivalence ratio, enabling the measurement of toxic product yields for various ventilation conditions, but provide no flammability data. On the other hand, common flammability bench scale tests such as the cone calorimeter provide key flammability data, but only under well-ventilated conditions. An existing bench scale test with the potential to provide both flammability and toxicity data, including the possibility of controlled ventilation, is the Fire Propagation Apparatus (FPA). This work presents significant modifications to the FPA in order to simultaneously measure flammability parameters (heat release rate, total heat release, time to ignition) as well as time-resolved and integral yields of key toxic species (solid particulate, CO, CO_2, HCN, HCl, HBr, among others) at a prescribed value of ϕ.

Keywords: Flammability, Toxicity, Calorimetry, Diagnostics

Introduction

Full-scale and large-scale fire tests have shown that toxic product yields are highly dependent upon the combustion conditions. Fire stages and types can be characterized in terms of the global equivalence ratio, ϕ, where $\phi<1$ represents well-ventilated conditions, while $\phi>1$ represents underventilated conditions [1]. A representative enclosure fire will typically start with well-ventilated conditions and eventually transition to under-ventilated conditions. Heat flux to the solid fuels in the enclosure is also expected to vary as a function of time due to fire growth. Due to these complexities, most bench scale tests can only address one part of the problem, at a reduced set of conditions. Cone calorimetry [2], for example, can provide key flammability parameters (heat release rate, total heat release, time to ignition), at a constant incident radiant heat flux (which can be varied from one test to another, but not as a function of time) and only under well-ventilated conditions. Cone calorimeters can only provide limited fire toxicity data (CO yields, indirect solid particulate measurements via laser extinction methods). A Steady State Tube Furnace, on the other hand, can be run over a wide range of ventilation conditions (including underventilated and well-ventilated), but is also typically run at a set furnace temperature, and can only provide yields of toxic species with no flammability data [3].

The Fire Propagation Apparatus (FPA) [4] is an alternative method to cone calorimetry, with the advantage of providing user-defined ventilation conditions as well as incident heat flux. Both ventilation and heat flux can be set over wide ranges and can even be time-dependent. Past research [5] has shown that FPA data correlates well with large scale tests, at least for yields of CO. Despite these advantages, a standard FPA is not instrumented adequately for measuring additional toxic species such as acid gases (HCN, HCl, HBr) and solid particulate is measured via laser extinction, which is known to be challenging due to significant signal noise, and translating this data to actual yields can lead to large uncertainties. This works aims at augmenting the capabilities of the FPA by introducing time resolved measurement of toxic acid gas species (HCN, HCl, HBr) via electrochemical sensors, and replacing solid particulate laser extinction measurements by time-resolved light scattering measurements coupled with gravimetric measurements, thus providing a more direct method for obtaining yields of solid particulate. This modified FPA is designed to provide simultaneous flammability and fire toxicity data over a wide range of ventilation and incident heat flux conditions, including user-defined, time-varying conditions.

Experimental

The standard FPA design has been modified by introducing a second gas sampling line dedicated to acid gas and solid particulate measurements. The gas is sampled from the FPA duct and split into 3 parallel lines transported over a short (< 1 m) line, each one connected directly to the corresponding sensor. One line is dedicated to HCN measurements (Dräger Polytron 7000), another line is dedicated to other acid gases (Dräger Polytron 7000, user selects between HBr, HCl or other species by replacing the sensor as needed), and the third line is directed to a laser scattering dust characterization device (TSI DustTrak II), recalibrated with simultaneous gravimetric measurements to provide time-resolved solid particulate mass concentrations. A schematic of this augmented gas sampling and sensing line is shown in Figure 1-a). Data from these sensors, along with standard O_2, CO, CO_2 measurements from a separate gas analyzer (California Analytical Instruments ZPA) as well as an unburned hydrocarbon sensor (Edinburg Sensors Gascard), in conjunction with a flowrate sensor in the duct (Armstrong International Veris Verabar) and gas temperatures in the duct measured with K-type thermocouples (Omega), can be used to reconstruct the mass concentration of each species of interest in the duct as a function of time, thus providing the time-resolved mass rate of production of species and consumption of O_2. These data, in turn, can be used to:

1. Obtain heat release measurements via Oxygen Consumption or Carbon Dioxide Generation calorimetry.
2. Calculate the instantaneous and total CO/CO2 ratio.
3. Integrate all other species mass rates of production to determine the total yields for each species (normalized by either initial sample mass or volatilized mass).

The combination of standard and augmented sampling lines can thus produce simultaneous flammability and toxicity measurements from a single sample, and the ventilation and incident heat flux can be chosen from a wide range, including time-dependent values for both ventilation and heat flux.

Results and Discussion

Preliminary tests on poly(methyl methacrylate) (PMMA) samples have shown that the system produces heat release rate measurements (Figure 1-b) consistent in accuracy with those reported in the literature, while the solid particulate analyzer provides nearly noise free, time-resolved measurements of soot concentration, even for low sooting fuels such as PMMA (Figure 1-c). Additional tests are underway to finalize the calibration of the solid particulate measurements in order to provide accurate quantitative mass concentration data for the solid products. Once this calibration is finalized, the apparatus will be used to test materials with/without flame retardants in order to obtain measurements of acid gas species in addition to the aforementioned standard measurements. Additionally, tests will be performed with time-resolved control of the mass flow of oxidizer in order to keep a constant ratio with respect to the mass flow of fuel, thus achieving conditions where the entire combustion of the sample occurs under a constant, controlled equivalence ratio, ϕ.

Acknowledgement: The authors would like to thank FM Global (Dr. Yi Wang, Dr. Dong Zeng, Dr. Gaurav Agarwal) for providing the seed funding and technical support for construction of the standard FPA. The authors would also like to thank Dr. Richard Lyon at the FAA Technical Center for his support

towards the additional fire toxicity measurements. The modifications to the FPA are supported by FAA Grant Number 692M152140009.

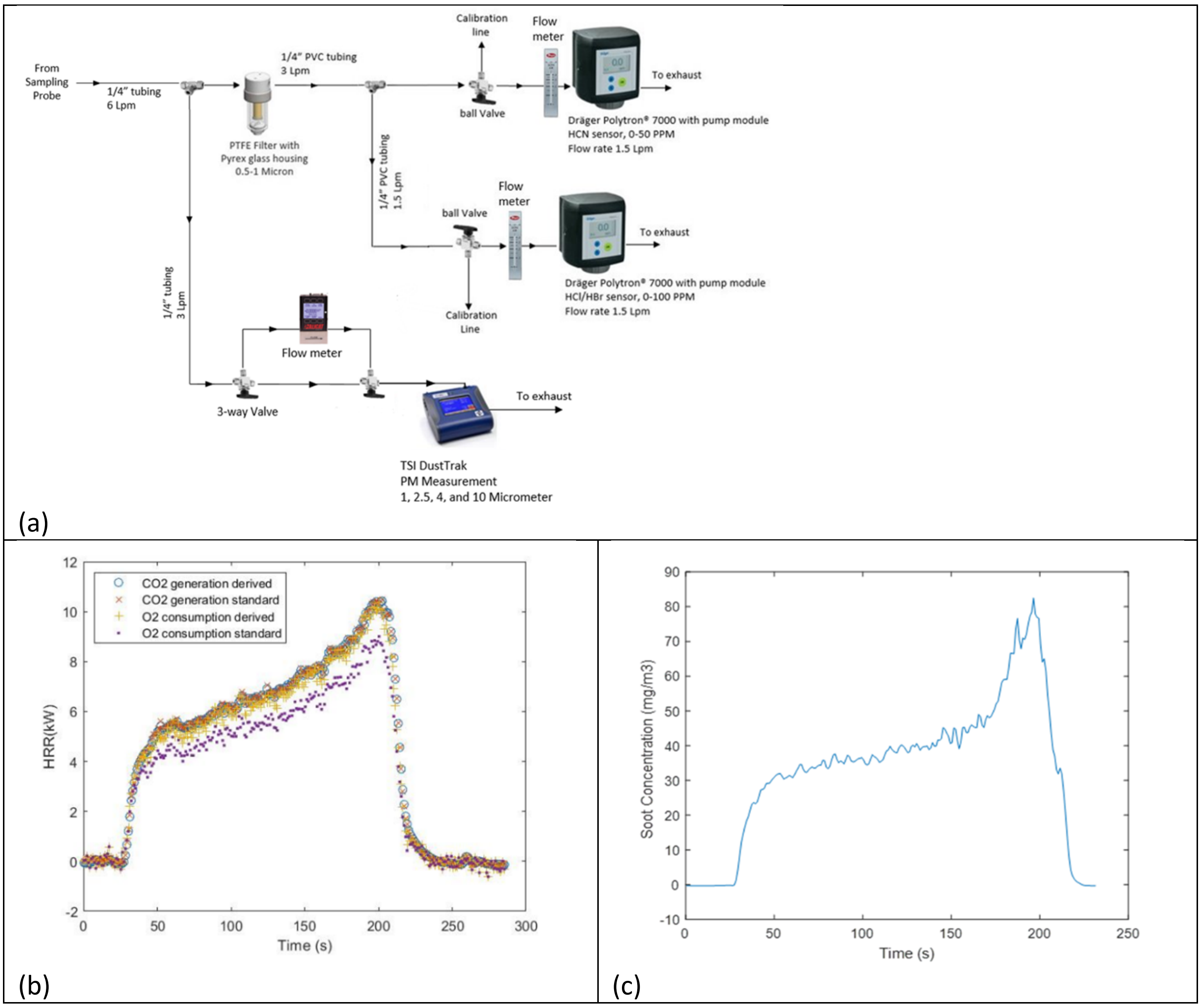

FIGURE 1. Modified FPA sampling line diagram (a). Heat release rate (b), and solid particulate yield (c) measured in the modified FPA.

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O17- Novel Analytical Toolkit for the Characterization and Development of Halogen Free Flame Retardants (HFFR) PP Formulations

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Conclusions

In the development of halogen free flame retarded (HFFR) formulations several factors have been found to influence the flammability of polymer materials. Main factors identified are thermal stability of materials and the ability of the materials to form char; surface or ignition temperature of the materials during burning; total amounts of volatiles formed and their chemical composition due to their flammability and finally the extent of radical quenching in the gas phase.

We have been working for several years to evaluate and develop analytical tools to quantify these parameters. In this presentation, I shall present our novel analytical toolkit aimed to determine quantitatively the following parameters for several of our model HFFR formulations:

1. Surface ignition temperature (Tign) and kinetic degradation parameters such as Arrhenius activation energy (Ea) and frequency factor (A) using Thermo Gravimetric Analysis (TGA)/SDTA.
2. Total volatiles formed due to burning of materials using Thermal Desorption (TD)/ Gas Chromatography (GC)/ Mass Spectrometry (MS).
3. Chemical composition of the volatiles using GC/MS.
4. Distribution of P in the gas and the condensed phase using ICP-SFMS.

We compared these experimental values to UL94V results and found a very good correlation between our results and UL94V tests.

Main implication of our new toolkit is that it allows us to estimate several of the quantitative parameters that control the fire resistance behavior of materials and allows us to understand the underlying principles for improved fire-resistance properties for different formulations. This also provides us with quantitative data to characterize and develop new HFFR formulations instead of using single UL94V test, which is relatively empirical.

Keywords: analytical toolkit, HFFR, TGA, TD/GC/MS, ICP-MS

Introduction

Polymer materials are made fire resistant basically by controlling either the bulk properties of polymers i.e., the condensed phase or by controlling the gas phase chemistry i.e., the volatiles that are formed due to polymer degradation under burning conditions or by controlling both.

This suggests that if materials could be designed with low specific mass loss rates under fire conditions, the amounts of volatiles formed would be substantially reduced resulting into less combustion and thereby less heat generation. The latter would result into less increase of surface or ignition temperature of the materials resulting into less thermal degradation of materials. This suggests that important parameters that control the condensed phase properties of polymers to make them fire resistant are surface or ignition temperature and the kinetic degradation parameters of the materials.

Another parameter that has a great influence on the fire properties is the gas phase chemistry, which in turn, is controlled by the volatiles formed during the burning process. The volatiles formed differs both with respect to flammability and generation of heat of combustion. This suggests that both the total amount of volatiles and the chemical composition of the volatiles formed because of burning are important to improve fire resistance properties of the materials. Therefore, preferred volatile compositions are also presumed to be effectively improve the fire properties of the materials.

Furthermore, in phosphorus (P) and Phosphorus-Nitrogen (P-N) based (PFR) halogen free flame-retardant systems, it has been suggested that formation of P and PO radicals in the gas phase are important to obtain good fire-resistant properties because they both function as effective radical quenchers and char formers resulting into less heat generation. For radical quenching presence of phosphorus in the form of P and PO radicals in the gas phase are important. This suggests that distribution of phosphorus both in the condensed and in the gas phase should play an important role in controlling the fire properties. This proposes that selection of suitable PFR compounds that renders a preferred P distribution in the gas and in the condensed phase is important to obtain good fire resistance properties.

Unfortunately, quantitative estimations of the above-mentioned parameters are lacking in the literature. In this presentation, we shall present a toolkit to experimentally measure these parameters for different HFFR PP model compounds and their correlations to the UL94V results. The study shows that we obtain a good agreement between these quantitative parameters and UL94V tests. This suggests that our toolbox could be very helpful and effective tool both to characterize and develop new and effective HFFR formulations instead of using single point UL94V tests that are being commonly used today.

Experimental

Analytical techniques that we have developed and used are summarized below:

1. Surface and ignition temperatures and kinetic parameters were determined using Thermogravimetric Analysis (TGA)/SDTA. These parameters were determined from non-isothermal TGA runs on model compounds using Mettler TGA 851 under nitrogen between 30-800°C at a heating rate of 30°C/min. Specific mass loss rate and maximum surface temperature for maximum mass loss rate during burning was determined.
2. For the analysis of volatiles, gas samples were collected on Tenax TA adsorbent tubes after thermally decomposing the samples in TGA in air under isothermal conditions at 800°C for 10 minutes. The gas samples collected on Tenax were then analysed by using thermal desorption (TD) using Unity 2 from Mark International Ltd. The adsorbent tubes were desorbed for different times preferably 10-15 mins at 270°C. The cold trap temperature used was -10°C with a suitable split ratio. Desorbed gases were then analyzed using Gas Chromatography (GC) and Mass Spectroscopy (MS). We used both Finnigan Polaris Q, an ion trap type MS and Finnigan Trace, a quadrupole type of MS for the analysis of volatiles. We used GC column, Rtx-5 Amine, 60m long and ID and OD of 0.25 mm and 0.39mm and 5m EZ guard for separation of volatiles. All analyses were running for 55 minutes ramping at 5°C/min. The initial start temperature for the analyses were 38°C.
3. Phosphorus distribution in the condensed and the gas phase were determined by analyzing the original compounds and the ashes from the compounds after pyrolyzing them in a muffle oven at 900°C. Phosphorus (P) contents were determined using Inductively coupled Plasma, ICP-SFMS according to SS EN ISO 17294-1, 2 (mod) and EPA-method 200.8 (mod) standards. Double focusing (electric and magnetic) ICP-MS, also called Sector Field (ICP- SFMS), was used due to its high sensitivity and low background.

Results and Discussion

1. Ignition temperature and kinetic parameters

We investigated the use of a single point measurement by TGA/SDTA presented by Lyon [1,2] to determine the surface ignition temperature and kinetic parameters for several model formulations with known UL94V results. A good correlation with UL94V tests will allow us to predict the fire properties of HFFR formulations in a more quantitative way as compared to subjective UL94V tests.

To determine these parameters, we analyzed our model compounds with TGA and determined the maximum specific mass loss rate and the maximum temperature for this maximum degradation rate. Critical degradation temperature (T_{cr}) that represents T_{ign} was estimated using equation 1 below [3] and for sustained ignition [4]:

$Tcr = (Ea/R) / \ln (A/ (Mcr/ (1 - \mu))$ equation 1

Where:
Ea = Arrhenius activation energy
A = Arrhenius frequency factor
R = universal gas constant and is 8.3145 J/mol
µ = inert/ char mass fraction
Mcr = specific mass loss rate [(mg/s)/mg]

Ea, A, µ and Mcr were determined using equations 2-4 below:

$Ea = [x'max/(1-\mu)]. [e.R. Tp^2]/ \beta]$ equation 2
$A = e. [x'max/ (1-\mu)]. e^{Ea/RTp}$ equation 3
$Mcr = m''cr / (\rho k/ h)$ equation 4

where,
x´max = maximum fractional mass loss rate
e = 2.71818 (constant)
ρ = material density (kg/m^3)
k = thermal conductivity (W/m.K)
h = coefficient of heat transfer from the TA furnace to the sample volume V(m^3) and surface area S(m^2)
m´´cr = critical mass flux determined from CC measurements for sustained ignition (3.2 ± 1.2 g/m^2.s)

Results on Tign and kinetic parameters such as Ea and A for a few of our model formulations and UL94V results are summarized in Table 1 below:

Table 1: Tign and kinetic results on a few of our model compounds

Model samples	Tign (°C)	Activation energy, Ea (kJ/ mol)	Frequency factor, A (s^{-1})	UL94V results
PPHD120MO: PP	561,83±8,77	260,5	$3{,}29e^{+16}$	flammable
BG582: PP + 28% PFR 1	615,3±14,07	183,8	$9{,}88e^{+10}$	V0
BG586: PP + 24% PFR 1 + 2% Pax	590,9±10,7	228,75	$1{,}04e^{+14}$	V0
BG1001-1: PP + 15% PFR 1+ 2.8% Pax	578± 9.4	251.8	$4.6e^{+15}$	V0
BG443: PP + 37% PFR 2	580.49±9.86	242.3	$1.11e^{+15}$	V1/ V2
BG455: PP + 25% PFR 2 + 2% Pax	590.14±11,04	221.3	$3.78e^{+13}$	V0

Note: Tign values are expressed in ±. Here ± does not represent standard deviation but instead the limiting values where we used both the lower and the higher value for mcr'' proposed by Lyon [4]. The main Tign value is the average of these two values.

The results in table 1 shows that all formulations that passes V0 test exhibit relatively high Tign values compared to PP without FR additive. Formulations showing V0 also renders comparatively high activation energy, Ea. This suggests that these parameters can successfully be used to predict the fire resistance properties of the materials.

2. Analysis of gas phase

To investigate the influence of gas phase we analysed the volatiles formed on pyrolyzing the model compounds and determined the total amount of volatile organic compounds (TVOC) formed and their chemical compositions. Results are summarized in Table 2 below. The results show that formulations that passes V0 forms comparatively lower amounts of TVOC compared to virgin PP. Moreover, composition of the volatiles formed differed for formulations that passed V0 compared to virgin PP and formulations that did not pass V0. TVOC values for a few of our model PP compounds and UL94V tests are summarized in the Table 2 below:

Table 2: TVOC values for a few model compounds

Sample Name	TVOC (ng tol.eqv./mg sample)	UL94V Results
PPHD120MO: virgin PP	17905; 17849; 18481	No rating, Burns
BG582: PP + 28% PFR 1	14086; 11092	V0
BG586: PP +24%PFR 1+ 2% Pax	15016; 12775; 14295	V0
BG840: PP + 31% PFR 3	8113; 8487	V0
BG1056: PP + 15% PFR 3	16762; 15542	No rating

3. Distrubution of phosphorus (P) in the condensed and in the gas phase

To determine distribution of P in the gas and in the condensed phase, we measured P contents in the model compounds containing PFR, in PFR used in the formulations and in the ash from the model compounds and calculated P concentration. Results on P distribution are summarized in Table 3 below:

Table 3: Distribution of P in the gas and in the condensed phase after pyrolysis

Name	%P remaining in the ash	%P disappeared in the gas phase	UL94V results
BG440: PP+ 4% PFR 4	56.8	43.2	V0 -V2
BG457: PP+16.5 PFR 4+2% Pax	80	20.0	V0 – V1
BG443: PP+37% PFR 2	35.8	64.2	V1 – V2
BG455: PP+25% PFR 2+2% Pax	66.2	33.8	V0

The results show that estimations of P concentration render important information if the used PFR functions as a char former or due to gas phase activity. It is interesting to note here that presence of Paxymer enhances the P-concentration in the condensed phase both for PFR 4 and PFR 2 resulting into more char formation. This explains why addition of Paxymer not only shows improved fire properties at lower dosage levels of PFR but also prevents dripping during burning eliminating risk pool fire.

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O18- DEVELOPMENT OF SUSTAINABLE FLAME RETARDED POLYPROPYLENE BY USING PREDICTIVE TOOLS

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Main message:
A sustainable flame retarded UL94-V0 PP formulation has been found avoiding time consuming experiments by using a predictive model for the dripping behavior and UL94 results. The optimal formulation does not contain any critical raw material since it is both halogen- and phosphorus-free. Moreover, the final filler content is extremely lower than that required by the only current counterpart solution, based on metal hydroxides.

Keywords: Flame retardants, melamine, N-alkoxy hindered amine, polypropylene, predictive models.

Introduction

Nowadays flame retarded PP (FR-PP) is obtained mainly by the use of halogen and/or phosphorus compounds. Very recently, there is a growing interest in developing alternative halogen- and phosphorous-free FR polymeric systems, since the phosphate rocks, i.e. the phosphorus FRs precursors, have been recently recognized as a critical raw material within the European Union [1]. Therefore, the main aim of this work is to develop UL94-V0 PP without any critical raw materials.

Experimental

Flame retarded PPs samples were developed by combining flame retardants (FRs) with different mechanisms of action in order to reach UL94-V0 rating with a thickness of 3.2 mm. To this end, we used melamine (MEL) and a phosphate ester (SolDP) to achieve “non-dripping” (ND) behavior. To obtain a “non-flaming dripping” (NFD) UL94-V0 PP, we employed also a radical generator compound, i.e. an N-alkoxy hindered amine (NOR). A statistical approach, based on design of experiment (i.e. extreme vertices design) and multiple regression, has been applied to develop predictive models, afterward used to assist the development of optimized formulations in terms of cost, total amount of fillers or phosphorus content.

Results and Discussion

For the most common ND behavior, we can state that UL94-V0 rating can be achieved when the dripping time t_d is large enough, i.e. it takes place after the complete sample extinguishment. Based on our results, in mathematical terms this can be expressed as [1]:

$$t_d > t_2 + 21 \quad [s] \tag{1}$$

where t_d and t_2 can be predicted as follow:

$$t_2 = 0.3802\ MEL + 2.946\ SolDP - 0.1276\ MEL*SolDP \tag{2}$$

$$t_d = 0.6923\ MEL - 0.698\ SolDP + 0.04675\ MEL*SolDP \tag{3}$$

being MEL and SolDP the % filler content. Very interestingly, both t_2 and t_d models show that the use of MEL or SolDP alone are not effective for achieving V0 rating since they both tend to increase the second afterflame time t_2 (their coefficients are positive) while SolDP also decreases the time of dripping t_d (its coefficient is negative). Moreover, both models show that there is a beneficial interaction between MEL and SolDP that is responsible for the enhancement of UL94-rating since it decreases afterflame time and increases dripping time.

In presence of NOR there is a cooling effect that can be used to suppress burning droplets [2], thus leading to UL94-V0 “non-flaming dripping” behavior. This means that the previous models, developed for ND behavior, can’t be applied since the dripping time loses importance. A new model based on V0 probability (i.e. the fraction of specimens out of 10 samples which can be rated as V0) has been developed. The final PP rating is V0 if the V0 probability is at least 0.9. The V0 probability can be predicted as follow:

$$\text{V0 Probability} = 0.00569\ \text{MEL} - 0.1089\ \text{SolDP} + 0.00554\ \text{MEL*SolDP} + 0.004668\ \text{MEL*NOR} \qquad (4)$$

The model shows that MEL has a beneficial effect in improving the V0 probability (positive fitting coefficient) while SolDP has a negative effect, probably because, promoting dripping, it facilitates the formation of flaming drops. Still more interestingly, the linear term related to NOR has been revealed to be statistically not significant. This means that NOR alone is not useful for increasing V0 probability, in agreement with what reported before on the use of NOR in thick sections, as our samples [3]. The model also shows that only two interaction terms are statistically significant: the combination between MEL and SolDP, in agreement with what reported before, and between MEL and NOR. Finally, the experimental results obtained have shown that this last model is able to predict in a reliable way also the behavior of ND FR-PP, although the use models based on a specific "physical constraint" (like condition on dripping time) is better.

To prove interactions between FRs in the solid phase, thermogravimetric analysis (Figure 1) have been obtained: it is evident that the thermal stability of MEL-SolDP and MEL-NOR mixtures is absolutely different from what can be anticipated by considering the weighted TGA curves of the neat components. This means that a reaction between the two additives takes place in the solid phase. Analysing the regression equations (eqns. 2 and 3 for ND, eq. 4 for NFD), it can be seen that only thanks to these synergies that V0 rating can be achieved for both ND and NFD formulations, since the neat additives alone, whatever they are (MEL, SolDP or NOR), are not enough to reach this very good fire reaction.

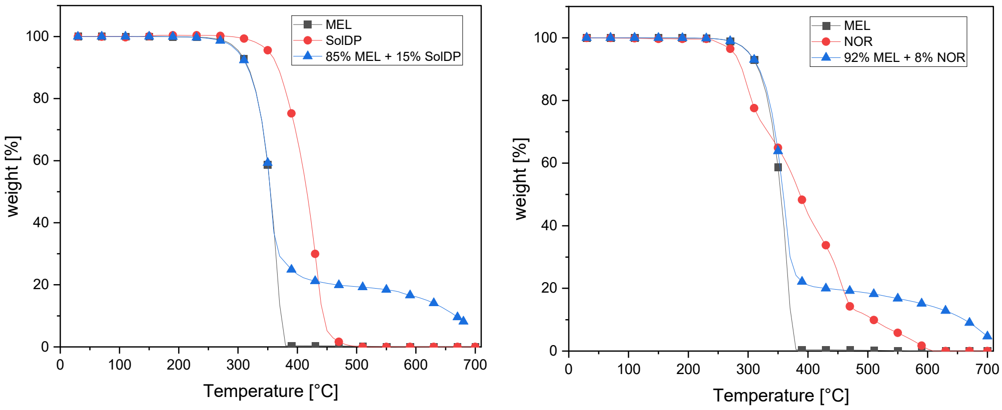

Figure 1 TGA curves in air for neat melamine, SolDP and a mixture of MEL and SolDP (on the left); TGA curves in air for neat melamine, NOR and a mixture of MEL and NOR (on the right).

The optimized formulations, developed through the use of the models, showed that filler contents around 40% are required to get V0 rating for FR-PP. Although this content is higher than that required by intumescent phosphorus-based system (27-30%), nevertheless, it is extremely lower than that required by using metal hydroxides (60-70%) which is the only current solution to obtain phosphorus-free UL94-V0 PP formulation. The phosphorus-free V0-PP formulation discovered in this work contains 40% of melamine and 3% of NOR.

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S8- EFFECTS OF FLAME RETARDANTS IN CARBON FIBRE REINFORCED COMPOSITES ON THE THERMO-OXIDATIVE PROPERTIES OF CARBON FIBRES

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Main message:
This work aims to assess the structural damage and electrical hazards of carbon fibres from heat/fire exposed carbon fibre reinforced composites (CFRCs) and the effects of different flame retardants and nanoparticles in mitigating identified hazards.

Keywords: Carbon fibre, CFRCs, composites, flame retardants, electrical conductivity

Introduction

When exposed to high temperatures, the resin within CFRCs decomposes and starts burning, exposing carbon fibres to the surroundings. Above 550°C the carbon fibres begin to oxidise, releasing fibrils [1]. The carbon being electrically conductive, exposed fibres and released fibrils can interfere with surrounding electronics [2]. Most often the resin matrix is modified with flame retardants and nanoparticles in order to reduce the flammability of CFRCs. While the effect of flame retardants and nanoparticles on the resinous matrix is well studied, there is absence of literature on their effect on carbon fibre. Since phosphorus-based flame retardants promote char formation, it is possible that a highly cross-linked char may encapsulate the carbon fibres and reduce the potential hazard. This work explores these aspects.

Experimental

PAN-based TR30S 3K 2x2 twill weave carbon fibre (Mitsubishi) and epoxy resin (Epilok 60-822 and Curamine 32-790) were used to make CFRCs. 15wt% of flame retardants 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), resorcinol bis(diphenyl phosphate) (RDP), and ammonium polyphosphate (APP)), as well as 5wt% nano-particles, octadecyl ammonium ion-modified montmorillonite clay (nano clay) and layered double hydroxides (LDH), were added to the epoxy resin. An epoxy control sample was also made. CFRCs were made by hand lay-up or resin infusion, and were 8/10 plies thick. Using a cone calorimeter they were exposed to a heat flux of 75kWm^{-2} for 600s. Fibres were retrieved from different plies through the thickness of the fire damaged CFRCs and examined with a scanning electron microscope (SEM) for structural damage and fibre diameter reduction. The electrical conductivity of composites and individual fibres, before and after fire exposure was determined by measuring an applied potential across them.

Results and Discussion

The cone's radiant heat flux of 75kWm^{-2} for 600s was high enough to cause oxidation to the carbon fibres in the CFRCs. The reduction in carbon fibre diameter was used as an indication and measurement of oxidation. Fibres were retrieved from plies P1 (top surface), P4/P5 (middle) and P8/P10 (unexposed surface) of the tested CFRCs. The SEM images of the as-received fibre, along with fibres from different plies of samples CC and CC_APP are shown in Figure 1. Twenty-five fibres were examined from each of these plies in all six CFRCs in order to obtain a mean diameter measurement for each ply. These results are given in Table 1 along with the mean fibre electrical resistivity (from 6 single fibre measurements).

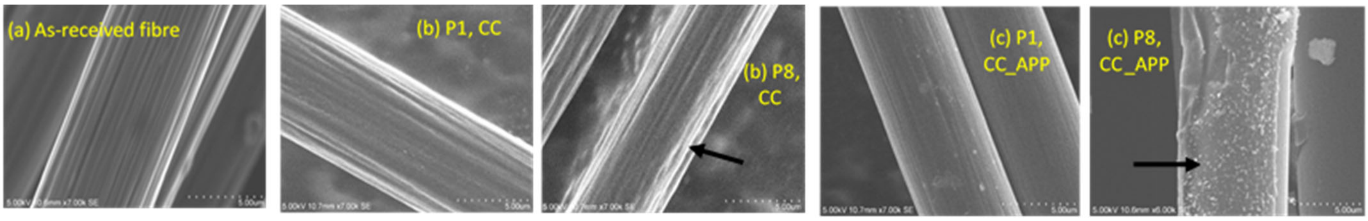

FIGURE 1. SEM images of (a) as-received fibre, and fibres removed from P1 and P8 of (b) CC and (c) CC_APP after 75kWm^{-2} exposure

TABLE 1. *Fibre diameters and electrical conductivity values of fibres from CC after 75kWm^{-2} exposure*

Sample	Mean fibre diameter/µm			Resistivity/Ωm 10^{-5}		
	P1	P4	P8/P10	P1	P4	P8/P10
CC	5.89 ± 0.11	6.69 ± 0.09	6.65 ± 0.22	2.20 ± 0.05	1.94 ± 0.04	2.27 ± 0.07
CC_APP	6.85 ± 0.06	6.91 ± 0.06	7.15 ± 0.11	1.43 ± 0.23	1.54 ± 0.07	1.78 ± 0.26
CC_DOPO	6.15 ± 0.22	6.44 ± 0.21	6.73 ± 0.17	1.60 ± 0.15	2.20 ± 0.15	1.75 ± 0.13
CC_RDP	6.22 ± 0.11	6.42 ± 0.23	6.63 ± 0.11	1.70 ± 0.07	1.45 ± 0.09	1.97 ± 0.04
CC_LDH	7.01 ± 0.10	7.17 ± 0.10	6.99 ± 0.12	1.97 ± 0.15		2.07 ± 0.03
CC_NC	6.72 ± 0.13	7.09 ± 0.10	6.81 ± 0.13	2.56 ± 0.41		2.20 ± 0.08

The reduction in fibre diameter was greatest for ply P1 in all CFRCs except CC_LDH. For the CFRCs with flame retardants, reduction was least for ply P8, indicating that in these CFRCs the upper plies provided a protective barrier in the form of physical shielding and impeded the flow of oxygen to the plies underneath. Residual fibres removed from CC_DOPO and CC_RDP underwent similar surface oxidation to fibres from CC, with only a small amount of char attached to underneath plies. However, there was a noticeable reduction in surface oxidation of carbon fibres recovered from CC_APP, with fibre diameter reduction less than CC. This was attributed to the large amount of char adhering to the removed fibres. Many of these fibres were encapsulated in char and bound together. This increased their mass, making them less likely to be transported by wind to interfere with their surroundings. Based on the char forming ability of APP [3], only this flame retardant resulted in the desired char formation and fibre retention effect. While CC_LDH had the least diameter reduction, pitting was observed on P5/P10 fibres indicating a potential reaction between the oxide residues formed during LDH's decomposition and the carbon fibre.

Even though incorporating flame retardants into the resin matrix reduced the electrical conductivity of the CFRCs, this did not translate into increasing the electrical resistivity of the exposed carbon fibres after heat testing. The phosphorus containing species remaining within the char attached to the fibres caused this small increase in their electrical conductivity. However, for CC_NC, the resistivity increased slightly, on P1 due to the presence of SiO_2 in the nanoparticles which migrated to the surface during testing.

Acknowledgement: DSTL for the funding given to this project

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S9- CORK EXTRACTS (*QUERCUS SUBER L.*): CHARACTERIZATION AND INTEGRATION IN FIRE-RETARDANT INTUMESCENT FORMULATIONS.

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Main message: This study aims to provide insights on the integration of natural extracts from cork oak as additives in intumescent formulations. Chemical analysis of samples obtained from "green" extraction of plant material indicated high concentrations of polyphenols which show good capabilities as carbon source in such formulations. Samples thermal stability and behavior were evaluated using bench-scale data from thermogravimetric analyzer and physical properties of char layers formed under cone heater.

Keywords: extracts, cork oak, thermogravimetric analysis, intumescence, analytical chemistry

Introduction

Virgin cork (*Quercus suber*) represents a vast volume of unvalorized biomass in cork-productive areas and is known to be rich in polyphenolic compounds that can be used in value-added products. Some studies have shown their ability to be integrated as carbon source in intumescent ternary formulations due to their high hydroxyls content [1]. Virgin cork can thereby be used as benchmark material to evaluate correlation between polyphenol concentration and efficiency in this type of flame-retardant.

Experimental

Plant material was grounded and sifted before being extracted with ethanol, water and mixtures of both using pressure-assisted extraction. Optimal parameters (temperature, static time) were determined by TPC (Total Phenolic Content) and ORAC (Oxygen Radical Absorbance Capacity) spectrophotometric measurements. Thermal stability was evaluated on pure extracts and their intumescent mixtures with ammonium polyphosphate. Two non-natural carbon sources were also studied: standard gallic acid (GA) as major phenolic compound in our material and pentaerythritol as literature control [2]. FTIR-coupled thermogravimetric analysis were performed on 5 mg samples at a heating rate of 20°C.min^{-1} from 80°C to 900°C under nitrogen flow.

Selected formulations were shaped into pellets of identical dimensions and weight (*d x h ;* 13 mm x 10 mm, 2 grams) and tested under cone-calorimeter for 15 minutes at 50 kW.m^{-2} irradiance with 60 mm separation from heater. Experimental setup included camera tracking and mass monitoring (before and after exposition) to evaluate their physical properties including expansion coefficient and mass loss over time. Char layers obtained were hermetically stored and analyzed using FTIR spectrometer to confirm the formation of aromatic phosphocarbonaceous structures.

Results and Discussion

Early chemical characterization of extracts obtained by pressure-assisted method highlighted high concentrations of phenolic compounds in our samples. TPC and ORAC measurements showed that solvent mixtures with 50% H_2O or more were the most efficient to obtain the richest extract in target metabolites with up to 0.51 $mg_{(GA\ Equivalent)}.mg_{(extract)}^{-1}$ in total phenolic content assay. These results are indicating the presence of hydroxyls and phenols functions which are the key sites for polymerization with acid precursor in intumescent reaction [2]. Thermogravimetric analysis of plain extracts confirmed the emergence of different thermal behaviors possibly correlated to their chemical compositions. Residual masses at 600°C and ORAC measurements of extracts showed high linear dependency with a correlation coefficient r = 0.991.

Extracts were selected as potential carbon source candidates following TGA and TPC/ORAC measurements. The comparison to control carbon sources was performed using the same apparatus and methodology. The figure 1 below shows the thermogravimetric analysis of mixtures containing extract obtained with 100% H_2O (Extract A) compared to pentaerythritol. Both plots indicate that the cork-based formulation has greater thermal stability with higher residual mass at any temperature and lower mass loss rate peaks on the derivative curve.

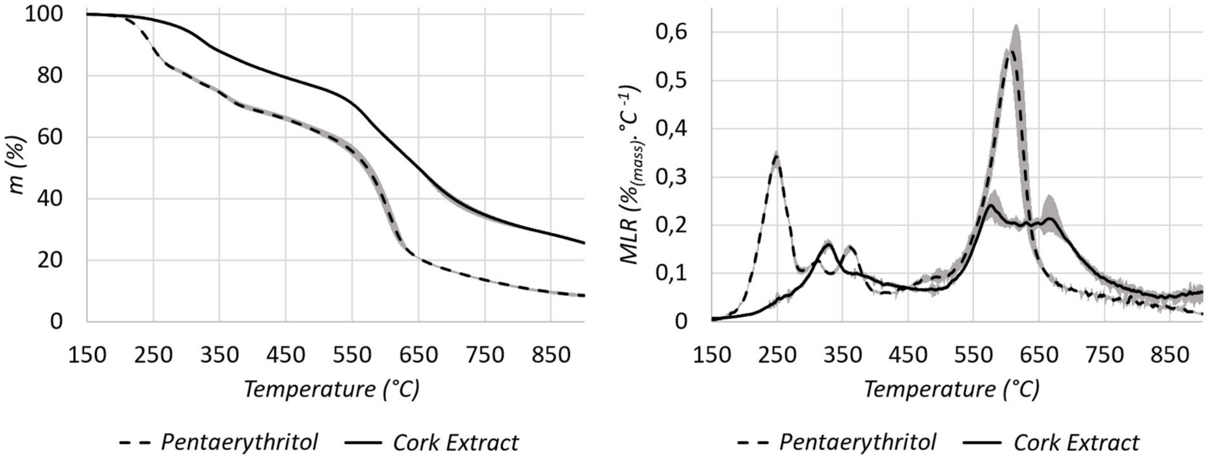

FIGURE 1. Thermogravimetric analysis of cork-based and control carbon sources mixed with APP (1:3 ratio)

Cone-calorimeter assays on pellets allowed to observe intumescence at a greater scale and confirmed the ability of cork extracts to initiate these types of reactions. These experiments showed a char thickness two times lower after 15 minutes exposure for our best performing extract compared to control with respectively 4.5 (±1) cm and 7.7 (±0.3) cm. However, time to initiate the reaction and mass loss after experiment were in the same range for both formulations giving encouraging results at macroscopic scale. Solid FTIR spectroscopy of char layers highlighted the formation of aromatic phosphocarbonaceous structure with similar bands and transmittance at 1610 cm^{-1} (C-C$_{(ar)}$), 1105cm^{-1} (P-O-C) and 960 cm^{-1} (PO_2 and PO_3) [3].

These results are encouraging for the integration of natural extracts with high polyphenols concentration as carbon source additives in intumescent formulations but also as a way to valorize waste and by-products from agriculture.

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K10- Recyclable Flame-Retardant Materials

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Main message: Recyclability is the key to the sustainable development of flame-retardant materials, which largely depends on precise structural design and advanced strategies. Our group are focused on developing a range of new methods to render flame-retardant materials recyclable. Here, we briefly outline our recent advances in recyclable flame-retardant materials by employing surface treatment, bulk-additive, and bulk-copolymerization approaches.

Keywords: Recycling, Flame retardancy, Materials

Introduction

Flame retardants largely mitigate the threat of fire from highly flammable polymeric materials [1]. However, traditional flame-retardant methods have serious problems, such as difficulty in flame-retardant wastes and environmental toxicity debt. In this presentation, we will show our typical studies for fabricating recyclable flame-retardant materials based on supramolecular assembly, intrinsic self-catalytic reaction, transesterification, etc., which endow the materials with high flame retardancy and dissociate them to monomers/precursors or small molecules for recycling.

Results and Discussion

Recyclable flame-retardant Coating. We show a durable flame-retardant coating that can be fully separated and recycled by regulating the interfacial interactions [2]. By exploiting π-π stacking and volatilization-induced self-assembly, a P-doped aromatic siloxane multifunctional coating was fabricated in an orderly manner on the surface of PET fabrics. At only 7.3 wt% coating loading, the limiting oxygen index (LOI) value of the fabric was significantly increased to 34.5%. The coated fabric after 50 machine wash cycles showed similar self-extinguishing properties with no droplet phenomenon. Notably, the coating of the fabric can be quickly removed by reversible assembly/disassembly in soaking in concomitant ethanol. The coating can be closed-loop recycled (~100%) over five recycling cycles, and the recycled coating imparted the same flame retardancy to the fabric. This study provides a new method for the sustainable development of recyclable flame-retardant coatings.

Recyclable bulk-additive flame-retardant materials. Flame-retardants incorporated in polymeric matrices make end-of-life flame-retardant materials difficult to handle. The dynamic reversible feature of supramolecular interaction upon facile stimulus provides us with inspiration. Driven by multiple directional intermolecular interactions, a phosphorus-doped nanosphere (PPNs) that exploits stimuli-responsive reversible assembly can be rapidly fabricated upon cooling assembly. By matching disassembly conditions, PPNs can be circularly dissociated into precursors, removed from application systems, reassembled, and reused sustainably. For instance, PPNs can be recycled and used in polyurethane foam. The corresponding polyurethane foam with only 3.5% PPNs manifested excellent self-extinguishing features and met the requirements of Cal TB 117. This closed-loop nanoscale recycling strategy based on reversible assembly paves the way for tackling the pressing issue of high-value flame-retardant nanomaterial sustainability.

Recyclable bulk-copolymerization flame-retardant materials. Recycling of copolymerized flame-retardant materials into monomers can effectively solve their waste problem. A novel strategy for the rapid recycling of flame-retardant PET was demonstrated by integrating flame retardancy and self-catalytic depolymerization activity into one reactive monomer that was chemically linked into the backbones of PET later. The resultant flame-retardant PET-copolymer possessed extremely low fire hazards with a UL-94 V-0 rating without dripping, a high limiting oxygen index of 33%, and largely decreased PHRR (-44%) and TSP (-67%). Taking advantage of the special self-catalytic phenomenon, the designed flame-retardant PET-copolymer can be depolymerized into BHET with a high recycling rate of 90% without adding other catalytic agents. The innovative strategy for the recycling of flame-retardant PET-copolymer represents a promising way to address the fossil fuel crisis.

Recyclable flame-retardant vitrimers. The reprocessability of flame-retardant thermoset materials is the bottleneck limiting their recycling. We reported an intrinsically flame-retardant epoxy vitrimer with rapid recyclability by introducing dynamic ester linkages with catalytic transesterification activity into the crosslinking networks [3-4]. Excellent flame retardancy with a UL-94 V-0 rating, a high LOI of 34%, and a reduction in the PHRR (-63%) and total heat release (-32%) of the designed epoxy vitrimer were achieved. By exploiting the dynamic feature of the transesterification network at selected temperatures, the epoxy vitrimer showed high malleability that could be reprocessed in 15 min at 200 °C without sacrificing its flame retardancy. We confirmed the topology rearrangement of a novel epoxy vitrimer composed of adaptable phosphate networks, which contributes to their reprocessing process. The design of flame-retardant epoxy vitrimers provides a new way to foster the cyclic utilization of flame-retardant thermosetting polymers.

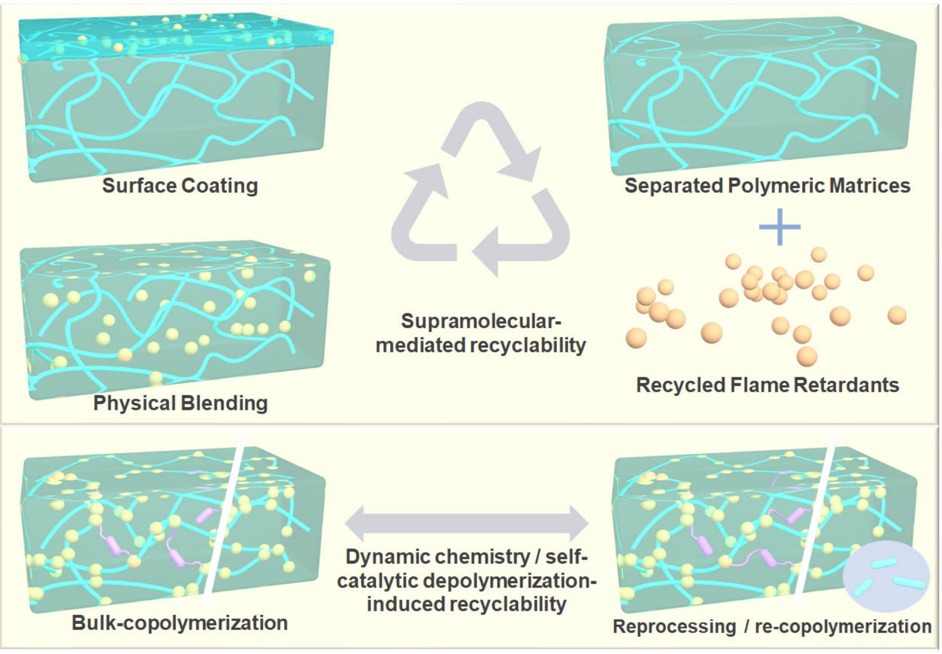

FIGURE 1. Schematic illustration of the recyclable flame-retardant materials developed by our group.

Acknowledgement: This work was supported by the National Natural Science Foundation of China 51991351 and 52122302.

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O19- Enabling reprocessability and recyclability of epoxy thermosets via reactive incorporation of phosphonate moieties

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Main message: The increasing amount of fossil-based plastic waste ending up in our environment is one of the most pressing issues of the oncoming decades. Thus, development of re-usable polymers with a prolonged useful lifetime heralds the switch for a transition towards a more circular economy. A novel dynamic phosphonate ester bonds rich thermoset has been designed and synthesized via a simple one-pot, two-step synthetic pathway, which demonstrated exceptional reparability, recyclability and flame retardancy. The covalent incorporation of phosphonate moieties in the thermoset matrix introduced sufficient dynamic P-O ester bonds, and promoted the exchange of network strands under moderate heating condition, resulting in scratch reparability and recyclability. Due to the presence of phosphorus in the structure, the thermoset also exhibited excellent flame retardancy in varied fire tests. Based on its above-mentioned properties, the application of the thermoset as fire protective coating on wood samples were explored. Fire tests on coated wood samples confirmed their excellent fire performance via intumescent mechanism. In addition to fire safe coating application, preliminary investigation of such phosphonate thermosets as matrix for natural fiber reinforced polymer composites was also performed.

KEYWORDS: flame retardant epoxy thermoset, phosphonate network, repairable and reprocessable thermoset, fire safe coating, flame retardant mechanism

Introduction

Various recyclable materials have been synthesized via incorporation of wide variety of covalent exchangeable bond. Some of these materials can "flow" again like thermoplastics through network topological rearrangement by thermally triggered catalytical bond exchanges. Such network structures are fixed at product operating temperatures when the exchange reaction kinetics are frozen. Among the various dynamic covalent bonds, phosphorous ester based transesterification reaction may provide a multifaceted solution, this functionality not only offers excellent fire protection, but also has industrial relevance due to ready availability of monomers and straightforward synthesis procedure. Phosphate triester based thermosets brought new inspirations into multifunctional vitrimer material.[2, 3] If we could replace the phosphate with phosphonate, the P-C bond will theoretically bring even better material stability and flame retardancy, as it is a chemically and thermally stable analog of a P–O bond.[4]

Results and Discussion

A one-pot and two steps procedure (FIGURE 1a) was developed to synthesize the multi-functional transparent epoxy thermoset with varied TDPSD contents. The chemical structures were confirmed by elemental analysis, ^{13}C and ^{31}P solid state NMR, and FTIR. As well studies in the bioorganic community, the replacement of the bridging oxygen in a phosphate ester with a CH_2 could introduce stability and confer inertness to phosphatase cleavage. In addition to the promising reprocessability of thermosets with phosphoester linkages (P-O) reported by researchers in the vitrimer field,[3] the phosphonate linkages could increase hydrolysis stability and reduce its potential leakage during usage and recycling. In addition, the presence of phosphorus offers inherent flame retardancy.[4] The reactive P-H bond of TDPSD allows direct covalent linkage to the epoxy, which could result in optimized fire performance at lower P loadings compared to a non-reactive approach.

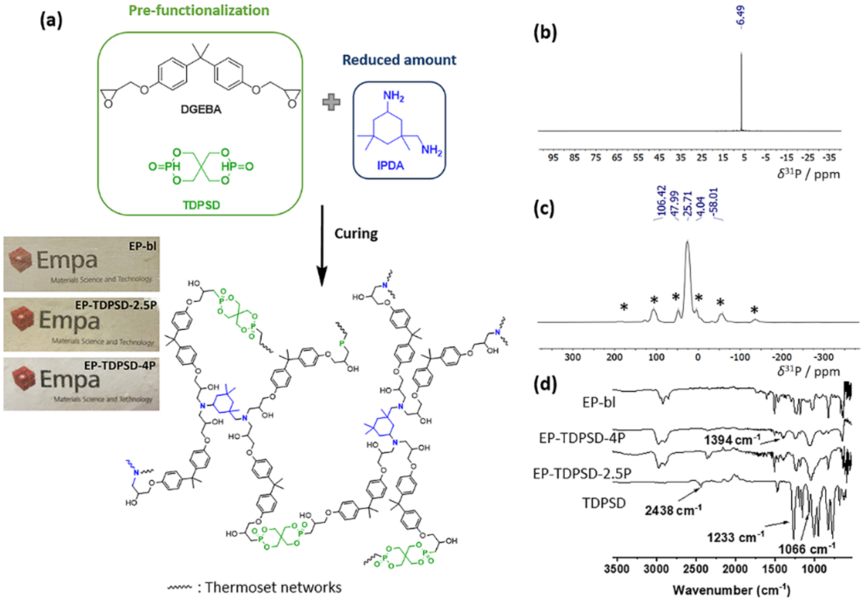

FIGURE 1. (a) The synthesis procedure of the spirocyclic bisphosphonate cured flame retardant EP-TDPSDs. (b) ^{31}P NMR spectrum the compound in solution, (c) solid state ^{31}P CP MAS NMR of EP-TDPSD-4P (* = spinning side bands), and (d) FTIR spectra.

The thermoset with 2.5% P demonstrated exceptional fire-resistance capability via intumescent charring effect, making them a suitable thin coating candidate for inflammable material protection, especially in the transportation and building industries.

Last but not least, thermo-mechanical recycling method enabled the vitrimer thermoset reformation by applying heat and pressure, as TDPSD promoted the reparability and recyclability of the thermoset EP-TDPSD-6P. The underlying concept is laying down at the sufficient reversible P-O ester bond exchange reactions by versatile transesterification that rearrange the network topology while keeping cross-linking and functionality of the covalent links. Flax fiber reinforced composites were fabricated via compression molding to demonstrate the malleability and reprocessability of the intrinsic flame retardant vitrimer. Such intrinsic flame retardant, repairable and reprocessable thermoset material is of great potential for various applications. In future studies, we will investigate in detail the use of these thermosets in manufacturing fiber (e.g. carbon fiber, glass fiber and natural fibers) reinforced composites and its full recyclability.

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O20- FLAME RETARDANCY SOLUTIONS FOR CARBON FIBRE–REINFORCED COMPOSITES DESIGNED FOR RECYCLING

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Main message: Currently, no technologies are available for the large-scale material recycling of fibre-reinforced polymer composites. For this reason, there is a need to develop innovative polymers and composites that enable an easy recovery and recycling of polymer matrices, fibres and additives, including flame retardants, contributing to the creation of a circular economy. This study reviews the current recycling methods, innovative polymers designed for recycling and their flame retardancy solutions.

Keywords: carbon fibre–reinforced composite, epoxy resin, vitrimer, flame retardant, chemical recycling.

Introduction

In many high-performance applications thermoset polymers are primarily used as composite matrices, forming crosslinked structures with irreversible covalent bonds, so their production, processing, and recycling require different technologies than thermoplastic systems. Although they are used in smaller quantities and have a longer lifetime, their recycling has become inevitable due to their increasing range and volume of use, higher price levels and the rapid growth in demand for carbon fibres.

Results and Discussion

Several recycling solutions exist despite the apparent difficulties, especially for fibre-reinforced composites [1,2]. These methods can be divided into three groups (Figure 1): mechanical (where the composite waste is reduced to a smaller size and the material, including the additives, is recycled), thermal (where thermal energy is used to recover energy or material or both) and chemical (where the polymer matrix is decomposed by the addition of various compounds and both the matrix and the fibre reinforcement are recycled). A major barrier to the uptake of these methods is that they can only be implemented for clean composite waste of known composition, and separating the received components and additives, and re-synthesising the polymers is technically challenging and expensive.

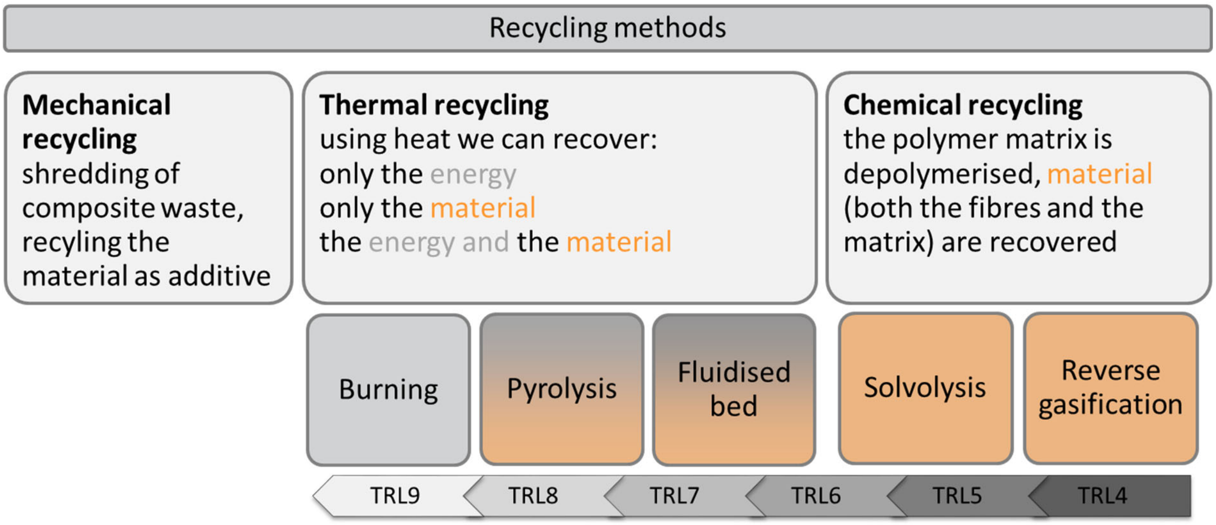

FIGURE 1. Current composite recycling technologies and their technology readiness level

But there are some promising innovative concepts aiming at recyclable-by-design thermoset polymers and composites. In 2011, Leibler et al. introduced a new family of thermoset materials, vitrimers, which behave like crosslinked systems below the glass transition temperature but can be reshaped or recycled similarly to thermoplastics above their vitrimer transition temperature. This thermally triggered reversible crosslinking is achieved via the dynamic rearrangement of covalent bonds in an associative manner. Vitrimers containing dynamic covalent diketoenamine bonds could be depolymerised at low temperatures and short reaction times, enabling the chemical separation of the monomer and the additives (e.g. solid flame retardants) as well [3]. Polyimine-based vitrimers could be the first commercial vitrimers to replace epoxy resins in structural composites, thanks to their high glass transition temperature [4]. Another approach is applying amine-type curing agents specially designed for recycling that enable the hydrolysis of the crosslinked epoxy network under mildly acidic conditions. After the hydrolysis fibre reinforcement is recoverable in its original state, the dissolved matrix can be precipitated by alkaline neutralisation in the form of a thermoplastic epoxy. Other possible alternatives are the ε-caprolactam based thermoplastic polyamide 6 systems, produced by in situ polymerisation, where a low viscosity monomer is impregnated into the reinforcing fabrics, and polymerisation occurs in the mould. Besides enabling short cycle times, these polyamide 6 based systems offer the possibility to produce self-reinforced composites, where both the matrix and the reinforcing materials are made from the same polymer resulting in simple recycling.

The application of these polymers designed for recycling in high-tech long-fibre reinforced composites requires an effective increase in thermal stability and reduction of flammability [5]. Flame retardants are typically added to the polymer matrix; thus, they can affect the viscosity of the matrix and, consequently, the available processing techniques. In the case of reactive polymer processing, such as the in situ polymerisation of ε-caprolactam, they may even interfere with the polymerisation mechanism. In addition, in composites prepared by liquid moulding techniques, the filtration and inhomogeneous distribution of solid flame retardants can be an issue, and fibre reinforcement can prevent the formation of a continuous protective layer as well. These issues are often avoided by using liquid flame retardants and/or flame-retardant coatings. A particular challenge of this field is to provide solutions where the flame retardant can be easily separated from or recycled with the matrix at the end of its life, in line with the principles of design for recycling.

Acknowledgement: This research was supported by the National Research, Development and Innovation Office (OTKA K142517 and 2018-1.3.1-VKE-2018-00011).

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O21- CHALLENGES AND OPPERTUNITIES USING INNOVATIVE TECHNOLOGIES FOR RECYCLING PLASTICS CONTAINING FLAME RETARDANTS

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Flame retardants serve an important role in plastics by preventing fires and as such contributing to lower CO2 emissions. Today being part of a circular economy, the most preferred option is material recycling as it has the lowest carbon footprint. Due to REACH and other legislation already more than 200 substances of very high concern (SVHC's) are present in these plastics and restrict the typically used re-melting recycling process. An overview of the different plastics with FRs will be presented including the potential of recyclability for these polymers.

New solvent based purification processes are developed but also chemical recycling is gaining more chances to get a place in the market

The CreaSolv® Process has been developed as a solution for plastics containing restricted substances, e.g., PS foam containing HBCD, which has been used in large quantities over decades. The process can also be used to remove all additives including brominated flame retardants in WEEE plastics mainly styrenics. The polystyrene value chain has built a demo plant (3300 mtons/y) in 2021 for recycling of waste PS containing HBCD including bromine recovery. We want to share the learnings of this startup plus using this experience for WEEE plastics for future demo plants to prove the technical and economic feasibility. Learnings in the presence of contaminants in the waste stream plus the analytical challenges for POPs will be shared.

An update will be given to this Demo plant for the different ongoing recycling projects using the dissolution purification technology compared with chemical recycling with focus on ABS, EPS and HIPS recycling containing BFRs and ATO

Keywords: Solvent based purification process, bromine recovery, circular economy, HBCD, POP PBDE's

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O22- RECYCLING OF BROMINATED PLASTICS FROM WEEE THROUGH SOLVENT-FREE UV-BASED TREATMENT.

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Main message: By irradiating plastic waste under UV-visible light, which has shown to be effective in degrading brominated flame retardants, this project aims to develop and optimize a process for decontaminating brominated plastic waste. The treated polymers can be used to produce non-harmful products without compromising their value.

Keywords: Recycling, halogenated plastics, WEEE, UV treatment.

Introduction

The use of brominated flame retardants, such as polybrominated diphenyl ethers (PBDEs), gradually became object of restrictions within the European Union and other countries due to their toxicity, persistence and bioaccumulation. However, these toxic molecules are still found in large quantities in the residues of obsolete electrical and electronic equipment. Therefore, plastic waste with brominated flame retardants cannot be recovered without prior treatment to ensure the elimination of the restricted additives. There is also a possibility that those compounds can be converted into more harmful substances, such as polybrominated dibenzo-p-dioxin (PBDD) and dibenzofurans (PBDF), when they are exposed to solar radiation.

Experimental

Different polymers have been filled with brominated flame retardants and submitted to artificial UV radiation. The radiative effect was followed mainly by means of infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC-MS) to evaluate the effect of different parameters on additives photodegradation.

Results and Discussion

The aim of our work is to develop and optimize a process for the decontamination of plastic waste by irradiation under UV-visible light, an economical technique that has proved to be effective for the degradation of brominated flame retardants, to obtain non harmful products without compromising the chemical and physical properties of the polymers which allows their revalorization.

The radiative effect on different pollutant/polymer systems was followed according to the exposure time to artificial radiation mainly by means of infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC-MS). A number of parameters influencing the photodegradation, in particular the duration of exposure and light intensity, were optimized in order to maximize the efficiency of the debromination process. Moreover, the mechanical and thermal properties of the decontaminated polymers appear to be maintained, which is advantageous for recycling purposes.

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S10- Basalt Fiber-Based Flame Retardant Epoxy Composites: Preparation, Mechanical Properties, and Flame Retardancy

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Main message: We aimed to study the impact of surface modification of basalt fiber (BF) on the mechanical properties of basalt fiber-based epoxy composites. Four different types of pretreatment approaches to BF were used; then a silane coupling agent (KH550) was applied to further modify the pretreated BF, prior to the preparation of epoxy resin (EP)/BF composites. The combination of acetone (pretreatment) and KH550 (formal surface treatment) for basalt fiber (BT-AT) imparted the EP/BF composite with the best performance in both tensile and impact strengths. Subsequently, such modified BF was introduced into the flame-retardant epoxy composites (EP/AP750) to prepare basalt fiber reinforced flame-retardant epoxy composite (EP/AP750/BF-AT). The fire behaviors of the composites were evaluated by vertical burning test (UL-94), limiting oxygen index (LOI) test and cone calorimetry. In comparison to the flame-retardant properties of EP/AP750, the incorporation of BF-AT slightly reduced LOI value from 26.3 % to 25.1 %, maintained the good performance in vertical burning test, but increased the peak of the heat release rate.

Keywords: epoxy resin, basalt fiber, flame retardancy, composites

Introduction

Epoxy resins possess intrinsic brittleness and high flammability which largely limits their application. Exolit AP750 (AP750) as a high efficiency intumescent flame retardant because of its machining stability, smoke suppressibility and non-toxic. Therefore, using AP750 as flame retardant, embedding reinforced fiber into the epoxy is great significance to both prepare flame retardant and mechanically reinforced epoxy.

Basalt fibers (BFs) are inorganic materials with high modulus, good strength and superb stability. They are easy to process, non-toxic, natural based, and cost-effective. However, due to the poor adhesive property of BF with EP, the application of basalt fiber-epoxy composite is very limited. The introduction of modified basalt fiber has been considered as one of the most effective methods to improve the performance of EP composites. Nevertheless, in comparison to the wide studies in the state of the art related to the GF, CF and/or natural fibers [1], the investigation on BF and its based epoxy composites is still very limited in both of fundamental and applied aspects. In this context, the main objective of this paper is to investigate the relationship between the surface modifications of BF and properties of BF reinforced epoxy composites.

Experimental

Firstly, four different pretreatment approaches were used for basalt fibers, such as acetone solution method (BF-AT), glacial acetic acid method (BF-AAT), NaOH method (BF-SHT) and high temperature method (BF-MFT). After that, the pretreated basalt fiber was modified formally by silane. Finally, EP, AP750, BF were mixed according to the formulations.

Results and Discussion

In **FIGURE 1(a) and (b)**, EP/BF showed lower strength in both of tensile and impact tests due to a poor interaction between the epoxy resin and basalt fiber. EP/BF-AT showed the best properties in both tensile and impact tests, which meant using acetone as pretreatment agent was a good option aiming at developing high performance basalt fiber. This pretreatment may efficiently assist the purification of the surface of basalt fiber without damaging its intrinsic properties; it would provide a good condition on the surface of fiber for further modification by silane. In **FIGURE 1(c)**, the tensile and impact properties of the EP/AP750 decreased as compared to EP, due to the introduction of AP750. It may be related to the poor compatibility between the AP750 and epoxy resin. Compared with sample EP, the addition of BF-AT into EP/AP750 obviously improved both of the tensile and impact strengths by 15.2 % and 27.8 %, respectively. [2] It meant two steps surface modification, pretreatment by acetone and further modification by KH550, to basalt fiber was an efficient approach to improve the interaction between the basalt fiber and resin.

In **TABLE 1**, the data of the LOI, UL-94, and cone calorimeter test are summarized. The LOI value of the EP/AP750 was 26.3 % and there reached V-0 rating and without dripping in the UL-94. However, as incorporating the BF-AT, the EP/AP750/BF-AT exhibited a slight reduction in the LOI value of 25.1 %, while the sample kept the similar phenomenon in the UL-94 test as EP/AP750. PHRR and THR values of EP were 950 kW/m^2 and 83 MJ/m^2, respectively. While the EP/AP750 sample was reduced sharply to 273 kW/m^2 and 48 MJ/m^2, registering a decrease of 71.3 % and 42.2 % in comparison to EP. In comparison, the introduction of BF-AT into EP/AP750, the value of PHRR and THR increased to 458 kW/m^2 and 51 MJ/m^2. [2] As expected, char layer formed during the combustion of EP/AP750 as physical barrier ensured the improvement of flame retardancy. The intumescent behaviors of EP/AP750/BF-AT during the combustion test was greatly suppressed due to the barrier effect of basalt fiber in the carbonaceous. This should be the main reason that led to the worse performance after introduction of BF-AT into EP/AP750 in the flame retardant test.

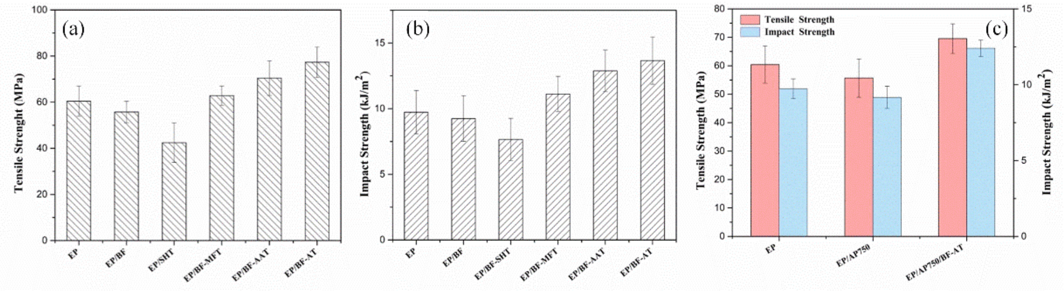

FIGURE 1. (a) Tensile strength, (b) unnotched impact strength behavior of epoxy-based composites; (c) Tensile and impact result of EP, EP/AP750, and EP/AP750/BF-AT [2]

TABLE 1. Parameters of EP and EP composites obtained from LOI, UL-94 and cone calorimeter test [2]

Sample	**LOI [%]**	**UL-94 [unit]**	**Dripping**	**PHRR [kW/m^2]**	**THR [MJ/m^2]**	**Char Yield [wt.%]**
Pure EP	23.2±0.2	NR	Yes	950±21	83±3	8.2±0.6
EP/AP750	26.2±0.2	V-0	No	273±12	48±5	32.8±0.3
EP/AP750/BF-AT	25.1±0.2	V-0	No	458±15	51±4	29.5±0.2

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O23- REPROCESSABLE, DEGRADABLE AND INTRINSICALLY FLAME-RETARDANT EPOXY VITRIMERS FOR CARBON FIBER REINFORCED COMPOSITES

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Main message: In this work, based on the typical dynamic covalent networks (CANs) of transesterification, firstly, we reported a facile way to prepare intrinsically flame-retardant epoxy vitrimers (EVs) combining rapid recycling and multiple shape memory effects by introducing dynamic ester-linkages with catalytic transesterification activity into the crosslinked networks of epoxy resins. Unfortunately, triaza-type catalysts usually show high cost, toxicity and low solubility in organic compounds. Therefore, it is of great importance and particularly urgent to develop a catalyst-free transesterification system. By adding the free phosphorus-containing diol, acting as both the flame-retardant moiety and the transesterification modifier with abundant primary hydroxyls and much higher reactivity than the *β*-hydroxyls, this work further proposed a new strategy to "kill two birds with one stone", in which the intrinsically flame-retardant carbon fiber composites with reprocessable matric resins and recyclable reinforced fibers were achieved. Afterwards, we utilized two kinds of the phosphorus-containing diols, with “trinity” structures containing phosphonate esters, primary hydroxyls and tertiary amine was applied in an epoxy-acid curing system to achieve the catalyst-free mixed transesterification within the adaptable carboxylate/phosphonate networks. Owing to the self-catalytic tertiary amine and highly reactive primary hydroxyls, the mixed transesterification within the adaptable carboxylate/phosphonate networks was accelerated, endowing facile reprocessibility and malleability of the vitrimers, which were further degraded into low-mass molecules by simple alcoholysis to achieve carbon fibers with nearly 100 % recyclability. This work provided a promising and feasible way to make sustainable and flame-retardant carbon fiber reinforced composites.

Keywords: Epoxy vitrimer; fire safety; transesterification; recycling; carbon fiber composites

Introduction

Fire risk and waste disposal are two major challenges for carbon fiber reinforced composites (CFRCs) due to the flammability and difficulty in recycling of either thermosetting matrix resins (typically epoxy resins, which possess the largest market share among the thermosetting polymers) or the carbon fibers. Moreover, many application fields of CFRCs usually require high flame retardancy, which is bound to require flame-retardant treatment of the composites. However, physically incorporating additive-type flame retardants or chemically introducing flame-retardant structures will further deteriorate the recyclability of the composites (Figure 1).

Covalent adaptable networks (CANs) provide new thought for the waste disposal problem of CFRCs, which makes the thermosetting matrix malleable or even degradable. Thanks to the CANS, these thermosets can change their topology by thermally triggered bond-exchange reactions [1]: at elevated temperatures they can flow like viscoelastic liquids and behave as reprocessable thermoplastics; while at low temperatures they behave like conventional thermosets, where the bond-exchanges are immeasurably frozen. Combining the advantages, these kinds of polymers containing associative CANs are named as vitrimers. Among them, ester bond in transesterification is relatively stable with a simple way to be incorporated by curing epoxy with acid or anhydride to construct epoxy vitrimers (EVs).

Regrettably, the application of catalyst-free transesterification-based EVs in CFRCs has rarely been reported, and the flammability problem of CFRCs is still of great difficulty to be solved at the same time. Herein, we reported a kind of flame-retardant EVs for CFRCs to solve the fire risk and recycling issues of CFRCs in a feasible and facile way.

Experimental

Flame retardancy of the vitrimers and their composites were evaluated by LOI, UL-94 V, cone calorimetry and smoke density test. Stress relaxation was performed on a dynamic rotational rheometer.

Results and Discussion

This work included four vitrimers and three relevant composites [2-4]. These vitrimer showed the expected fire safety with an LOI values higher than 30 and UL-94 V0 rating, as well as suppressed heat release and smoke generation during the burning test. More importantly, such flame retardancy can be greatly retained after reprocessing, and the resin matrix can be dissolved as the small-molecule diol participate in bond exchange reactions to achieve carbon fibers with nearly 100 % recyclability.

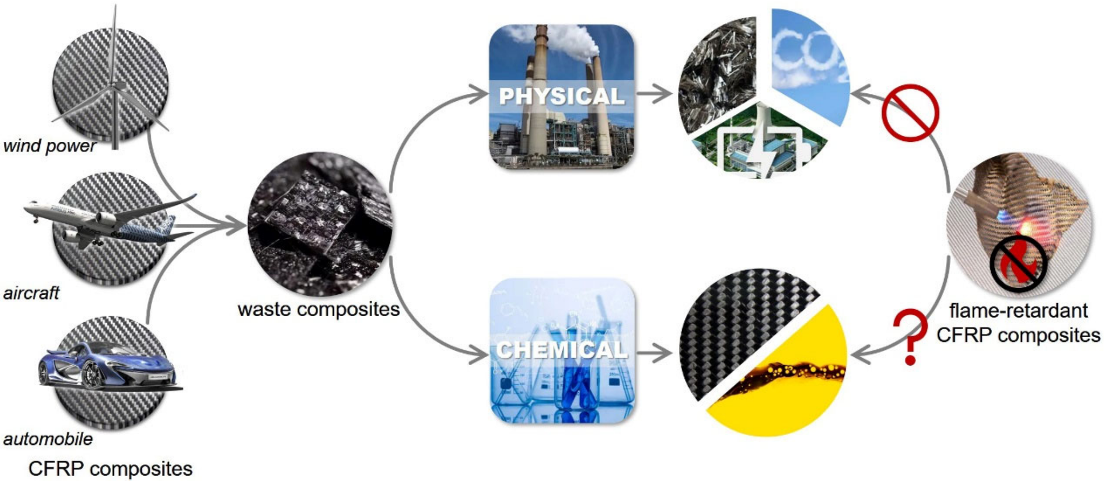

FIGURE 1. Conventional physical and chemical recycling route of waste composites and the dilemma of flame-retardant composites

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O24- Sustainable few-bilayers nanocoating for flame retardant polyester fabric

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Main message: Water-based polyelectrolyte solutions composed of chitosan (CH) and pectin (P) as carbon-rich biomacromolecules, and low molecular weight mono ammonium phosphate (MAP) were deposited on enzyme/corona discharge treated PES via layer-by-layer (LbL). With the deposition of 4 BL 0.5% CH_3/(1% P-30% $MAP)_{4.2}$, the fabric became self-extinguishable on a vertical flame test and exhibited a 42.6% lower peak heat release rate and nearly 40% reduction in the fire growth capacity compared to uncoated PES.

Keywords: chitosan, pectin, layer-by-layer assembly, multilayer nanocoating, monnoamonim phosphate.

Introduction

Despite its good mechanical properties, and low cost, PES is highly flammable [1]. While burning, it melts and produces ignited drops that can spread the fire. Many chemistries are employed to impart flame retardancy to PES, but many of them are toxic and environmentally persistent [2]. In our previous work, an intumescent system composed of chitosan, pectin, and monoammonium phosphate is applied to PES via the LbL assembly. Four bilayers (BL) of this system make PES self-extinguishing.

Experimental

100% polyester woven fabric (186 g/m^2) was used as a substrate for the LbL deposition. Esterase TEXAZYM PES was purchased from INOTEX Ltd. (Dvur Kralove, Czech Republic). Chitosan (CH) with Mw= 190,000-310,000 g/mol was supplied from Carbosynth Limited (Compton, Berkshire, UK). GRINSTED pectin LC 810 (P) was supplied from P.I.C. Co. DOOEL (Skopje, North Macedonia). Hydrochloric acid 37% (HCl), sodium hydroxide-pellets (NaOH), and monoammonium phosphate (MAP) were supplied from Sigma-Aldrich (Milwaukee, WI). 1 wt% CH was dissolved in DI water with pH 1.7 (the pH was adjusted using 37% HCl) and stirred until homogenous solutions were obtained [1]. Afterward, the pH of the solutions was adjusted with 1 M NaOH to pH 3. 1 wt% P was dissolved in DI water, and then the pH was adjusted to pH 4.2 (using 1M NaOH). The polyelectrolyte solution 1% P-30% MAP was prepared by dissolving 30 wt% MAP, respectively, in the already prepared 1 wt% P solution and then adjusted to pH 4.2. The pH value of every solution is given by the subscript number. Three samples for each LbL recipe were vertical flame tested following the ASTM D 6413 standard. The combustion behavior was tested with a micro cone calorimeter (MCC) according to ASTM D 7309, using an MCC-2 instrument (Govmark, Farmingdale, NY).

Results and Discussion

Images of the uncoated, coated with 20 BL 1% CH_3/1% $P_{4.2}$ and 4 BL PES 1% CH_3/(1% P-30% $MAP)_{4.2}$ presented in Fig. 1 show self-extinguishing behavior on VFT on the PES coated with 4BL MAP-containing recipe.

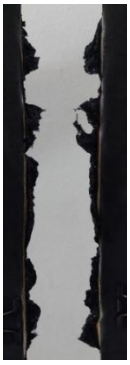
Recipe	Uncoated	1% CH_3/1% $P_{4.2}$	1% CH_3/(1% P-30% MAP)$_{4.2}$
BL		20	4
Picture after VFT			
Weight gain	/	8.49%	42.1%
Burning rate	10.7 mm/s	13.71 mm/s	/
Residual weight	No residue	38.65%	94.4%
Self-extinguishing	NO	NO	YES

FIGURE 1. Pictures from VFT of uncoated and LBL-coated PES with 20 BL 1% CH_3/1% $P_{4.2}$ and 4 BL PES 1% CH_3/(1% P-30% MAP)$_{4.2}$.

The results obtained from MCC are presented in Table 1. Polyester coated with 4 BL 1% CH_3/(1% P-30% MAP)$_{4.2}$ has a 42.6% lower peak heat release rate and 39.2% lower fire growth capacity than uncoated polyester fabric.

Table 1. MCC results for uncoated and LbL coated polyester.

Recipe	BL	T_{pkHRR} (ºC)	ΔT_{pkHRR} (%)	pkHRR (W/g)	ΔpkHRR (%)	THR (kJ/g)	ΔTHR (%)	FGC (J/g-K)	ΔFGC (%)
Uncoated PES	-	467.8		434.0		16.0		320.6	
1% CH_3/1% $P_{4.2}$	20	463.7	-0.9	309.8	-28.6	13.8	-13.8	248.2	-22.6
1% CH_3/(1% P-30% MAP)$_{4.2}$	4	407.3	-12.9	249.1	-42.6	12.4	-22.5	195.6	-39.2

Acknowledgement: The authors would like to thank the NATO Science for Peace and Security (SPS) program for their funding through the G5905 (MULProTex) project.

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K11- Advances on Flame Retardant Materials for Batteries in New Energy Vehicles

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Main message: Ni-rich lithium batteries and lithium-sulfur batteries have attracted extensive attention owing to their high energy density. However, their further developments are still restricted by the unsatisfactory electrochemical performance and the potential fire hazard. This presentation introduces our recent efforts on improving the fire safety and electrochemical performance of polymeric materials for batteries in the last 5 years. Multifunctional micro-nano flame retardant phosphazene microspheres are delicately designed and constructed for simultaneously improving the electrochemical properties and flame retardancy of batteries.

Keywords: Flame retardant, Phosphazene microspheres, Ni-rich cathode, Lithium polysulfide, Lithium-sulfur batteries

Introduction

The rapid market growth of electric vehicles puts forward high demand for a new generation of high-energy-density and high-safety lithium batteries. However, the limited energy density and unsatisfactory safety character of current liquid lithium-ion batteries (LIBs) cannot meet the requirments. Hexachlorocyclotriphosphazene cross-linked tannic acid microsphere (HT) is applied to gel electrolytes or separators to improve the fire safety and the performance for Ni-rich batteries and lithium-sulfur batteries (LSBs).

Experimental

HT was synthesized by a simple one-step precipitation polymerization [1]. The feed ratio was controlled with P-Cl to Ph-OH at a ratio of 1:3 or 3:1 (mol). The gel electrolyte with HT applied in Ni-rich batteries (15 wt% polyethylene glycol diacrylate and 85 wt% LEs (1M $LiPF_6$ in EC/DMC (v/v)) with an additional 1 wt% as-prepared HT) was prepared by in-situ polymerization (named as PEGGPE@HT). The separator applied in LSBs was prepared by a slurry coating method. As-prepared HT, SP, and PVDF were mixed well for 12 h in NMP in a mass ratio of 4:4:2 and coated on a commercial PP separator (named as H-CMP@SP separator).

Results and Discussion

As-prepared HT is a typical sphere with a smooth surface, which is attributed to multiple functionalities in hexachlorocyclotriphosphazene (HCCP) and tannic acid (TA). The diameters of HT are in the micro-nano scale with an average particle size of 192 nm, and its small size facilitates immersion in separator and electrodes (FIGURE 1.a) [2]. The flame-retardant properties of electrolytes and separators after the introduction of HT can be evaluated by ignition test (FIGURE 1.b). The PEGGPE@HT is difficult to be ignited in the first ignition, and the self-extinguishing time (SET) in the second ignition is only 6.0 s g^{-1}. The high flame-retardant efficiency of HT not only attributes to the abundant P-related free radicals released in wider temperatures but also to the synergistic char-forming reactions between HCCP and TA. The NCM811//Li battery matched with PEGGPE@HT features a higher initial capacity of 168.4 mA h g^{-1} than that of PEGGPE, and 143.6 mA h g^{-1} is retained after 200 cycles with an improved retention rate to 85.3% compared to PEGGPE (FIGURE 1.c). Furthermore, as shown in (FIGURE 1.d), the NCM811//Graphite pouch cell with PEGGPE@HT features excellent safety characters under extreme mechanical abuse conditions.

The HT exhibits excellent flame-retardant effect as a separator coating material (FIGURE 1.e). The combustion flame is indistinct and self-extinguished rapidly with the SET of only 0.32 s mg^{-1}. Furthermore, only a small area of the PP separator is burned in the process. The pouch cell with the coating is hard to burn and is quickly extinguished after two ignitions by a butane spray. On the contrary, the pouch cell without a PP separator is prone to violent combustion. The temperature in the fire is significantly decreased by 317.1°C with the coating, which will prevent the fire from spreading between the cells. The LSBs with the PP separator deliver only 414.6 mA h g^{-1} remained after 100 cycles with a low-capacity retention of only 37.8 % owing to the severe shuttle effect. Conversely, the LSBs with H-CMP@SP coating exhibit a high capacity of 1183.5 mA h g^{-1} at the initial cycle and remain 865.8 mA h g^{-1} after 100 cycles with an observably improved capacity retention of 73.2 %, which is resulted from the H-CMP@SP coating that provides stable adsorption and conversion sites for LiPSs [3].

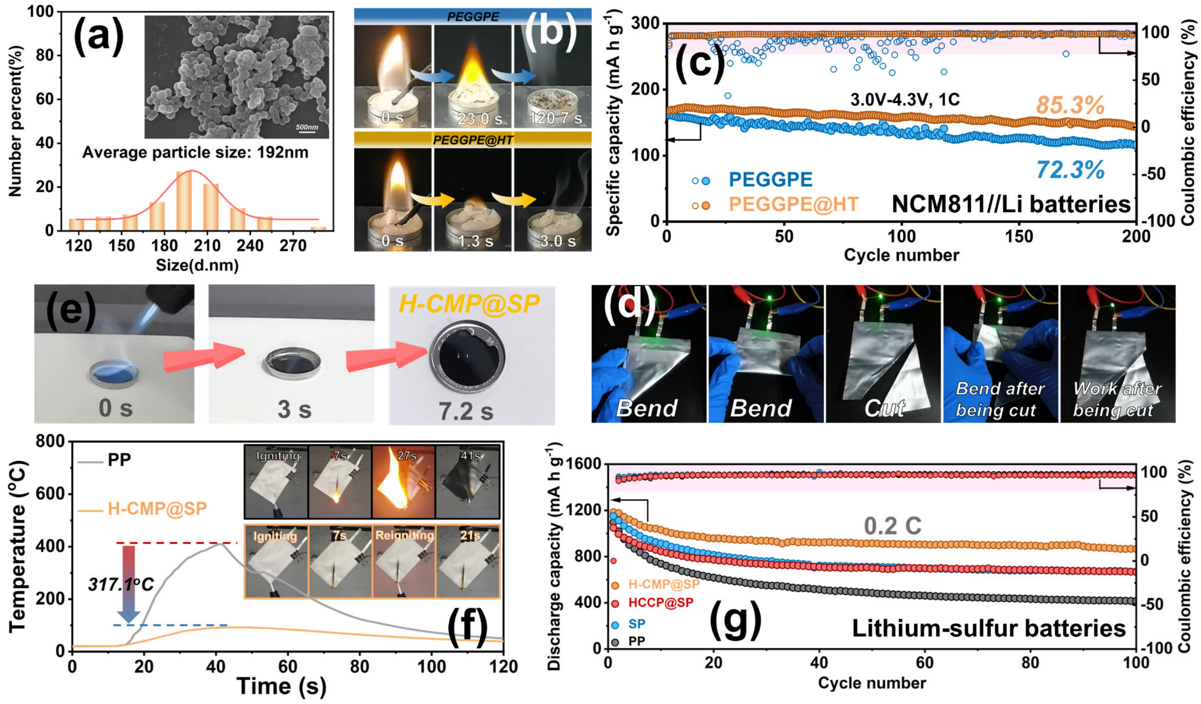

FIGURE 1. (a) Particle size distribution of HT (inset: the SEM image of HT). (b) Ignition test of PEGGPE@HT. (c) Cycle performance of NCM811//Li batteries. (d) Mechanical abuse tests of the NCM811//Graphite pouch cell. (e) Ignition test of H-CMP@SP separator and (f) pouch cells. (g) Cycle performance of lithium-sulfur batteries.

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O25- New chlorinating agents-free synthetic route for preparation of P-N and P-O dibenzooxaphosphacycles derivatives

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Main message:
The research concerned the investigation of a new synthetic route to functionalize P(=O)-heteroatom derivatives of dibenzooxaphosphacycles, such as 6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO) and dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (BPPO), by formally replacing the P-bonded hydrogen atom with N- and O-containing fragments to develop a more sustainable preparation of organophosphorus additives as flame retardants in polymeric matrices, avoiding the use of chlorinating agents.

Keywords: DOPO-derivatives, BPPO-derivatives, chlorinating agents free, synthetic route, flame retardants

Introduction

Dibenzooxaphosphacycles derivatives (with P-N or P-O bonds) are two relevant classes of Flame retardants (FR). To form them is necessary undergo a reaction to activate P-atom, which is based on the use of CCl_4, dangerous towards ecosystem and human health. [1] Alternatives to CCl_4 have been identified, [2a,b] but all require the use of chlorinating agents, with environmental and health impact. [3] This research proposes a new approach to P-atom functionalization for P-N or P-O FR compounds.

Experimental

The experimental activity was started trying to find unusual approaches for the functionalization of DOPO and BPPO. The substrate reacted with different amines and alcohols once a stoichiometric amount of I2 was added to the reaction mixture as oxidant. The amine plays three roles in the reactions: its conjugate base forms a new P-N bondwith the phosphorous atom of DOPO and BPPO. Moreover, the amine neutralizes the HI formed as by-product of I2 reduction and supports the deprotonation of the nucleophile. The products were easily isolated with high purity and moderate-good yield.

Results and Discussion

Due to the crescent restrictions to the use of halogen-based flame retardants from European commission since 2002, Organic Phosphorus Flame Retardants (OPFRs) are rising as one of the most promising alternatives for plastic fireproofing in a wide range of applications.

6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO) and its derivatives are considered suitable alternatives to halogenated FRs for their nontoxic proprieties as well as for their versatile flame extinguishing behavior in both gas and condensed phase.

On the other side, dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (BPPO) is a phosphonate compound considered as possible candidate as phosphorous flame retardant only recently. His derivatives have mainly been investigated only in form of P-C compounds through phospha-Michael additions or Pudovik reactions, to avoid use of chlorinating agents.

The objective of this research has been to develop a one-pot synthetic route, potentially industrializable, involving the oxidation of dibenzooxaphosphacycles, such as DOPO or BPPO, and the simultaneous functionalization of the phosphorous atom. This route allows to avoid the use of

chlorinating agents for the preparation of P-N and P-O derivatives of DOPO and BPPO, that could be used as flame retardants, as some of them are already know in literature.[4]
The synthetic route has been tested on different substrates, from amines to alcohols, and with different solvents. The reaction worked with aromatic amines such as aniline, p-toluidine, N-methylaniline and 4-aminostyrene as well as cyclic and linear aliphatic amines, such as morpholine, N-acetyl piperazine and butylamine.
The experimental outcomes suggest that DOPO reacts with I2 and the P-H bond is readily broken, possibly forming an intermediate compounds with a labile P-I bond which is readily undergo substitution by the nucleophilic group. The qualitative comparison with the same reactions carried out with DOPO indicated higher reactivity of BPPO, that required lower reaction times.

Decomposition was observed in compounds such as dimethylamine, piperidine or allyl-amine, which could be ascribed to their difficult deprotonation, that is instead favored by conjugated aromatic groups or electron- withdrawing fragments in the skeleton. The formal deprotonation of an amine is related to the electron density on the nitrogen atom, that also affects the basicity of the species. It is worth noting that the amines that reacted with DOPO and I2 are characterized by relatively low basicity. For instance, the pKa of piperidine is 11.1, while the values for morpholineand N-acetyl piperazine are 8.5 and 7.9, respectively.
The formation of the desired products was confirmed by NMR spectroscopy. In all the cases only a single sharp signal in the range 14.3 - 7.7 ppm was present in the 31P {1H} NMR spectra.
The disappearanceof the P-H resonance was confirmed by 1H NMR and FR-IT spectra. The first showed the disappearanceof the P-H resonance (δ = 8.05 ppm, 1JPH = 592.5 Hz, CDCl3, 298 K), while in the second ν-PH band (at 2438 cm-1 for DOPO) was absent.
The formation of new P-N bonds was highlighted in the case of aniline, p-toluidine and 4-aminostyrene by the NH resonance, falling around 8.5 - 8.7 ppm in DMSO-d6 solution, with a 2 JPH coupling constant of 9.1 Hz. The assignment was confirmed by the lack of HSQC cross-peaks. 13C {1H} NMR spectra confirmed the formation of the desired products, being the number of CH and C-ipso resonances in agreement with the proposed formulations.
The NMR characterization of cyclic aril amines, demonstrated the formation of the desired product as it has been possible to observe diastereotopic signals for morpholine molecule due to the formation of a chiral center in the phosphorous atom, in both morpholine and acetyl piperazine. In the latter it has been also observed the lack of rotation of acetyl group, forming a mixture 1:1 of regioisomers at room temperature, as confirmed by the 13C {1H} NMR spectrum.

I2-mediated functionalization of DOPO was extended to oxygen-containing compounds, alcohols in particular. In this case a supporting base is required, and triethylamine was used because of its inability to behave as nucleophile. The alcohols considered were methanol, allyl alcohol, 2-hydroxyethyl methacrylate and eugenol, the respective products have been synthesized with moderate yields. As for the previous cases, the proposed formulations were confirmed by the NMR spectra and FT-IR.

In order to fully avoid use chloro-based chemicals in the synthetic route, the functionalization of DOPO using green solvents has been investigated, selecting 2-methyl-tetrahydrofuran, a volatile cyclic ether generated by the chemo-catalytic treatment of biomass. The formal replacement of the P-H bond of DOPO with P-N by reaction with suitable aliphatic and aromatic amines and I2 was successfully carried out in Me-THF at room temperature between 40% and 72% and high purity.
The comparison with parallel runs carried out in dichloromethane showed that the reactions are generally slower in Me-THF. Acceptable yields were however obtained keeping the reaction mixtures overnight under stirring, and it is likely to suppose that further optimizations of the reaction conditions could improve the syntheses. The results of the synthetic route are promising and have been object for the drafting of a patent. The technology will be further investigated in a European project (FOREST project, grant agreement No. 101091790) to enhance flame retardancy of composites for mobility products.

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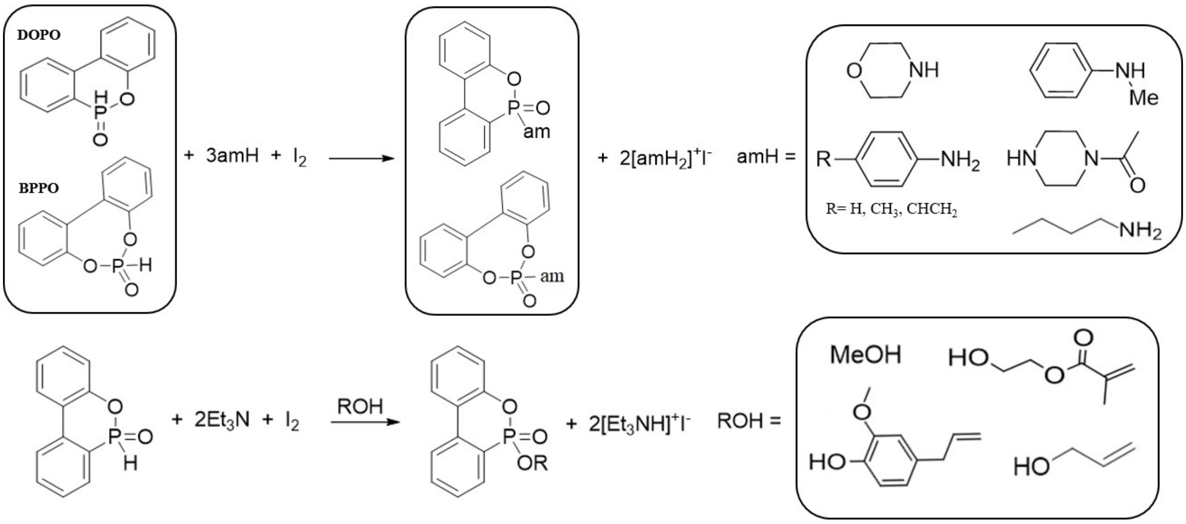

FIGURE 1. One-pot synthetic route for preparation of P-O and P-N derivatives of dibenzooxaphosphacycles DOPO and BPPO.

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O26- USE OF RECYCLED HIPS TO DEVELOP FLAME RETARDED MATERIALS FOR EEE – WHAT ARE THE CHALLENGES?

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Main message: Objective: to determine in the case of HIPS what are the challenges linked with the use of recycled materials in new products that have to present FR properties. Results: (i) the FR performance obtained using brominated and phosphorus-based FR additives are lower when using rHIPS and (ii) rHIPS contains pollutants and contaminants coming from various steps of the life cycle of the products. Conclusion: Challenges appear in the understanding of the role of pollutants in the FR mechanism of the different formulations and on the development of specific depollution techniques.

Keywords: HIPS, WEEE, recycling, pollutants, GWIT

Introduction

Nowadays, numerous regulatory and voluntary initiatives have brought the subject of plastics recycling and of their integration into new material as an urgent need. As an example, European Parliament resolution of 10 February 2021 on the New Circular Economy Action asks the European Commission to work on binding targets concerning the recycled content of new products with the objective to increase it. In that frame, the aim of this study is to determine the challenges the development of flame-retardant materials faced when recycled polymers are used instead of raw materials. The study focuses on HIPS from WEEE.

Experimental

Recycled materials were supplied by Coolrec and Skytech in the frame of the PEPSI-r project. They were first fully characterized using various techniques (TGAs performed on a TA Instruments Q600, in a N_2 atmosphere at 10°C/min from 25 to 600°C – DSC performed on a TA Instruments Discovery in a N_2 atmosphere at 10°C/min from -20 to 200°C – SEM images taken using a JEOL JSM 7800F LV at 5 kV– XR Diffraction – -X-ray fluorescence using a spectrometer of the S2 Ranger type from Bruker – ATR infrared spectra recorded in a range 400 and 4000 cm^{-1} with a spectrometer Nicolet iS50). The contaminants of the recycled materials were extracted using micro-wave assisted extraction and then characterized using GC-MS (Shimadzu). Two types of flame retardant additives were used: brominated FR [1] (BrFR1 and BrFR2 added in the polymer at a 5wt% Br content) and phosphorus-based FR (PhFR1 [2] and PhFR2 [3], added as recommended by the supplier respectively at 5 and 13wt.-%). Formulations were prepared using extrusion (Extruder Haak Rheomex OS, Thermo Scientific) and the FR properties were evaluated according to glow-wire flammability index, GWFI (DS/EN IEC 60695-2-12).

Results and Discussion

The first step of the study has the objective to evaluate if the flame retardant performance achieved with virgin HIPS can also be reached with the same amount of additives using rHIPS i.e. HIPS manufactured from post-consumer plastic. rHIPS obtained for various categories of WEEE were considered including category 1 (large household appliances cold; LHA), 2 (small household appliances, SHA), 3 (IT Equipment and Telecommunications) as well as multipurpose based-waste (MP). Results are presented in Table 1 for rHIPS(I) and rHIPS(MP) and for the two types of FR additives: brominated- based and phosphorus-based flame retardant. Those results show that whatever the type of FR additive and of rHIPS, the performance are lower when recycled materials are used. Moreover, it can also be concluded that the decrease in performance depend both on the type of FR additive and onthe type of rHIPS. Indeed, in the case of BrFR, the performance are better using BrFR1 in rHIPS(MP) whereas using BrFR2, better performance are achieved in the case of rHIPS(I).

TABLE 1. GWFI obtained for FR formulations based on virgin HIPS and rHIPS obtained from category 1 WEEE (rHIPS(I)) and from multipurpose WEEE (rHIPS(MP))

GWFI (°C)	HIPS	rHIPS(I)	rHIPS(MP)
BrFR1	950	650	750
BrFR2	950	850	650
PhFR1	850	650	650
PhFR2	950	750	650

The second step of the study was, as a consequence, dedicated to the characterization of the recycled materials to better explain why the FR performance of rHIPS are lower. The objective is to identify if differences between HIPS and rHIPS exist, if they vary depending on the origin of the waste from both qualitative and quantitative aspects. The strategy followed for that purpose is illustrated in Figure 1. Moreover, as an example of this part of the work, Figure 1 also presents the SEM images of HIPS and of rHIPS obtained for rHIPS(I) and rHIPS(MP). HIPS is a two-phase system formed by the immiscibility of polystyrene and polybutadiene. Polystyrene forms the continuous phase (matrix) and polybutadiene does the disperse phase (elastomer nodules). From the SEM images, the distribution and size of the elastomer nodules can be determined. We thus demonstrated that the size and distribution of the size of the nodules vary depending on the WEEE categories used to manufacture rHIPS. It could, at least partially, explained the difference in term of FR performance. Various type of pollutants and additives were also identified in rHIPS including plasticizers, other type of polymers (mainly PP and PE), stabilizers as well as degradation products of HIPS.

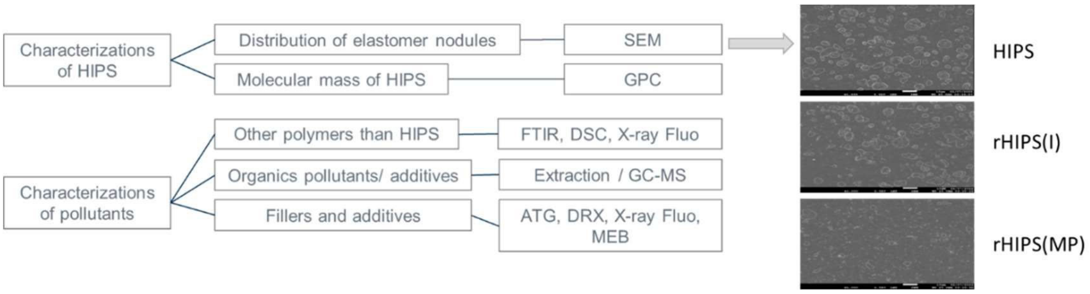

FIGURE 1. Strategy followed in the study to fully characterize rHIPS and example of results (SEM images of HIPS and rHIPS.

Conclusion: We can thus conclude that the pollutants will affect the performance of the FR formulations. Challenges thus appear in the understanding of the role of pollutants in the FR mechanism of the different formulations and on the development of specific depollution techniques.

Acknowledgement: The authors want to thank EcoSystem for its financial support. They also want to thank all the partners of the project PEPSI-r (Coolrec, Skytech, Haëger, Legrand and Ecosystem) for helpful discussion and to supply the material.

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O27- TOWARDS RECYCLING OF FIRE RETARDED POLYAMIDE 12 FOR LASER SINTERING

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Main message: One of the main concerns of Laser sintering (LS) is the recyclability of the polymer powders (mainly polyamides). Indeed, post condensation reactions are prone to increase the molar mass of PA leading to an increase on part porosity. This increase highly impacts its mechanical properties as shown by various works on the literature. However, at the best of our knowledge, no work evaluated the influence of flame retardants on polymer processability and on the fire behavior of parts made with recycled PA12.

Keywords: Laser sintering, polyamide 12, recycling, fire behavior.

Introduction

Polyamide 12 is the main polymer used for LS, accounting for about 80% of the global market. Various works on literature evaluated the influence of recycling PA12 in terms of mechanical properties, part porosity and crystallinity of polymer powder. Furthermore, the influence of oxygen content on build chamber was also evaluated and thermo-oxidation effects were highlighted [1] but no work evaluated its influence on fire behavior of parts. Thus, the present work aims to evaluate the influence of two flame retardants on the recyclability and fire behavior of parts made by LS.

Experimental

Polyamide 12 (PA2200) powder with a median diameter (D50) of 58 µm was supplied by EOS. Based on the results of a previous work, two flame retardants were evaluated: Ammonium Polyphosphate (Exolit AP 422) and zinc borate (Firebrake ZB from Rio Tinto Minerals) at 30wt% [2]. Test specimens (sheets of 70×70×4 mm^3) were produced with a LS equipment (SnowWhite from Sharebot-Italy). First build process starts with virgin PA12 or blends of PA with FRs. After each build process the partcake material was used entirely for further processing cycles without refreshing. The resulting partcake powder was sieved and mixed (15 min, 60 rpm) after each build process in order to obtain a homogeneous powder blend.

A cone calorimeter from Fire Testing Technology was used with an irradiance of 35 kW/m^2 to test SLS plates. Thermal stability of individual components and FR compositions were investigated using thermogravimetric analysis (SETSYS Evolution from Setaram) under nitrogen flow (40 mL/min) from 50 to 750 °C at 10 °C/min. The determination of SLS processing windows regarding the incorporation of the different FR additives was carried out using differential scanning calorimetry (DSC Pyris Diamond from Perkin-Elmer). A temperature ramp of 10 °C/min was applied to investigate fusion and crystallization processes defining the SLS processing window. IRFT spectroscopy (Bruker Vertex 70) was used to investigate modifications of absorption bands through reprocessing of FR compositions.

Results and Discussion

Figure 1 shows cone calorimeter results of neat PA12 and PA12 with 30wt% of APP and ZB with four recycling cycles and Table 2 regroups results of selected formulations. For neat PA12, a decrease on TTI and pHRR is observed for the first 3 recycling cycles, compared to virgin PA12 (PA-0). Interestingly, increasing to four cycles, an increase on pHRR and TTi is observed (PA-4). Moreover, it seems that the addition of APP does not lead to significant differences on the fire behavior of samples along the recycling cycles. Significant changes are observed when mixing PA12 and zinc borate. For the first and second cycles (ZB30-1 and ZB30-2 respectively) an increase on pHRR is observed. Moreover, increasing the recycling cycles (ZB-3 and ZB-4) a very different behavior is observed, with a pHRR that appears later compared to ZB30-0 and the HRR curve profile that changes. Various works on the literature shows that post condensation reactions take place when polyamides are exposed to heat which leads to an increase of the polymer molar mass, which have an impact on porosity and mechanical properties of LS parts [3,4]. Beyond post condensation reactions, Yang et al. [1] also showed that laser beam may have an important influence on PA12 degradation. However, the addition of a FR able to absorb part of the laser irradiation could decrease the rate of polymer degradation, improving the recyclability of polymer/FR blends.

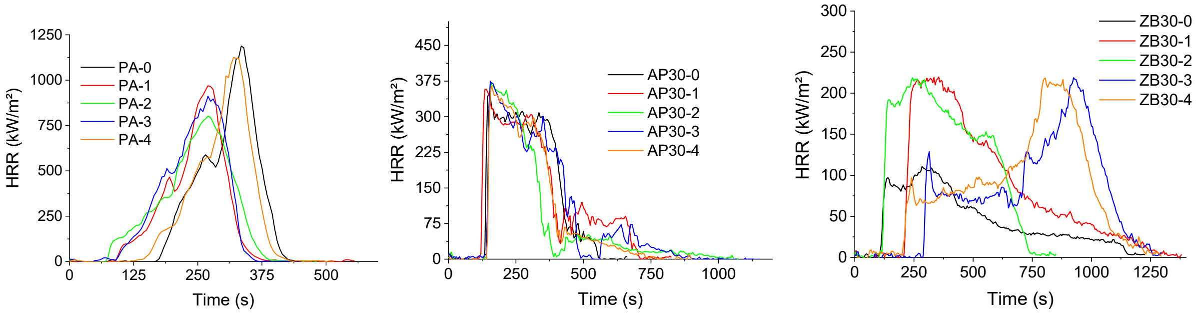

FIGURE 1. Cone calorimeter results of flame retarded formulations.

TABLE 1. Selected properties of flame retarded polymeric samples

Sample	TTI (s)	pHRR (kW/m^2)	THR (MJ/m^2)	Residue (%)
PA-0	154±10	1416±200	131±5	-
PA-2	80±5	893±98	120±1	-
PA-4	193±20	1037±102	115±4	-
AP30-0	122±10	351±5	92±6	31±2
AP30-2	144±1	373±2	81±6	27±1
AP30-4	143±2	374±14	86±5	27±1
ZB30-0	115±20	125±15	95±8	38±3
ZB30-2	189±5	175±61	98±6	33±1
ZB30-4	180±20	220±22	95±5	29±2

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O28- Effectiveness of phosphinates and radiation crosslinking on fire-retardancy of unfilled and wood-filled bio-based polyamides for application in E&E

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Main message: Fire-retarded compounds with bio-based polyamides (PA) 6.10, 10.10 and 11 were developed which reach UL94-classification V-0 (1.6 mm) and fulfil requirements of the glow-wire test and for comparative tracking index (CTI). Three types of phosphinates were evaluated. The effectiveness of radiation crosslinking was investigated as a potential route to improve fire-retardancy, thermal stability and mechanical performance of composites for application in electrical and electronic equipment (E&E).

Keywords: Bio-based polyamides, phosphinates, wood particles, radiation crosslinking, fire testing.

Introduction

The objective of this research project was to develop fire-retarded bio-polyamides with and without wood particles for application in E&E. There are currently only few fire-retarded compounds available with a high bio-based content. Phosphinates and particularly diethyl aluminium phosphinate (AlPi) have proven their effectiveness in polyamides [1]. The fire retardancy mechanism of AlPi as single FR and in combination with melamine polyphosphate in glass-fiber reinforced PA 6 has been investigated in detail by Braun et al. [2]. To confer high temperature stability to the composites, in this project, radiation crosslinking was performed which represents an innovative strategy to improve functional properties of bio-composites [3].

Experimental

In total, 20 formulations (compounds) were prepared using a laboratory kneading mixer and mini injection-molding. Bio-based PA6.10, 10.10 and 11 (Ems-Grivory; Arkema) were combined with phosphinates (Exolit OP 1312, OP 1400 and OP 1230; Clariant Plastics and Coatings). Depending on the thermoplastic melting point, wood particles (J. Rettenmaier & Söhne) were also included. Trimethallyl isocyanurate (TAICROS M; Evonik) was used as cross-linking agent in formulations subjected to electron beam irradiation (66 kGy in the case of formulations with PA 6.10, and 165 kGy for PA 10.10 and 11). The following tests were performed: degree of crosslinking (gel content), UL94, glow wire test, comparative tracking index, cone calorimeter, thermogravimetric analysis, tensile and notched impact strength tests, dynamic mechanical analysis (DMA).

Results and Discussion

Following optimization, all formulations which contained phosphinates reached V-0 classification in UL94 tests at 1.6 mm thickness. When TAICROS M was included and materials were irradiated, in some formulations, classification worsened. This could not be attributed to burning dripping but long burning times. However, when wood particles were included, no change in classification was determined for irradiated samples. In the glow wire test, 960°C was reached for most of the non-irradiated formulations. Values were slightly lower when TAICROS M was included and samples were irradiated. Regarding comparative tracking index (Figure 1), 600 V was reached for most of the non-irradiated formulations (irradiated samples were not tested).

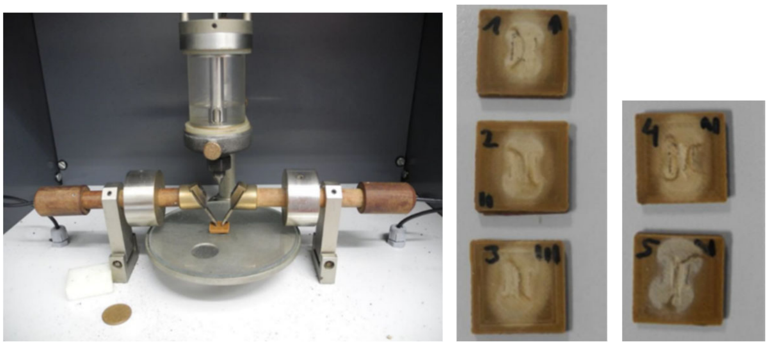

FIGURE 1. Set-up of comparative tracking index measurement (left) and samples after test (right). Pictures provided by Hager Electro GmbH & Co. KG, Blieskastel, Germany.

Cone calorimetry results are shown in Table 1. Sample size was 100 mm x 100 x 3 mm. Peak heat release rates and maximum average rates of heat emitted (MARHE) were significantly reduced when wood particles were included in formulations while time to ignition was reduced.

TABLE 1. Cone calorimeter results for fire-retarded bio-based PA (heat flux: 35 kW/m^2).

Sample	pHRR [kW/m^2]	MARHE [kW/m^2]	THR [MJ/m^2]	TSP [m2]	TTI [s]	Residue [%]
PA6.10[1]	263 (3)	79 (2)	71 (2)	11 (5)	39 (1)	8.5 (0.3)
PA10.10[1]	567 (69)	81 (4)	60 (2)	18 (1)	50 (1)	10.5 (1.8)
PA10.10[2]	174 (38)	38 (12)	49 (12)	16 (3)	40 (1)	16.6 (2.2)
PA11[1]	645 (46)	124 (21)	77 (1)	20 (2)	56 (1)	9.7 (0.8)
PA11[2]	151 (84)	43 (21)	62 (17)	16 (2)	42 (1)	17.5 (4.2)

[1] excluding wood particles; [2] including wood particles; standard deviation in parentheses.

Using DMA, it was determined that the stiffness (storage modulus) of crosslinked, fire-retarded PA was significantly increased in the high-temperature region compared to non-crosslinked PA. Glass transition temperature was also increased for crosslinked PA. Temperature stability was highest for PA6.10 and lowest for PA11. Cross-linking increased tensile strength and MOE but decreased notched impact bending strength. Further results will be presented at the conference.

Acknowledgement: Funding for this research project (grant number FKZ 22022717) was provided by the Federal Ministry of Food and Agriculture (BMEL) and their funding agency Fachagentur Nachwachsende Rohstoffe (FNR) e.V.

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K12- Sustaining the CHNOPS building blocks of life, but Phosphorus-based flame retardants first!

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In addition to the well-known Green Chemistry principles that have revolutionized optimizing and sustaining linear processes, Circular Chemistry[1] moves beyond value extension and aims at making chemical processes and production cycles circular by using waste (or ideally products) as resource.

I will highlight the importance of using waste as resource, as well as stress the need to develop Circular Technologies, which use chemistry as enabling tool to target the conservation of, in particular the key biogenic elements CHNOPS, as well as contribute to solving pressing connecting waste problems.[2] Such an endeavor will combine molecular design and synthesis with the environmental fate and impact of current products targeting safe by design (no persistent, bio-accumulative, and toxic compounds; green chemistry) and design for re-use, recovery and recycling (circular chemistry).

In this lecture, I will focus on phosphorus sustainability in general,[3] and sustainable strategies to synthesize phosphorus compounds for flame retardant applications in particular.[4]

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O29- Synthesis by reactive extrusion, properties and ageing of flame retardant PBT vitrimers

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Main message: Flame retardancy of a vitrimer matrix has been obtained for the first time using an additive approach. A flame retarded PBT vitrimer matrix containing aluminum phosphinate has been successfully prepared via reactive extrusion. Aluminum phosphinate has been proven to act as a catalyst in the vitrimer formation enabling quicker exchange reactions. Similar thermal and flame-retardant properties as with a PBT matrix were obtained. Ageing of the flame retarded sample was studied.

Keywords: vitrimer, poly(butylene terephthalate), flame retardant additive, UL-94 test, ageing

Introduction

Addition of fillers and flame retardant in a vitrimer matrix to functionalize it is not a trivial thing. The properties of these covalent adaptative networks are indeed conditioned by the possibility to make exchange reactions in their networks.[1] The occurrence of such reactions in presence of additive has barely been investigated. Addition of aluminum phosphinate salt in a PBT vitrimer matrix during its synthesis by reactive extrusion has been investigates as well as their properties and ageing.

Experimental

PBT (Valox 315, Sabic), DGEBA (DER 332, Aldrich), zinc acetylacetonate (Aldrich) and aluminum phosphinate (DEPAL, Clariant) were used to synthesized the materials. 8 minutes extrusion were performed at 270°C, 60rpm in a DSM microextruder. Stoichiometric ratios 2:1 [epoxy]/([OH]+[COOH]) and 0.11:1 [catalyst]/([OH]+[COOH]) were used. DEPAL was incorporated at 10, 15 and 20 wt.-% during the synthesis. Gel ratio were measured after immersion in HFIP. UL-94 tests were performed to evaluate the fire reaction properties. DSC and TGA were performed on a TA discovery apparatus. Two types of ageing scenarios have been performed: 7 days at 70°C and an immersion in water at 50°C for a month.

Results and Discussion

Demongeot et al have described the synthesis by reactive extrusion of PBT vitrimers from PBT epoxy and a transesterification catalyst.[2] Based on this work, the formulations detailed in table 1 have been prepared. Formulations containing PBT, epoxy and DEPAL were consequently prepared with and without the transesterification catalyst as well as references with only PBT and DEPAL. Crosslinked networks were obtained for all formulations containing epoxy. The crosslinking without the Zn catalyst shows that DEPAL is able to act as catalyst of the transesterification reactions. It is indeed able to partially dissolve in the matrix as highlighted by electron probe microanalyser (EPMA). Al and P mapping show homogeneous dispersions of the DEPAL without presence of aggregates in the gel part. In addition, the ^{27}Al and ^{31}P NMR analyses of the gel part of the materials show the appearance of new small peaks attributed to changes in the P and Al environments. It is assumed that similarly to what occurs with the zinc acetylacetonate, Al is able to connect with the matrix. This leads to a partial loss of coordination between Al and phosphinate. The gel ratio is the same in presence of 10, 15 and 20wt.-% of DEPAL as the one of the non flame retarded vitrimer. The stress relaxation test results prove that the networks formed are able to relax quicker in presence of the DEPAL. Thermal analysis confirms that the PBT chains between the crosslinks is still able to crystallize but to a lower extent. The thermal stability of the materials analyzed by TGA are not modify by the partial crosslinking.

The UL94 ratings of the flame retardant vitrimers are identical to the non vitrimer equivalents. However, the impact of the vitrimer matrix is visible on the behavior and dripping of the materials. Indeed, the presence of crosslinks prevents the flowing of the matrix as it can be seen on the figure 1 compared to the non-crosslinked materials. The melt flow is decreased. This enable to prevent the elongation and the flowing of the material during the UL test. It is clearly demonstrated thanks to the residual weight measurements of the sample after the test. All the vitrimers present lower mass losses and consequently a reduced dripping compared to the thermoplastic materials.

Accelerated ageing tests have been performed on vitrimers and thermoplastic formulations containing 20% of DEPAL. Two different conditions have been selected: 7 days at 70°C and one month of immersion in water at 50°C. The gel ratio decreases with the ageing treatments particularly when the sample is immerged in water. However, in the chosen conditions, it was possible to keep a reduced dripping of the materials. The UL94 rating was not impacted by the ageing of both the thermoplastic and the vitrimer samples.

TABLE 1. Details of the formulations, their gel ratios and UL-94 rating

Sample	Composition	Ageing	Gel ratio [%]	UL94 rating
PEZ	PBT+ epoxy + Zn(acac)$_2$	None	68 ± 4	NC
PA 10%	PBT + DEPAL	None	0	V2
PEA 10%	PBT+ epoxy + DEPAL	None	65 ± 4	V2
PA 15%	PBT + DEPAL	None	0	V0
PEA 15%	PBT+ epoxy + DEPAL	None	66 ± 4	V0
PA 20%	PBT+DEPAL	None	0	V0
		Aged for 7d at 70°C	0	V0
		Aged for 30d at 50°C in water	0	V0
PEzA 20%	PBT+ epoxy + Zn(acac)$_2$ + DEPAL	None	68 ± 6	V0
PEA 20%	PBT+ epoxy + DEPAL	None	63 ± 5	V0
		Aged for 7d at 70°C	45 ± 4	V0
		Aged for 30d at 50°Cin water	15 ± 4	V0

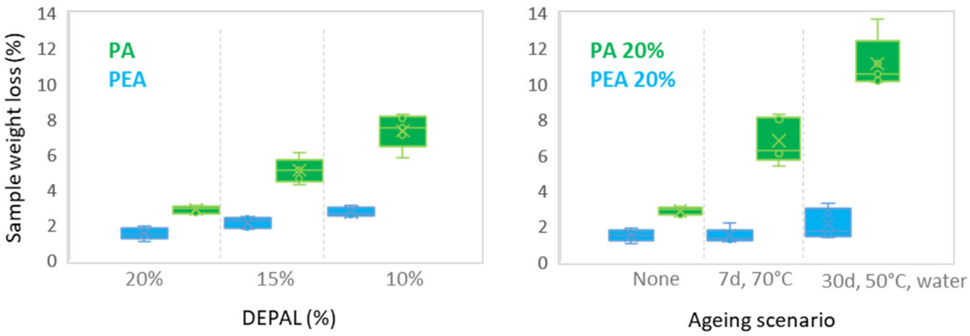

FIGURE 1. Box plots of the average weight loss of 5 UL94 samples after the test versus the DEPAL contents on the left and versus the ageing scenarios for samples containing 20% of DEPAL (on the right).

Acknowledgement: Financial support of the university of Lille and the French region “Hauts de France”

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S11- BENCH-SCALE FIRE STABILITY TESTING OF CARBON FIBRE REINFORCED POLYMER LAMINATES WITH PROTECTIVE LAYERS

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Main message: Fire resistance testing of components made of carbon fibre reinforced polymers (CFRP) composites usually demands intermediate-scale or full-scale testing. In this study, a bench-scale test is presented as a practicable and efficient method to assess the improvement in structural integrity of CFRP with different protective layers during fire.

Keywords: Fire stability, Bench-scale fire resistance testing, Carbon fibre reinforced polymer

Introduction

Fire stability is one of the biggest issues of carbon fibre reinforced polymer (CFRP) composites, particularly when they are using in load bearing applications. As soon as the glass transition temperature of polymer matrix (100-200°C) is achieved, the composite loses its structural integrity, what leads to the distortion and failure.[1,2] Generally, the fire stability testing of components in realistic conditions requires intermediate-scale or full-scale investigations.[2,3] The proposed bench-scale setup offers the possibility to simulate the key parameters for a proper assessment of fire resistance of composites during their development.[4,5]

Experimental

The possibilities of bench-scale fire stability testing were presented by investigating new types of laminate structures, which exhibit promising flame retardancy and fireproof properties. There were two different approaches to protective concepts of CFRP composites: CFRP laminate systems with combinations of different internal fireproof layers: metal foil, thermoplastic foil, ceramic plate, rubber tape Pyrostat, basalt fibres and kenaf fibres and laminate systems with different protective coatings: paper with a thickness in the range of µm consisting of cellulose nanofibre (CNF)/clay nanocomposite, nonwoven mats with thickness in the range of cm and intumescent coatings with a thickness in the range of mm.

The principal fire stability test is based on simultaneous application of fire and mechanical load. Since the carbon fibres can transfer the tensile loads quite well, the compression load is chosen as a required mechanical load for a test. The fire tests were preceded by a static load test at room temperature to determine ultimate failure load. The specimen was loaded with a compression force until the failure load was reached, which was observed as a buckling. The bench-scale setup is presented at Figure 1a. For the fire tests, 10% of compression failure load and direct flame of a fully developed fire (heat flux ≈ 180 kW m-2) were applied simultaneously to the specimen, while the time to failure was measured. Figure 1b presents the fire resistance test of CFRP composite in bench scale.

Results and Discussion

The time to failure of CFRP composite was 17s. All specimens with coatings showed a significant extension of time to failure. Figure 1c shows the comparison of time to failure of each of the system for CFRP laminates with intumescent coatings. The other approach of CFRP laminate differs with a protective concept. Every system consists of two different interlayers, where the one layer constitutes the fireproof protection, that delays the rise of temperature in the rest of laminate, and the second layer provides very good structural connection with carbon fiber layers, thus improves the mechanical integrity of CFRP composite in fire.

Although bench-scale tests are limited with respect to assessing the performance of components and structures, they are valuable in the assessment of different materials concepts. Furthermore, the reduced effort of conducting bench-scale test (lower costs, time, personnel resources) makes it more practical and effective.

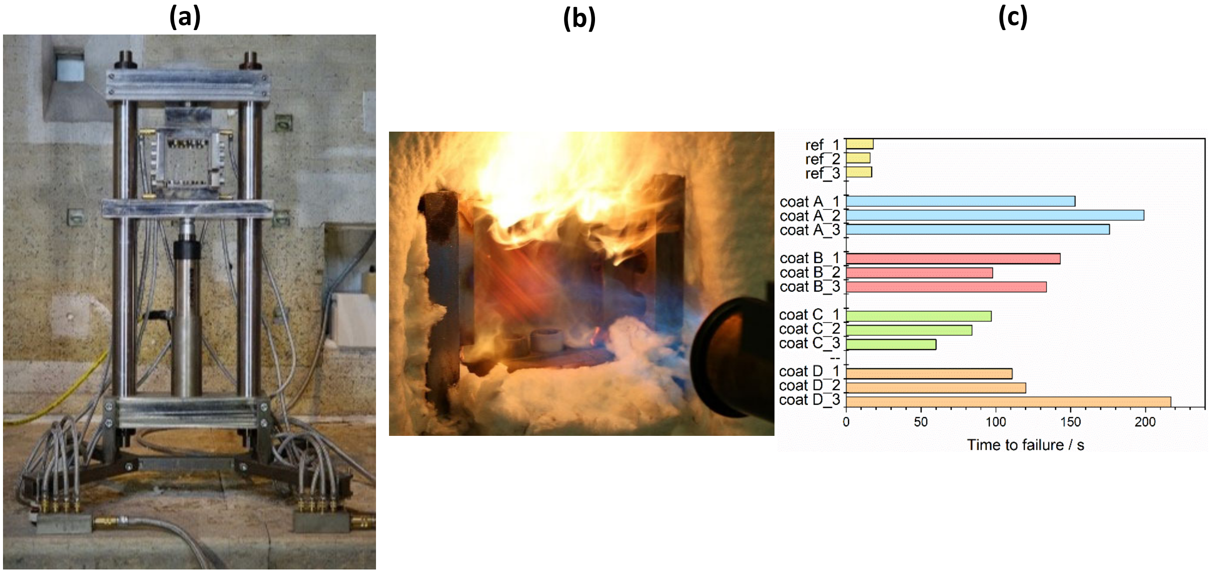

FIGURE 1. (a) The isometric view of the bench-scale compression device; (b) fire resistance test of CFRP composite in bench scale; (c) the comparison of time to failure of each system of pure CFRP composite (ref) and laminates with intumescent coatings (coat A-D).

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S12- MODELLING OF THE SWELLING BEHAVIOR OF A FIRE RETARDED MATERIAL UNDER A CONE CALORIMETER

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Main message: The swelling behavior of intumescent materials controls their pyrolysis process. It must be therefore considered to improve the predictability of pyrolysis models. In this work, a swelling model was developed in order to predict the behavior of samples of EVA/ATH polymer (ethylene vinyl acetate containing aluminum trihydroxide). This material is used for electrical cables. The model was validated against our own experiments, including the swelling rate, and was found to obtain good results. The originality of this model is its ability to model the pyrolysis process without imposing the densities of the intermediate and final materials, hence making it more predictive than existing models.

Keywords: Modelling; swelling; deformation; EVA/ATH; cone calorimeter experiments.

Introduction

Electrical cables used in nuclear power plants, and elsewhere, are made with materials that can swell (or deform/shrink) under heat flux. This is the case of EVA/ATH or PVC cables. However, this phenomenon is not considered in the existing literature dedicated to the modelling of the pyrolysis of electrical cables [1,2,3]. Indeed, this phenomenon has an important impact on the pyrolysis process by modifying the exposure of the combustible surface to the external heat flux. In addition, the transport of pyrolysis gases is also impacted. Therefore, this phenomenon must be considered to improve the reliability of pyrolysis models of these materials.

The objective of this work was to develop a model that represents the swelling of EVA/ATH samples. The model was implemented in Gpyro [4] and compared to our own experiments performed with a cone calorimeter. The originality of the model lies on the fact that it is more predictable than existing works. It allows to successfully predict the mass loss, the swelling of the sample as well as density evolution in function of time. This last parameter, density, has an important influence on the behavior of the material and is usually imposed as a fitting parameter in the literature.

Experimental and Modelling

The deformation model is an adaptation of the model presented in [5], which was written for an intumescent coating. The model was modified and adapted to represent the swelling of EVA/ATH. In addition, the model was further enhanced to account for the action of the porosity on the deformation process.

FTT (Fire Testing Technology) Mass Loss Calorimeter was used to evaluate samples of EVA/ATH following the procedure defined in ASTM E 906. The equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain heat release rate (HRR) rather than employing the oxygen consumption principle. External heat flux of 35 kW/m² was applied. This heat flux corresponds to mild fire scenario. The mass loss calorimeter permits to determine the mass loss and the heat release rate (HRR). When measured at 35 kW/m2, HRR is reproducible to within 10%.

The sample thicknesses studied were 1mm and 4mm. To characterize the swelling, experiments were carried out to measure the evolution of the sample thickness as a function of time. In addition to the mass loss, the temperature at the back of the EVA/ATH sample was measured by a thermocouple. The evolution of the density with time was also measured by measuring the volume of the sample by tomography, as well as its mass.

Results and Discussion

Figure 1 compares the results obtained by the model with those measured experimentally for the 4 mm sample (similar results were obtained for the 1 mm sample). The evolution of the thickness predicted by the deformation model is in good agreement with the experiments. The model is also compared to the classical models used in the literature (based on imposed densities of the intermediate and final materials), showing a better prediction of the deformation model. The model presented a good prediction of the evolution of the density as a function of time. Being able to predict the density is an important result because this parameter is a must for the use of pyrolysis models. Moreover, it is difficult to measure experimentally and is most often used as a fitting parameter in the literature. Thus, the deformation model shows an ability to improve the overall predictability of the pyrolysis model.

Further results will be presented at the conference.

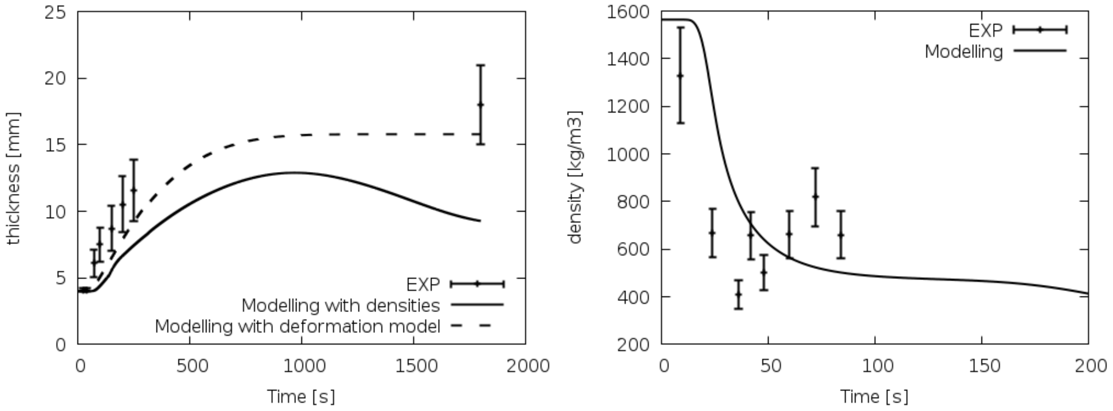

FIGURE 1. Comparison of the thickness (left) and the density (right) predicted by the deformation model and the one measured experimentally.

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S13- COMPARISON OF FIRE RETARDANT TIMBER TREATMENTS

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Main message: Fire retardant impregnated plywood shows low heat release during flaming combustion and high char yields, but releases a significant amount of carbon monoxide during under-ventilated flaming. Plywood painted with fire-retardant intumescent coating provide similar fire protection, but with lower char yields and significantly lower yields of toxic products. Fire risk assessment should include both flammability and toxicity.

Keywords: Intumescent coatings, smoke toxicity, fire stages, fire effluents

Introduction

Sustainable, combustible materials like timber are having a renaissance in construction. Ensuring combustible materials can safely replace non-combustible materials requires systematic study to assess fire-retardant timber treatments (e.g. untreated, vs. painted and impregnated plywood). Fire behaviour under different fire stages, smoke development and toxic yields are determined in order to assess fire risk in modern buildings. A scenario with acoustic panelling (figure 1, left) is discussed.

Experimental

Thermal degradation of untreated plywood and Euroclass B-s1, d0 fire retardant impregnated and painted plywood was investigated with thermogravimetry (TGA), combustibility with micro combustion calorimetry (MCC) and reaction-to-fire tests with cone calorimetry (CC) under well-ventilated conditions. Replications of different fire stages with the steady state tube furnace (SSTF) [1,2] allowed quantification of toxic products during flaming combustion as a function of ventilation. Fire effluent was sampled to quantify specific fire gases with ion chromatography (HPIC) [3].

Results and Discussion

CC experiments demonstrated significant fire protection of timber with reduced total heat release for both coated (- 21%) and impregnated timber (- 45%) and increased times to ignition (+ 468% vs. + 748%), shown in table 1. In addition, higher char yields of impregnated timber may provide greater structural stability in the later stages of a fully developed fire.

TABLE 1. Extracted properties from CC, 50 kW m^{-2}. TTI: time to ignition, pHRR: peak heat release, THR: total heat release, char yield: mass after end test to initial sample mass.

	TTI **[s]**	**pHRR** **[kW m^{-2}]**	**THR** **[MJ m^{-2}]**	**Char yield** **[%]**
Untreated	25 ± 8	280 ± 19	127 ± 4	3 ± 2
Impregnated	142 ± 57	186 ± 28	70 ± 11	18 ± 2
Painted	212 ± 58	223 ± 20	100 ± 4	13 ± 1

Microscale decomposition of impregnated timber showed combustible gases continuously released above 200°C in air, but under inert atmosphere only a very low contribution to heat release was observed (THR 4.4 kJ g^{-1}). Part of the explanation is reduction of combustible content per kg timber as tested (the impregnated fire retardant will add to its mass). This is not the case for intumescent coating that increases the quantity of combustible material released over a narrow temperature range (≈ 100°C). However, the coating builds a char layer that limits gas release to the combustion zone.

Further, mass loss in TGA showed release of other, non-combustible gases (NH_3 and H_2O [4]) that dilute the available oxygen under flaming coinciding with cellulose decomposition. Flaming combustion of wood is mainly fed by the rapid mass loss upon decomposition of cellulose around 355°C [5]. Thus, fire protection mechanisms of timber treatments target different regions of flaming combustion.

From both well-ventilated fire tests in CC representing developing fires, and controlled fire conditions in SSTF a dramatic difference in toxic product yields was evident. In under-ventilated fires, large yields of carbon monoxide (CO) evolved from impregnated timber (figure 1, right). Hydrogen cyanide, phosphoric acid and CO were detected for both timber treatments in under-ventilated fires. CO was the most toxicologically significant species, differentiating clearly between timber treatments.

Fire protection of timber tends to focus on a combination of reduced heat release, reduced ignitability, and high char yields. However, overall fire risk assessments should also include smoke toxicity.

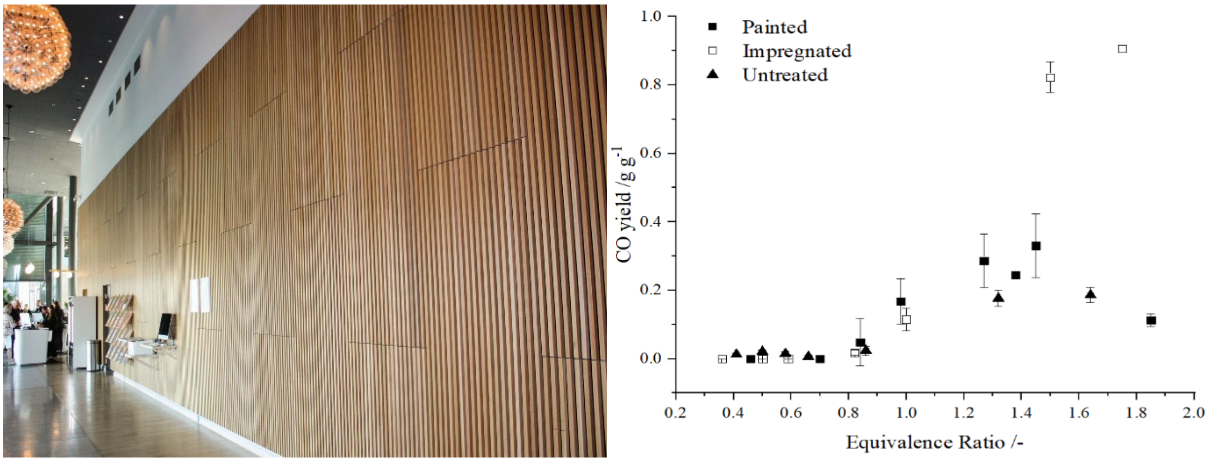

FIGURE 1. (Left) Acoustic panels in ribbon mounting. (Right) Carbon monoxide yields obtained from SSTF runs during flaming combustion with variation in ventilation (measured as equivalence ratio).

Acknowledgement: Innovation Fund Denmark, Grant no. 9065-00233B.

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PL7- CARDANOL AS A VERSATILE BUILDING BLOCK FOR FABRICATION OF BIO-BASED FLAME RETARDANT EPOXY THERMOSETS

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Main message: For fabrication of the cardanol-based epoxy thermosets, the main starting materials are inexpensive and extensive, and the synthetic technology is simple and easy to operate for scalable production. This study paves the way for broadening applications of cardanol in the fabrication of high-performance bio-based thermosetting polymers with excellent comprehensive properties.

Keywords: Cardanol, Bio-Based Epoxy Thermosets, Flame Retardancy, Toughening

Introduction

Presently, flammability and brittleness are two major problems for EP which has restricted its development and application in industry. Under the global advocacy of green and sustainable development, developing bio-based flame-retardant and toughening agents that can endow epoxy resins with high fire resistance and satisfactory mechanical properties is of significant demand for industrial applications [1, 2].

Experimental

Three kinds of cardanol-derived epoxy monomers, including cardanol-formaldehyde glycidyl ether (CFGE), epoxidized cardanol-formaldehyde resin (ECF), and epoxidized cardanol-formaldehyde glycidyl ether (ECFGE) were synthesized according to a previous report (**Figure 1**) [3]. In addition, a cardanol-derived phosphate (DPP-CFR) was also synthesized according to a previous report [3].

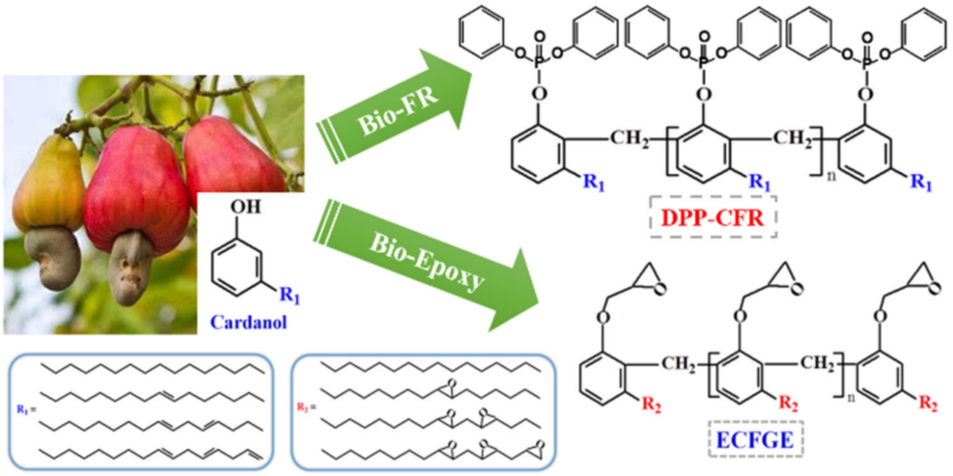

FIGURE 1. Synthesis of DPP-CFR and ECFGE epoxy pre-polymer from cardanol

Results and Discussion

Table 1 summarizes the LOI values and UL-94 combustion classification. The LOI of the cured ECFGE/DDM sample is 26.0%, which is easy to ignite and cannot self-extinguish after ignition. After flame-retardant modification, the LOI values of the cured ECFGE/DDM-1, ECFGE/DDM-2 and ECFGE/DDM-3 are increased to 28.0%, 29.0% and 31.0%, respectively, indicating that DPP-CFR has a good flame-retardant effect on the cured ECFGE/DDM systems. With the addition of 15 wt% DPP-CFR, the cured ECFGE/DDM-3 can pass the UL-94 V-0 classification, showing excellent flame-retardant and self-extinguishing effects. In addition, the PHRR and THR values of the cured ECFGE/DDM are 349.4 W/g, and 42.3 kJ/g, respectively. After flame-retardant modification by DPP-CFR, the PHRR and THR values of the cured ECFGE/DDM/DPP-CFR composites decrease gradually with increasing DPP-CFR content. This is because the addition of DPP-CFR promotes the early decomposition of the cured ECFGE/DDM system. As a result of enhanced charring capacity by adding DPP-CFR, the residual yield increases gradually. The higher char formation yield can play a better role in reducing the heat release rate during the thermal decomposition process. Furthermore, when the content of DPP-CFR is 15%, the tensile strength and elongation at break of the cured ECFGE/DDM-3 are 48.20 MPa and 5.19%, respectively, which are 12.8% and 130.6% higher than those of the cured ECFGE/DDM system. The main reason is that the introduction of DPP-CFR reduces the cross-linking density of the system, and the flexible long aliphatic side chain in the structure improves the toughness of the system.

TABLE 1. The LOI, UL-94, and MCC data of the cured ECFGE/DDM and its DPP-CFR composites

Sample	PHRR [W/g]	THR [kJ/g]	Reduction in PHRR [%]	Residue [%]	UL-94	LOI [%]
Cured ECFGE/DDM	349.4	42.3	/	10.7	NR	26.0
Cured ECFGE/DDM-1	322.3	34.9	7.8	17.3	NR	28.0
Cured ECFGE/DDM-2	248.2	34.2	29.0	18.2	V-1	29.0
Cured ECFGE/DDM-3	181.7	33.3	48.0	32.7	V-0	31.0

Acknowledgement: We gratefully acknowledge financial support from the National Natural Science Foundation of China (No.: 22075265) and the Youth Innovation Promotion Association of CAS (No.: 2021459).

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K13- Reactive Flame Retardants for Aerospace-Grade Epoxy Flame Retardants: Design Considerations and Example Chemistries

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Main message: Recent work has found phosphorus-based flame retardants for aerospace carbon-fiber composites that copolymerize with the epoxy while maintaining and slightly increasing glass transition temperature. The phosphorus-based flame retardants utilized a bifunctional epoxy with a similar chemical structure to bisphenol A epoxy. The flame retardant was assessed for its heat release reduction by Cone calorimeter and microscale combustion calorimeter. Measurements found mixed vapor phase and condensed phase fire protection that varied depending upon carbon fiber presence.

Keywords: Epoxy, Composites, Aerospace, Flame Retardants

Introduction

Aerospace grade composites (those used for aircraft and upcoming electric vertical takeoff and landing) require fire protection to meet aviation based fire risk scenarios. The fire protection will need to consider flame retardant approaches that are compatible with epoxy processing conditions, while maintaining use temperatures and a balance of flammability and other properties. Ideally, the flame retardant approach should be use of reactive chemicals that copolymerize with the epoxy while maintaining glass transition temperature of the epoxy after composite fabrication.

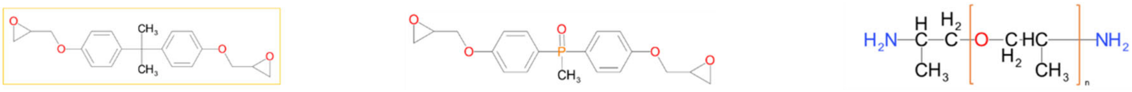
Experimental

Epoxy + carbon fiber composites were prepared via hand-layup methods, and were fabricated using aerospace grade bisphenol A epoxies and autoclave processing. Flammability testing was conducted via cone calorimeter (ASTM E1354, 3" square specimens, 50 kW/m^2 heat flux) and microscale combustion calorimetry (ASTM D7039).

Results and Discussion

A bisphenol A epoxy resin (DGEBA), a phosphorus-based epoxy (P-DGEBA), and an aliphatic amine curing agent were combined together (Figure 1) to produce flame retardant carbon fiber epoxy composites. Differential scanning calorimetry of the blends of these materials found that T_g was 68.5 °C for the control sample (no P-DGEBA present), and T_g increased to 72.9 °C when the ratio of DGEBA to P-DGEBA was 1:1. Degree of cure for this 1:1 material was 95% after heating, and the T_g + % degree of cure results indicate that P-DGEBA is very compatible with this particular epoxy system. After the epoxy was used to generate carbon fiber composites, fiber volume fraction measurements were conducted to determine the quality of the final composites made for the 100% DGEBA system, and the 1:1 blend of P-DGEBA and DGEBA. The results found equivalent volume fractions for the 1:1 system when using a water submersion method (0.52 volume fraction of carbon fiber to epoxy for the 1:1 system, 0.51 volume fraction of carbon fiber to epoxy for the 100% DGEBA control), further indicating that the P-DGEBA has high compatibility with DGEBA in producing good quality composites.

After fabrication, flammability was measured via microscale combustion calorimetery (MCC – ASTM D7309) and cone calorimeter (ASTM E1354). MCC testing found that the 1:1 system had a peak HRR reduced to 300 W/g, a Total HR of 22.5 kJ/g, and a char yield of 13.4wt%, compared to the 100% DGEBA sample which had a peak HRR of 530 W/g, a total HR of 25.4 kJ/g, and a char yield of 5.4wt%. MCC results suggest a mostly char formation mechanism of flame retardancy. Cone calorimeter data (Table 1) indicates that the P-DGEBA does lower heat release, but has more of a vapor phase effect when carbon fiber is present, as indicated by the lack of char increase in the wt% lost data, and the reduction in average effect heat of combustion and the heat of combustion for the gaseous pyrolysate data. The data from flammability testing indicates that P-DGEBA would be a good candidate for further study in aerospace epoxy systems, as it shows good compatibility with the epoxy, but may need to have stronger flame retardant performance (lower peak HRR and lower Total HR) against severe fire threats present for aerospace applications. However, in its current form it may be appropriate for some internal cabin applications.



A. Epoxy resin
EPON 825 (DGEBA) (liquid)

B. Flame Retardant (P-DGEBA)
Phosphorus-Diglycidyl Ether of Bisphenol A (Synthesized by UD Chemistry Dept. faculty)

C. Curing Agent
Epikure 3274 (liquid)

Figure 1. Epoxy Chemical Structures

Table 1. Heat Release Data for Epoxy and Epoxy + P-DGEBA Systems

Sample Description	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m2)	Starting Mass (g)	Final Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m2)	Avg. Effective Heat of Comb. (MJ/kg)	Heat of Comb. for Gaseous Pyrolysate (MJ/kg / 1-char yield)
baseline	3.0	45	625	34.80	21.95	12.9	36.9	44.6	27.43	74.34
Epon 825	3.0	45	634	34.91	21.63	13.3	38.0	45.2	26.88	70.74
Epikure3274	3.0	47	662	35.83	21.93	13.9	38.8	50.4	28.66	73.87
Average Data	3.0	45	640	35.18	21.84	13.3	37.9	46.7	27.66	72.98
P-DGEBA	3.0	41	462	35.44	21.99	13.5	38.0	33.7	19.79	52.08
Epon825	3.0	37	486	37.20	22.18	15.0	40.4	38.3	20.11	49.78
Epikure3274	3.0	43	434	33.01	21.76	11.3	34.1	28.4	19.91	58.39
Average Data	3.0	40	460	35.22	21.98	13.2	37.5	33.5	19.94	53.41

Acknowledgement: This work was self-funded by the University of Dayton.

O30- GREEN, FIRE SAFE AND LIGHTWEIGHT INSULATING MATERIALS FROM LAYER-BY-LAYER COATED NATURAL FIBERS

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Main message: Green lightweight materials are produced from Layer-by-Layer functionalized natural fibers. Electrostatic complexation of bio-based components is exploited as a green approach to material development. The foam produced show structural integrity thanks to the deposited coating while also displaying extremely high fiber content (80-90%wt). These materials combine high mechanical strength, excellent thermal stability and flame retardancy thanks to the achieved control over the nano and micro structure.

Keywords: natural fibers, layer-by-layer assembly, lightweight materials, flammability, cone calorimetry.

Introduction

Societal demands towards more sustainable products and circular economy have led to a growing interest in the use and recycling of natural resources [1]. Within this context natural fibers represent a tremendous opportunity for the development of green and functional materials capable of meeting the above mentioned demands. Here natural fibers have been Layer-by-Layer (LbL) coated in order to enable their assembly into lightweight, mechanically strong and flame retardant foams (Figure1).

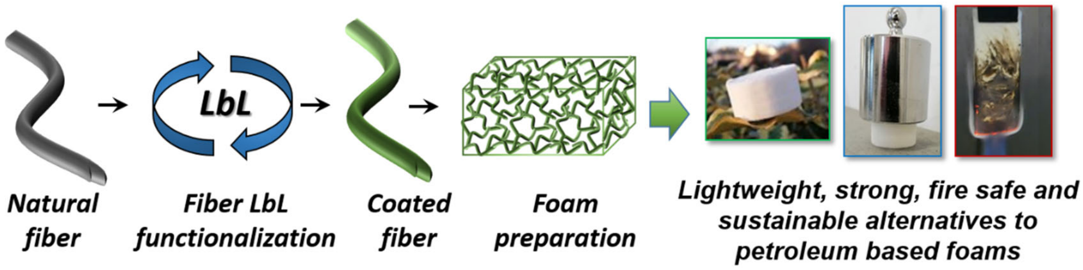

FIGURE 1. Schematic representation of the procedure adopted for the production of foams from LbL functionalized natural fibers

Experimental

Commercially available cellulose fibers with different aspect ratios were employed. Chitosan and sodium polyphosphate were selected for the LbL assembly. The coated fibers were dispersed in water at different ratios and then freeze-dried in order to achieve fiber-based foams with different densities. Coating growth and assembly on natural fibers was monitored by means of infrared spectroscopy and charge titration, respectively. The morphology of the coated fibers and produced foams was investigated by SEM. Thermogravimetric analysis (TGA) in was carried out in a TGA-Discovery (TA, Newcastle, USA) from 50 to 800°C at 10°/min in both nitrogen and air. The flammability of the prepared samples was evaluated in both horizontal and vertical configuration. The sample (80x25x10 mm^3) was ignited from its short side by a 20 mm blue methane flame (flame application time: 2x6 s). The after-flame time (s), char length (mm) and final residue (%) were evaluated. Cone calorimetry (Noselab ATS) was employed to investigate the combustion behavior of square samples (50x50x15 mm^3) under 35 kW/m^2 in horizontal configuration. Time to ignition (TTI, s), peak of heat release rate (pkHRR, kW/m^2), total heat release (THR, MJ/m^2), smoke production rate (SPR, m^2/s), total smoke release (TSR, m^2/m^2) and final residue (%) were evaluated.

Results and Discussion

The coating growth was first studied by FT-IR to establish the best deposition conditions. A linear growth regime was found for the chitosan/ sodium polyphosphate pair. When applied to the cellulose fibers this assembly produced continuous and homogeneous coatings with only 1,2 and 3 deposited bi-layers (BL). Thermogravimetric analyses highlighted an improved char forming ability for the LbL coated fibers. Self-standing 3D structures based only on the coated fibers were achieved by means of freeze-drying. SEM observations pointed out the formation of a porous fiber network where the deposited LbL coating is acting as a glue conferring structural integrity. The cellulose fiber content ranged between 80-90%wt highlighting the potentialities of the proposed approach in delivering lightweight porous structure with extremely high fiber content.

Flammability tests in horizontal configuration evidenced a self-extinguishing behavior for foams prepared from 1BL coated fibers. At 3BL the foams showed a non-igniting behavior where no flame persisted on the sample after the removal of the methane flame. The same 3BL foams also self-extinguished the flame during flammability tests in vertical configuration.

By cone calorimetry the prepared foams showed very low HRR values (pkHRR < 100 kW/m^2) as well as extremely limited smoke production (TSR < 50 m^2/m^2). These results clearly show the FR potentialities of the prepared foams especially if compared with commercially available petroleum based foams, such as PU, that normally display higher HRR and TSR values under the same testing conditions [2]. The proposed approach will allow for the production of advanced materials encompassing high natural fiber content where functional properties such as mechanical properties, flame retardancy and sustainability are optimized.

Acknowledgement: The financial support from Italian Ministry of University (MUR) call PRIN 2017 with the project 2017LEPH3M “PANACEA” is acknowledged.

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O31- FLAME RETARDANT AND SMOKE SUPPRESSIVE PROPERTIES OF EPOXY RESIN COMPOSITES WITH ORGANIC PHOSPHATES AND THEIR MESOPOROUS SILICA HYBRIDS

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Main message: In this work, we prepared mesoporous silica (m-SiO_2)/nano-zinc amino-tris-(methylenephosphonate) (m-SiO_2@Zn-AMP) hybrid, and found that the epoxy resin (EP) composite with 5% m-SiO_2@Zn-AMP achieved a UL 94 V0 rating with a 45.2%, 57.8 % and 53.1 % reduction in total heat release and peak heat release rate and total smoke release, respectively compared with the ones of untreated EP. Moreover, the EP/m-SiO_2@Zn-AMP composites exhibit excellent mechanical properties.

Keywords: Epoxy resin, Flame retardation, Smoke Suppression, Organic phosphates, Mesoporous silica

Introduction

Mesoporous silica (m-SiO_2), due to its unique mesoporous structure, is commonly used to reinforce polymers, however, its flame-retardant efficiency is relatively low [1,2]. Organic phosphates are efficient flame-retardants for EP [3]. Therefore, in this study, the m-SiO_2@Zn-AMP hybrid was synthesized and used as a flame-retardant additive for EP, and the flame-retardant, smoke suppressive and mechanical properties of EP/m-SiO_2@Zn-AMP composites were evaluated.

Experimental

Preparation of m-SiO_2@Zn-AMP was carried out according to the publication [4]. Preparation of EP nanocomposites: A certain amount of m-SiO_2@Zn-AMP was first introduced into EP at 125 °C with vigorous stirring to guarantee the good dispersion. Then, DDS was incorporated into the mixture and stirred for 30 min. After the complete dissolution of DDS, the mixture was degassed, and subsequently, was cured at 150 °C for 2 h, 180 °C for 2 h and 200 °C for 1 h.

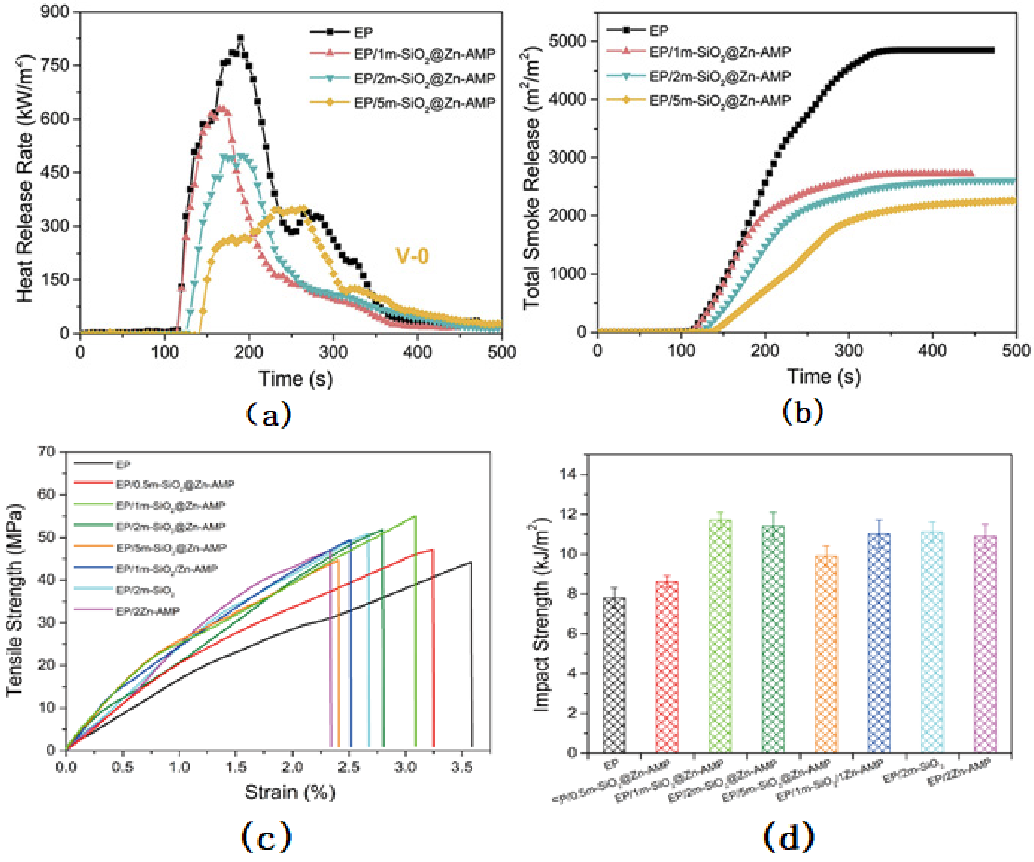
Results and Discussion

In this work, the m-SiO_2@Zn-AMP hybrid was prepared by self-assembly method and confirmed by FTIR, XRD, XPS, TEM and EDS. The limiting oxygen index (LOI), UL-94 and cone calorimeter test results of flame retarded EP composites are shown in Fig. 1 and Table 1. The EP composite with 5% m-SiO_2@Zn-AMP achieved a UL 94 V0 rating with a LOI of 28.5 %. The total heat release (THH), peak heat release rate (PHRR) and total smoke release (TSR) values decrease by 45.2%, 57.8 % and 53.1 %, respectively compared with the ones of untreated EP.

TABLE 1. Combustion properties of flame retarded EP composites

Sample	LOI [%]	UL-94 Rating	PHRR [kW/m^2]	THR [MJ/m^2]	TSR [m^2/m^2]
EP		NR	827	104	4850
EP/0.5m-SiO_2@Zn-AMP		NR	709	72	3248
EP/1m-SiO_2@Zn-AMP		NR	627	61	2726
EP/2m-SiO_2@Zn-AMP		V-1	497	59	2610
EP/5m-SiO_2@Zn-AMP		V-0	349	57	2277

The addition of 1% m-SiO_2@Zn-AMP into EP increased the storage modulus, impact strength, and tensile strength by 29.9, 50.0, and 23.5 %, respectively. The incorporation of 2% and 5 wt% m-SiO_2@Zn-AMP did not further increase the impact and tensile strength of EP, but the strengths were all higher than those of untreated EP.



(a) (b)

(c) (d)

FIGURE 1. EP and its composites, (a) HRR curves; (b) TSR curves;
(c) Tensile properties; (d) Impact Strength

Acknowledgement: The work was financially supported by the National Natural Science Foundation of China (21975185).

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S14- AN IN-SITU PHOSPHAZENE FLAME RETARDANT DERIVED INTERFACE LAYER IN $LiFePO_4$ CATHODE IN LITHIUM ION BATTERY

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Main message:
As one of the co-authors, I participated in the methodology and data analysis, including cell assembly for in situ XRD measurements, operation of cyclic voltammetry tests to analyze full cell oxidation/reduction, participation in cone calorimetry tests, and preparation of separators. Meanwhile, I proofread the manuscript and supplement the experimental data according to the review comments.

Keywords: Lithium ion battery (LIB); liquid electrolyte (LE); fire safety; flame retardant (FR) additives; electrode-electrolyte interphase.

Introduction

Safety concern is one main obstacle for the application of LIBs in portable electronic devices, electric vehicles, and energy storage stations, which is intrinsically related to the high flammability of LEs[1]. This work provides valuable insights into the fire suppression mechanism of fluorinated phosphazene (EPCP) in LEs and its effective role in inhibiting corrosion attack by forming a FR-derived passivation layer on the surface of lithium iron phosphate (LFP) cathode.

Experimental

To investigate the effect of EPCP on battery performance and to understand the fire suppression mechanism, we arranged the following main experiments:

1. *Sturcure characterization:* Qualitative GC mass spectrum (GC-MS), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy were used to characterize the structural information of modified LEs;
2. *Thermal/fire safety:* The combustion behaviors of the separator/electrolyte were compared by cone calorimetry test (CCT), micro-combustion calorimetry test (MCC) and thermogravimetric analysis (TGA), to clarify the real combustion behavior and fire suppression mechanism;
3. *Morphology and structural information:* X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field (HAADF) images, energy dispersive spectrometry (EDS) elemental mapping, and 2D Optical profilometry images were used to analyze the surface topography and structural features of the LFP cathode before and after cycling;
4. *Electrochemical performance:* Electrochemical impedance spectroscopy (EIS) was used to test the ionic conductivity; galvanostatic charge/discharge (GCD) was used to evaluate long-term cycle and rate performance; cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed to understand the effect of EPCP on the electrochemical performance of batteries;
5. *Composition of cathode electrolyte interface (CEI):* For the first time, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was employed to investigate the CEI layer.

Results and Discussion

This study revealed that fluorinated phosphazene-based electrolytes with content up to 6% (by vol.) cannot be considered non-flammable because they will burn when exposed to a sufficient amount of heat flux. However, they exhibit a certain ignition-delay behavior, which is highly dependent on the heat flux supplied to the electrolyte sample as well as the content of the fluorinated phosphazene-based additives[2]. The fire suppression mechanism investigations also showed that the presence of EPCP additive effectively slowed down and suppressed the amount of flammable volatiles released by the electrolyte under heating conditions. In addition, the corrosion of HF seriously affects the performance of $LiFePO_4$, whereas the addition of EPCP has a significant effect on the chemistry and properties of the CEI layer formed on the surface. We found that the formation of a robust and uniform P- and N-species-rich CEI layer in EPCP-LEs correlates with enhanced battery key performance indicators, such as rate capability, cycle performance, and coulombic efficiency[3].

These findings provide strong evidence to decipher the superior cycling performance observed with EPCP-LEs. While our findings of the chemical composition of the CEI layer provide a deeper insight into the chemical composition of the complex CEI layer, specific studies are still required for different electrode and electrolyte chemistries, especially when using different FR additives.

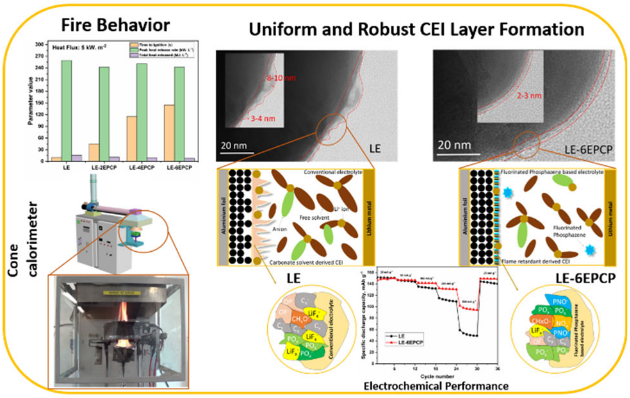

FIGURE 1. The fire suppression mechanism of fluorinated phosphazene-containing electrolytes and their effective role in the inhibition of corrosion attack through the formation of FR-derived passivation layer on the surface of LFP electrode.

Acknowledgement: We acknowledge the financial support of this work by the IMDEA Materials STRUBAT Project, BIOFIRESAFE Project funded by Ministerio De Ciencia E Innovación (MINECO), Spain with the project number: PID2020-117274RB-I00BIOFIRESAFE and PEJ-2018 MINECO.

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PL8- FIRES CAUSED BY ELECTRIC VEHICLES: FLAMMABILITY AND SMOKE TOXICITY

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Main message: Fires from Lithium-ion (Li-ion) batteries represent one of the fastest growing and potentially largest fire threats in the coming decade. The combination of high energy density, reactive chemistries separated by fragile membranes, and lack of strategies for their mitigation, will lead to uncontrollable fires with highly toxic emissions, putting Li-ion vehicles at the top of the fire safety agenda.

Keywords: Li-ion, vehicle, fire, hazard, toxic.

Introduction

Use of Li-ion batteries is growing rapidly. Their use has become widespread and well-established in small devices, with surprisingly limited increase in fire-related incidents. In the medium-scale there have been surges in fire deaths. E-bikes are the largest cause of fire deaths in Vancouver, and a similar trend is emerging in NYC. The recent surge in Li-ion car ownership has been accompanied by infrequent, but uncontrollable fires, which may become more frequent as the vehicle fleet ages, alongside the cumulative effects of minor accidental damage.

Overview

Li-ion batteries arrays for vehicles are composed of hundreds to thousands of individual cells. Li-ion cells are inherently flammable, with typical heats of combustion 10 times greater than the energy they store[i]. The main causes of ignition are rapid charging or discharging, and mechanical damage. Contaminants or manufacturing defects act as initiating sites for failure, causing breakdown of the separators, particularly the delicate passivating layer on the solid electrolyte interface, but also the main porous polyolefin membrane, leading to thermal runaway as the stored energy drives the battery's decomposition[ii]. The heat released causes neighbouring cells to reach a critical temperature, also resulting in thermal runaway. In each case, the heat volatilises the electrolyte, usually a mixture of organic carbonates and lithium hexafluoro phosphate ($LiPF_6$), rupturing the cell and releasing hot, flammable gases.

The likelihood of ignition of Li-ion batteries is obviously dependant on the manufacturing quality, with cheap, unbranded imports being blamed for the spate of fast-food delivery e-bike fires in Vancouver and NYC. Different Li-ion battery cathodes are used for vehicles, which have different critical temperatures, with lithium iron phosphate (LFP) offering higher thermal stability but greater weight, compared to lithium nickel manganese cobalt oxide (NMC) batteries. Both have better thermal stability than the lithium cobalt oxide (LCO) cathodes used for Li-ion batteries in consumer electronics. The state of charge of the battery at the time of the incident has a profound effect on the severity of the fire, and the toxicity of the smoke[iii].

Li-ion battery fires usually start with the release of a white vapour cloud. In the absence of a flame, its toxicity is greatest, but the rate of heating and vapour release will accelerate rapidly once flaming occurs. Several studies have measured the toxic components in Li-ion battery and Li-ion vehicle smoke[iii, iv]. These show that the most toxicologically significant components identified include carbon monoxide (CO), hydrogen fluoride (HF) and phosphoryl fluoride (POF_3). Depending on the component chemistry, sulphur dioxide (SO_2) is also present. However, in a comparison between electric, hybrid and internal combustion engine vehicles it was shown that a significant amount of HF actually came from burning the air conditioning refrigerant. In all large-scale fire tests, it is a challenge to make the test scenario representative of a typical fire scenario. Small variations in manufacturing defects, or mechanical damage after a collision; the ventilation condition and geometry (such as whether in a garage or outside in a wind); and the factors affecting incapacitation and escape, will all have a large impact on the outcomes. There are also concerns over adverse impact on firefighters' health and the need for decontamination of personal protective equipment after tackling Li-ion vehicle fires.

Finally, Li-ion battery vehicles have demonstrated the need for new firefighting strategies and agents. None of the traditional firefighting agents, water, powder, carbon dioxide etc., are effective at controlling thermal runaway, apart from cooling neighbouring cells, before they go into thermal runaway. This has led to new approaches. In China perfluorinated hexanone ($CF_3CF(CF_3)C{=}OCF_2CF_3$)(PMP) is routinely used, although concerns have been raised about the hazards of its decomposition products[v]. It is reportedly capable of extinguishing Li-ion battery fires at concentrations of 4 to 6%. In the UK, an aqueous vermiculite dispersion is being marketed as the solution. After a fire, Li-ion battery vehicles can reignite several days after extinction, either spontaneously or when disturbed. This is believed to result from stranded electrical charge driving thermal runaway.

Conclusions

In combination with greener electricity generation, Li-ion vehicles offer an urgently needed reduction in carbon emissions, while improving urban air quality. While charging, discharging and mechanical damage lead to thermal runaway, this is more likely for poorly manufactured or fully-charged cells, and those with a lower critical temperature for decomposition. The main toxic components of Li-ion battery smoke appear to be CO, HF, POF_3, organofluorines and sometimes SO_2. The high energy and relative novelty of the chemistry of Li-ion batteries is likely to produce substances of unknown, and potentially very high toxicity, which have yet to be identified and characterised.

The behaviour of Li-ion batteries in thermal runaway, and the effects on vehicles and occupants is unfamiliar two firefighters and other emergency responders, and requires more comprehensive investigation. New techniques need to be developed to reduce Li-ion battery fires and to contain them. Agents and strategies need to be developed to access and control Li-ion battery fires, particularly when they are inaccessibly located on the vehicle chassis. Even at low fire incident rates, certain scenarios, such as underground car parks or alongside the outer walls of taller buildings with combustible façades, may lead to unexpectedly large fire disasters.

References

K14- PASSIVE FIRE SAFETY IN CONVENTIONAL AND E-VEHICLES: STATUS AND TRENDS

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Abstract

The existing fire safety requirements and tests for conventional passenger cars and buses are too low, and with the exception of cables in buses, electrotechnical products are virtually not regulated. Emerging, increased fire hazards stemming from electrical systems with voltages of now 400 to 600 V compared to voltages of 12 or 48 V used to date, and from the profusion of small devices operated by electrical motors, must be considered. This also applies to e-vehicles, where in addition, fire safety requirements and tests were developed to address new fire safety challenges for electric powertrains and Li-ion batteries. Fire and overheating requirements for enclosures, plugs, and sockets used in e-vehicle charging stations have been introduced as well.

Currently, all passenger cars, including e-vehicles, only have to meet the fire safety requirements for car interiors to FMVSS 302 in the United States, or similar requirements and tests in other countries of the world. These requirements are based on an old (1972) horizontal small flame test and are rather low. In recent years, a U.S. research program conducted to evaluate the flammability of interior automotive materials found that the microscale combustion calorimeter (MCC) test is a promising test method, providing quantitative (i.e. heat release based) data related to the fire hazard of materials. Additional work is under way.

Buses basically also have to meet the FMVSS 302 requirements worldwide. In North America, (some U.S. States and Canadian provinces) additional requirements for school bus seating, based on a full-scale seat test, must be met. In Europe and other countries, the UNECE Regulation No. 118 specifies additional melting behavior, and vertical burning rate tests, as well as a flame propagation test for electrical cables.

For e-vehicles, the UNECE Regulation No. 100 Annex 8E, a mandatory fire resistance test of the Rechargeable Energy Storage System (RESS) against fire from outside, is requested.

For Li-ion batteries used in e-vehicles, fire safety requirements do not specifically address fire performance requirements for materials and components, but rather the whole battery system. The focus is on mechanical, thermal, and electrical abuse tests such as the ‘‘Projectile and external fire test’’ and the ‘‘Internal short circuit or internal fire test’’.

For charging stations, fire safety requirements and glow wire/open flame tests apply for plastic components used in enclosures, plugs, and sockets of charging stations.

Passive fire safety requirements in these applications are generally met by using products containing flame retardants based on phosphorus, bromine, nitrogen and other compounds, because of their efficiency, easy processing and reasonable cost. In specific cases, inherently flame retarded products are used, but may be difficult to process and expensive. To prevent thermal runaway of battery packs in e-vehicles, intumescent coatings, non-combustible sheets, and ceramifying products may be used.

S15- Construction of hierarchical $Ti_3C_2T_X$@PHbP-PHC architecture with enhanced free-radical quenching capability: Effective reinforcement and fire safety performance in bismaleimide resin

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Main message: Here, a hindered amine and polyphosphazene modified $Ti_3C_2T_X$ ($Ti_3C_2T_X$@PHbP-PHC) was obtained. With the loading of $Ti_3C_2T_X$@PHbP-PHC in the bismaleimide resin (BMI) increased to 2 wt%, an 43% reduction was achieved in the peak heat release rate (PHRR), and a 47% reduction in the total heat release rate (THR). Meanwhile, the total smoke production (TSP) exhibited a similar decreasing trend. Furthermore, 0.5 wt% BMI system exhibited the highest storage modulus (2629 MPa) and impact strength (13.7 MPa), which were 21% and 76 % higher than pure BMI, respectively. Therefore, the developed functionalized $Ti_3C_2T_X$ can be effectively used in BMI matrix, thereby providing reliable source material for the design of high-performance BMI resins that meet various application scenarios.

Keywords: $Ti_3C_2T_X$; Hindered amine; Toughness; Fire safety.

Introduction

With excellent heat resistance, high mechanical strength and excellent dielectric properties, BMI resin occupies a high position in the fields of transportation, aerospace, construction, and electronics [1]. However, the strict and symmetrical structure of BMI resin brings inevitable shortcomings (such as high melting and solidification temperature), and inherent brittleness and low impact resistance due to its molecular network characteristics and large crosslinking density [2]. Therefore, this work carries out new research based on 4,4'-bis-methyleneiminodiphenylmethane (BDM)/2,2'-diallyl bisphenol A (DBA) systems to develop a more effective fire safety and toughness enhancement strategy for BMI resin. $Ti_3C_2T_X$, polyphosphazene and hindered amine, with different flame-retardant functions, was selected to prepare the new nanomaterial $Ti_3C_2T_X$@PHbP-PHC. The effect of hindered amine light stabilizer on free radical quenching can be combined with the cross-linked polyphosphazene containing –P=N- structure to improve the flame retardant efficiency of titanium carbide ($Ti_3C_2T_X$) in both gas phase and condensed phase. Subsequently, $Ti_3C_2T_X$@PHbP-PHC was incorporated into BMI matrix to study its effect on the fire safety and mechanical performance of BMI.

Experimental

In this work, 4-Amion-2,2,6,6-Tetramentylniperidine and cyanuric chloride were selected to synthesize a novel hindered amine flame retardant (PHC) with free radical quenching function that retained an active chlorine site, it then reacted with the surplus amino group on the cross-linked polyphosphazenes produced on the surface of $Ti_3C_2T_X$, the generated PHC was successfully grafted onto the surface of $Ti_3C_2T_X$@PHbP. Subsequently, $Ti_3C_2T_X$@PHbP-PHC was introduced into the BMI matrix to study its positive effect on the fire resistance and toughness of the nanocomposite.

Results and Discussion

As an effective strategy, cone calorimeter was widely applied to analyze the smoke emission and combustion characteristics of BMI and its nanocomposites [3]. As far as PHRR, THR and TSP were concerned (Figure 1a and b), BMI nanocomposites presented a significant decreasing trend with the increase of $Ti_3C_2T_X$@PHbP-PHC (from 0.5-2.0 wt%). When the loading reached 2wt%, the nanocomposites achieved a 43% reduction in PHRR, a 47% reduction in THR along with a 30% decrease in TSP. In terms of reducing heat release and smoke release, $Ti_3C_2T_X$@PHbP-PHC showed a more significant effect than $Ti_3C_2T_X$@PHbP and $Ti_3C_2T_X$, implying the synergistic flame-retardant effect of $Ti_3C_2T_X$, PHbP and PHC.

Considering the mechanical properties, dynamic thermomechanical analysis and Izod impact test were applied to evaluate the storage modulus and impact strength of BMI nanocomposites, and the test results were shown in Fig. 1d-f. With the increase of load, the storage modulus (Fig. 1d) of BMI nanocomposites increased first and then decreased. This is mainly due to $Ti_3C_2T_X$@PHbP-PHC It can limit the migration of polymer chain and improve the rigidity of the material, but the crosslinking degree of BMI will be reduced when the content of flame retardant is too high. In addition, the fact that the glass transition temperature (Tg) (Fig. 1e) of the nanocomposites shifted to the low temperature region under high $Ti_3C_2T_X$@PHbP-PHC loading can be used as a further proof of this view. Similar to the change trend of energy storage modulus, the impact strength (Fig. 1f) of BMI composites increases at first and then decreases with the increase of flame-retardant content, which is also attributed to the agglomeration characteristics of a large number of $Ti_3C_2T_X$@PHbP-PHC. In addition, on comparison with the impact strength of BMI nanocomposites at 2% filler content, $Ti_3C_2T_X$@PHbP-PHC and $Ti_3C_2T_X$@PHbP nanocomposites exhibited higher values than the $Ti_3C_2T_X$ counterparts. The result indicated that the covalently functionalized $Ti_3C_2T_X$ was beneficial to enhance the toughening modification effect of BMI resin.

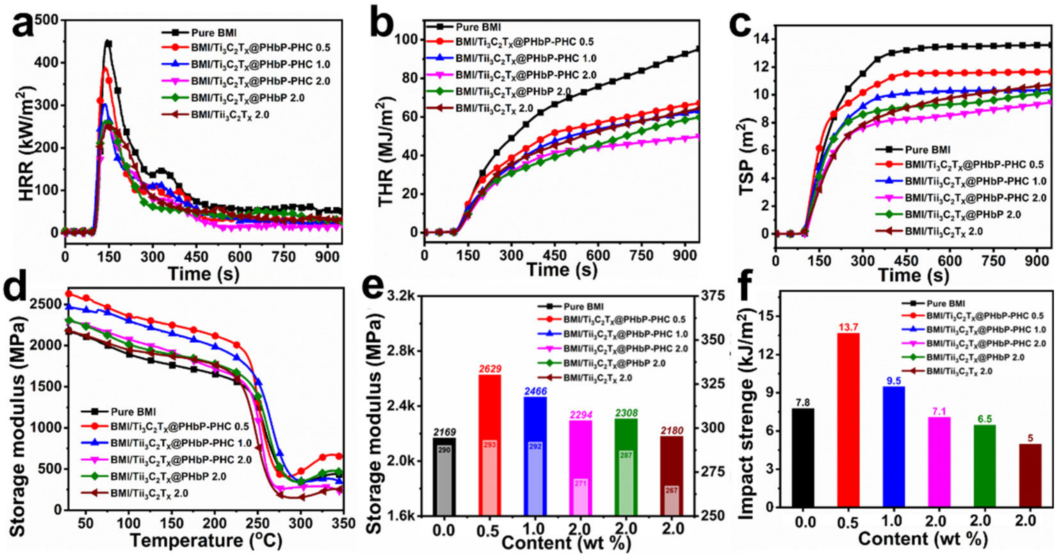

FIGURE 1. (a) HRR, (b) THR and (c) TSP vs. time curves of pure BMI and its nanocomposites; (d) Storage modulus (E') curves, (e) the corresponding storage modulus (E') (left Y coordinate) and Tg (right Y coordinate) histogram and (f) impact strength results of BMI and its nanocomposites.

Acknowledgement: This work was financially supported by the National Natural Science Foundation of China (21975239).

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S16- FIRE TESTS OF FLAME RETARDANT THERMOPLASTICS FOR ELECTRIC VEHICLE BATTERY PACK APPLICATIONS

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Main message: The rapid development of electric vehicle (EV) market share [1] poses both opportunities and challenges for high-strength, lightweight, and flame retardant (FR) thermoplastic composite materials. In coping with fire safety specifications for EV battery pack applications, various fire testing standards have been developed to evaluate FR performance under abusive thermal conditions [2,3]. Short glass fiber filled SABIC® FR PPc (polypropylene compound) H1030 and long glass fiber filled FR STAMAX™ resin have demonstrated effective flame resistance and thermal insulation.

Keywords: Thermoplastics, Electric Vehicle, Battery Pack, Fire Safety, Flame Retardant.

Introduction

Use of thermoplastics can provide a promising material solution for EV battery pack technologies for their light weight, high strength, functional integration possibilities and lower manufacturing costs. However, the thermal abusive bonfire and thermal battery runaway risks pose challenges in its implementation. The conventional sample bar scale UL94 flammability tests cannot fully evaluate materials' FR performance under these extreme scenarios. Therefore, specific fire test methods are required for materials screening and qualification to meet the automotive industry's needs.

Experimental

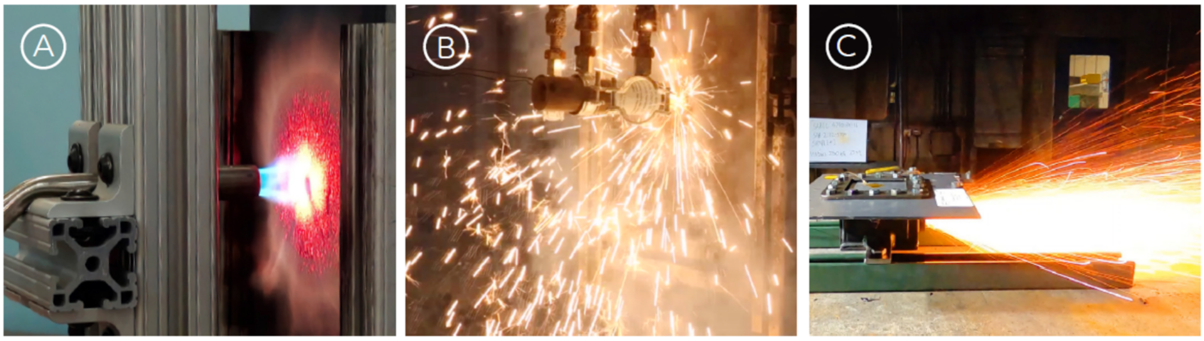
A series of fire test methods and equipment have been developed for different battery pack applications: protection cover, tray, and cell/module thermal barriers. These include torch flame test, weight-loaded pool fire test, pyrotechnic test, grit-flame burner test, and battery thermal runaway tests with both cylindrical and pouch/prismatic cells. These tests simulate the high temperature, pressure, severe grit impingement, and their cumulative impact at the same time at the plaque scale. The advantages and limitations for translating the test results to the application level will be discussed.

Results and Discussion

SABIC's thermoplastics and composite solutions were tested extensively using the methods mentioned above, with thermocouple and infrared camera temperature measurement systems showing the thermal insulation performances, and displacement sensor/Thermographic Digital Image Correlation (TDIC) system showing the structural response. Fig. 1 (A-E) shows some images from typical fire abuse tests, including the flame torch test, pyrotechnic impact, and the UL2596 [4] battery pack thermal runaway test, among other fire tests which will also be discussed.

In these tests, the FR thermoplastic materials passed the high temperature, pressure, and harsh grit impingement tests – based on specific engineering designs for different EV applications. Table 1. summarizes the recommended plaque thickness of the LGF (long glass fiber) filled FR polypropylene (FRPP) STAMAX™ resin and SGF (short glass fiber) filled SABIC® PPc H1030 under various fire test conditions. The results and their implications for end applications in an EV battery pack design will be discussed.

In addition to the various fire tests, advanced Computational Fluid Dynamics (CFD) and Finite Element Analysis (FEA) models were developed to understand the pyrolysis chemistry and physics including intumescence and charring, fire-polymer interactions, and thermomechanical response to the flame exposure, as shown in Fig. 1 (F). Our ongoing work in this area continues to provide insights and guidelines into high performance thermoplastic composite solutions for EV battery packs.



1100°C flame test of a 4 mm plaque in a vertical setup, after 5-minute flame exposure.

Pyrotechnic abuse test with grit impingement on a 3 mm (w/ 2 mm Organo sheet laminate) plaque.

UL2596 battery pack thermal runaway test on a 4 mm plaque.

1100°C flame test on a 4 mm ribbed structure in a horizontal setup.

A view of the post-test plaque after the flame test shown in D

A CFD simulation of the fire-polymer test highlighted in D, showing the intumescence and char formation on the polymer.

FIGURE 1. Typical fire abusive tests on SABIC thermoplastics for various EV battery pack applications.

TABLE 1. Recommended thickness of selected FRPP materials to pass fire tests for EV applications.

Fire Test Method	*STAMAX™ 30YH570 (30% LGF-PP)*	*STAMAX™ 30YH515 (30% LGF-PP)*	*SABIC® PPc H1030 (30% SGF-PP)*
UL94 V0	1.3 mm	1.5 mm	1.5 mm
5 minute 1100°C flame test	4 mm	4 mm	4 mm
20 second pyrotechnic test	3 mm + 2mm Organo sheet laminate	-	4 mm + 2 mm UD tape laminate
UL 2596 Battery TRA test	4 mm	-	-

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Poster Section

P1- POLARITY ADAPTED SILANIZATION OF FUNTIONAL MATERIALS FOR FLAME RETARDANT POLYMER ADDITIVES

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Main message: In this work, we address the surface modification of targeted fillers (e.g., aluminum trihydroxide, glass beads, wood flour) with N-P silanes in order to adapt the polarity to the respective matrix polymer (PE, PA, PP). This should not only improve the flammability of the novel composites, but also give the composite additional properties such as improved compatibility and hence mechanical properties.

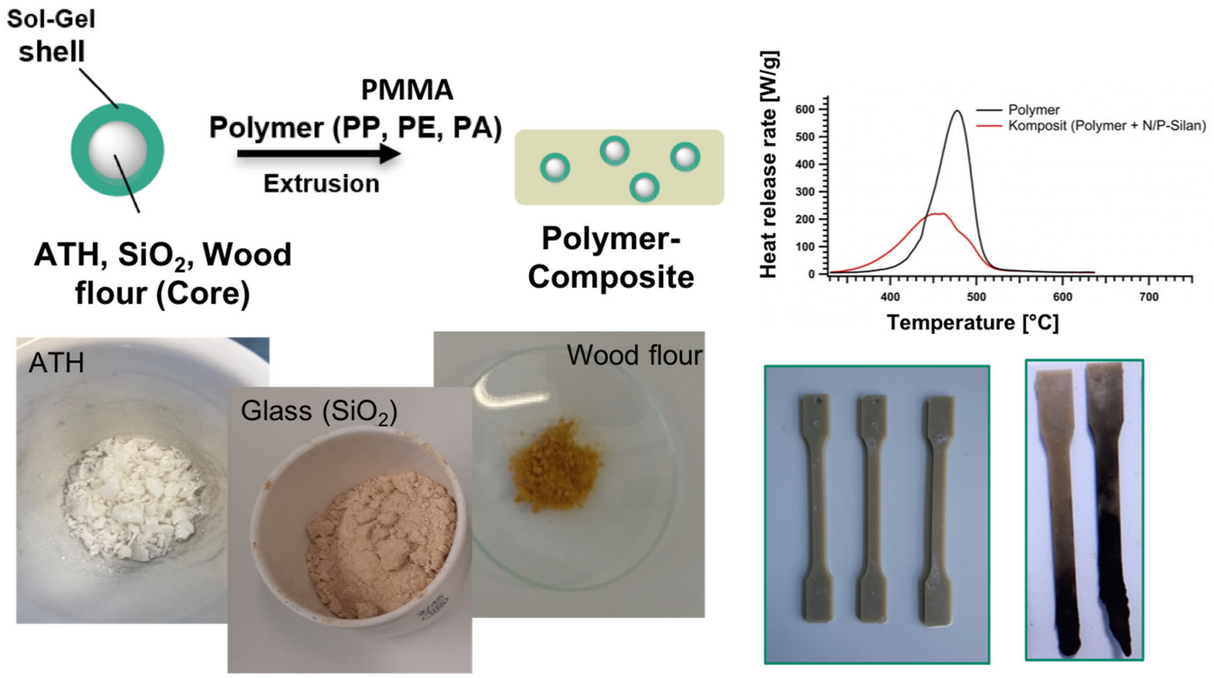
Keywords: composites, surface modification, N-P silanes, polymer additive, mechanical properties.

Introduction

The highest demands are placed on plastics, especially when it comes to safety aspects such as fire protection. Due to the growing environmental criteria, new flame retardants (FRs) have become essential, which have a low toxicological risk potential. This applies to all areas in which the release of substances into the environment cannot be ruled out. In this context, N-P silanes are a good alternative to the frequently used halogenated FRs. The compatibility and the homogeneous incorporation of the FRs in the polymer matrix also play a decisive role in the mechanical properties of the final product.

Results and Discussion

Within this work, the surface of functional materials, namely glass balls, wood flour and aluminum hydroxide $Al(OH)_3$, were modified with novel flame retardant based on N-P-silane compounds (see Figure below). The proof of the successful modification could be provided with appropriate analysis methods. The incorporation of the different filler systems into the respective polymer matrix was initially carried out using microextrusion technology. With the help of this method, the smallest amounts could be subjected to a pre-evaluation of the flame retardant effectiveness using MCC and TGA analysis. The analysis results of the microextrusion tests showed the successful use of FRs fillers in polymers. The focus was placed on polyamide with modified glass beads for processing using conventional compounding technologies and subsequent injection molding processing. With the help of compounding technology, modified glass beads could be incorporated into polyamide at the intended concentrations. A comparison of twin screw extrusion to planetary roller extrusion could be made. The analysis according to test methods customary in practice showed that the impact strength target could be significantly improved compared to the reference material. However, it was also shown that flame retardancy according to UL94 V-0 could not be achieved and further optimization is still required for the extrusion process regarding the concentration and the homogeneous incorporation of the FRs.



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P2- HALOGEN-FREE STYRENIC TERPOLYMERS WITH SELF-EXTINGUISHING PROPERTIES

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Main message:

A synergistic combination of two halogen-free flame-retardants copolymerized with styrene is employed to increase the flame-inhibiting properties of the resulting material. Comonomers include elemental sulfur and acrylate bound phosphate esters. The self-extinguishing properties of the resulting terpolymers are analyzed by thermogravimetric analysis and evaluated by UL 94 V and DIN 4102 B2 flame tests.

Keywords: Polystyrene, sulfur, phosphorus, flame-retardant, halogen-free.

Introduction

Styrene-based polymers are highly flammable and pose therefore significant fire and safety hazards for their applications. Due to the negative impacts of halogenated flame-retardants on human health and the environment, halogen-free alternatives that can circumvent these unwanted properties are gaining increasing interest. Integrating halogen-free flame-retardants to a polymer backbone is additionally advantageous due to a prevention of leaching as well as a facilitated REACH process.

Experimental

Terpolymers were synthesized by copolymerization of styrene, elemental sulfur and diphenyl(acryloyloxyethyl)phosphate at 130 °C for 72 h. After cooling, the solid product was dissolved in tetrahydrofuran and precipitated in methanol to obtain a white powder. Terpolymers were analyzed by ^{1}H- and ^{31}P-nuclear magnetic resonance spectroscopy as well as size exclusion chromatography. Thermogravimetric analyses were performed to analyze the thermal degradation behavior. The flammability of the synthesized terpolymers was evaluated by UL 94 V (DIN EN 60695) and preliminary DIN 4102 B2 tests.

Results and Discussion

This work investigates the self-extinguishing properties of intrinsically flame-retardant styrenic terpolymers.[1] Two variants of theses copolymers prepared with a feed of 1 wt% sulfur and 1 wt% phosphorus monomers (CP-1) as well as with a feed of 1 wt% sulfur and 5 wt% phosphorus monomers are used in the following. Both copolymers passed a preliminary DIN 4102 B2 test and were able to achieve UL 94 V-2 ratings with short afterburn times and a burning melt drip. In order to gain a better understanding of the underlying flame extinguishing processes for CP-1 and CP-2, thermogravimetric analyses (TGA) were performed and corresponding derivate (DTG) curves generated (**Fig. 1**). Although the TGA curves of both copolymers (Fig. 1 a) show a similar thermal degradation behavior compared to homopolystyrene (HPS), several differences can be detected. The onset degradation temperatures decrease from 381 °C for HPS, to 376 °C for CP-1 and 368 °C for CP-2. This behavior is most likely caused by the thermal instability of the diphenyl(acryloyloxyethyl)phosphate monomer, as similar molecules were also shown to decompose at temperatures below 300 °C.[2] Additional influences from sulfur carrying species like disulfides within the copolymers that decrease the decomposition temperature of polystyrene can also be expected.[3,4]

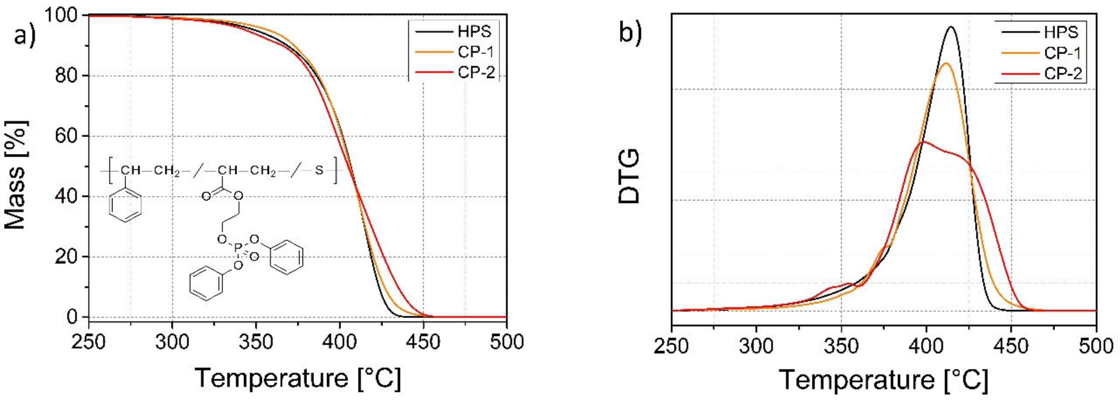

FIGURE 1. a) TGA of homopolystyrene (HPS), styrenic copolymer with 1% sulfur 1% phosphorus monomer feed (CP-1) and the styrenic copolymer with 1% sulfur and 5% phosphorus monomer feed (CP-2). b) DTG curves of copolymers with HPS as a comparison.

The DTG results in Fig. 1 b show a small decomposition step at 375 °C for CP-1 and at 350 °C for CP-2, which might be attributed to a phenol release from the phosphorus monomer.[4] In comparison to HPS and CP-1, a new pronounced degradation process at 398 °C can be detected for CP-2. This process is likely the result from interactions of the phosphorous monomer with the degradation of the residual polymer. Further analyses of the decomposition and flame-regarding mechanisms of those copolymers will pe presented in upcoming works.

Acknowledgement: The author gratefully acknowledges the financial support from the Hamm-Lippstadt University of Applied Sciences.

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P3- Bilayer Coating with Coupled Intumescent and Creamification Effects toward high fire safety and fire structural survivability of fiber-reinforced polymer composites

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Main message: Fire safety and fire survivability are of great importance for the emerging application of fiber-reinforced polymer compos ites (FRPs) [1]. Herein, we demonstrated that flame retardancy, fire resistance, and fire structural survivability can be achieved by employing a feasible surface bilayer coating strategy with coupled intumescent and creamification effects for FRPs. This work provides a promising approach to the design of structural polymer composites.

Keywords: Fiber-reinforced composite, flame retardancy, fire resistance, fire mechanical properties.

Introduction

Most polymer matrices of FRPs tend to be highly flammable and impart low heat/fire survivability for FRPs compared to metal/alloys [2]. Applying surface fire protective coating stands out among choices with nearly no compromise on the mechanical strength of polymer composites. To the best of our knowledge, few works have demonstrated a result of achieving simultaneously ideal reaction-to-fire properties, strong fire resistance properties, as well as improved fire survivability of FRPs.

Experimental

Two layers of surface coating by using commercial gel coat epoxy resin and multiple fillers were applied onto the surface of glass fiber reinforced FRPs. Cone Calorimeter tests were done under 50 kW/m^2, 25mm distance for samples with one, two layer of surface coating as well as not coated. The fire resistance test for the composite panel was designed and performed by using a method like the vertical burning mode of the Cone test (50 kW/m^2, 60mm distance) with the addition of a thermal camera aimed at the reverse side. In addition, after 120s of heat and fire attacks, samples were cooled down and screened to get the apparent tensile strength values by the universal testing machine. A homemade accessory for *in situ* tensile fire test mounted on the Cone Calorimeter was designed, manufactured, and employed to screen the failure time of composite coupons under simultaneously 50 kW/m^2, 25mm distance and varied tensile force [4].

Results and Discussion

Two coating layers of 1mm each were applied by the film applicator on the composite surface of one side. Different fillers were selected and added to the coating matrix to apply intumescent effects on the top layer and creamification effects in the middle layer [3]. In the results of the Cone test, around 50% reduction of PHRR and 65% reduction of TSP for samples with two layers of coatings, as shown in Figure 1 (a), (b). Strong effects of delaying matrix decomposition are also shown in Figure 1 (c). In the fire resistance test, the composite panel with bilayer coating never showed burn-through failure compared to that of the two other panels. And the T_B for the bilayer-coated sample was below 300 ℃ even when flame out, as shown in Figure 1 (e).

The fire survivability of composite coupons was screened by *in situ and postmortem* tensile tests. After 120s (time to PHRR) of heat and fire attack, coupons with bilayer coating preserved around 79% of the original tensile strength, while almost no post-fire tensile strength was retained for composites without coatings, as shown in Figure 1 (f). By using a homemade accessory, the *in situ* tensile fire test showed that fire protective coating could significantly prolong failure time for composite under simultaneous fire and tensile stress, as shown in Figure 1 (g).

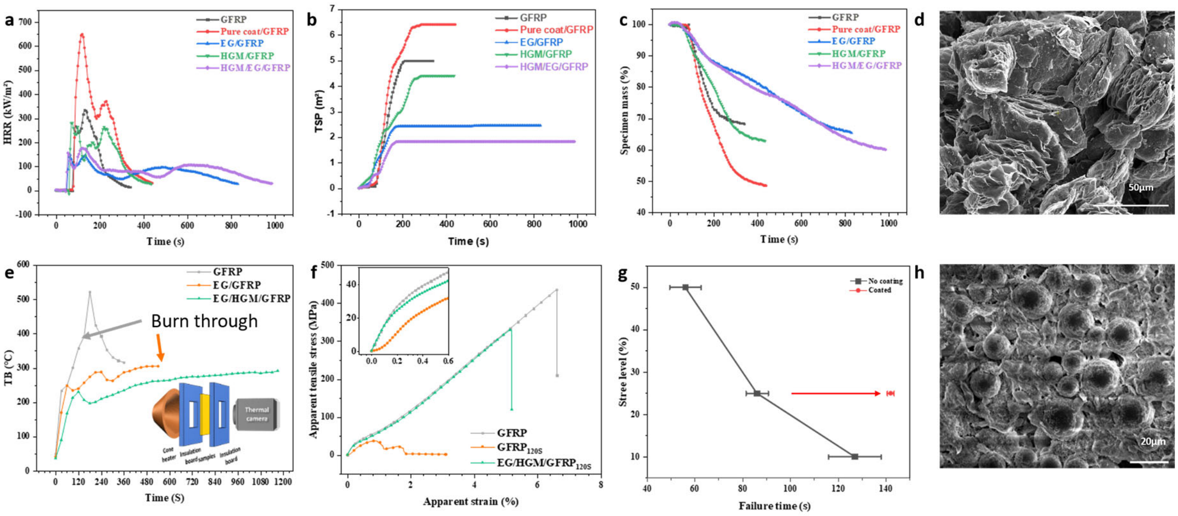

FIGURE 1. Results from Cone test: (a) Heat release rate vs time curve, (b) Specimen mass vs time curve, (c) Total smoke production vs time curve. (d) char residue of the top coating layer after the cone test. (e) Back face temperature (T_B) at central point vs time curve. (f) Apparent stress vs strain curve of coupons after damage. (g) Stress level vs failure time curve for *in situ* tensile fire test. (h) char residue of the middle coating layer after the cone test.

The char residue of composite panels after cone tests was also screened by SEM, XRD and FTIR measurements. As shown in Figure 1 (d), (h), results displayed a top intumescent porous char layer with a dense, compact middle char residue layer upon the glass fabric residue of composite panels, indicating a strong condense phase charring behaviour. Based on the results above, a fire protection mechanism was proposed. The top intumescent coating layer produces a highly porous char layer hindering mass and heat transfer after ignition. In contrast, the middle creamification layer produces a compact, insulative char layer, which further enhances thermal insulative effects. Thus, the bilayer-coated sample showed simultaneous idea reaction-to-fire properties, strong fire resistance properties as well as improved fire survivability.

Acknowledgement: This research is partly funded by China Scholarship Council under Grant CSC No. 202006630011.

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P4- IMPROVEMENT OF PLA FIRE PROPERTIES WITH AUTOPOLYMERIZABLE ADDITIVES

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Main message: Autopolymerizable compounds are used as additives to improve PLA fire properties. These additives are able to self-polymerize under heating, leading to high thermal stability cross-linked network. Their incorporation into PLA matrix permit to improve fire properties of this biobased polymer.

Keywords: PLA, Biopolymer, Autopolymerizable additive, Extrusion, Fire retardancy

Introduction

Poly(lactic acid) (PLA) displays good mechanical properties and could be an alternative to common petroleum-based polyolefins (PP, PE, PS..) for long-lasting applications. [1] Nevertheless, its poor flame resistance is a major obstacle to its progression on this market. Therefore, autopolymerizable additives were used to provide improved fire retardancy of PLA. The influence of the polymerization rate of these additives was also studied by heating the additive at different temperatures prior to be mixed with PLA.

Experimental

Commercial PLA (grade 4032D, 98% of *L*-lactide from NatureWorks) and 10 or 20 wt.% of an autopolymerizable additive (r-FR) were mixed using a twin-screw extruder. The r-FR was pre-polymerized for 60 and 120 min at 100°C and for 80 min at 150°C before being mixed with PLA. TGA and DSC analysis were performed under nitrogen atmosphere with heating rates of 10 $K \cdot min^{-1}$ from 50°C to 800°C and from 20°C to 400°C respectively. Then, the fire properties were assessed using mass loss cone (MLC) at an external heat flux of 35 kW/m^2 on hot pressed 10x10 cm^2, 3mm thick plates.

Results and Discussion

Based on the results of MLC test (Figure 1), the autopolymerizable additive had a positive effect on PLA fire properties indeed the incorporation of 20 wt-% of r-FR prepolymerized 80 minutes at 150°C allows to reduce the peak of heat release rate (pHRR) by 43 %. Moreover, the pre-polymerization improved the fire barrier of the blend compared to both neat PLA and PLA mixed with unpolymerized additive. All of these results will be fully detailed in the communication.

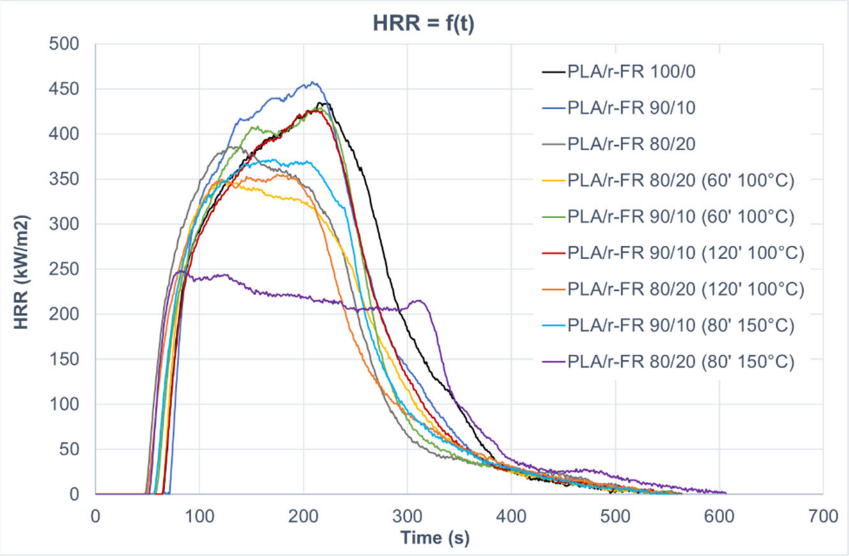

FIGURE 1. HRR as a function of time for different PLA r-FR formulation

Acknowledgement: This work is part of PLARE project (ANR-20-CE93-0004) funded by the Agence Nationale pour la Recherche (ANR) and Swiss National Science Foundation (SNF, grant No. 200021L 196923).

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P5- Commercial and biobased halogen-free flame retardants for thin polyurethane materials used for textile coatings

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Main message: Flame retardants (FR) for polyurethane (PUR) bulk materials show an insufficient effect regarding fire safety in thin films. Furthermore, FR incorporated in thin films show a completely different flammability than the same FR incorporated in the functional layer of a coated textile.
A mixture of a commercial ammonium polyphosphate (APP) and organic phosphorus shows the best FR properties and synergistic effects, as well as modified biobased residuals (starch residues) appear promising.

Keywords: polyurethane, (biobased) flame retardants, thin films, coated textile

Introduction

The polymer PUR can be used as alternative for polyvinyl chloride (PVC) to produce e.g. coated fabrics for furniture and interior of cars, trains and cruisers. In case of fire, no halogenated, corrosive and toxic gases are released by PUR. However, the intrinsic flame retardancy of PVC is missing, making FR necessary. Halogen-free FR exist, but are usually designed for bulk materials. Therefore, we screened the flame retardancy of conventional and biobased FR in thin films and coated textiles.

Experimental

Thin films were prepared from a high solid reactive aromatic PUR prepolymer with the according crosslinker. Except for the FR, no additives were used to ensure that no other substances influence the flammability. For the screening, 16 commercial FR and three biobased residual materials considered as FR were applied. These residual materials – starch residues, bark and keratin – were modified using a phosphate/urea reaction system, to ensure that flame-inhibiting groups were present [1].
The FR concentration was varied in a range of 5 – 30 phr, mixtures of FR were used and possible synergists added. Thin PUR films were manufactured with a lab coater in a transfer coating process. The same formulation as for the thin films was used for the functional interlayer of a coated textile. The layer was embedded between a knitted cotton fabric and a top layer based on polycarbonate ester polyurethane. Both, thin films and coated textiles were investigated by cone calorimetry, horizontal and vertical flammability tests, limiting oxygen index (LOI) and thermogravimetric analyses (TGA).

Results and Discussion

Burning and decomposition behaviour of several thin films and coated textile samples with different FR were compared. The investigated FR belong to different substance groups like phosphates, phosphinates, phosphate ester, ammonium polyphosphates and phosphonates.

Thin films containing phosphinate had a lower LOI and a higher peak heat release rate (PHRR) than the flame-retardant free reference film, indicating a higher combustibility. Despite identical formulations in thin films and functional interlayers of coated textiles, the latter showed an opposite effect: PHRR decreased and LOI increased, suggesting an enhancing effect of added FR. Therefore, the encapsulation of the functional layer is important. Contrary to phosphinates, organic phosphorous compounds showed a flame-retardant effect in thin films and in coated textile samples.

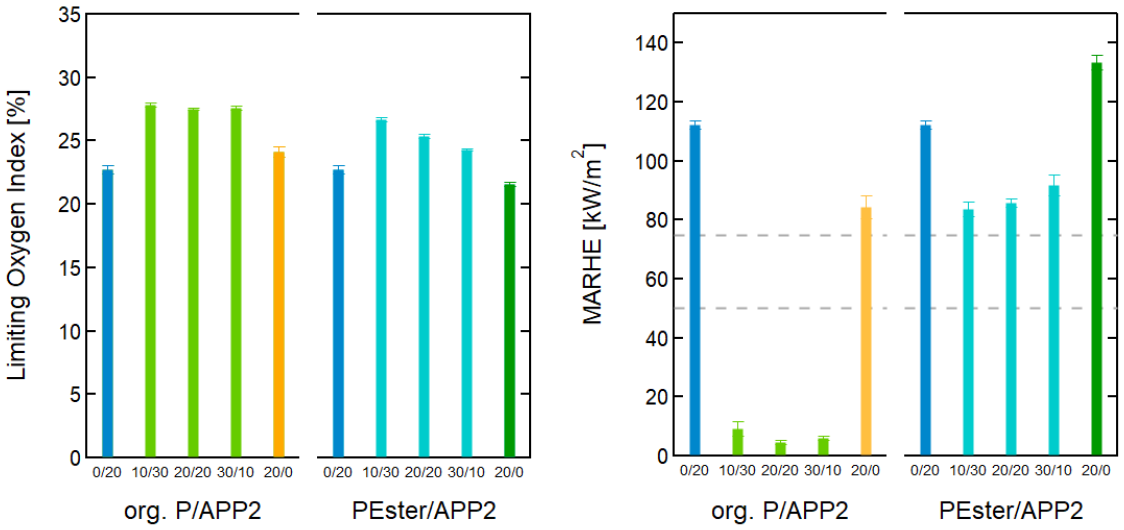

FIGURE 1. Limiting Oxygen Index (left) and Cone Calorimetry measurements in form of MARHE (maximum average rate of heat emission) value (right) of two flame retardant mixtures – organic phosphate (org. P) with ammonium polyphosphate (APP) and phosphate ester (PEster) with APP in different ratios compared to the results of only one FR.

The best flame retardant properties were found for mixtures of at least two FR (Fig. 1). The mixture of org. P and APP showed an enhanced LOI and a significant decreased MARHE, independent of the FR-ratio. The second mixture of PEster and APP shows also improved values but the MAHRE threshold of 75 kW/m² was not reached. Both mixtures showed enhanced flame retardancy compared to the corresponding system with only one FR.

Comparing the biobased residual materials, starch residues improved the fire resistance the most. Adding 5 phr led to an increase of LOI of around 3 % and the MAHRE value decreased from 76 kW/m² to 34.8 kW/m².

Adding synergists based on Bentonit and Hindered Amine Light Stabilizers (HALS) had no effect.
While the flame retardancy could be improved by increasing the FR concentration up to 30 phr in coated textiles, the opposite was observed in thin films, where 5-10 phr FR showed the best results.
In conclusion, predictions of flammability of coated textiles based on results of thin films are not feasible. It is always necessary to investigate the entire product. These results contribute to the gain of systematic knowledge on the impact of FR in PUR thin materials.

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P6- POLYAMIDOAMINES DERIVED FROM NATURAL α-AMINOACIDS AS EFFECTIVE FLAME RETARDANTS FOR COTTON

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Main message:
In the continuous seeking of new efficient and sustainable flame retardant (FR) solutions, bioderived and bioinspired synthetic polymers named polyamidoamines (PAAs) have been proposed. The results collected up to now demonstrated the ability of PAAs to retard or completely inhibit the combustion of cotton textiles by modifying cellulose thermal decomposition. The results obtained with the α-amino acid-derived PAAs reported here confirmed this hypothesis.

Keywords: polyamidoamines, α-amino acids, intumescent flame retardants, functional coatings, cotton fabrics

Introduction
Polyamidoamines are synthetic polymers synthesized by the aza-Michael polyaddition of primary amines or secondary diamines to bisacrylamides in H2O, at room temperature, without catalysts. Previous studies showed that PAAs bearing different functionalities in the structure turned out to be efficient FR for cotton in different fire scenarios [1-4]. The aim of this work was to ascertain the FR efficiency of nine different α-aminoacid-derived PAAs [5] and to set up structure-property correlations.

Experimental
Polyamidoamines were synthesized from *N,N'*-methylene bisacrylamide (MBA) and a specific α-aminoacid using H2O as solvent, in basic environment and at room temperature. The α-amino acids used were *L*-alanine, *L*-leucine and *L*-valine, chosen for their hydrophobic side chain, *L*-serine, *L*-asparagine and *L*-glutamine for their neutral side chain, *L*-aspartic acid and *L*-glutamic acid for their acidic side chain, and *L*-histidine for its basic side chain. In addition, PAA derived from glycine was synthesized and studied as model.
The resulting PAAs were structurally characterized by hydrogen nuclear magnetic resonance (^{1}H-NMR) and Fourier transform infrared spectroscopy/attenuated total reflectance (FT-IR/ATR). Cotton fabric samples (6 x 3 cm^2) were impregnated with PAA aqueous solutions and then dried for 4 min at 100 °C. The total dry solid add-on (wt.-%) was determined by weighing each sample before (Wi) and after impregnating and drying (Wf). The add-on was calculated according to Equation (1):
Add-on% = [(Wf - Wi)/Wi] x 100 Eq. 1

Results and Discussion
In order to study the thermal stability of PAAs and PAA-treated cotton fabrics, thermogravimetric analyses (TGA) were carried out in nitrogen and air. In addition, in order to deeply investigate PAA action mechanism as FRs, residues of M-GLY-treated cotton obtained by heating fabrics in an oven at 300, 350 and 420 °C were analyzed by X-ray photoelectron (XPS) and Raman spectroscopies [4].
TGA showed a higher stability of PAA-treated cotton fabrics in comparison to untreated cotton, in terms of residual mass fraction above 300°C. This is due to the high thermal stability of PAAs in nitrogen and air and to their intumescent feature in air, intrinsically characteristic of this polymer family, as already demonstrated [1]. XPS analysis of the residues of M-GLY-treated cotton obtained in the oven

revealed the formation of aromatic nanographitic char at lower temperature with respect to untreated cotton. Raman spectroscopy of these residues provided indications on the degree of graphitization of treated and untreated cotton at 300, 350 and 420 °C. Further XPS analyses on the nine α-aminoacid-derived PAAs studied demonstrated that this mechanism of protection is common to all PAAs.

The efficiency of PAAs as FRs was studied by specific combustion tests: specifically, ignition tests on PAA powders, horizontal flame spread tests (HFSTs) and oxygen consumption cone calorimeter tests on PAA-treated cotton fabrics. None of PAAs ignited by direct flame impingement apart from the leucine-derived PAA, which burned for a few seconds and then self-extinguished; however, its final residue was about 93%. For each polymer, 10%, 7% and 5% add-ons were applied on cotton fabrics and specimens with 7% add-on were characterized by FT-IR/ATR, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA).

All samples were tested by HFSTs: at 10% and 7% add-ons, all specimens were able to extinguish the flame, obtaining different residual mass fractions (RMFs); in particular, it was observed cotton treated with *L*-alanine, *L*-leucine and *L*-valine-derived PAAs produced lower RMF (at 7% add-on, 69%, 80% and 74%, respectively). These results are in agreement with those already observed in the ignition tests, PAAs were able to extinguish the flame thanks to their intrinsic intumescence and their ability to form a thermally stable carbonaceous structure (char) when they are exposed to heat in air that protected the cotton fabric. Reducing the add-on to 5%, samples burned, except for cotton fabrics treated with *L*-glutamic acid (Figure 1) and *L*-glutamine-derived PAAs, which suppressed the flame leaving high RMFs (respectively 84% and 74%).

Combustion tests in cone calorimeter revealed that all PAAs, regardless of structure, were able to increase FR cotton performances, as evidenced by the significant reduction of the heat release rate peak values (down up to -33%) and the RMF values (up to 5.5 % for PAA-treated cotton fabrics in comparison to a negligible residue left by of untreated cotton).

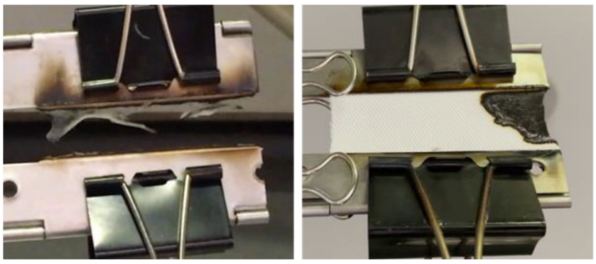

FIGURE 1. Results of HFSTs on untreated cotton (left) and cotton fabric treated with *L*-glutamic acid-derived PAA (right), add-on 5%.

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P7- EPOXY VITRIMERS – THERMAL BEHAVIOR AND FLAME-RETARDANT PROPERTIES

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Main message:
Vitrimers offers a great potential in terms of recyclability of thermosets. However, vitrimer-based materials must also pass safety requirements of the product use phase in terms of flame retardancy. Here we report the thermal behavior and flame-retardant properties of epoxy vitrimer-based composites.

Keywords: Epoxy vitrimers, flame retardant, composites

Introduction

Linear plastic economy leads to an unmanageable accumulation of plastic waste in the ecosystem. A change towards a sustainable circular plastics economy must be achieved. However, the end-of-life phase and plastic recycling is still the greatest challenge in this respect. To reduce the environmental harm of plastics and to achieve the transformation towards a circular plastics economy, more safe-, sustainable- and recyclable-by design polymeric systems are needed.

Especially the recyclability of thermosets and thermoset composites is limited and challenging. The development of reprocessable, reusable and recyclable thermosets is therefore of great importance.

Vitrimers offer great potential in terms of recyclability as the incorporation of dynamic covalent bonds into a thermoset network provides a powerful method to recycle and reshape these plastics by topology rearrangements.

For many applications especially in the transportation sector the thermal and mechanical properties of plastics are essential. Currently, thermoset based composites are mainly and extensively used for several interior applications and secondly in structure applications due to weight saving. Vitrimers show very similar mechanical properties to thermosets. However, vitrimers consist of a dynamic covalent network, which changes its topology by thermal activation – offering a great potential to be more safe-, sustainable- and recyclable-by design.

For application in the transportation sector, the thermal behavior and flame-retardant properties are of great importance.

Experimental

The thermal behavior and flame-retardant properties were investigated using differential scanning calorimetry (DSC), thermal gravimetric analyses (TGA), and thermal gravimetric mass spectrometry (TG-MS) as well as limiting oxygen index (LOI) tests, UL94 tests, and cone calorimeter tests.

Results and Discussion

The thermal behavior and flame-retardant properties of different types of epoxy vitrimers as well as different types of glass fiber and carbon fiber reinforced epoxy vitrimer-based composites were studied. The vitirmer properties were achieved by a hardener, which contains disulfide bonds. An example of a cured glass fiber reinforced epoxy vitrimer plate and the mechanism of the dynamic covalent disulfide bond exchange are shown in Figure 1.

During flame treatment, epoxy vitrimer-based composites showed charring and the release of large quantities of soot. Without any flame retardant, epoxy vitrimers and epoxy vitrimer-based composites do not pass the UL94 test. The LOI values of the studied cured fiber-free epoxy vitrimer is 20.9 O_2% and increases with increasing fiber content.

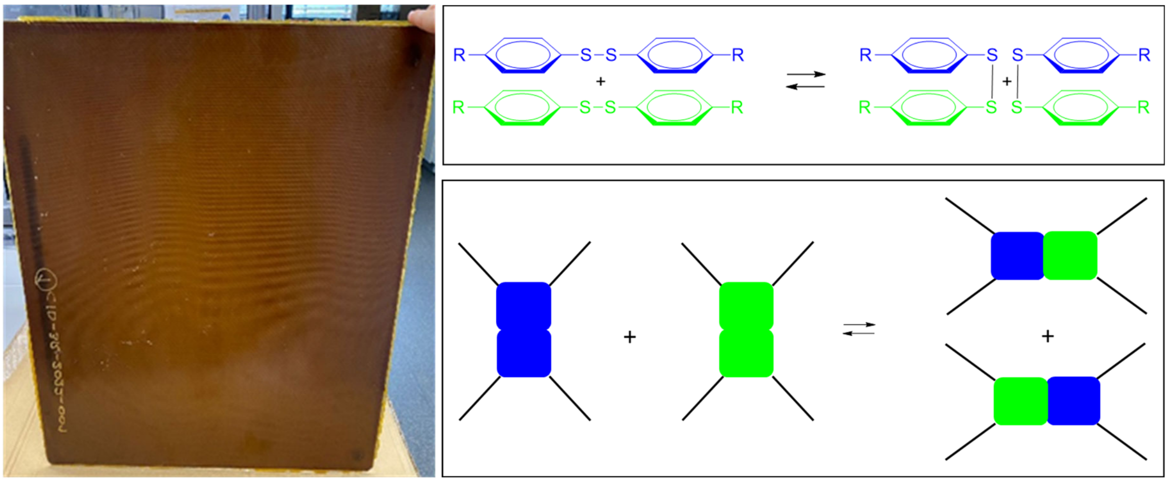

FIGURE 1. Left: cured glass fiber reinforced epoxy vitrimer plate; Right: dynamic crosslink – aromatic disulfide exchange [1]

This presentation provides a more detailed overview about the thermal behavior and the flame-retardant properties of epoxy vitrimers.

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P8- USEFUL TRICKS WITH BIOBASED FLAME RETARDANTS

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Main message: Novel flame retardancy mechanisms have been explored through physical and chemical modifications—such as fibre formation, surface treatment or encapsulation—of various polysaccharides and by utilising synergistic interactions between the active ingredients of biocomposites, respectively.

Keywords: poly(lactic acid), polysaccharides, biocomposites, intumescence, electrospinning

Introduction

The potential of various carbonising agents of renewable origins—such as cellulose, cyclodextrins, alginates, and bioresins—are comprehensively investigated in different intumescent flame retardant formulations. Novel strategies, including physical and chemical modifications, of the biobased carbonising agents are shown to significantly enhance the efficiency of intumescent flame retardant systems in various polymer matrices.

Experimental

Cellulose fibres, flax fabric, cyclodextrin, sorbitol-based bioepoxy resin and Na-alginate were used in neat and modified forms to create flame retarded biocomposites (Figure 1). Composition-structure-property relationships were evaluated using morphological, spectroscopic, thermal, flammability and mechanical analyses.

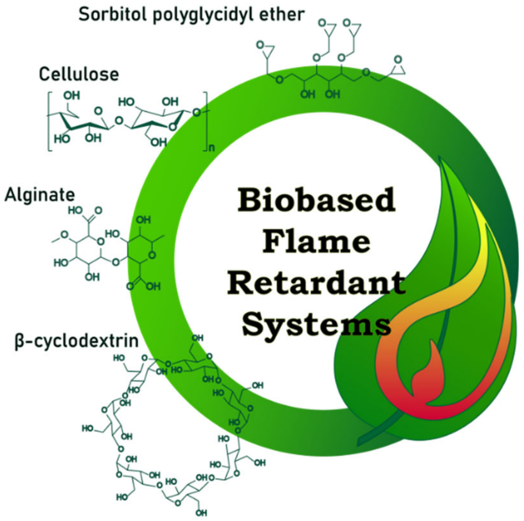

FIGURE 1. Compounds investigated as biobased carbonising agents

Results and Discussion

Chemical modification

Outstanding flame retardant efficiency has been observed for a newly synthesized, phosphorous-silane-modified alginate compound due to the efficient carbonisation of the modified alginate catalysed by phosphorus, as well as the ceramising effect caused by silicon.

Microencapsulation

A new process of microencapsulating the widely used ammonium polyphosphate (APP) flame retardant with sorbitol-based bioepoxy resin has been developed. The bioresin shell effectively promotes the charring of the APP-loaded poly (lactic acid) (PLA) composites, besides providing increased water resistance to the flame retarded biocomposite [1].

Multiphase approach

It has been demonstrated that natural fabric-reinforced polymer composites, when flame retarded with a combined approach—i.e. balanced distribution of phosphorus-containing additives between the matrix and reinforcing phases—gain improved mechanical performance and fire retardancy at the same time [2].

Specific surface area

It was found that the formation, swelling ability, structure and mechanical resistance of a fire-protecting char can be noticeably affected by the length (or aspect ratio) of the used cellulosic fibres; thereby, it can determine the efficiency of the flame retardant system.

The flame retardant effectiveness of a cyclodextrin-type biobased carbonising agent has been evinced to noticeably increase when used in a microfibrous form produced by electrospinning method [3]. The flame retardant performance of the high-surface-area electrospun cyclodextrin microfibres could be further enhanced by reactive surface modification with a phosphorous silane compound [4].

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P9- Mechanical Recycling of PET Fibers containing Phosphorus Flame Retardants

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Main message: It is challenging and has enormous potential to recycle flame-retarded PET fabric waste. In this study, PET/FR compounds show a fascinating behavior in stabilizing viscosity over a long time. During the rheological investigation, a DOPO derivative (DOPO-PEPA, shortened DP) shows a stabilizing function over the viscosity of molten PET; while a phosphonate compound (Aflammit PCO 900, shortened AF) exhibits a branching/crosslinking effect on the compounds. Moreover, a mix of DP and AF of a specific composition shows an improving stabilizing effect. Therefore, It is very promising to improve the recycling quality of PET fabric waste by studying the FR effects on PET melts.

Keywords: PET, fibers, mechanical recycling, rheology

Introduction

Recycling polyethylene terephthalate (PET) fabrics containing flame retardants (FRs) is a significant and challenging issue because FR is hazardous, not to mention the downgrading of PET during mechanical recycling [1]. For these reasons, tons of PET fabric waste ends up being incinerated. Some research reports the effects brought to recycling by existing additives in fabric waste [2,3].

Experimental

ICP-OES, GPC, and NMR were employed to characterize the phosphorus components and polymers. To study the rheological behavior of PET/FR compounds, time-resolved frequency sweeps (TRFS) were implemented.

Results and Discussion

The results show that DP has the potential to stabilize the viscosity of molten PET over a long period, while AF leads to branching/crosslinking structures. Meanwhile, a hybrid composition of DP and AF exhibits an improved stabilizing effect on the viscosity of PET melts. This fascinating performance also exists in studying the processability and recyclability of PET/FR compounds by repeated extrusion. After extrusion cycles, the recycled PET/AF showed an undesirable mechanical performance, while other compositions exhibited superior properties. Notably, the hybrid composition stabilizes the viscosity of PET melts during rheological measurements and processing experiments. It can hinder the degradation of PET and inhibit branching/crosslinking effects introduced by AF.

It is significant to study molecular events to achieve a better picture of the stability of molten PET/FR. Therefore, computational simulations are also involved in helping understand the behavior. It is promising to design flame-retarded PET fabrics and improve the recycling quality based on this phosphorus FR study.

Acknowledgment: For the funding of this research, we acknowledge the Zürcher Stiftung für Textilforschung (Switzerland), and EmpaInternal Research Call 2020 in the framework of the "RePET" project.

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P10- Flame Retardant and Transparent Polymethylmethacrylate Composites Based on Phosphorus-nitrogen Flame Retardants

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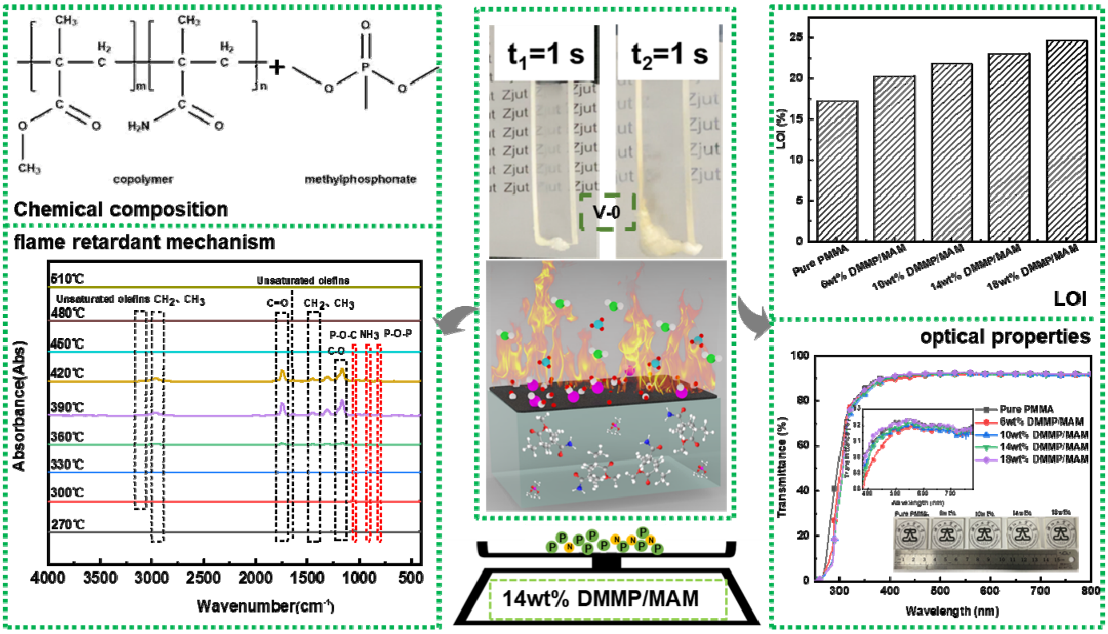
With the advantages of high transparency, low density and electrical insulation, polymethylmethacrylate (PMMA) has become a substitute for many traditional materials However, because of its low limiting oxygen index (LOI) and extreme flammability, PMMA will drip seriously during combustion, which greatly limits the application of PMMA. It puts forward higher indexes for the performance of flame-retardant PMMA materials in the fields of architecture, transportation and national defense. Therefore, it is necessary to carry out flame retardant modification on PMMA. PMMA materials with excellent flame-retardant properties, optical and mechanical properties can meet the needs of more applications It is urgent to prepare flame retardant PMMA products with excellent comprehensive performance, which is of great significance for the application of PMMA. With an eye to the concept of green, low-carbon and environmental protection and the cost of flame retardants, flame retardants of halogen-based, boron-based and silicon-based are gradually eliminated. Inorganic flame retardants are not widely used because of their poor compatibility with PMMA matrix. The single phosphorus flame retardant has low flame retardant efficiency and large addition, which has great influence on the mechanical properties of PMMA products. For improving the flame retardant efficiency, domestic and foreign scholars gradually emphasize the research of phosphorus-nitrogen synergistic system. How to maximize the flame retardant efficiency of nitrogen -phosphorus synergistic flame retardant system has become a problem worthy of attention. Researches have demonstrated that the structure of flame retardant and the proportion of nitrogen to phosphorus have important influence on flame retardancy. In the case of nitrogen-phosphorus synergistic flame retardant system, the proper phosphorus-nitrogen ratio has obvious effect on flame retardant effect.

In this article, dimethyl methylphosphonate (DMMP) and methacrylamide (MAM) were used as flame retardants to develop an efficient synergistic flame retardant system of phosphorus and nitrogen, and P(MMA-co-MAM)/DMMP products were prepared by free radical polymerization, which had excellent flame retardant effect and high transparency. When only 14 wt% DMMP/ MAM is added, the LOI value of PMMA can reach 23.1%, and the vertical combustion grade can attain V-0. The flame retardant ways of DMMP/MAM flame retardant mainly include terminating free radical chain reaction and gas phase dilution, which indicates that gas phase flame retardant plays an important role in PMMA flame retardant. Meanwhile, the optical properties of P(MMA-co-MAM)/DMMP products are almost the same as those of pure PMMA. In addition, when 14 wt% DMMP/ MAM is added, the mechanical properties of P(MMA-co-MAM)/DMMP products only slightly are changed, and the Vicat softening temperature is 65℃ higher than the long-term service temperature of commercial PMMA, which can fulfill the needs of most markets. This research provides a valuable method for preparing transparent flame retardant PMMA products.

Keywords: PMMA, transparent, Phosphorus-nitrogen ratio, efficient flame retardant, flame retardant mechanism



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P11- Ultra washing durable flame retardant coating for cotton fabric by the covalent bonding and interface polymerization

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Main message: In this work, a formaldehyde-free flame retardant cotton fabric (Cotton-PEI/APP-TMC) with ultra washing durability was prepared via covalent bonding of ammonium polyphosphate (APP) and polyethyleneimine (PEI) followed by the interface polymerization between PEI and trimesoyl chloride (TMC). The prepared fabric exhibited excellent flame retardancy. Even after 300 washing cycles, the cotton-PEI/APP-TMC sample was still self-extinguishing in the vertical flammability test (VFT).

Keywords: Flame retardant; Washing durability; Cotton fabric

Introduction

Cotton fabrics are widely favored. However, the inherent inflammability of cotton fabric poses many fire hazards[1]. As alternatives to halogen-based flame retardants, a variety of flame retardant finishing agents have been developed to endow the fabric flame retardancy. Although considerable progress has been made in the development of flame retardant cotton fabrics, the challenge in this field is that the fabrics would gradually lose their flame retardancy after washing.

Experimental

The mercerized cotton fabrics were impregnated in the solution which contained 25 % APP, 8 % PEI, and 5 % dicyandiamide with a bath ratio of 1:30 at 70 °C for 30 min. Then, the fabrics were padded with 1.6 MPa pressure. After that, the fabrics were pre-baked at 110 °C for 30 min and baked at 170 °C for 6 min. Subsequently, the cotton fabrics were wetted with deionized water, immersed in 0.4 % TMC n-hexane solution at ambient temperature for 5 min, and then dried at 70 °C for 1 h. Finally, the cotton fabrics named cotton-PEI/APP-TMC were immersed in deionized water for 1 h to remove unstable flame retardants and then dried to constant weight.

Results and Discussion

The cone calorimeter test (CCT) under the heat flux of 35 and 50 kW/m^2 was performed to simulate the fire performance of the control cotton and cotton-PEI/APP-TMC samples, respectively. The key data were collected in Table 1. Under the irradiation of 35 kW/m^2, the control cotton fabric burned violently, with a time to ignition (TTI) of 24 s, a peak of heat release rate (pk-HRR) of 204.0 kW/m^2, a total heat release (THR) of 11.3 MJ/m^2, and a final residue of 6.8 %. However, the cotton-PEI/APP-TMC fabric was not ignited and glowed slowly with no flame. The pk-HRR and the THR value of cotton-PEI/APP-TMC were 34.8 kW/m^2 and 5.1 MJ/m^2, which was reduced by 82.9 % and 54.9 % respectively in comparison with that of the control cotton sample. The total heat release (TSP) value of the cotton-PEI/APP-TMC (0.51 m^2) was higher than that of control cotton (0.13 m^2), which was attributed to incomplete combustion.

As predicted, the control cotton showed an earlier TTI (7 s) and higher pk-HRR value (296.4 kW/m^2) under 50 kW/m^2, compared to the results under 35 kW/m^2. Unexpectedly, the cotton-PEI/APP-TMC sample remained unignited under 50 kW/m^2 and there was almost no change in pk-HRR and THR value compared to the results under 35 kW/m^2 irradiation CCT, as listed in Table 1. The FIGRA (fire hazard

index) value of control cotton was 16.5 kW/m^2·s, while that of cotton-PEI/APP-TMC was 0.32 kW/m^2·s. The above results indicated the PEI/APP-TMC coating effectively prevented the spread of flame.
The mean effective heat combustion (mean-EHC) value of cotton-PEI/APP-TMC (38.4 MJ/kg) was higher than that of control cotton (26.0 MJ/kg), indicating that the flame retardant coating mainly took effects in the condensed phase.

TABLE 1. The key data from CCT

Sample	**Control cotton**		**Cotton-PEI/APP-TMC**	
Heat flux [kW/m^2]	**35**	**50**	**35**	**50**
TTI [s]	24 ± 2	7 ± 1	–	–
pk-HRR [kW/m^2]	204.0 ± 9.2	296.4 ± 12.1	34.8 ± 2.2	34.4 ± 2.5
$t_{pk\text{-}HRR}$ [s]	60 ± 4	18 ± 2	123 ± 9	109 ± 8
THR [MJ/m^2]	11.3 ± 0.1	11.4 ± 0.2	5.1 ± 0.1	5.1 ± 0.1
TSP [m^2]	0.13 ± 0.02	0.10 ± 0.02	0.51 ± 0.04	0.64 ± 0.04
Residue [%]	6.8 ± 0.3	7.4 ± 0.4	33.3 ± 0.5	28.6 ± 0.5
FIGRA [kW/m^2·s]	3.4	16.5	0.28	0.32
Mean-EHC [MJ/kg]		26.0 ± 1.1		38.4 ± 1.8

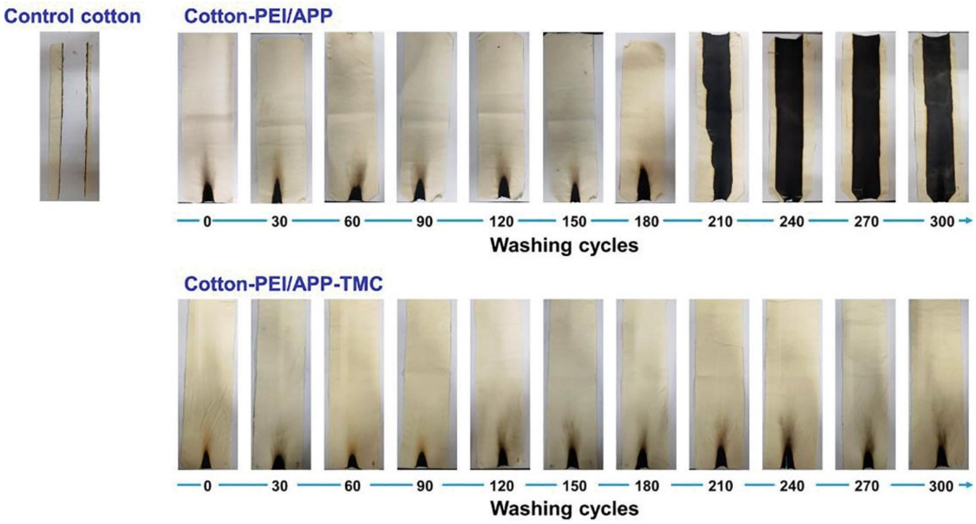

FIGURE 1. The digital photos of cotton fabric samples from the vertical flammability test

After 300 washing cycles, the LOI of cotton-PEI/APP and cotton-PEI/APP-TMC decreased to 26.0 % and 35.3 %, respectively. With the increase in washing cycles, the flame retardancy of the cotton-PEI/APP fabric gradually deteriorated. However, the washing cycles had minimal effect on the vertical burning properties of the cotton-PEI/APP-TMC sample, even after 300 washing cycles.

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P12- SMOKE SUPPRESSANT FLAME RETARDANTS FOR NATURAL FIBRE REINFORCED COMPOSITES

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Main message:
With a global strive towards energy-efficiency and resource-responsibility, lightweight construction plays a key role in modern automotive, aviation, and naval design. Natural fibre reinforced composites offer a promising approach to provide a green alternative to artificial fibre reinforcements.[1] However, the combination of flammable natural fibres and a smoke producing polymer matrix limits their usability. These challenges are addressed with smoke suppressant flame retarding additives.

Keywords: Composites, smoke suppression, flame retardant, natural fiber reinforced, halogen-free

Introduction

Classical halogen-based flame retardants are classified as toxic and environmentally concerning, thus, halogen-free replacements must be developed.[2] Several organophosphorus and -nitrogen compounds are reported but lack smoke suppressing capabilities. Boric acid derivatives, in contrast, are effective smoke suppressants, but are classified as SVHC under REACH.[3] As a safer solution, PIN-organoboron flame retardants (non-SVHC) are investigated for natural fibre reinforced composites.

Experimental

A common and straightforward approach to protect fibre reinforced polymeric composites against fire is to introduce a flame retardant (FR) into the polymer matrix prior to or during merging matrix and reinforcement into a composite. This technique, however, distributes the flame retardant over the composites volume, including the surface, leaving water-soluble FRs vulnerable to environmental influences.

To ensure persistency against leaching, the newly developed phosphorous-, nitrogen-, and boron-containing (P/N/B)-FRs are applied as organic-inorganic hybrid polymers to the textile reinforcement, where covalent bonds between the substrate and the FR are formed. Using well-established techniques for textile finishing, such as pad-dry-cure from aqueous media, a simple transfer into the industry is granted. Chemical synthesis of the FR-precursors is optimized to high-yield and low-effort protocols. Various P/N/B-FRs were tested during screening on flax, rayon, and cotton textiles and the most promising candidates were processed into composites, using polypropylene (PP) and bio-based Greenpoxy (GP) matrices, respectively. Composite samples were thoroughly tested for flame retardancy and smoke suppression via LOI, MCC, TGA, and standardized methods, such as smoke density (ASTM D2843) and flame spread testing (DIN 75200).

Results and Discussion

Among the >20 boron-containing precursors synthesized and tested, only a few candidates fulfilled all requirements in terms of processability (i.e., high-yield synthesis, simple work-up, solubility in water/ethanol, reproducible add-on) and function (limited flame-spread/self-extinguishing effect during screening). Combinations of the promising boron-organic compounds with P/N-based FR-precursors were investigated under variation of their P/N/B-ratios and the most effective add-on values on flax, rayon and cotton as textile substrates were identified. After successful implementation of the FR-finished textiles into the polymer matrices, the obtained composites were tested regarding their flame spread and smoke emission, alongside composites containing only the P/N-, and the B-FR, respectively, as well as pristine composites. While P/N-finished composites showed a decreased flammability, compared to the pristine composites, the smoke emission during ASTM D2843 smoke-chamber test increased, due to the incomplete combustion, promoted by the flame retarding effect. While the addition of B-FRs showed a negligible effect on flammability, the measured smoke density was significantly lowered, confirming boron's smoke suppressing effect. LOI, MCC, and TGA measurements underline the flame retardancy, achieved by the introduction of the newly developed P/N/B-FR.

The chemical integration of boron, nitrogen, and phosphorous in an organic-inorganic hybrid polymer, combined with immobilization of the flame retardant on the textile as well as the embedding of the textile in the polymer matrix are expected to prohibit environmental exposure while providing smoke suppressant and flame retardant properties to the composite.

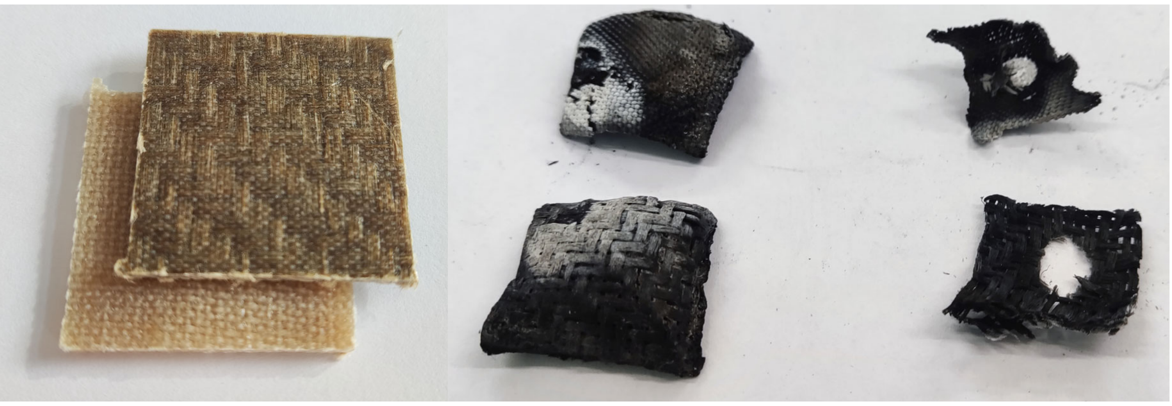

FIGURE 1. Left: Flax(top) and rayon(bottom) reinforced PP-composites. Center: Char residue of the P/N/B-FR finished composites after 4 min. flame impingement (ASTM D2843). Right: Char residue of the pristine composites.

Acknowledgement: *The research project (IGF Nr. 21318 N) is funded by the Bundesministerium für Wirtschaft und Klimaschutz within the program Industrielle Gemeinschaftsforschung (IGF) by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen e. V. (AiF)*

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P13- DEVELOPMENT OF AN ALGINATE-BASED ADDITIVE FOR FLAME RETARDANCY OF POLYLACTIC ACID

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Main message: Our goal was to develop a bio-based flame retardant (FR) additive for PLA using sodium alginate as starting material. To increase the FR activity of the alginate, it was reactively modified with a phosphorus-silane compound. The thus obtained new biobased FR additive was characterised using spectroscopic and thermal analytical methods, while flame retardant efficacy was evaluated in PLA matrix using standard flammability tests.

Keywords: alginate, biobased, PLA, intumescence, synthesis

Introduction

Despite polylactic acid's (PLA) comparable properties to common technical polymers, it is mostly only used in single-use products. The large-scale distribution of PLA in technical fields is primarily limited by its low heat resistance, brittleness and increased flammability. In this research, PLA's biobased, green flame retardancy possibilities were investigated using neat (Na-Alg) and chemically modified alginate in combination with ammonium-polyphosphate (APP). Due to the rapid growth of algae and its use in many industries, alginate can be a very economical and environmentally friendly additive.

Experimental

In order to increase the flame retardant efficiency, Na-Alg was reactively modified with a phosphorous silane (PSil) compound [1], obtained by the by-product-free addition reaction of a phosphorus-containing polyol and 3-(triethoxysilyl)propyl isocyanate. The modified PSil-Alg was then coagulated by dripping it into an aqueous calcium chloride solution (see Figure 1).

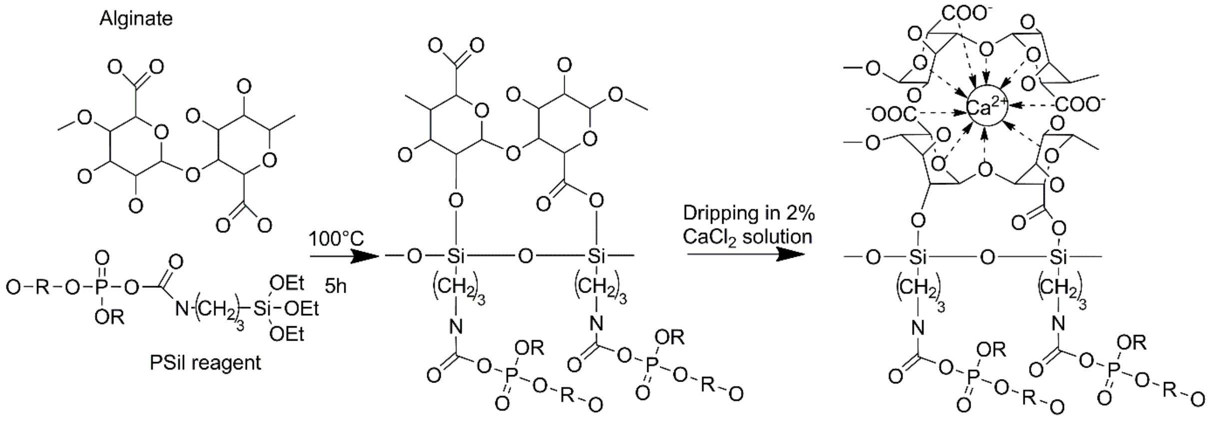

FIGURE 1. Synthesis of the PSil-Alg additive and subsequent coagulation in $CaCl_2$ solution gaining the Ca-Psil-Alg additive

The Ca-PSil-Alg additive was obtained after drying and grinding the modified hydrogel and then comprehensively characterised by spectroscopic and thermoanalytical methods. Its flame retardant effect was evaluated at 1-5% loading in PLA matrix besides 15% APP flame retardant using standard flammability testing methods.

Results and Discussion

Our experimental results show that as low as 5% of the newly synthesised alginate-based additive increases the limiting oxygen index of the 15% APP-containing PLA composite from 26% to 34%. It also reduces the total heat emission during cone-calorimetric measurements by more than 60%, besides the formation of a significant amount (approx. 40%) of charred residue.

The outstanding flame retardant effect of the PSil-Alg is explained by the efficient carbonisation of the modified alginate catalysed by phosphorus and the ceramising effect caused by silicon, which together contribute to the formation of a thermally and mechanically resistant fire protecting layer.

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P14- One-dimensional transient pyrolysis model for intumescent fire retardant polymers usage in Electric Vehicle battery pack applications: validation with fire-retarded polycarbonate

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Main message

The aim of this study is to set up modelling tools that help to understand the behavior of materials in battery packs of Electrically propelled Vehicles (EVs) exposed to external fire hazards.

The pyrolysis model used is based on the one-dimensional transient finite element model of Statler Jr and Gupta [1] which predicts the heat release rate for polycarbonate (PC) from cone calorimeter data at 50 kW/m^2 heat flux.

The results showed a good prediction of the built model thanks to the introduction of the non-constant heat at the sample expanding and the char cracking behaviour observed during the combustion.

Keywords: Electrical vehicle batteries packs, pyrolysis model, fire-retardant polycarbonate

Introduction

Electric Vehicles (EVs) have become an increasingly important part of the vehicles market in recent years. The main reason for this is to reduce the number of petrol-driven vehicles, which are suspected to be harmful to global warming. However, due to their on-board battery technology, EVs present a higher risk of fire compared to fuel vehicles when exposed to external fire hazard, such as fire pools. The presence of the battery will increase and accelerate the destruction of the vehicle (thermal runaway phenomenon) [2].

A one-dimensional transient pyrolysis model was developed by Statler Jr and Gupta [1] for predicting the heat released rate during a cone calorimeter test. The Statler Jr and Gupta [1] model is based on mass and heat transfer equations and considers two distinct zones. The polymer zone (PZ) (x0-x1) accounts for the pyrolysis reaction; the polymer is consumed and gas is produced. The char formation zone (CFZ) (x1-x2) accounts for the char growth and acts only as a barrier to heat and mass transfer. For modelling purposes, the CFZ is assumed to be initially small (~ 1 nm). The PZ is assumed to be constant and the thermal expansion is implemented by applying a moving boundary condition at the char front x2. The following assumption has been added to the Statler Jr and Gupta [1] ones :

(1) **Non-constant heat at the char front boundary**: during the combustion, the material expands and sees its front subjected to the cone heater, the heat increases with time. This behaviour was not taken into account by Statler Jr and Gupta [1] and has a significant effect on the heat release predicted by the model [3]. This effect is implemented by applying an additional non-constant heat flux condition at boundary x2:

$$Q_{add} = \frac{Q_{cone} * t}{t_{comb}} + Q_i \qquad \text{Equation 1}$$

Where Q_{add}, Q_{cone}, Q_i are respectively the added heat flux, cone calorimeter heat flux [50 kW/m²] heat to initiate the ignition [20 kW/m²] and t_{comb} the combustion time [600 s].

(2) **Second peak of heat release curve**: the char cracking observed during the combustion of charring polymers was implemented by considering a Dirac function for the coefficient of gas diffusion in the char ($D_{char} = \delta * D$)

Experimental

All the model parameters were obtained from direct property measurements and can be found in the Statler Jr and Gupta [1] paper. The model was validated against the results from cone calorimeter data for polycarbonate (PC). The data were taken at a frequency of 1 Hz and the radiant heat flux was 50 kW/m^2. The boundary and initial conditions also are the same as Statler Jr and Gupta [1] for PC.

Results and Discussion

The comparison between the predictions and experimental data i.e. heat released rate (**FIGURE 2. a)** and growing char thickness (**FIGURE 2. b**) from cone calorimeter under a 50 kW/m² radiative heat flux on PC (self-intumescent) [1] shows a good prediction by the built model. The simulated curves show that the PC expands to ~ 2 cm, i.e. ten times the initial thickness of virgin polymer (3 mm).

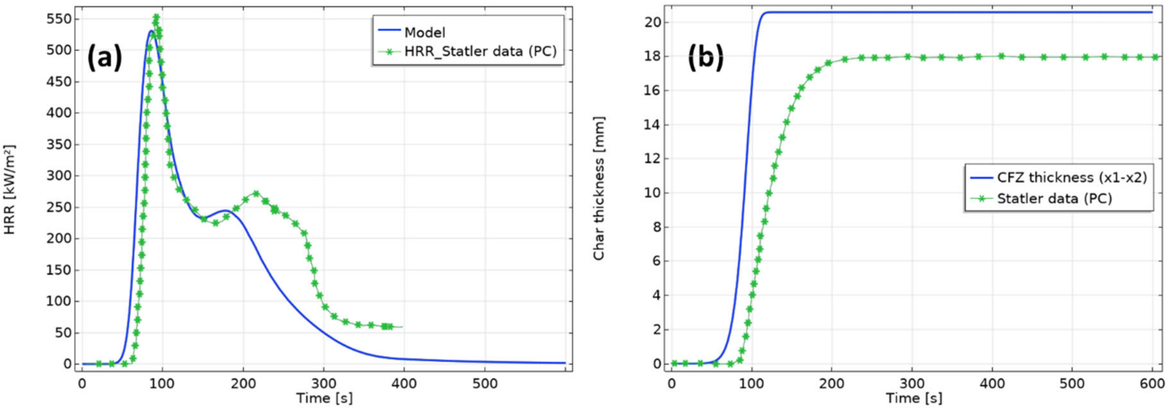

FIGURE 2. (a) Predicted heat released rate from Statler Jr and Gupta [1] cone calorimeter at 50 kW/m², (b) verification of the moving boundary condition: thermal expansion

Acknowledgement

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P15- Combination of ionic liquids and phosphorus-containing flame retardants for carbonate-based battery electrolytes

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Main message: The effect of ionic liquids and phosphorus-based flame retardants in battery electrolytes. How do the two components affect the fire properties. New molecules for flame protection of carbonate-based electrolytes.

Keywords: Ionic liquid, electrolytes, phosphate and phosphonate based.

Introduction

The increasing market share of electric vehicles leads to an increased need for reliable battery systems. Damaged or defective batteries lead to a high fire risk. The risk reduction can be achieved by preventing the battery from igniting, therefore the flammability of the battery must be reduced. A leakage of the electrolyte holds the highest risk, therefore, it is favorable to equip the electrolyte with a flame retardant. To achieve this, phosphates and phosphonates are used as flame retardants.[1] However, these can degrade essential properties such as conductivity. Ionic liquids can increase the flash point of the electrolyte and contribute safe electrolytes.[2]

Experimental

Various methods can be used to test the effectiveness of flame retardants. The flammability and flame spread of electrolytes were tested using glass fibre wicks soaked with electrolyte. For this purpose, carbonate-based model electrolytes are mixed with various flame retardants and the impregnated wicks are exposed to a defined flame (50 W) for 10 s. It is measured whether the flame propagation and if so, its speed. From this, knowledge can be gained about the flammability and flame propagation when using certain flame retardants.

Cone calorimetry is used to obtain further insights into the fire properties and the effectiveness of the flame retardants.

Results and Discussion

Cone measurement show an increase in time to ignition using ionic liquids (Figure 1). This is done by reducing the total heat release during the fire.

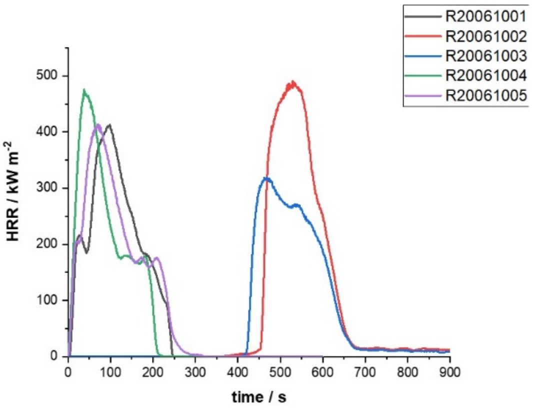

FIGURE 1. Heat release rate measurements of electrolytes without flame retardants (green, purple, black) and comparable electrolytes with ionic liquids as additives (blue, red).

The curves show that a fire can be prevented by ionic liquids and if inflammation does occur, less heat is released.

Different phosphorus-containing flame retardants show different efficiencies depending on the mass concentration. Triphenyl phosphate (TPP), for example, shows a better flame-retardant effect as Dimethyl methylphosphonate (DMMP) (Table 1) but has a large negative influence on conductivity. A lower concentration of TPP is needed to make it self-extinguishing in the test performed. But even lower concentrations slow down the spread of the fire The ionic liquids do not show this deterioration but have a negative influence on the electrodes.

TABLE 1. Time until the wick soaked with electrolyte is self-extinguished or, in the case of non-self-extinguishing samples, the propagation velocity averaged over 150 mm.

Sample	**Time until self-extinction [s]**	**Propagation speed [mm·s^{-1}]**
0% FR	-	13
25% DMMP	-	5
50% DMMP	96	-
25% TPP	27	-
50%TPP	0	-

New flame retardants combine the flame-retardant properties of the two classes of compounds.

Acknowledgement: This study has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement n° 875568/ COBRA/2020-2024).

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P16- SAFE AND SUSTAINABLE BY DESIGN: REDESINING FLAME RETARDANTS USING A COPUTER-AIDED FRAMEWORK

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Main message: Meeting increasing environmental concerns about flame retardants, we present a case study applying the concept of Safe and Sustainable by Design on the molecular redesign of hazardous halogenated organophosphate flame retardants. Our approach combines computational and experimental methods following a design-make-test-analyze cycle with the aim of reducing environmental impacts while preserving the flame retardant function of the molecules [1].

Keywords: Safe and Sustainable by Design, Environmental impact, Organophosphates, Chemical redesign, Green and Circular chemistry

Introduction

Environmental concerns about organophosphates applied as flame retardants are growing as they are frequently detected in many compartments and further adverse effects are discovered [2]. At the same time, the concept of Safe and Sustainable by Design is gaining traction in research and policy spheres as new paradigm for the development of chemicals to advance towards the EUs goal of a non-toxic environment. However, there are limited examples of the practical application of this concept.

Experimental

We build on a computer-aided approach using *in silico* generation of a large number of chemical structures (>6 million) similar to the original chemical and available, established, and applicable QSAR models (US EPA Episuite, VEGA) to predict PBMT related properties. Multicriteria analysis ranked generated structures according to predictions and inspection of the top-scoring compounds identified promising structural features to inform our design. Elements of sustainable production were considered by favoring retrosynthetic fragments with a high potential to be sourced sustainably in the future. Chosen alternative chemicals were synthesized for experimental testing. Experiments are currently ongoing evaluating acute and chronic aquatic toxicity to daphnia, chironomids and algae (following OECD guidelines) and studies of primary biodegradation (using LC-MS/MS) and mineralization (following CO_2 evolution) are in preparation. Flame retardancy tests are planned to assess the performance of the designed alternatives.

Results and Discussion

For this work we selected a case study of redesigning the flame retardants tris(2-chloroethyl) phosphate (TCEP), listed as substance of very high concern under REACH due to its toxic effects on reproduction [3], and its analogue tris(3-chloropropyl) phosphate (TCPP), for which less data is available. We propose two alternative chemicals for TCEP and TCPP, respectively. With a straight-forward design choice we strive to give a clear-cut example of the feasibility of tuning environmental properties by molecular design. To gain possible clues about the relationship between ecotoxicological effects and structural trends of OPFRs, we also tested the structural intermediates tris(ethyl) phosphate and tris(propyl) phosphate, which are themselves used as polymer additives.

Our results can help operationalize Safe and Sustainable by Design for industrial chemicals like flame retardants. The approach can be expanded and further verified to reach its full potential in the mitigation of chemical pollution and to help enable a safe circular economy.

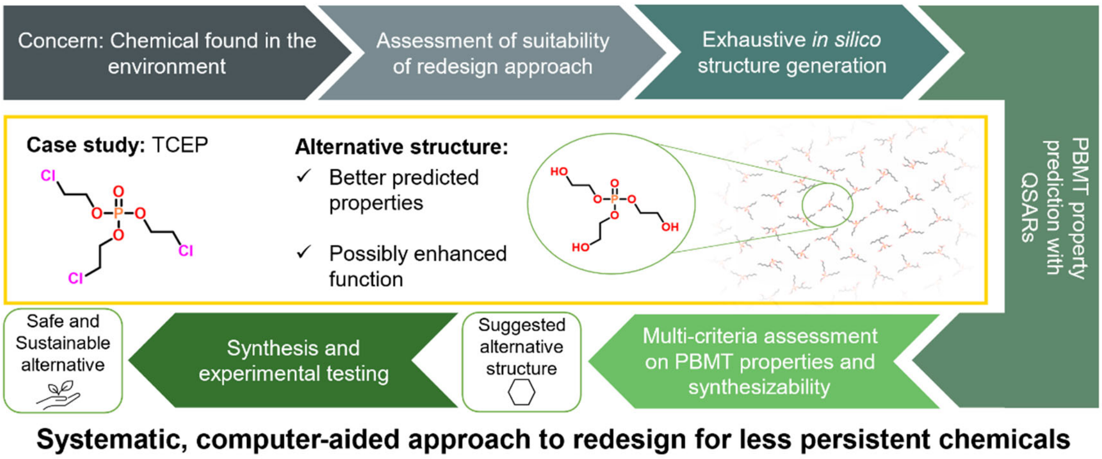

FIGURE 1. Systematic, computer-aided frame work for Safe and Sustainable redesign applied to TCEP.

Acknowledgement: We thank the Science and Design Doctorate program of the Zero Waste research theme of the University of Amsterdam for funding and support.

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P17- INTUMESCENT ALKALI SILICATE AND GEOPOLYMER COATINGS AGAINST HYDROCARBON FIRES

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Main message:
Inorganic intumescent coatings were developed for fire protection of the steel under hydrocarbon fires UL1709 standard. A best performing kaolin-based geopolymer coating exhibited a promising fire protection. Pure alkali silicate coatings based on Na, K, or a mixture of these with Li exhibited high initial expansion but followed by melting. Geopolymer coatings with additional Al-sources (kaolin, metakaolin or fly ash) and $CaCO_3$ displayed improved thermal stability and better protection.

Keywords: Intumescent coatings, Inorganic, Geopolymer, Alkali silicate, Fire protection

Introduction

Steel loss 50% of its loading capacity at high temperatures. Intumescent coatings are applied to prolong the time before structural collapse through swelling and producing thermal barriers [1]. Organic systems suffer from drawbacks of toxicity and exothermic decomposition [2]. Developing inorganic coatings systems is in demand. Hydrated alkali silicates and geopolymer coatings are inherently intumescent and their applications in fire protection have been suggested [3]. Their performance under severe conditions as described in UL1709 were discussed here [4].

Experimental:

Typically, a geopolymer solution was prepared from an efficient dispersion of Na-silicate solution, Al-source, $CaCO_3$ and fumed silica using high-speed disperser. Subsequently, the coating was prepared by applying the solution to the steel plate inserted in a mold to control coating thickness. The coating was cured in a climate chamber at 25 °C and 50% relative humidity for approximately 6 days until a stable weight was obtained. The prepared coating was subjected to a modified laboratory oven for the fire protection test. The performance was evaluated by the critical time reaching to the failure temperature of steel, 500 °C. In situ blue light laser and camera were placed at the opposite side of the exposed coating to measure the coating expansion during furnace experiments.

Results and Discussion:

Pure alkali silicates coatings were evaluated initially. They exhibited a high initial expansion but followed by a melting behavior at high temperature expect for Li-based coating with slightly shrinkage instead. Increasing SiO_2/Na_2O molar ratio improved the performance, explained by the lower melting behavior proposed by global thermodynamic calculations.

Compared to pure alkali silicates, geopolymer coatings with kaolin, metakaolin, or fly ash and additional $CaCO_3$ exhibited higher thermal stability with little to no melting and thereby better fire protection. Especially, the kaolin-based coating displayed the best fire protection along with a critical time of 37.6 min, explained by highest expansion (FIGURE 1). Kaolin and $CaCO_3$ amount were optimized in terms of critical time, expansion, and thermal stability. It was conclude that the volatiles (H_2O and CO_2) content along with its evolution of the internal structure was of importance to ensure good fire protection.

A state-of-the-art commercial organic epoxy-based hydrocarbon coating within 44.2 minutes critical time exhibited better fire protection than the optimized geopolymer coating. This is explained by a high proportion of macropores in the developed coating (FIGURE 1) other than microporous structure observed in commercial coating.

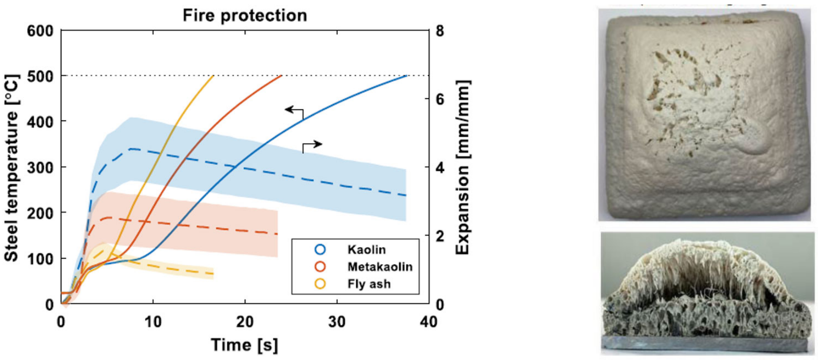

FIGURE 1. Fire protection of geopolymer coatings (left). The thickness of kaolin, metakaolin, and fly ash coatings was 4 mm, 4 mm, 4.1 mm, respectively. Images of kaolin-based geopolymer coating taken post-exposure from top and cross section (right).

Acknowledgement: Financial support from the Sino-Danish Centre for Education and Research, and the Hempel Foundation is highly appreciated.

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P18- Development of HDPE cap waste for flame retarded outdoor products

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Main message: We developed recycled high-density polyethylene (rHDPE) nanocomposites by combining ammonium polyphosphate (APP) flame retardant and montmorillonite. To upgrade the UV stability of the compounds UV absorber was also used. A synergistic effect was achieved by combining APP with nanoclay leading to increased limited oxygen indices (LOI) and reduced combustion parameters during cone calorimeter tests. V0 rating according to the UL 94 standard is achievable at 25 wt% flame retardant loading.

Keywords: recycled HDPE, flame-retardant nanocomposites, phosphorus-based flame retardant, montmorillonite

Introduction

Nowadays, international trends show that the packaging industry processes most plastics. However, packaging materials, due to their function, have a very short lifetime (even just a few days) and therefore become waste within a short time. With the increased consumption of mineral water, there is a significant amount of HDPE cap waste in addition to PET bottles [1]. The aim of the research was the upcycling of rHDPE by preparing flame retarded nanocomposites. Based on the literature, 20-30 wt% intumescent flame retardant is needed in order to achieve acceptable levels of flame retardancy in polyolefins [2-4].

Experimental

Recycled HDPE flakes originating from collected HDPE mineral water caps were used as matrix material. Exolit AP 766 was used as a flame retardant which is a combined ammonium polyphosphate and charring agent containing intumescent flame retardant additive. Cloisite 30B montmorillonite (MMT) was used as nanofiller. To upgrade UV stability, Hostavin ARO 8 hydroxy-benzophenone UV absorber was used.

The flame retarded recycled HDPE compounds were prepared using a Brabender Lab-Station internal mixer. Then the compounds were hot pressed to form 3 mm thick sheets for flammability tests in a Collin P200E type hot press.

Results and Discussion

In our research, we investigated the effect of the amount of APP and the presence of MMT in the rHDPE-based compounds on the UL 94 rating, LOI and combustion characteristics. Based on UL 94 tests, samples containing 20 wt% APP flame retardant were classified as HB, regardless of whether the compound contained MMT or not. However, we found that if the sample contains at least 25 wt% APP flame retardant, a V0 rating is achieved. It was also observed that the presence of MMT in the flame retardant formulation reduces the burning time in the UL 94 test. The limited oxygen index of the reference rHDPE was 18.0%, which gradually increases with increasing flame retardant contents. The LOI of the sample containing 20 wt% APP did not change when MMT was added. However, for samples with 25 wt% and 30 wt% flame retardant content, a synergistic effect was achieved by combining APP with MMT leading to increased LOI values, as shown in Table 1.

TABLE 1. UL 94 rating and LOI values of the investigated reference and flame retarded compounds

Sample	**UL 94 rating**	**LOI [vol%]**
rHDPE	-	18,0
rHDPE + 20 wt% APP + 0.2 wt% UV stab.	HB	25,5
rHDPE + 20 wt% APP + 1.5 wt% MMT + 0.2 wt% UV stab.	HB	25,5
rHDPE + 25 wt% APP + 0.2 wt% UV stab.	V0	28,0
rHDPE + 25 wt% APP + 1.5 wt% MMT + 0.2 wt% UV stab.	V0	28,5
rHDPE + 30 wt% APP + 0.2 wt% UV	V0	30,0
rHDPE + 30 wt% APP + 1.5 wt% MMT + 0.2 wt% UV stab.	V0	31,0

Cone calorimeter tests also confirmed advantageous interaction between APP and MMT. At identical APP contents, 10 to 17% reduction both in peak of heat release rate and total heat emission were measured when MMT was also added to the system.

The outdoor application potential of the effectively flame retarded and stabilized rHDPE composites is demonstrated in colorful wall coverings.

Acknowledgement: The project was funded by the National Research, Development and Innovation Fund of Hungary in the frame of the 2019–1.3.1-KK-2019–00004 project. The research was funded by the Hungarian Scientific Research Fund, grant number FK128352.

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P19- A novel flame retardant based on cellulose and sugar alcohols

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Main message: Novel cellulose and sugar alcohol-based flame retardants were found to be thermally very stable, which renders them suitable for processing in different thermoplastic polymers. In addition to being compatible with polyolefins and partially bio-based polyamides, the new flame retardants also exhibit good flame-retardant effects, which could be further enhanced by the addition of suitable synergists. The bio-based flame retardants could be synthesized, thoroughly characterized, and successfully processed in thermoplastic polymers to create a novel set of flame retardant polymer compounds.

Bio-based flame retardants, cellulose, halogen-free, polypropylene, partially bio-based polyamide.

Introduction

Flame retardants, with a polymer additive market share of approx. 6 wt. %, are important additives as they prevent losses caused by fire, and thus can save human lives. However, a large proportion of flame retardants are still halogenated, and render toxic and persistent properties. Additionally, they are not rated as not sustainable as they are based on fossil raw materials. Halogenated flame retardants have been detected in rivers and in the atmosphere, potentially harming humans as well as the environment. In contrast, the new flame retardants presented in this work are made from renewable raw materials, are environmentally compatible and toxicologically harmless, while maintaining a high flame retardant efficiency. [1,2,3,4]

Experimental

All bio-based flame retardants were prepared on lab-scale. Compounding was carried out on a ThreeTec 12 mm extruder (Seon, Switzerland), and on a Haake MiniJet Pro (Thermo Fisher Scientific, Karlsruhe, Germany) injection molding device, which was used to prepare the various test bars. Thermal stabilities of the used flame retardants were detected by thermogravimetric analysis, pyrolysis GC-MS, and TG-FTIR before and after processing. The efficiencies of the synthesized flame retardants were tested in standardized fire tests, e.g. UL 94 V, DIN 4102 (B2), and others. Furthermore, the mechanical and rheological properties of the flame retardant compounds were tested by tensile test or melt flow index.

Results and Discussion

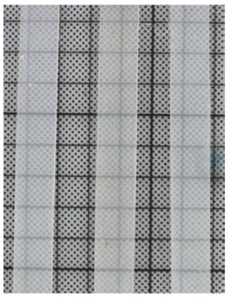

Figure 1: Polypropylene with bio based flame retardant (FR-1)

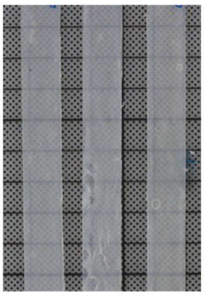

Figure 2: Polypropylene with commercial flame retardant

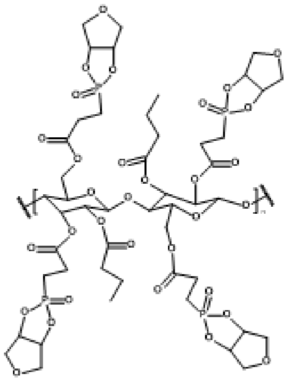

Figure 3: structure of the bio-based

flame retardant (FR-1)

The structure of flame retardant FR-1 is shown in Fig. 3. FR-1 shows a good compatibility with polyolefins, exhibiting good transparencies and low yellowing. Fig. 1 shows FR-1 in polypropylene at a loading of 10 wt. %. The UL 94 test bars show a homogeneous distribution in polypropylene by visual inspection. In contrast, Fig. 2 shows UL-94 test bars containing Aflammit® PCO 900 in polypropylene at a loading of 10 wt. %, where agglomerates and structural irregularities can be seen on the surface of the prepared injection molded specimens.

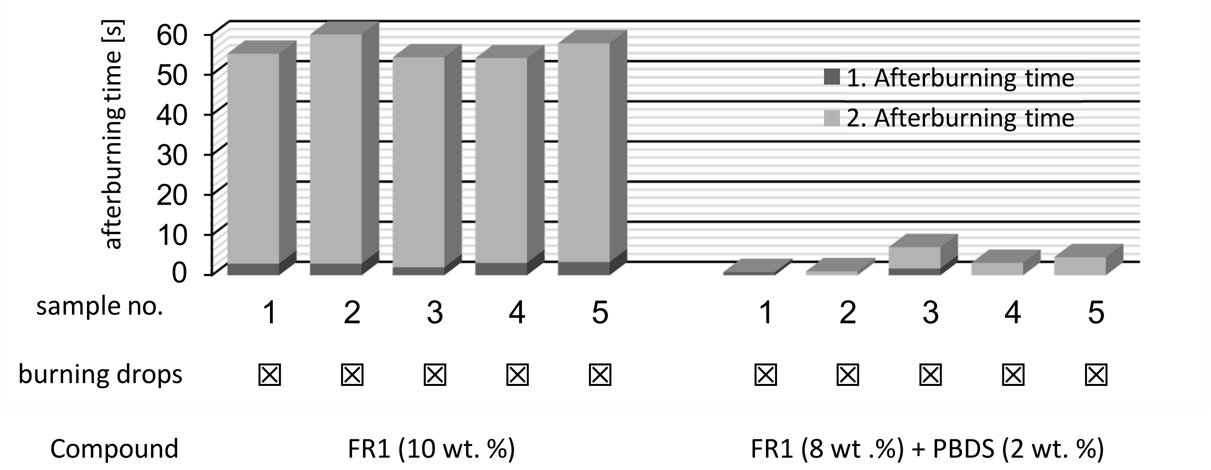

*Figure 4: UL 94 V test results according to DIN EN 60695-11-10 in Moplen RP 320M, *PBDS = poly (tert. - butyl pheno disulfide)*

A flame-retardant effect of the bio-based flame retardant can be observed even at low dosages. PP compounds containing only FR-1 at 10 wt. % loading extinguished already after the first flame treatment. However, after the second flame treatment, a burn to the clamp can be observed. With the same total loading, extremely short burning times after the first and second flaming could be achieved with PBDS as synergist. Those UL-94 test bars achieved a V-2 classification with mean afterburning times of < 6 seconds.

In the bio-based polyamide Ultramid® Flex F29 (BASF SE, Ludwigshafen, Germany) FR-1 is already very effective as sole flame retardant. At a loading of 18 wt. % UL-94 test bars already reached a V-0 rating with 1.6 mm sample thickness.

Acknowledgement: This work was supported by the Federal Ministry of Education and Research (031B0719) and the *Fachagentur Nachwachsende Rohstoffe e.V.* (220NR032), Germany.

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P1- EFFECTS OF COMBINING CORK POWDER AND APP IN THE MECHANICAL AND FLAMMABILITY BEHAVIOR OF ABS

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Main message: The use of biobased industrial residues, such as cork dust, as a substitute of the charring agent in intumescent flame retardants is a powerful tool to promote circular economy and reduce the consumption of non-renewable resources. In this work, it has been studied the combination of ammonium polyphosphate (APP) and cork powder as an intumescent flame retardant system in the fire behavior and mechanical properties of Acrylonitrile-butadiene-styrene (ABS) composites.

Keywords: ABS composites, ammonium polyphosphate, cork powder, thermomechanical dynamic properties, flammability.

Introduction

Cork industry produces a high amount of cork dust every year, approximately 30% of total cork production [1]. Several studies reported that APP combined with bio-based materials [2-4] improve thermoplastics fire retardancy by producing a thermally stable foamed char that protects the underlying material against fire propagation. In this sense, using cork powder as a charring agent for IFR systems would give added value to this industrial by-product and would help to reduce the environmental impact of flame retardant polymer formulations.

Experimental

In this work, ABS, ELIX^{TM} 128 IG, composites with a total of 30 wt% of an IFR system composed by cork powder and APP, Exolit® AP422, with different weight proportions were prepared by using a melt compounding technique. Also, the effect of this novel and more environmentally friendly IFR system on the mechanical and flammability behavior of ABS composites was analyzed. The fracture surface morphology of the composites was analyzed using a JEOL JSM-5610 scanning electron microscope (SEM). Dynamic mechanical thermal analysis (DMTA), DMA Q800, was used to study the viscoelastic response of the samples and flexural test was conducted according to ASTM D 790. The flammability behavior was investigated by the UL-94 test according to the ASTM D 3801 standard. Linear burning rate (LBR) was also calculated through LBR = 60 L/t, where L is the damaged length in mm and t is time, in seconds. Limiting oxygen index (LOI) measurements were performed in an oxygen/nitrogen atmosphere, in accordance with ISO 4589 standard.

Results and Discussion

ABS composites exhibited a homogeneous microstructure with cork and APP particles well dispersed in the ABS matrix. SEM micrographs also showed that some of cork cells were filled with APP and that matrix covered the commented particles.

The glass transition temperature of SAN, obtained by DMTA analysis, was not significantly affected by the presence of the IFR system. Nevertheless, a clear decrease in the intensity of tan δ and storage modulus of the flame retarded ABS composites, was registered. However, APP and cork particles showed different contributions to the flexural properties of ABS composites. A 58% increase in flexural moduli was registered in the case of ABS composite with 30 wt% of APP, due to the higher stiffness of APP particles. On the other hand, by substituting APP with cork, the flexural moduli decreased following the same trend observed for the storage moduli.

The presence of a 30 wt% of APP increased LOI of the ABS from 18 to 23.1, and no effect on LOI value was observed by replacing APP with cork particles (up to 20 wt%). A decrease of LBR was observed when replacing 3 wt% of APP with cork (see TABLE 1). This synergistic effect can be related with a cross-linking reaction between cork and APP in the condensed phase that led to the formation of a more protective physical barrier reducing heat and mass transfer.

TABLE 1. LBR under horizontal UL-94 and LOI values of of ABS and ABS composites.

Material	LBR [mm/min]	LOI values
ABS	44	18
ABS/30APP	24	23.1
ABS/3C/27APP	19	23.1
ABS/10C/20APP	28	23.1
ABS/20C/10APP	24	23.1
ABS/30C	41	19.1

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P21- Combination of optical diagnostics and pyrolysis fragment analysis to investigate flame retardant mode of actions

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Main message: Different flame retardants in polypropylene are investigated regarding their fire behavior, pyrolysis fragment analysis and impact on the OH radical signal intensity in the gas phase. By combining different methods of the flame retardant and combustion research, a more detailed clarification of the ongoing processes during the combustion process can be achieved. This interdisciplinary approach unlocks the high research potential complementing the mode of action of flame retardants.

Keywords: flame retardant mode of action, pyrolysis fragment analysis, OH-PLIF, OH radical detection

Introduction

Phosphorus-containing flame retardants can decompose into reactive radicals which are able to scavenge highly reactive OH radicals in the flame and thus poisoning the flame. To investigate the mode of action of flame retardants, it is important to understand the impact of flame retardants on the combustion process and the flame.

Experimental

The experimental setup for simultaneous thermal analysis (TGA/STA coupled to FTIR) and Cone Calorimeter was described in Goedderz et al. [1] and Geschwindner et al. [2] The experimental setup for planar laser-induced fluorescence spectroscopy of OH radicals (OH-PLIF) was described in detail in Köser et al. [3,4]

Results and Discussion

Different phosphorus-containing and inorganic flame retardants were analyzed regarding their impact on the OH radical signal intensity in the gas phase of the combustion of polypropylene. First, characteristic decomposition products of the flame retardants were identified by TGA-FTIR to evaluate possible species involved in the flame inhibition effect within the gas phase. The ignition and combustion of micrometer-sized particles and polymer sticks was investigated using OH-PLIF, which enables a detailed observation of processes and interactions in the gas phase.

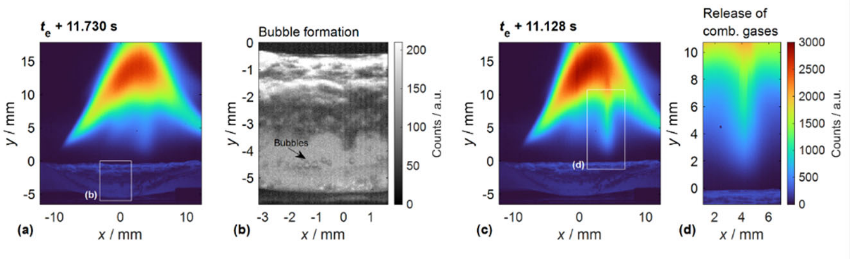

FIGURE 1. High-speed luminosity imaging of polypropylene containing 10 wt% flame retardant with formation of bubbles (a,b) and combustible gases (c,d) causing jet-like flames.

The inhibition effect of the flame retardants regarding the OH radical signal intensity is similar for both experimental setups. The flame topology could be investigated in detail using the external flame test stand and polymer sticks revealing ongoing transport processes in the gas phase (Figure 1). This work enables a more efficient flame retardant formulation development by using the gained detailed knowledge about the mode of action of flame retardants.

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P22- How reactions between smoke suppressants in flame retardant polyamide 6.6 (PA66) change the burning behavior and smoke emission.

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Main message:
Smoke suppressants (SP) affect the burning behavior and smoke release due to changes in the decomposition pathway. Zinc stannate (ZnSt) and melamine polyphosphate (MPP) accelerate the decomposition of the polymer backbone, while hydrotalcite (HT) hydrolyzes the amide group. Silicon dioxide (SiO2) acts as an inert filler. ZnSt reduces the optical density and fixes toxic precursors in a char. ZnSt reacts with aluminum diethyl phosphinate (AlPi), resulting in less flame inhibition and less toxic smoke.

Keywords: Smoke suppressant, flame retardant, smoke, toxicity, particles.

Introduction

AlPi in PA66 can act in the gas or condensed phase, depending on the interactions to different additives [1]. Flame inhibition promotes the formation of CO and HCN, which causes high toxicity. Furthermore, incomplete combustion results in higher smoke density. SPs are added to reduce smoke release. To achieve good flame retardancy and smoke suppression, it is crucial to understand the interactions between SP, FR and the polymer. Changes in decomposition affect burning behavior and smoke emission.

Experimental

The tests on pyrolysis, flammability, and forced flaming behavior were conducted compliant with the established standards and using the required specimen size. The smoke density was measured according to ISO 5659-2 and the toxic gases analyzed according to EN 17084. Additionally, an electrical low-pressure impactor (ELPI) was coupled to the smoke density chamber to monitor particle emissions during smoldering.

Results and Discussion

The flammability tests (see **Table 1**) indicate that all SPs used had an impact on the reaction to a small flame compared to the flame retarded reference (PA_FR). Zinc stannate (PA_ZnSt) decreased the UL94-V rating and the OI. This reduction is attributed to the accelerated decomposition behavior observed in the TGA. Silicon dioxide (PA_SiO2) increased the OI due to fuel replacement. Its UL94-V rating remained unaffected. The hydrotalcite (PA_HT) decreased the UL94-V rating but did not affect the OI. The decrease in the UL94-V rating is attributed to the release of water, which hydrolyzes the amide group according to the mechanism described by Hornsby et al.[2] Additional decarboxylation led to a release of combustion gases. Melamine polyphosphate (PA_MPP) caused a decrease in OI, suggesting accelerated decomposition behavior. Polyphosphates can catalytically decompose the polymeric backbone of PA66, which results in a smaller OI. [3]

Under forced flaming conditions, each SP material showed improved flame retardancy. A reduction in the PHRR was observed for all materials. PA_ZnSt, PA_MPP and PA_SiO2 reduced the PHRR by up to 40% compared to PA_FR. All SP materials showed a reduced HRR, which is attributed to enhanced charring behavior or the formation of a protective layer. Since the residues of PA_MPP and PA_HT exhibited a black surface, the charring appeared to dominate, whereas PA_SiO2 and PA_ZnSt showed a mixture of ash and char. The THE was reduced in PA_MPP and PA_SiO2, whereas HT and ZnSt tended to increase the THE. The increase in THE is attributed to the enhanced decomposition of the polymeric backbone. PA_ZnSt showed an increase in the EHC, which indicates that the flame inhibition effect of

AlPi was decreased. The change in the mode of action indicates a reaction between AlPi and ZnSt in the condensed phase. The reaction becomes visible in the white inorganic residue on the surface, which can act as a protection layer as well.

TABLE 1. Characteristic values for flammability, smoke and heat release, and toxicity in different fire scenarios

Sample	OI [vol.-%]	UL94-V	PHRR [kW·m^{-2}]	THE [MJ·m^{-2}]	EHC [MJ·kg^{-1}]	$D_{s,max}$	CIT_8
PA_FR	33.7 ± 0.2	V0	359 ± 30	42.3 ± 1.2	22.6 ± 0.6	429 ± 45	0.52 ± 0.12
PA_ZnSt	31.1 ± 0.2	V1	252 ± 9	45.4 ± 3.0	26.0 ± 1.3	173 ± 19	0.39 ± 0.02
PA_SiO2	36.1 ± 0.2	V0	218 ± 17	36.3 ± 1.2	22.1 ± 0.5	441 ± 27	0.54 ± 0.21
PA_HT	33.6 ± 0.2	V1	334 ± 26	45.6 ± 1.4	23.9 ± 1.0	406 ± 26	0.67 ± 0.05
PA_MPP	30.1 ± 0.2	V0	266 ± 10	40.8 ± 0.2	23.0 ± 0.5	423 ± 43	0.92 ± 0.25

The maximum of the specific optical density $D_{s,max}$, see **Table 1**, shows that PA_SiO2, PA_HT, and PA_MPP have less impact on $D_{s,max}$, whereas PA_ZnSt exhibited a strong reduction. Similar effects for ZnSt were observed by Horrocks et al. in an AlPi flame retardant high-temperature polyamide. [4] The overall reduction of D_s in PA_ZnSt is attributed to a crosslinking mechanism induced by ZnSt and phosphorus in the condensed phase. The crosslinking reaction fixes isocyanates, which are precursors for HCN, in a stable char. This fixing of HCN reduces the CIT_8, as displayed in **Table 1**. The mode of action of AlPi in PA_ZnSt changed between the gas phase and the condensed phase, lowering CO emission, and reducing flame inhibition. PA_HT, PA_MPP and PA_SiO2 reduced D_s after reaching $D_{s,max}$. This reduction is attributed to the emission of larger particles, which settled due to gravitation. Since the transmission is based on the Beer-Lambert-Bouguer law, the reduction in the concentration of the particles led to increased transmission.

As shown, it is crucial to understand the interactions of SP in flame retardant materials, because they influence the burning behavior and the smoke emission of the materials due to changes in the mode of action and decomposition pathways.

Acknowledgements: The authors would like to thank Tina Raspe and Patrick Klack for their technical support.

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P23- INFLUENCE OF BENTONITE PROPERTIES ON WEATHERING RESISTANCE IN FLAME RETARDANT CABLE MATERIALS

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Main message: Distributing filler in a polymer on a nanometer scale can greatly improve its flame retardancy. This however impedes the long-term stability of the thus resulting formulation which in turn leads to the early formation of cracks in the component, that can lead to great safety concerns. A correlation between the fillers and the long-term stability of the resulting nanocomposite is established, which greatly facilitates material selection.

Keywords: Polymer nanocomposites, improved long-term stability, cable flame retardancy, filler additive interactions

Introduction

Regulations for the flame retardancy of cable materials have become more demanding. This leads to an increase in the development of higher performing flame retarded materials. To reach those higher regulations, the use of nanocomposites has already been well established. However, regarding overall material composition, concerns have arisen that the nanoscale fillers interact and deactivate some of the additives and thus decrease the long-term stability of the material. The goal of this project was to understand the interactions of all components and improve the material stability overall.

Experimental

Polymer nanocomposites were processed using a twin screw extruder and dumpbell-samples were created by injection molding. To show the flame retardancy of polymer nanocomposites, cone calorimetry is used. Weathering of the samples was done by Q-LABs QUV/spray chamber for 3000 h. The degradation of samples was checked in intervals of 500 h using FT-IR-spectroscopy, tensile strength tests and yellowness index. Analysis of the bentonite products were done in the polymer formulations: The Surface properties of various bentonite materials was investigated using nitrogen-adsorption measurements and evaluated using the BET-model; XRD-measurements to determine interlayer distance; SEM was used to evaluate particle size of bentonite products; thermal analysis was applied to investigate the contents of organic modifier on bentonites.

Results and Discussion

The nanocomposites were produced with four different bentonites. The properties of the different bentonite products for use as flame retardants alongside aluminium hydroxide in PE/EVA-formulations as cable sheaths were evaluated. One of these bentonite products (NaClay) was an unaltered, natural bentonite whereas the three other products were all organically modified using dimethyldihydrotallowalkylammonium chloride (oClay_1, _2 and _3) to improve compatibility with the matrix polymers.

The improvement of the flame retardancy using nanocomposites is shown via Cone calorimetry as seen in Figure1. All three nanocomposites with the organomodified bentonites show a reduction in the total heat release. After the artificially weathering for 3000 hours the nanocomposites show intact flame retardancy. Table1 shows the values from the cone calorimetry before and after the weathering. For the polymer nanocomposites the minor changes in the time to ignition (TTI), mass loss and peak heat release rate (pHRR).

For the oClays the organomodification can be quantified by using thermal analysis. XRD measurements show the interlayer distance of the bentonite products and therefore show the degree of intercalation of the organomodifier into the galleries, which leads to the degree of exfolation. Since exfolation directly relates to specific surface area, and this in turn is very likely to affect stability by adsorption and deactivation of stabilizers onto the filler [1] this aspect would be very likely to affect the long-term properties of the nanocomposite and lead to a lesser extent of destabilization using this bentonite. Gas adsorption measurements of the bentonite using N_2 shows vast differences in surface properties of oClays. Whilst all nanocomposites with oClays show wider pores than NaClay, corresponding to their degree of exfoliation examined by XRD, these pores are less common overall. Small pores lead to a decreased interaction between filler and stabilizers during processing. These results are underlined by the SEM-imaging of the four bentonite products.

To test the conclusions drawn by the various analytical methods, the dumpbell samples were weathered and their properties monitored regularly. For all applied methods of tracking deterioration of the samples, the same was true: A formulation without any bentonite whatsoever has the highest weathering resistance. A formulation with unmodified bentonite shows the lowest amount of destabilization by its bentonite-filler. Whilst the three organomodified bentonites clearly resulted in the lowest overall stability. As shown in TABLE 1 the flame retardancy is still functional in the materials after the weathering, the issue with the material stability itself can cause major security problems. To solve this, some modifications of the material composition were tested. The most effective improvement was the addition of a bisphenol A based epoxy resin shows an improved long-term stability. Their function is to deactivate active species of the filler by reacting with the groups of the filler and thus making them inaccessible or unreactive for interaction with additives. The use of the epoxy shows a significant increase in the photooxidation set compared to the epoxy-free formulation.

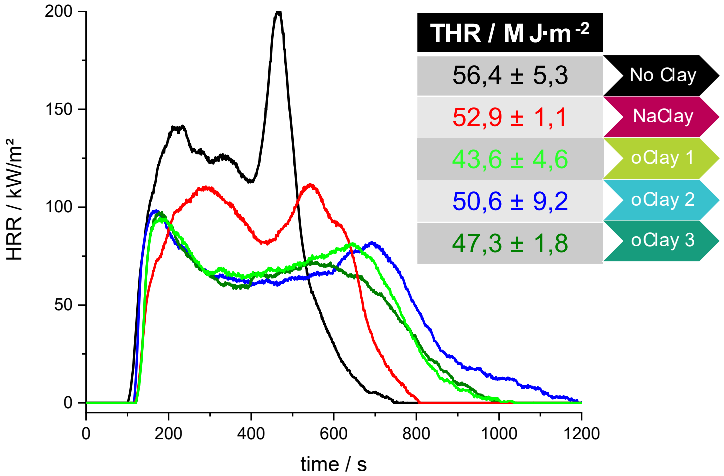

FIGURE 1. Weathering resistance of cable compounds is greatly impacted by the type of filler used. Adding no clay results in the most stable compound.

TABLE 1. Influence of weathering on flame retardant properties Cone Calorimetry @ 35 kW/m².

#	TTI [s]		Mass loss [%]		pHRR [kW/m²]	
	0 h	3000 h	0 h	3000 h	0 h	3000 h
NoClay	100 ± 11	102	41,5 ± 4,6	44,6	145 ± 14	130,3
Na_Clay	96 ± 10	109	44,1 ± 1,3	44,6	162 ± 43	105,5
oClay_1	103 ± 25	127	48,9 ± 1,5	46,9	103 ± 14	88,9
oClay_2	109 ± 3	93	48,3 ± 0,9	50,2	98 ± 8	87,0
oClay_3	122 ± 1	95	47,9 ± 2,4	47,8	89 ± 1	85,0

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P24- Insight research on the thermal degradation mechanism of PET

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Main message: Thermal degradation mechanism of PET was essential for flame retardant research. The computer simulation with thermal analysis experiment suggested that the generation of free radicals in PET was essential due to its lower activation energy. Furthermore, the oxygen attacked the benzene free radical and produced lots of heat to ignite the matrix in the air atmosphere. This free radical mechanism was helpful for specialized free radical flame retardant design.

Keywords: PET; Thermal degradation mechanism; computer simulation; homolytic cleavage reaction;

Introduction

The thermal degradation of PET was essential for discussing the combustion process and guiding to design of specialized free radical flame retardant. Nowadays, some thermal degradation research without oxygen of PET was raised to illustrate the mechanism[1,2]. However, the mechanism could not wholly explain the thermal degradation, especially the generation and disappearance of the benzoic acid. In this work, the experiment and simulation are adopted to prove the thermal degradation of PET.

Experimental

PET was synthesized in the laboratory. The thermal oxidation degradation mechanism of PET was determined by TG, TG-IR-MS and XPS combined with Quantum chemistry, including Reaxff MD, Fukui function, and DFT calculation.

Results and Discussion

The thermal degradation of PET was studied by TG-MS, TG-IR, and Py-GC-MS methods. A theoretical study on the thermal degradation mechanism in the nitrogen atmosphere of PET and PET copolymer was carried out using density functional theory (DFT). The homolytic cleavage reaction of PET was dominant at first, followed by the β-cis-elimination reaction, which resulted in the generation of abundant benzoic acid and 4-carboxybenzaldehyde, instead of terephthalic acid, as the main product

However, the experiments are still hard to reveal the thermal-oxidative degradation of PET. Therefore, computer simulation was another efficient way to assist with the interpretation of the thermal-oxidative reaction of PET. However, with oxygen influencing, the thermal-oxidative reaction was complex to propose a distinct reaction path of PET. Herein, the Reaxff as an efficient simulation of thermal degradation was applied in the thermal oxidation of PET.

The products of the reaction in 2000 K and 3000 K were abundant and the product information was counted and shown in Figure 1. The trend of the result in 2000 K was similar to the initial stage result in 3000 K, in that products were increased. However, all products were stable or decrease besides the CO. The process was shown in figure Sn, which was observed in the generation of char residue. Combine with the decrease of the products of CH_2O and C_2H_4, the process in 3000 K could reflect the thermal degradation of char residue in the second degradation in TGA. On the other hand, the 2000 K result could more obviously demonstrate the initial degradation of the PET.

The CO_2, CH_2O, and C_2H_4 increase sharply at beginning of the reaction with less consumption of oxygen in both 2000 K and 3000 K, demonstrating that oxygen had less influence in the initial thermal degradation. And the oxygen-containing products were mainly from the ester group in PET. Lastly, the

H, OH, and O free radicals in traditional combustion theory were considered the most important part to trigger the combustion and be captured by flame retardants. However, these free radicals in degradation keep at a low content that could not be the essential part of the combustion mechanism of PET.

More detailed products in 2000 K were studied to observe how oxygen influences the chain of PET. The beginning and final structures was shown in Figure 1a. And some valuable structure was picked and shown in Figure 1b. The homolytic reaction reacted at first, and carbonyl and carboxyl functional groups will leave at the subsequent reaction. The oxygen was hard to react with the PET chain. However, the oxygen will attack, react and connect two benzene free radicals by a peroxy bond. The peroxy bond was cleavaged as soon as possible and generate the C-O free radical. The result supported that oxygen at the beginning of the combustion would not observe influence the thermal degradation of PET.

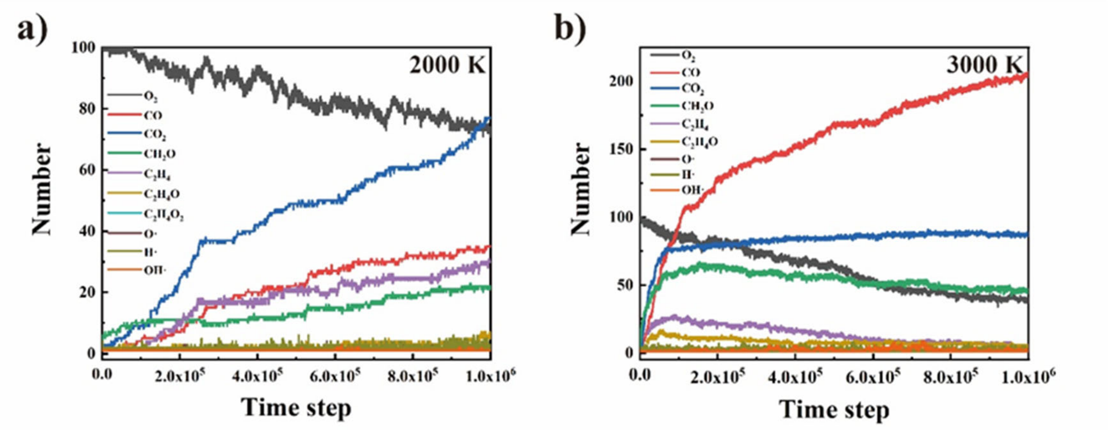

FIGURE 1. The Reaxff production of PET at 2000 K and 3000 K.

Acknowledgement: Beijing Scholars Program (RCQJ20303).

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P25- Constructing cross-functional intumescent flame retardants with UV resistance for polypropylene

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Main message: Cross-functional additives were carefully designed for polypropylene (PP) composites to enhance the flame retardancy, UV resistance, and mechanical properties. In this work, firstly, ammonium polyphosphate (APP) was coated with polysiloxane to avoid the pyrolysis of APP under UV irradiation; secondly, the charring formation agent (CFA) with triazine groups was selected to enhance the absorbance of UV radiation. Hindered amine light stabilizer (TEMP) was reacted with sodium lignin sulfonate (SLS) to obtain SLS-TEMP. By using 19 wt% (SiAPP/CFA)/2 wt% SLS-TEMP, the limiting oxygen index (LOI) of the PP composite was increased to 33.5 and the UL-94 grade was achieved to V-0. The peak heat release rate and peak smoke release rate were reduced by 76% and 74% compared with that of the control PP sample, respectively. Moreover, the aging process of the PP composite sample was delayed. the tensile and impact strength of the PP/19wt%(SiAPP/CFA)/2wt%SLS-TEMP sample was decreased by 13.4% and 27.8%, respectively after 60 h UV irradiation, which was significantly lower than that of control PP (50.9% and 68%). The change of LOI before and after aging was minimal and the sample still passed UL-94 V-0 grade after 100 h UV-aging test. It was proved that the SLS-TEMP has an excellent synergy effect on improving the flame retardancy and UV resistance of PP. This cross-functional additive strategy provides a good solution for obtaining high-performance PP composites.

Keywords: Polypropylene, lignin, hindered amine, flame retardancy, UV resistance.

Introduction

Due to excellent performance and relatively low cost, polypropylene (PP)-based products have been widely used indoors and outdoors. However, two key issues must be considered during the service life of PP products. One is their inflammability, they can be easily ignited in the atmospheric environment, accompanied by concentrated heat and smoke emission. The second is the pendulous -CH_3 groups in PP molecules are easy to be oxidized under UV radiation, as a result, their mechanical performance could be worsened obviously and their service life is shortened. The popular solutions were blending flame retardant and anti-aging agents in the PP matrix.

Ammonium polyphosphate (APP) is a widely used flame retardants (FR). Unfortunately, it was found under UV irradiation, APP tended to pyrolyze and release phosphoric acid and P· free radicals, which would react with the hindered amine, the most used UV-resistant agent in PP [1]. As a result, the coexistence of APP and anti-aging agent contributed to the antagonism decrease in both flame retardancy and anti-aging efficiency. To cope with the complex issue, some cross-functional fillers should be specially designed.

In this work, APP was coated with a popular silane to avoid the reaction between APP and the hindered amine, at the same time the cross-linked Si-O surface can shield some UV irradiation [2]. Triazines are used as a charring formation agent (CFA), and they can also adsorb UV irradiation and be used as a UV-shielding agent.

Sodium lignin sulfonate (SLS) was also used as a charring agent and antioxidant [3]. The 4-amino-2,2,6,6-tetramethylpiperidine (TEMP) is a reactive intermediate to prepare hindered amine stabilizers, which possessed high efficiency in capturing free radicals. Unfortunately, they were easy to migrate due to their low molecular weight, and hence the anti-aging ability attenuated rapidly. In this work, TEMP was reacted with SLS, and the molecular weight of the obtained SLS-TEMP was much higher than TEMP, so it is not easy to emigrate from the PP matrix. The product was used as a synergist to improve both flame retardancy and UV resistance. It is expected this work can provide a comprehensive solution to guarantee the required flame retardant and anti-aging performance of PP.

Experimental

Materials

PP was provided by Maoming Petrochem. APP (DP⩾1000) was produced in Jin Ying Tai Chem. Tetraethoxysilane/ triethyl orthosilicate (TEOS) were supplied by Xilong Science. Alkylphenol polyoxyethylene (OP-10), ammonia solution (25 wt%, AR), and ethanol are AR grade. Sodium lignin sulfonate (SLS) was obtained fromMacklin. 4-amino-2,2,6,6-tetramethylpiperidine (TEMP) was provided by Aladdin. Charing formation agent (CFA) was provided by Guangzhou Yinyuan New Materials. All the materials were used directly without purification.

Preparation

The TEOS was added into an ethanol/H_2O solution containing APP, OP-10, ammonia dropwise under continued stirring for 2 h. After cooling, washing, filtration, and drying, the APP was microencapsulated and abbreviated as *SiAPP*.

TEMP was mixed with SLS solution under stirring at 70 °C for 15 min, heating to 85 °C and 10 wt% HCHO solution was added dropwise in 3 h, after cooling, precipitation and washing with ethanol. The obtained product was named *SLS-TEMP.*

Characterization

The FTIR, LOI, SEM, XPS and CONE test was implemented.

Results and Discussion

For the control PP, its LOI was only 19% and it cannot pass any UL-94 rating. The addition of 25% (APP/CFA) lifted the LOI to 34.3%, and the sample passed UL-94 V-0 grade. By using 19%(SiAPP/CFA)/2%SLS-TEMP, the LOI reached 33.5 and it passed UL-94 V-0 grade.

In the CONE test, the PP/19%(SiAPP/CFA)/2%SLS-TEMP sample exhibited obviously decreased heat and smoke release, at same time An intumescent char was left.

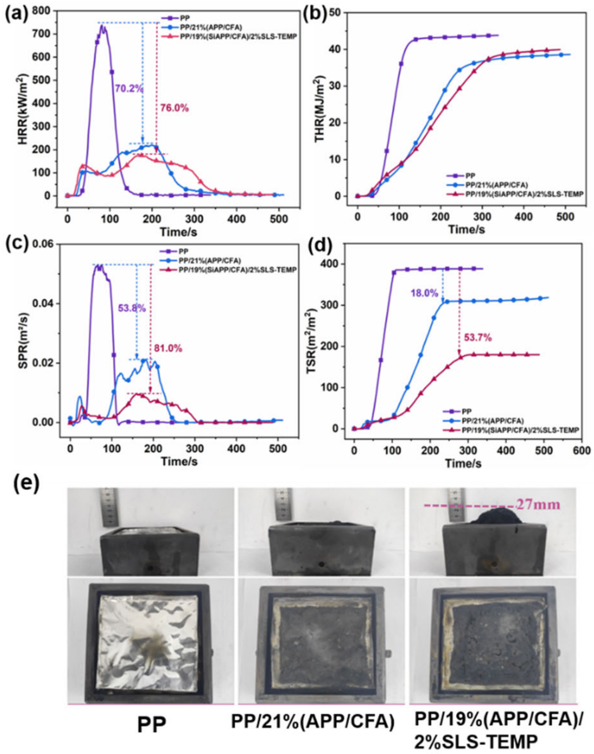

FIGURE 1. The cone calorimeter test results

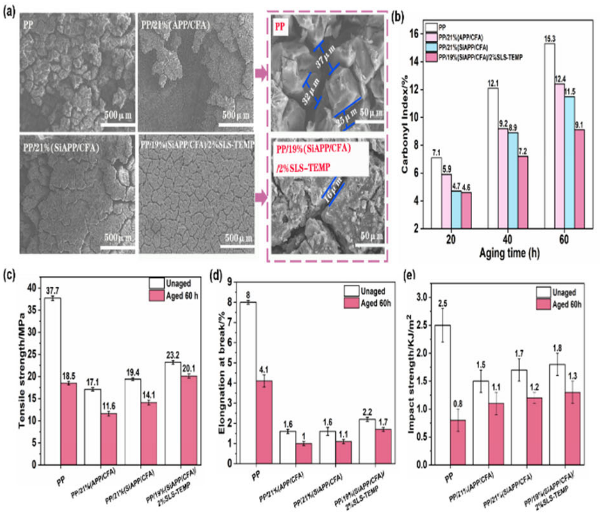

FIGURE 2. (a)SEM (b)Carbonyl index (c)tensile strength (d)elongation at break (f) impact strength

The surface topography of all the samples aged for 60 h was observed by SEM and shown in Fig.2 (a). It could be found the control PP became wrinkled with many big cracks, even some areas were sunken. However, for the PP/19%(SiAPP/CFA)/2%SLS-TEMP sample, the whole surface kept continued with some small and shallow cracks. It is suggested that the filler of 19%(SiAPP/CFA)/2%SLS-TEMP improved the UV resistance of PP.

Generally, the pendulous -CH_3 groups of PP were easy to be oxidized to C=O under UV irradiation. Therefore, the carbonyl index (CI) is used to evaluate the aging [35]. The CI of the control PP and PP composites was shown in Fig.2.(b). The CI of the control PP was 7.1 after being irradiated for 20 h, with the aging time increased, the CI increased to 15.3. For the PP/19%(SiAPP/CFA)/2%SLS-TEMP sample, the CI was still lower than the control PP at the same aging time, after aging for 60 h, the CI was 9.7.

It shows that the tensile strength and elongation at the break of the control PP were pulled down by the fillers. Especially by using APP/CFA. The fast aging of the control PP resulted in a sharp decrease in tensile and impact performance. However, the filler of 19%(SiAPP/CFA)/2%SLS-TEMP kept much mechanical performance after aging, especially for the impact strength, it was only decreased by 28%, which was significantly lower than that of aged PP.

Based on the above analysis, the anti-aging mechanism was concluded. The polysiloxane coating on APP protects the APP from pyrolysis by shielding the UV irradiation. The antagonism between flame retardant and anti-aging was eliminated and then the anti-aging efficacy of SLS-TEMP was kept. In this work, the lignin and TEMP ring in the structure of the obtained product SLS-TEMP simultaneously captured the free radicals during the UV aging process.

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P26- THE ASSESSMENT OF THE SMOKE TOXICITY OF FURNITURE FABRICS AND FILLINGS

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Main message:
Most UK fire deaths result from smoke inhalation of burning upholstered furniture. The toxicity of the smoke has been found to vary considerably, depending on the flame retardant treatment. The smoke toxicity of 3 fillings and 8 fabrics are reported. Halogen and organophosphate flame retardants cause the largest increase in toxicity.

Keywords: Smoke, toxicity, retardants, halogens, phosphorus

Introduction

In 1980s, the change from natural to synthetic polymers in upholstered furniture led to an increase in fire deaths, because they were more flammable and produced more toxic smoke. In response, the British government implemented legislation that set limits on the flammability of upholstered furniture. However, the legislation is only based on the material's flammability and not its smoke toxicity. Inhalation of toxic smoke is the major cause of death and injury in fires. In this study, the smoke toxicity of the materials was assessed under a range of fire conditions [1].

Experimental

This investigation used the steady state tube furnace (ISO 19700), an apparatus designed to replicate specific fire conditions, connected to gas analysers to quantify the main toxic components, such as asphyxiants (CO, HCN as well as CO_2 and O_2) and acid gas irritants (HBr, HF, HCl, NO_2, NO_3, SO_2, and SO_3). This instrumental setup facilitates testing of the smoke effluents in specific fire stages, which can be replicated for different materials [2].

TABLE 1. List of samples used and their fire retardants (FR)

Use	Sample type	Control (no FR)	Sample 2	Sample 3	Sample 4
Fabric	Woven polyester	No fire retardant	Brominated	Expandable graphite	-
Fabric	Cotton	No fire retardant	Proban	-	-
Fabric	Mattress fabric	No fire retardant	23% Kanecaron	29% Kanecaron	30% Kanecaron
Filling	PU foam	No fire retardant	TCPP + Melamine	Melamine	-
Filling	Non-woven polyester	No fire retardant	-	-	-
Tape	Tape	No fire retardant	63% Kanecaron	-	-

Samples were provided by Silentnight as representative materials for headboards or beds, both without fire retardants (NFRs) and with typical fire retardants (FRs). Thus, the polyester fabric was also tested with a brominated or expandable graphite back-coating; cotton was also tested with Proban (tetrakis-hydroxymethyl phosphonium chloride) treatment; the polyurethane foam was also tested with either melamine, or a melamine and tris-(chloropropyl) phosphate (TCPP) treatment. Finally, Kanecaron, a blend of PVC and acrylonitrile fibres was tested as fabrics at 23, 29, 30 and 63% Kanecaron loading.

The samples were tested under conditions of flaming combustion being most representative of likely fire scenarios: well-ventilated flaming; and small under-ventilated flaming, typical of a developed fire in a medium-sized bedroom [2].

Results and Discussion

The investigation took an assortment of typical fabrics and fillings used for making beds, with and without fire-retardants, and compared their smoke toxicity, using the steady state tube furnace. There were three groups of materials, each with an NFR control, with various FRs applied. The materials were tested both as singular components and as a composite materials, in order to understand the interaction between the different fire retardant treatments and bed components.

Flame retardants can act in the gas phase as free-radical flame quenchers, or in the condensed phase as fillers, barrier layers or char formers. The results showed that gas phase FRs increased the yields of products of incomplete combustion in both well-ventilated and under-ventilated flaming condition. For example, decabromodiphenyl ethane (DBDPE) in the back-coating of the polyester fabric released HBr, which inhibited flaming combustion by gas phase quenching, increased yield of carbon monoxide. In contrast the uncoated fabric, while the fabric coated with expandable graphite showed similar yield of carbon monoxide to the NFR fabric [2,3].

Although classed as an inherently FR free material of low flammability, the Kanecaron showed the highest toxicity and the greatest potential to increase the smoke toxicity of other fabric components, such as viscose.

The study showed interaction between the halogenated treatments and nitrogen-containing compounds resulting in the largest increase in smoke toxicity, higher than either element produces on its own.

Acknowledgement:

We gratefully acknowledge Silentnight Beds for provision of samples, technical support and advice.

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P27- MODIFIED COTTONID AS A FIRE RETARDANT LAYER

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Main message: Cottonid or vulcanfibre is one of the oldest known bioplastics. The basis of this product is paper made of cotton, pulp or a mixture of both, which is soaked in a zinc dichloride solution for a specific time at a certain temperature. The modified cottonid can be used as a protection layer especially for timber constructions by adding a fire retardant, with the aim to stop the spread of flames. Due to the similar properties of wood and cottonid, new opportunities can arise from a combination.

Keywords: Sustainability, Cottonid, Flame Retardant, Timber Constructions, Biodegradable

Introduction

Metal hydroxides, ammonium phosphates or other phosphorous-based fire retardants often cause limitations to the mechanical properties of a material. [1] A modified cottonid probably does not suffer any losses due to addition of the flame retardant. The modified cottonid, which is made of renewable resources, is also less harmful to the environment than most of the common fire retardants and could be biologically degraded at the end of its service life.

Experimental

The modified cottonid is prepared in a parchmentizing process multiple layers of paper. The fire retardant is integrated between the single paper layers during processing. An aqueous zinc dichloride solution is used as a parchmentizing solution.

Tensile tests are carried out to determine the mechanical properties of the test specimens.

Flame tests are executed to characterize the test bodies. Data was recorded by a thermal sensor on the fire averted side of the specimen and a thermal camera on the fired side. Scanning electron microscopy is used to investigate the surface structure of the material and for the characterization of the inserted fire retardant material.

Results and Discussion

The manufacturing process of the samples showed that a modification with the fire retardant can easily be implemented.

Untreated cottonid is inherently flame retardant and can withstand flames for a short time. Flame tests, where a sample is placed horizontally 15 cm above the flame of a propane gas burner, demonstrated that our modified cottonid drastically increases the durability against fire and heat. As of now, a 15 fold extension could be achieved. During that flame test, the temperature on the fire averted side of the specimen stayed constant at around 120 °C, at which the cottonid is still resistant to continuous heat exposure, while the temperature at the fired side is over 450 °C.

The adhesiveness of wood and cottonid was also tested with standard wood glues, to investigate the usability of this combination. The tensile shear tests were carried out according to DIN EN 302-1 and the results indicated that the connection between cottonid and wood is sufficiently good. Therefore, modified cottonid is suitable as a sustainable cellulose-based fire retardant for timber constructions.

Acknowledgement: This research has been funded by the Federal Ministry of Food, Agriculture and Consumer Protection in the project “Entwicklung eines material- und energieeffizienten Holzbausystems aus Laub- und Nadelholz” (project number 2220HV045X).

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P28- New approach for electric vehicle composite battery housings: Electromagnetic shielding and flame retardancy of PUR/UP-based sheet moulding compound

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Main message: In an electric vehicle, the battery housing performs important safety tasks. Both the cells inside a battery as well as the outside environment must be protected in the event of an internal battery failure or an external battery-damaging event. Electromagnetic shielding and flame retardancy are two of the major safety functions of a battery housing. Composite materials offer significant potential in the production of battery housings due to cost-efficiency, mechanical performance, and formability of complex structures. However, both electromagnetic shielding and flame retardancy require specific material modifications.

Keywords: Thermosetting resin, Sheet moulding compound, Flame retardancy, Electromagnetic shielding

Introduction

In a battery electric vehicle, the battery housing fulfils important safety functions such as electromagnetic shielding and flame retardancy. Composites like sheet moulding compounds (SMCs) offer significant potential in the production of battery housings. However, to achieve both electromagnetic shielding and flame retardancy in one material, conventional SMCs must be modified. This study examined the electromagnetic shielding and flame retardancy of unsaturated polyester polyurethane hybrid (UPPH) resin-based SMCs containing either glass- or carbon-fibre reinforcement as well as carbon black, carbon nanotubes, carbon nanostructures or expandable graphite filler.

Experimental

The electromagnetic shielding was tested using test plates and test housings. The flame retardancy was investigated by limiting oxygen index (LOI) tests, UL94 tests, cone calorimeter tests and bench-scale fuel fire tests [1].

Results and Discussion

The best results in terms of electromagnetic shielding and flame retardancy were achieved by using UPPH composites with 50 wt.-% carbon fibres and 11.5 wt.-% expandable graphite [2].

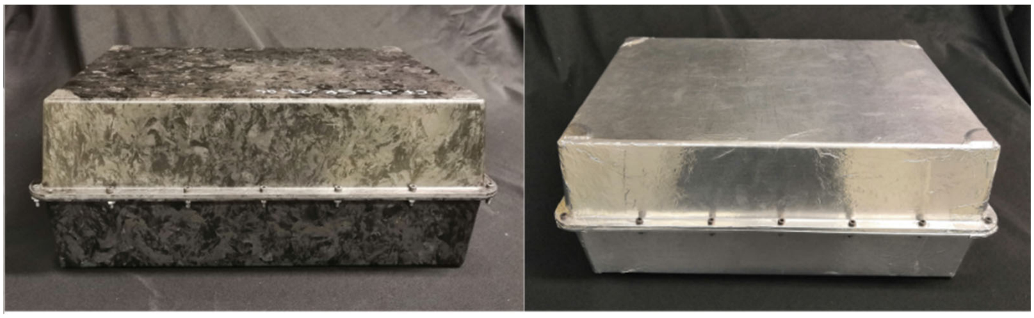

FIGURE 1. Box-like test housings for electromagnetic shielding tests. Left: UPPH composite with 50 wt.-% carbon fibres and 11.5 wt.-% expandable graphite. Right: UPPH composite with 40 wt.-% glass fibres and covered with aluminium foil.

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P29- RIGID POLYURETHANE FOAMS WITH LIMITED FLAMMABILITY

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Main message: Rigid polyurethane-polyisocyanurate (PUR/PIR) foams are insulating materials for constructional components, using in the building industry. Presented results of investigations concern our conception of halogen-free flame retardant systems (HFFRS) and PUR/PIR foams with their participation. The purpose was to develop HFFRS effective enough to enable their use in the smallest possible amounts in PUR/PIR foam compositions.

Keywords: flame retardants, rigid polyurethane foams, halogen-free additives.

Introduction

Limited flammability of PUR/PIR foams, is essential for theirs practical application. In industry, halogen additives are still used for this purpose, for example TCPP [1]. They are consistently substituted by halogen free additives - unfortunately often characterized by a lower efficiency in decreasing the flammability [2,3]. HFFRS which might be used with similar quantity like halogen additives, for obtained satisfied results of reduced flammability of PUR/PIR foams, were developed.

Experimental

The HFFRS, containing nitrogen and phosphorus compounds were obtained by synthesis or by physical mixing of individual components. Syntheses of HFFRS from melamine and cyanuric acid were carried out in the presence of nitrogen, phosphorus and other compounds in the environment of the reaction [4]. The results of the researches of the modified with HFFRS PUR/PIR foams, were compared with results of foams without additives, made in the same way and conditions. The flammability properties of the prepared compositions were examined by using vertical and horizontal burning test (UL 94) - PN-EN 60695-11-10, limiting oxygen index (LOI) - ISO 4589-2 and ignitability of products subjected to direct impingement of flame method (PN-EN ISO 11925-2). Additionally fire resistance tests (tests done in bigger that laboratory scale) were carried out. Building of artificial wall, simulating real conditions, were necessary. Particular elements, modified and unmodified PUR/PIR foams, were obtained specially for this purpose in our laboratory. The wall was subjected to one-sided heating. Increase of temperature was measured with 20 thermo-elements on the outer surface.

Results and Discussion

During the fire resistance tests, the following parameters were observing: temperature (increasing of temperature) on the outer surface of the wall (on each element), behaviour of each element in the wall, time of destruction of each element. On the picture (**FIGURE 1**), fire resistance tests results are shown. The time, in which the sample exceeded the temperature (on the outer surface) increase of 140°K and then 180°K, was used as the parameter. Longer time means better result. Ten samples (two of each type) were tested according to the above procedure: TCPP(P) – PUR/PIR foam, with halogen compounds tris(2-chloro-1-methylethyl)phosphate (commercial sample), 0 – reference sample without additives, MC(S) – foam, with flame retardant obtained in the process of synthesis, DIPER(K) – foam, with flame retardant based on dipentaerythritol, APP(K) – foam, with flame retardant based on ammonium polyphosphate. Only one of two of reference samples 0, survived until a temperature increase of 140°K was reached, but undergo destruction as a result of further increase of temperature. Analysing results of test, there is clearly a positive effect of modification of PUR/PIR foam with HFFRS.

Results of fire resistance tests PUR/PIR with HFFRS are much better that reference sample and better or comparable with PUR/PIR modified with halogen flame retardant.

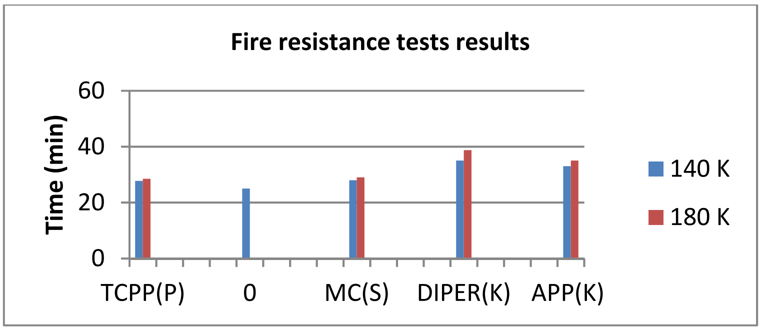

FIGURE 1. Fire resistance tests results.

Effectiveness of HFFRS can also be seen in the results of other flammability tests – LOI and vertical and horizontal burning tests. All PUR/PIR samples modified with HFFRS achieved much better parameters of LOI and results of vertical and horizontal burning tests, compare with unmodified sample 0 and better results that commercial sample, but modified with halogen flame retardant TCPP(P) (**TABLE 1**).

TABLE 1. Results of flammability tests - LOI, vertical and horizontal burning tests

Nr	symbol of composition	oxygen index (%)	vertical flammability class	horizontal flammability class
1	TCPP(P)	23.5	V0	HB40
2	0	21.0	fails	fails
3	MC(S)	27.8	V0	HB40
4	DIPER(K)	27.0	V0	HB40
5	APP(K)	26.8	V0	HB40

As a result of our work the PUR/PIR foams with reduced flammability with HFFRS were received. Developed solutions are competitive with other PUR/PIR foam on the market using for insulation of building. Additionally other PUR/PIR foam are modified with halogen compounds. Developed HFFRS, are currently being tested in the process of obtaining PUR/PIR with limited flammability with other additives: modified aerogel (that increases its thermal-insulation properties) and antifungal and antibacterial compounds.

Acknowledgement: The project was carried out by Łukasiewicz Research Network – Professor Ignacy Mościcki Industrial Chemistry Institute (Poland) and was supported by the National Centre for Research and Development in Poland within the framework of the European program - Operational Programme Smart Growth 2014-2020 (Application Projects).

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P30- PROFOUND CHARACTERIZATION OF NOVEL PHOSPHORUS-CONTAINING FLAME RETARDANTS BASED ON CELLULOSE AND SUGAR ALCOHOLS

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Main message: An innovative, sustainable and highly efficient synthesis for bio-based phosphorylated cellulose ester derivates with a profound characterization by *NMR* spectroscopy, Gel permeation chromatography *GPC* and thermal gravimetric analysis *TGA* has been elaborated. The synthesis is based on an activation and implementation with a carboxylic acid/acrylic acid anhydride mixture to form a fully functionalized mixed cellulose ester, followed by a *Phospha-Michael-Addition via* phosphorylated anhydroerythrite.[1]

Keywords: biobased flame retardant, cellulose ester, acrylic acid anhydride, sugar alcohol, NMR

Introduction

Thermal stability, migration, compatibility, etc. are typical challenges sustainable and biobased flame retardant additives need to face nowadays.[2] Due to its unique backbone, cellulose offers a wide range of modifications to overwhelm those issues. This led to a novel class of flame retardants and intrinsically flame retarded polymers with versatile properties and applications. Subsequently, this new class requires customized characterization methods which will be discussed hereinafter.

Experimental

The two main sources for cellulose were drawn from 100 % organic cotton (*ebelin*®, DM, Karlsruhe) and totally chlorine free softwood pulp (*Mercer International Inc.*). The conversion to mixed cellulose esters was realized by an in-house made acrylic acid anhydride mixture (pre-synthesized from acrylic acid) with different carboxylic acid anhydrides. The phosphorylated anhydro sugar alcohol was based on erythrite from Xucker®. NMR spectroscopy was carried out on a *BRUKER Avance 300 MHz*, GPC was performed on an *Agilent Infinity 1200* with Dimethylacetamide/0.1 % LiCl as mobile phase (1 mL/min), two *PSS Gram* columns as stationary phase and a poly(ethylene oxide) calibration. For thermal analysis a TGA/DSC device from *Mettler Toledo DSC822^e* was used.

Results and Discussion

Synthesis: The general two-step procedure is schematically represented in FIGURE 1.[1] 1stStep describes the formation of the mixed cellulose ester. Both, the catalyst as well as the activation process determine the degree of chain length shortening to the desired molecular weight, which is quite useful regarding to the application. For flame retardant additives a preservation of the high molecular weight is desirable, to lower the migration out of the polymeric matrix and to increase the thermal stability. Therefore, zinc(II)-chloride turned out to be the most promising catalyst in combination with the organic cotton cellulose, due to a milder activation process. To increase the compatibility with the polymeric matrix, different saturated acid anhydrides (propionic/butyric acid anhydride) were additionally esterified. Longer alkyl chains might increase the compatibility even more, expanding the application to a broader range of polymers. Lowering the molecular weight might also be useful for other purposes, where the cellulose esters are used as macro-comonomers in different applications typical for acrylates to form polymers with intrinsic flame retardancy. For such a purpose, harsher activation and stronger catalysts are necessary, which favor degradation to lower molecular weights and open the possibility to use less reactive and cheaper cellulose sources, such as totally chlorine free (TCF) softwood pulp.

Hereby, only a small fraction of acrylate groups is converted to flame inhibiting functional groups by 2nd Step, the *Phospha-Michael-Addition*, whereas the vast majority of acrylate groups is still available for curing applications.

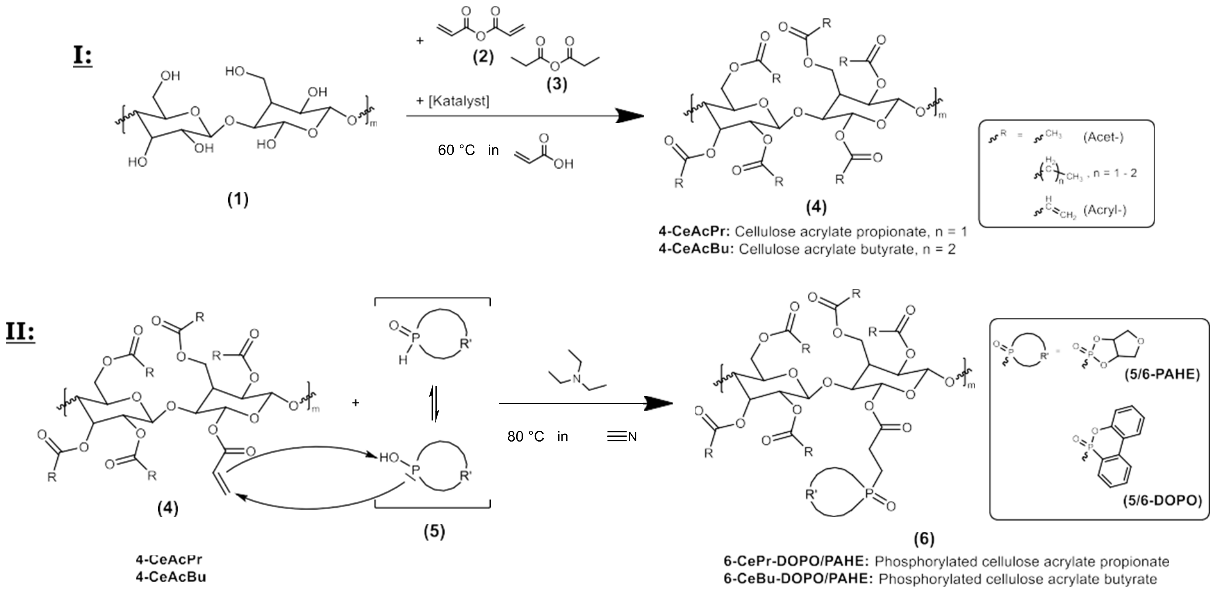

FIGURE 1. Schematic representation of the **(I)** cellulose esterification (**4**) followed by the (**II**) Phospha-Michael addition (**6**).

Characterization:

Nuclear magnetic resonance spectroscopy NMR turned out to be a powerful tool to characterize the produced acrylates and flame retardant. *^{1}H-*, *^{13}C-*, *^{31}P-* as well as *2D-DOSY-NMR* spectroscopic results provide important information on the composition of the macromolecule, such as degree of functionalization (*e.g.,* acrylate/alkanoic ester: 70/30 or *vice versa*!), certainty of chemical attachments rather than aggregation, stability of the phosphorous cycle and conversion of the same. Even the esterification of primary/secondary hydroxyl groups is visible and quantifiable by *^{13}C-NMR*.

Gel permeation chromatography GPC is a powerful tool to evaluate the degree of degradation our unique activation process and specific catalysts have upon cellulose. Unfortunately, raw cellulose is difficult to measure by *GPC*. Still, a relative comparison of the products facilitates a distinction of different parameters and their impact on the molecular weight ($\bar{M}_w$: 40 kDa up to 120 kDa).

T*hermal gravimetric analysis TGA* is a simple and elementary tool to get first insights into the thermal behavior/stability of the produced flame retardants and esters upon thermal heat. The collected data clearly prove an improvement in thermal stability, which is still dependent on the used catalyst and molecular weight (*e.g.,* T_{dec}^{raw} ≈ 360 °C ➔ $T_{dec}^{modified}$ ≈ 280 °C).

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P31- FLAME RETARDANT IN-MOULD COATINGS FOR ε-CAPROLACTAM-BASED POLYAMIDE 6 FIBRE-REINFORCED COMPOSITES

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Main message: We developed an ε-caprolactam-based flame retardant in-mould coating for continuous fibre-reinforced polyamide 6 composites prepared by anionic ring-opening polymerisation of ε-caprolactam. Magnesium oxide, red phosphorus, and expandable graphite were used as flame retardants. A synergistic effect was achieved by combining flame retardants with a different mode of action leading to a significant reduction in total and peak heat release rate.

Keywords: flame retardancy, anionic ring-opening polymerisation, polyamide 6, in-mould coating

Introduction

Using recyclable thermoplastic matrix composites with long fibre reinforcement and outstanding mechanical properties is becoming increasingly important in the automotive industry. One of the most widely used matrices in this sector is polyamide 6 (PA6), produced by anionic ring-opening polymerisation of ε-caprolactam [1,2]. Strict automotive safety regulations require the effective flame retardancy of these thermoplastic matrices. Flame retardants can be added to the matrix, or a coating can be created on the composite surface, even by in-mould coating [3].

Experimental

To prepare the PA6 matrix, ε-caprolactam monomer and C20P activator were heated to 120 °C and mixed using a magnetic stirrer. After adding Dilactamate® initiator, the system was injected into a 100 mm x 100 mm x 2 mm aluminium mould. This mould was used to model the thermoplastic resin transfer moulding (T-RTM). Five layers of unidirectional carbon fibre reinforcement in $[0]_5$ layup were pre-placed in the mould, and the closed mould was preheated to 150 °C.

To create a 0.5 mm thick flame retardant coating, first, we placed the prefabricated 100 mm x 100 mm x 2 mm PA6 composites into a 100 mm x 100 mm x 2.5 mm aluminium mould, then the closed mould was preheated to 150 °C. To provide good adhesion between the composite and the coating, we prepared the coating by polymerising ε-caprolactam as in the case of the PA6 composite matrix. We used magnesium oxide (MgO), red phosphorus (RP), and expandable graphite of two different particle sizes (EG ES100 and EG ES350) as flame retardants.

After characterising the coating by differential scanning calorimetry and thermogravimetric analysis, we investigated the effect of flame retardant coatings on the fire performance of composites by mass loss calorimetry (MLC). Dynamic mechanical analysis (DMA) was used to determine the mechanical properties. In addition, we investigated the effect of different flame retardants on the hardness and adhesion of the coatings.

Results and Discussion

RP and MgO as single additives did not significantly reduce the flammability of the samples. However, when combined with expandable graphite, a synergistic effect was observed, resulting in a reduction in both total and peak heat release rates. Figure 1 shows the heat release rate of the reference and the coated composites. The flame retardant coatings can reduce the maximum heat release by up to

27% and the total heat release by 37% compared to the reference composite. Due to the expandable graphite acting in the solid phase, a protective char layer was formed on the surface of the samples. Furthermore, this protective layer increased the residual mass. When 10% EG ES350 was used, due to the large particle size and significant sedimentation, the flame retardant remained in the inlet, and only a small amount was injected into the mould. For this reason, the maximum heat release rate of the PA6/10%EGES350 sample was higher than the reference. These results suggest that only expandable graphite with a small particle size is suitable for the coating as a synergistic flame retardant additive.

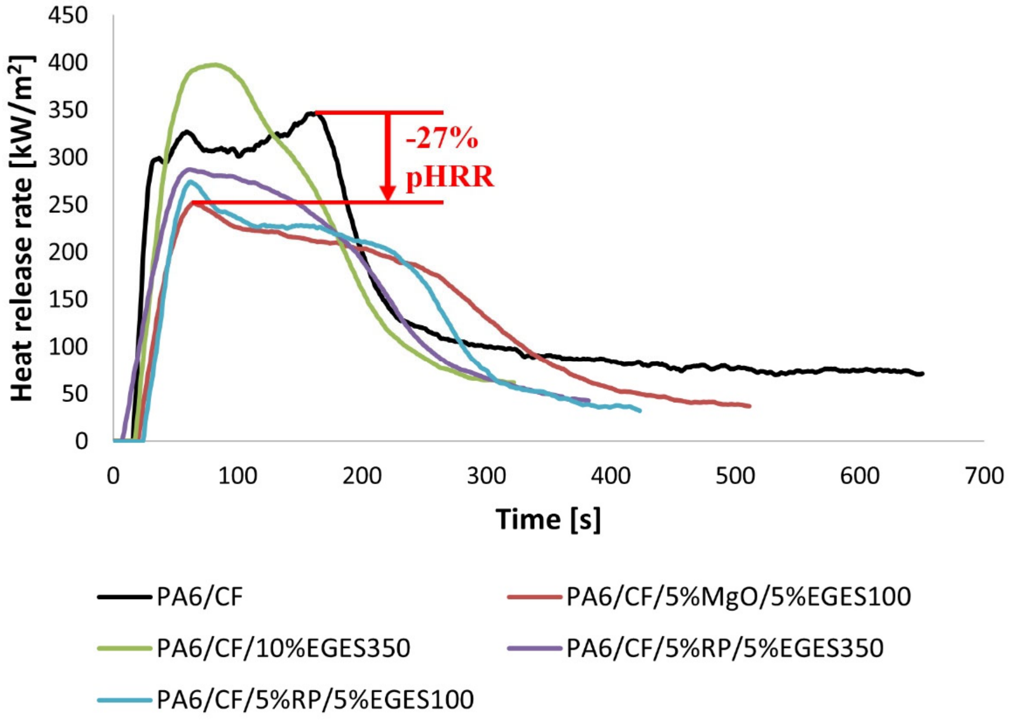

FIGURE 1. The heat release rate of reference and flame retarded polyamide 6 composites with coatings containing red phosphorus (RP), magnesium oxide (MgO) and expandable graphite (EG ES100 and EG ES350)

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P32- Effect of Different Fire-Retardant Mechanisms on Fire and Smoke Behavior of Upholstered Furniture

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Main message: Fire-retardants (FR) using gas- and condensed-phase mechanisms were used individually or in combination to produce nine fabric-filling composites, representative of UK upholstered furniture. The fire and smoke behavior of these composites were assessed using cone calorimetry. Generally, FRs reduce the flammability of the composite, either by reducing its ignitability and/or reducing the rate of combustion. Inclusion of gas phase FRs in the composite dramatically increases it smoke toxicity.

Keywords: Upholstered furniture, Smoke toxicity, Fire behavior, Cone Calorimetry

Introduction

The UK implemented the Furniture and Furnishings (Fire) (Safety) Regulations (FSRs) in 1988, making the use of chemical FRs ubiquitous within mass market upholstered furniture. Furthermore, since the introduction of the FSRs the most common cause of casualty has become gas, smoke, or toxic fumes [1]. The FRs most used to meet the FSRs function in the gas-phase. However, condensed phase FRs have become more widely available and have the potential to reduce smoke toxicity while maintaining fire safety.

Experimental

Upholstered furniture composites for the cone calorimeter were manufactured and tested using a The CBUF Cone Calorimeter Test Protocol [2]. However, some modifications to the protocols method of composite construction were made to replicate changes in furniture manufacture since protocols publication in 1996.

In brief, cone calorimetry was carried out in triplicate and in accordance with ISO 5660, using an irradiance of 35 kW m^{-2}. The specimen was placed in the sample holder. However, the retainer frame was not used. The end of the test was reached once all the following three criteria had been met; a minimum of 5 minutes had elapsed; flaming had stopped; the rate of mass loss had dropped below 150 g m^{-2} min^{-1}.

Additional gas sampling was carried out by drawing a metered volume of effluent gas, which was collected at a depth of 45 cm below the mouth of the chimney stack during the test. The sampled gas was drawn through bubblers to trap individual toxic components. The concentrations were determined using ion chromatography (HPIC) and a spectrophotometric technique in accordance with ISO 19701.

Results and Discussion

A single quality of polyester upholstery fabric was used; without FR treatment (NoFR); with a brominated FR backcoating (BrFR); with expandable graphite laminated to the back of the fabric (EGFR). The upholstery fabric failed to meet FSRs without the use of a FR treatment. All three fabrics were used to make composites with each of the fillings. A polyurethane foam without any FR treatment (NoFR-PU) that is noncompliant with the UK's FSRs. A combustion modified high resilience PU (CMHR-PU) treated with tris(1-chloro-2-propyl) phosphate, complying with the FSRs. Finally, polyethylene terephthalate (PET) wadding which also meets the FSRs. The fire and smoke behavior of each composite was assessed in triplicate using the cone calorimeter. In all instances the composite lost at least 85 % of its mass.

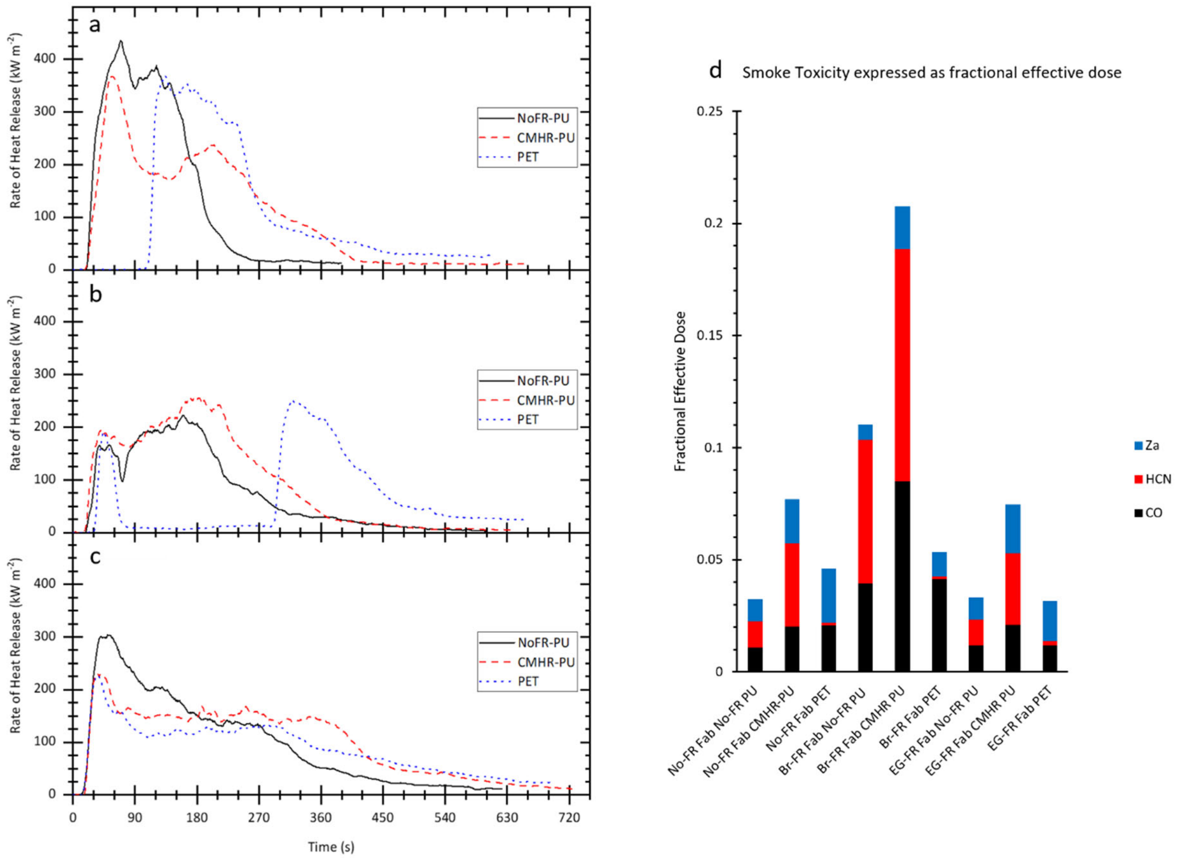

Figure 1. a-c Representative rate of heat release (RHR) profiles of fabric-filling composites in the cone calorimeter for: a NoFR Fabric, b BrFR Fabric, c EGFR Fabric over the three different fillings: NoFR-PU foam, CMHR-PU foam and PET wadding. d smoke toxicity of the various fabric filling combinations expressed as fractional effective dose using ISO 13344, where Za is the acidosis factor.

As shown by the rate of heat release (RHR) profiles (Figure 1.), the use of FSRs compliant fabrics and/or fillings, lowers the peak RHR while extending the length of time a significant RHR (>50 kw m^{-2}) is observed for [3]. Furthermore, use of inherently low flammability PET wadding fillings can delay the time to ignition, as result of PET's large temperature difference between melting and ignition. The use of gas-phase FRs in the filling (CMHR-PU) or fabric (BrFR) significantly increases the smoke toxicity of the sample. Especially when the two FR treatments are used in combination (figure 1 d).

Acknowledgement: The authors would like to thank InnovateUK KTN for funding the project (KTP partnership number KTP011934), and Mrs Tracy Fortune for her invaluable knowledge and understanding of the UK's Furniture and Furnishings (Fire) (Safety) Regulations and relevant standards.

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P33- BIORENEWABLE POLYELECTROLYTE NANOCOATING FOR FLAME-RETARDANT COTTON-BASED PAPER

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Main message

Cotton-based raw paper, made of 100% cellulose, is used to make humidity-sensing, cottonid-based actuators. Despite its renewability and excellent mechanical properties, it is inherently flammable. In an effort to reduce its flammability, thin films of renewable and environmentally benign polyelectrolytes, chitosan (CH) and phytic acid (PA), were deposited on raw paper via layer-by-layer (LbL) assembly. With only four bilayers of the CH/PA coating, self-extinguishing behavior is achieved [1].

Keywords: sustainability, cellulose, chitosan, renewable resources, layer-by-layer assembly

Introduction

Intumescent coatings constructed via LbL are known for imparting flame-retardant (FR) behavior on cellulosic material. An effective intumescent system contains an acid source, a blowing agent, and a carbon source, which react upon heating to form an insulating and protective char layer on the surface of the substrate. Renewable and environmentally benign intumescent systems have previously been deposited on cotton fabric by coupling cationic chitosan and anionic phytic acid.

Experimental

LbL deposition was carried out by immersing the pretreated cotton based raw paper in a phytic acid solution first and then in a chitosan solution. Characterization of the finished samples before and after vertical flame testing was carried out via micro combustion calorimetry (MCC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR).

Results and Discussion

Following LbL assembly, uncoated and coated samples were characterized using ATR-FTIR spectroscopy. Untreated raw paper contains a broad band at 3332 cm^{-1} that corresponds to the hydroxyl groups of cellulose. The absence of the O−H band is observed in the CH/PA-treated raw paper spectrum, while new bands are observed at 1635, 1532, 1153, and 965 cm^{-1} corresponding to the $C=O$ (amide) stretching, N−H bending, $P=O$ stretching, and P−C−O bending vibrations, respectively. These findings confirm that the coating components were interacting with the raw paper, indicating successful deposition onto the substrate.

Self-extinguishing behavior of the raw paper was evaluated by performing vertical flame testing, according to ASTM D6413. Coated and uncoated raw paper samples (12 × 3.5 in.) were exposed to a direct flame for 12 s. Upon exposure to the flame, uncoated raw paper burned completely, leaving little residue behind. In contrast, paper coated with four bilayers of CH/PA self-extinguished immediately after ignition, resulting in a 95% residue and a char length of 4.5 in.

The thermal degradation and decomposition process of uncoated and coated raw paper was monitored by thermogravimetric analysis (TGA) under air and nitrogen atmospheres. The decomposition shows three stages of mass loss. The first mass loss starts at 100 °C, corresponding to evaporation of moisture. The second stage (300−380 °C) involves dehydration and decomposition reactions of cellulose, which produce nonflammable gases, aliphatic char, and levoglucosane. The third step, around 490 °C, is attributed to the conversion of aliphatic char into aromatics, producing CO and CO_2 due to simultaneous carbonization [2].

The coating decreases the degradation temperature of the raw paper from 343 to 329 °C. This earlier onset of decomposition is due to the activation of the instumescent ingredients, which form a char layer that suppresses combustion and protects the underlying material from the flame [3]. While the raw paper burns completely in the absence of the coating, the coated raw paper yields a char residue of ∼15%. TGA of uncoated and coated raw paper under nitrogen atmosphere shows a single degradation step attributed to the depolymerization of cellulose into volatile gases and aliphatic char. Under pyrolysis conditions, the coated raw paper leaves behind a greater char residue (30%) when the temperature reaches 700 °C. This CH/PA coating in either atmosphere delays the maximum decomposition of the raw paper.

Further analysis of flame-retardant properties was carried out using MCC. MCC can measure several fire reaction parameters such as mass loss, heat release rate (HRR), peak heat release rate (pkHRR), and total heat release (THR), and can quantitatively explain the combustion phenomena of materials [4]. Four bilayers of CH/PA intumescent coating provides fire protection by reducing the pkHRR by 69% and THR by 70%, while increasing the char residue by 75%. These results correlate with the data obtained from TGA by demonstrating that the intumescent coating decreases the onset decomposition temperature of the raw paper. The effectiveness of this renewable intumescent coating relies on the decomposition of the phosphate groups in PA, which then catalyze the dehydration reaction of cellulose toward the formation of an aromatic char [3]. The char is then expanded by gases produced in the decomposition of the blowing agent. Chitosan acts as both a carbon source and a blowing agent, so there is a continuous release of foaming gases over the entire char-forming area. This char layer slows the heat flow from the fire to the raw paper [5].

Acknowledgments:
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P34- Highly-sensitive fire alarm system based on cellulose paper with low-temperature response and wireless signal conversion

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Main message

In this paper, Xiaolu Li as the first author, undertakes the main work except the design and preparation of wireless signal transmission device. Specifically, the contribution of this work mainly contains initial experimental design, sample preparation, all the data testing and analysis, graphs design and arrangement, manuscript writing and revision, sentence polishing, the reply of reviewer's comments, proof, etc.

Keywords: fire alarm, graphene oxide, MXene, wireless signal, cellulose paper

Introduction

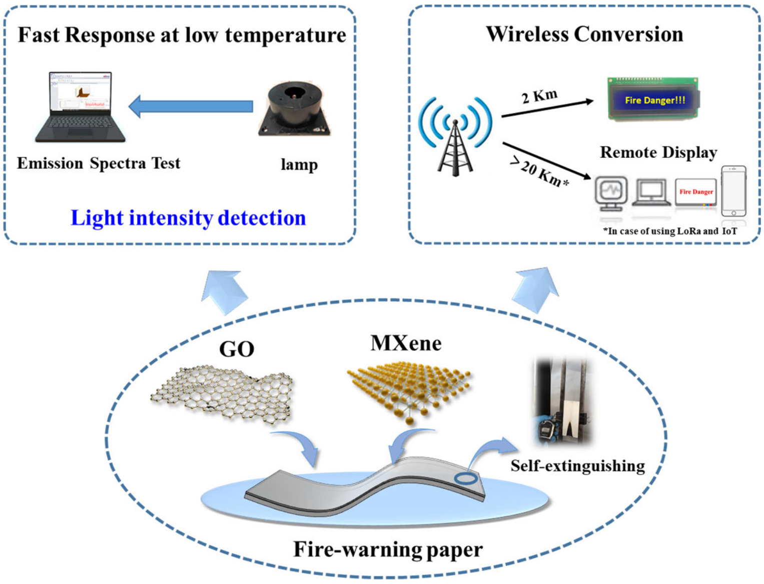
Highly sensitive smart fire sensors with remote warning capabilities are urgently required to improve the fire safety. Here, a novel fire alarm is designed by using flame-retardant cellulose paper loaded with graphene oxide (GO) and titanium carbide (Ti_3C_2, MXene), which also is coupled to a self-designed wireless communication interface to conveniently transmit fire signal remotely. It can transmit a message of "FIRE DANGER" to screen within a short response time of 2 s at 250 °C.

Experimental

Firstly, cellulose paper was immersed into phytic acid (PA) solution several times and dried at room temperature. Cellulose paper after PA modification were named as PAx, where x was PA concentration. Next, the homogeneous MGO suspensions with different concentration ratio of GO to MXene were prepared for next usage. By using simple dip-coating way to put PAx samples into MGO suspension (GO suspension), final PA@MGOy (PA@GO) papers were obtained, where y meant concentration ratio of GO to MXene.

Results and Discussion

A highly-sensitive fire-warning system based on PA@MGOy cellulose paper was successfully prepared via a simple dip-coating method. The modified PA@MGO5 paper exhibited a highly-sensitive response to abnormal temperature, showing a rapid response time of 2 s at a low temperature of 250 °C. Most importantly, a novel method based on "Light Intensity Change" to calculate response time was proposed, which is more quantifiable and precise after a comparison to the one based on "Electric Resistance Change". Notedly, self-designed wireless signal conversion device was provided to achieve remote message transmission, presenting the cooperation between new generation fire sensor with smart network.



SCHEME 1. Schematic illustration of the structural feature and fire-warning process for cellulose paper-based fire-warning system.

TABLE 1. Achievement of cellulose paper-based fire-warning system

Sample	**Response Time /s**		
	150 ºC	**200 ºC**	**250 ºC**
PA@GO	2303	76	21
PA@MGO20	2027	64	20
PA@MGO15	859	50	12
PA@MGO10	531	41	7
PA@MGO5	114	21	2

Acknowledgement: This work is supported by China Scholarship Council, China under the Grant CSC (201908110272).

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P35- Achieving high flame retardancy and high transparency Polycarbonate based on low addition of linear polysiloxane borane

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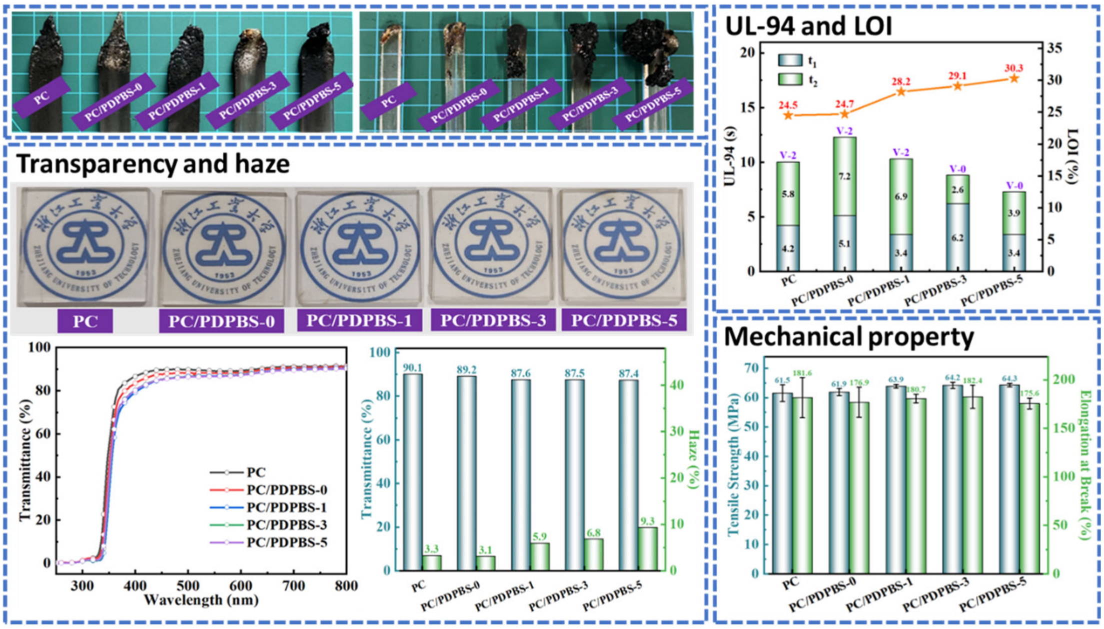
As the only transparent material among the five general engineering plastics, polycarbonate (PC) has been widely used in high-tech fields such as smart cars, precision electronics, building materials and 5G equipment because of its high transparency and balanced mechanical properties. However, the fire hazard caused by its inherent flammability seriously threatens people's personal and property safety and hinders the practical application of PC. Especially in the high-end manufacturing field, it is very necessary to modify the flame-retardant of PC while maintain its high transparency and mechanical strength. To solve this problem, many flame retardants such as bromine, phosphorus, sulfur, silicon and various compounds have been developed to improve the flame retardancy of PC. With the improvement of corresponding standards, PC is required to maintain excellent transparency and mechanical properties while achieving flame retardancy. As the most suitable flame retardant for PC, sulfonates can make PC achieve high flame-retardant efficiency with very low addition, but often sacrifice the transparency and mechanical properties of PC. Silicone-like flame retardants have little influence on the mechanical properties and transparency of PC, but they can't be used on a large scale because of their high cost. Boron-like flame retardant can improve the density of carbon layer in the combustion process, thus playing the role of condensed phase flame retardant, but adding it alone will seriously affect the transparency of PC matrix. How to combine silicone and boron compounds to improve the flame-retardant efficiency, so as to give consideration to the flame-retardant performance, transparency and mechanical properties of PC composites, has become a problem worthy of attention.

In this paper, a kind of polysilborane flame retardant PDPBS was synthesized, which endowed PC with excellent flame retardancy and transparency, while maintaining good mechanical properties. With the addition of only 3 wt% PDPBS, the LOI of PC composites is 29.1%, reaching the V-0 level of UL-94 test. Especially, this work can improve the flame retardancy of PC composites while still maintaining good transparency, and PC composites containing 3 wt% PDPBS can still maintain 87.5% transparency and haze below 10%. In addition, the tensile strength and elongation at break of PC composites are kept at the same level as those of pure PC. This work provides a new method to obtain PC flame-retardant composites with both flame-retardant and transparent properties, and makes the practical application of polycarbonate in the above industries.

Keywords: Polycarbonate; Flame retardation; Anti-dripping; Transparency;



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P36- NANOCELLULOSE BASED POLYELETROLYTE COMPLEXES AS EFFICIENT FLAME RETARDANT SOLUTION FOR TEXTILES AND OPEN CELL FOAMS

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Main message:
In this work cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC)have been used as building block for the preparation of polyelectrolyte complexes (PECs) able to confer flame retardant properties to cotton fabrics and flexible polyurethane foams (PU). Few deposition steps yielded efficient nanostructured coating capable of conferring self-extinguishing behavior to PU and cotton fabrics.

Keywords: Polyelectrolytes complexes, nanocellulose, coatings, polyurethane foams, cotton fabrics.

Introduction

The use of water-based PECs is a promising FR approach capable of delivering functional coatings with an industrially viable number of deposition steps. Nanocellulose, has attracted interest as a plant-based building block for water-based nanostructured composites and coatings [2]. Here, CNF is employed in combination with other environmental benign polyelectrolytes (e.g. gelatin, phytic acid) in order to develop highly efficient PECs capable of conferring FR properties to fabrics and open cell foams (Figure1).

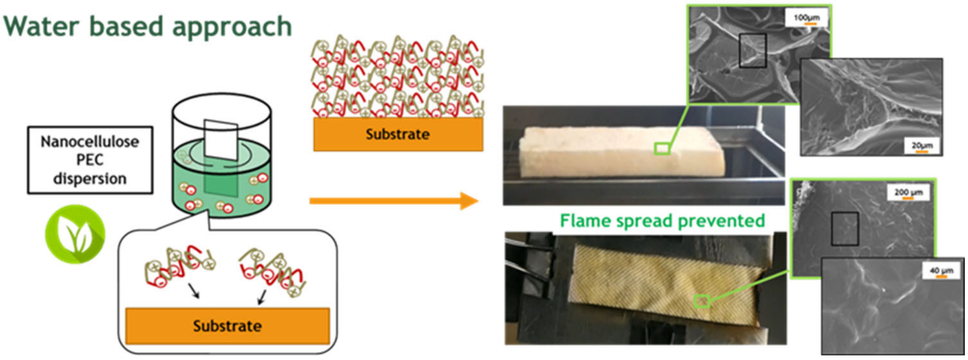

FIGURE 1. PECs deposition on different PU and cotton fabric. SEM micrographs of substrate surfaces and pictures after flame application in flammability test.

Experimental

In this work commercially available cellulose nanofibrils with carboxymethylated functionalization, and in lab synthetized cellulose nanocrystals have been used as main component for the formulation of PECs while cotton fabric and open cell flexible polyurethane foams have been used as substrates. Atomic force microscopy (AFM) and dynamic light scattering (DLS) have been employed to characterize the cellulose nanocrystals (CNC) dimensions, whereas infrared spectroscopy and scanning electron microscopy (SEM) were employed in order to study the coating deposition on PU and cotton fabric.
Thermogravimetric analysis (TGA) was carried out in a TGA-Discovery (TA, Newcastle, USA) from 50 to 800°C at 10°/min in both nitrogen and air. The flammability of the prepared samples was evaluated in horizontal configuration. The cotton or PU sample was ignited from its short side by a 20 mm blue methane flame (flame application time: 1x6 s). Cone calorimetry (Noselab ATS, 35 kW/m^2 heat flux, in

horizontal configuration) was used to investigate the combustion properties of PU samples (100x100x20 mm^3). Time to ignition (TTI, s), the peak of heat release rate (pkHRR, kW/m^2), the total heat release (THR, MJ/m^2), the total smoke release (TSR, m^2/m^2) and final residue (%) have been evaluated. SEM and Raman spectroscopy were employed for post-combustion analysis of cone calorimetry residues.

Results and Discussion

Flame retarded PU, were prepared by single step deposition of a Gelatin/Phytic acid/Cellulose nanofibers (Gel/PhA/CNF) complex. Different CNF concentrations have been investigated. SEM observation pointed out the formation of a continuous and homogeneous coating only at low CNF concentration (< 0.25%wt).

Flammability test in horizontal configuration showed a self-extinguishing behavior within few seconds after the removal of the blue methane flame. Interestingly, samples coated by (Gel/PhA/CNF) complexes with 0.1%wt CNF showed the deposition of a more homogenous coating that resulted in a non-igniting behavior (i.e. total absence of flame spread after 6s of flame application). By cone calorimetry, (Gel/PhA/CNF) exhibited a decrease of smoke release if compared with neat PU. Then, the reuse of prepared PECs solution was considered. The excessing solution from the deposition step was reused for the preparation of new samples that showed self-extinguishment immediately after the flame removal in flammability test.

Cotton fabrics were directly coated with a CNC/BPEI complex by a simple doctor blade approach. SEM micrographs showed the presence of a dense and compact layer efficiently adapted to the fabric surface morphology. During flammability tests treated samples exhibited self-extinguishment immediately after the flame removal as well as the suppression of the after-glowing phenomenon, typical of cotton fabrics. The same properties have been maintained even after a washing step (deionized water for 10 min under stirring at 40°C) thus demonstrating the durability of the coating in these conditions.

The present work demonstrates the possibility of using nanocellulose as effective building block for the preparation of FR PECs. The achieved results make it possible for the development of industrially viable approaches where the efficiency of the process and the flame retardant results are maximized.

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P37- FIRE PERFOMANCES OF POLYISOCYANURATE FOAMS WITH VERY HIGH INDEX

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Main message:
The main aim of this work is to compare in a systematic way the thermal stability and fire behavior of polyisocyanurate (PIR) foams of very high index (up to 900) based on aliphatic or aromatic polyester polyols. In this way it is possible to assess the effect of polymer chain flexibility, crosslinking density and aromatic content on the isocyanurate yield and, therefore, on fire and thermal performance of the foams.

Keywords: isocyanurate, aliphatic and aromatic polyols, relation formulation-properties.

Introduction

It is well known that PIR foams show better fire behaviour with respect to polyurethane rigid foams. This has been generally explained considering that the higher the isocyanurate content the better the fire performance. However. it seems that there is a lack of systematic investigation of the effect of the polyol structure on the isocyanurate yield that greatly influences thermal stability as well as fire behavior.

Experimental

The raw materials employed in the synthesis of polyisocyanurate foams were several polyester polyols, characterized by the same, low functionality, different molecular weight and aromatic content (Table 1). Pentane-blown PIR foams with NCO index ranging from 400 to 900 have been synthesized by varying the isocyanate content with respect to the polyol one.

TABLE 1. Selected properties of polyols.

Polyol	Chemical structure	nOH [mgKOH/g]	Molecular weight [g/mol]
ALI_MW	aliphatic	160	701
ALI	aliphatic	240	467
MID_AR	aromatic (medium content)	240	467
HIGH_AR	aromatic (high content)	240	467

Results and Discussion

The polyols used in this study have been chosen in order to understand the relation among chain flexibility or aromatic content of the polyol and the isocyanate conversion, isocyanurate yield as well as fire and thermal stability of the PIR foams prepared in a wide range of NCO index (400-900).

The experimental results (Figure 1) have shown that the NCO conversion was almost complete, although it decreased when NCO index increased and/or the aromatic content was high. This can be explained considering the high crosslinking density of the system for high NCO index and/or the reduced chain mobility of the highly aromatic polyol: indeed, NCO terminal groups in the polymer chain need a certain flexibility to be able to assume proper orientation to further react and when the polymer is extremely crosslinked or stiff this becomes increasingly difficult [1]. As expected, the isocyanurate content increased when increasing NCO index (Figure 1) and it was always lower than the maximum allowable one. This is due to the huge numbers of reactions which can take place between isocyanate and other compounds present in the polymer: isocyanate can react with itself to give isocyanurate but also with urea and urethane to give carbodiimide, biuret and allophanate. However, due to the presence of specific trimerization catalysts in the formulation, the formation of isocyanurate is favoured amongst the other ones.

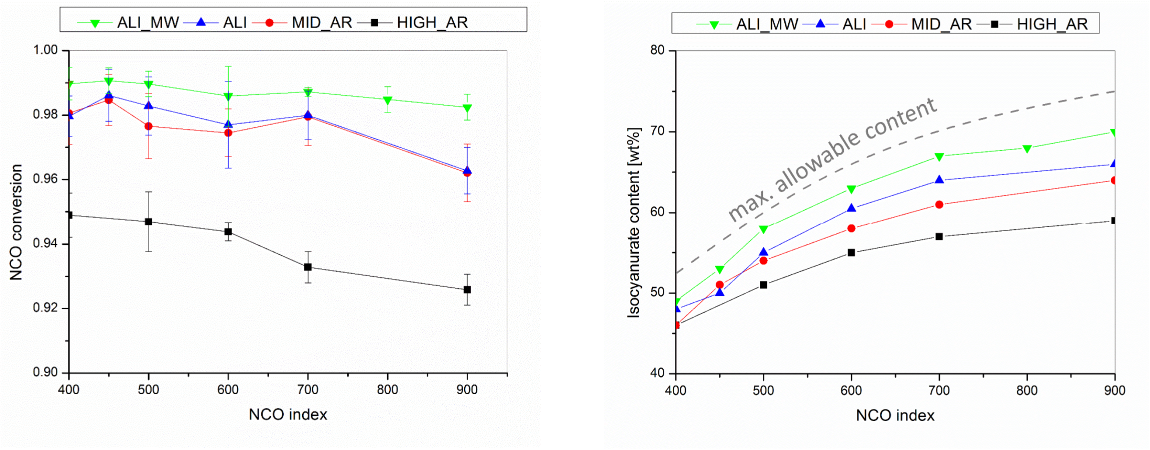

FIGURE 1. NCO conversion (left) and isocyanurate content (right) as a function of NCO index.

Thermogravimetric analyses have shown that the thermal stability of the foams is higher for higher NCO index, as expected, because of the higher content of thermally stable isocyanurate. It has also been demonstrated that PIR foams based on aromatic polyols have greater thermal stability with respect to their aliphatic counterparts; however, the effect of the chemical nature of the polyols becomes less and less important as the NCO index increases. Cone calorimeter data show the same trend: the peak of heat release rate and the total smoke production are lower for higher NCO index as well as for foams based on aromatic polyols. Similarly to TGA data, also cone results show decreasing effect of chemical nature of the polyols when the NCO index increases.

In conclusion, we can state that fire performances as well as thermal stability of PIR foams are greatly affected by the chemical nature of the polyol at low NCO index (400), where the isocyanurate content is almost similar for different polyol kinds while at higher NCO index(900) the low thermal stability of the aliphatic polyols is counterbalanced by the low isocyanurate content of aromatic foams, so no significant differences can be noted.

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P38- RELATIONSHIP BETWEEN HEAT EXPOSURE EQUIPMENT AND INTUMESCENT COATING PERFORMANCE

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Main message: Intumescent coatings are certified based on tests in industrial furnaces, which are costly and use a lot of energy. This leads researchers to use lab-scale methods. However, there is no method to correlate industrial and lab-scale test results. This work aims at understanding how various testing methods differ from each other and to find a way to predict the coatings behavior in industrial furnaces. Here, coatings are exposed in an industrial furnace, a new prototype named CoaST-Fire and a lab-scale modified electric oven.

Keywords: Intumescence, fire protection, thermal resistance, industrial scale testing.

Introduction

Intumescent coatings must be tested according to fire safety standards to be commercialized. These standards require cubic meter sized industrial furnaces for the final approvement of intumescent coatings, which consume a lot of time, energy, and money. Therefore, there is a need to develop precise correlations between various test set-ups and to improve current fast screening methods for intumescent coatings for a more rapid and reliable performance assessment.

Experimental

Cellulosic and hydrocarbon coating formulations were supplied by Hempel Spain. Their composition is confidential and the formulation that its results were provided in this work will be referred to as C- WB-A. This formulation was tested using cellulosic fire curve in 3 different testing set-ups to investigate how different methods affect the fire protection performance of a coating. Substrate dimensions and the exposed areas were chosen in a way to equalize the section factor to 200 m^{-1}. The dry film thicknesses were chosen as 0.7, 1.0, 2.0 and 3.0 mm.

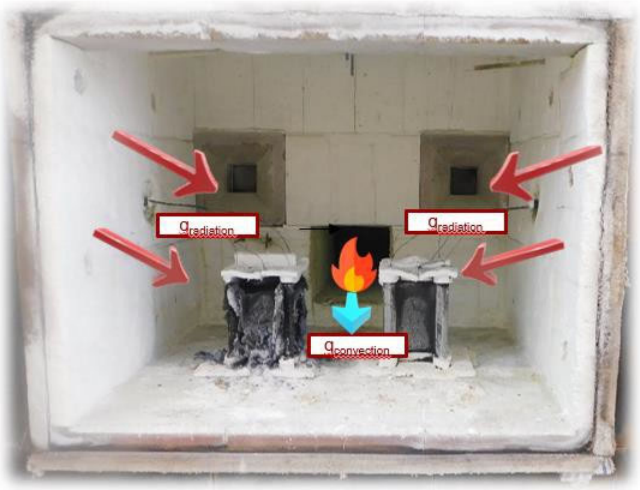

FIGURE 1. Industrial furnace used in Hempel Spain.

Industrial furnace (Fig.1) testing was performed in Hempel Spain using the standard of ISO 834 cellulosic fire curve. The furnace with a volume of 7,5 m^3 was fired with natural gas while 4 samples were tested simultaneously by mounting them in the 4 openings on the furnace wall. The samples tested in this set-up had the dimensions of 5 mm x 200 mm x 300 mm. Samples are coated on one side that faces the inside of the furnace. The uncoated backside of the steel was thermally insulated with 5 cm fiber blanket to minimize the heat losses. The steel temperature was measured by attaching two K-type thermocouples to the steel backside. The furnace temperature was simultaneously measured with K-type thermocouples. The test was ended when all the steel substrates reached the critical temperature of 550°C.

The first lab scale method used for comparison to the industrial furnace was the CoaST-FIRE (Fig. 2) set-up, which was developed at the Technical University of Denmark[1]. This vertical furnace has 3 temperature zones and the sample cup is placed at the bottom of the furnace. Depending on the desired heating curve, the sample is pushed upwards with a certain velocity profile. For this work, the ISO 834 cellulosic fire curve was chosen to align with industrial tests in Hempel Spain. The test was ended when the steel temperature reached the critical temperature of 550°C. The steel disc substrates had a diameter of 90 mm and 5 mm thickness and were covered with coating on the side exposed to heat. The steel temperature was measured with a K-type thermocouple on the uncoated backside of the substrate.

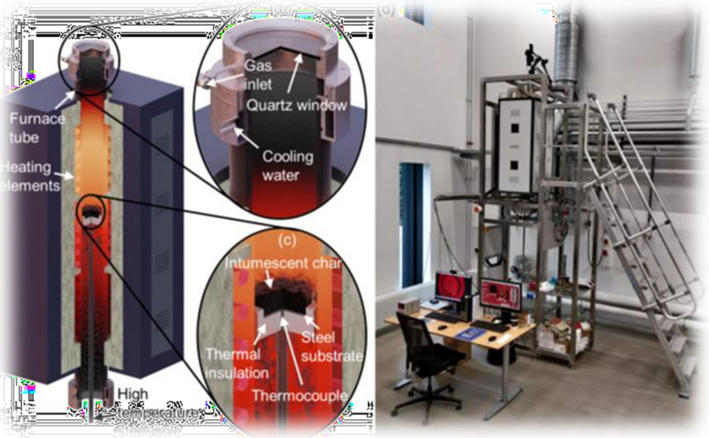

FIGURE 2. CoaST-FIRE set up designed at DTU[1].

The second lab scale method used was a modified version of a small electric oven (Fig. 3) LHT 01/17D from Nabertherm[2]. The ISO 834 cellulosic fire curve was used. Substrates with dimensions of 3 mm x 60 mm x 60 mm were coated on the side facing the oven interior. The uncoated backside was thermally insulated with 10 mm of ceramic fibers and 25 mm of Skamol in order to minimize the heat loss from the backside of the steel. The furnace temperature was measured using B-type thermocouple while the steel temperature was measured using a K-type plate thermocouple.

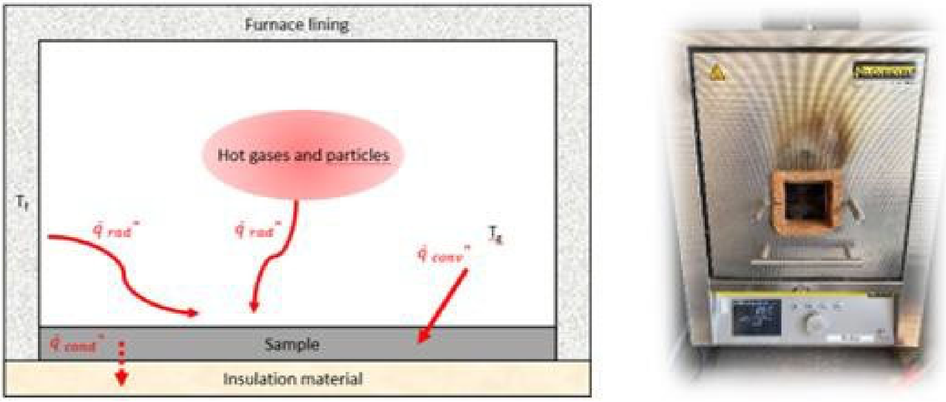

FIGURE 3. Small Electric Oven modified at DTU.

Results and Discussion

Tests were done with 2 repetitions for each sample namely, C-WB-A-0,7 mm, C-WB-A-1 mm, and C-WB-A-3 mm. Time-temperature curves and expansion ratios are seen in Fig.4 while some key parameters can be seen in Table 1. Tests done in the industrial furnace show that increasing the dry film thickness (DFT) also increases the time to reach the critical temperature but decreases the expansion ratio. The thinnest coating was chosen as 0.7 mm and it has the lowest fire protection performance with a time to reach critical temperature of 38.45 minutes. The coating with the highest thickness (3 mm) also has the highest fire protection performance with 66.25 minutes.

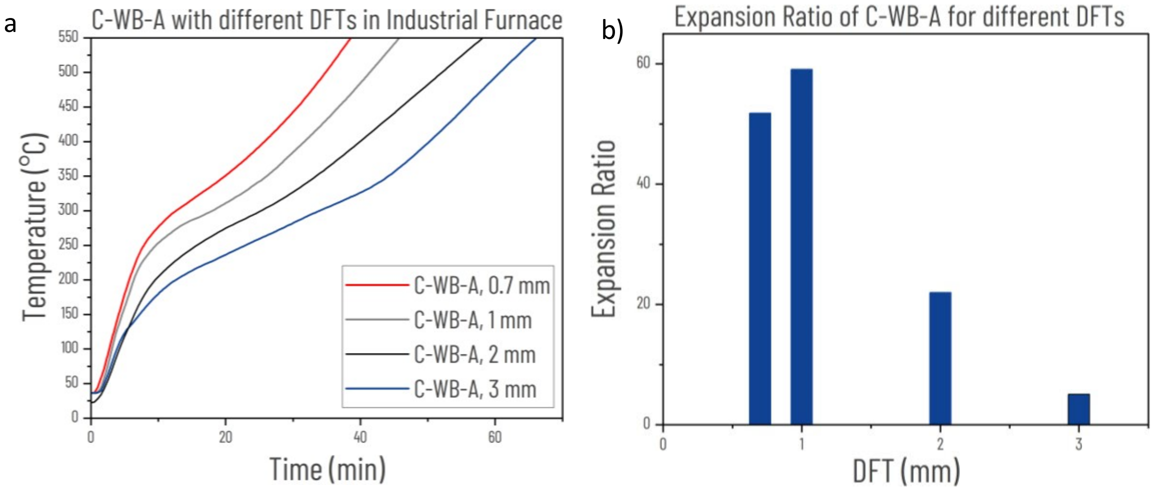

FIGURE 4. a) Time-Temperature curves and b) expansion ratios of sample C-WB-A with different DFTs in industrial furnace.

TABLE 1. Selected properties of sample C-WB-A with different DFTs.

Sample	**Time to Critical Temp. [min]**	**Thickness before [mm]**	**Thickness after [mm]**	**Expansion Ratio**
C-WB-A, 0,7 mm	38.45	0.701	37	51.8
C-WB-A, 1 mm	45.75	0.987	63.3	59.1
C-WB-A, 2 mm	60	2.25	51.75	22
C-WB-A, 3 mm	66.25	2.92	17.65	5.1

Samples with the same coating DFT were placed diagonally on the furnace door and they can be observed in Fig. 5 after the fire exposure. The char from the 1 mm thick coating was easily detached from the surface, indicating that the adhesion was not very good. No cracking was observed on the surface. The char consisted of several homogeneous layers with different structures. One being the softer and lighter char with larger poresand the other being the brittle char at the bottom layer having smaller pores. The char from the 3 mm thick coating has similar characteristics to the 1 mm sample but with a much smaller expansion ratio, resulting in a more compact char. It is thought that this compactness gives a better fire protection performance since a good char must have a pore structure that is stable and has a fairly uniform cell size distribution .

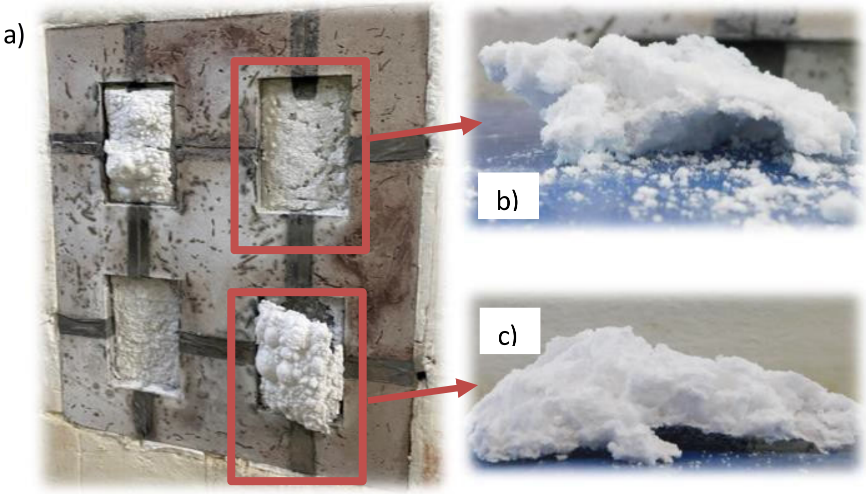

FIGURE 5. a) Post burn of Sample C-WB-A in industrial furnace door b) with a DFT of 1 mm and c) 3 mm.

Tests in the small electric oven and CoaST-FIRE with different formulations (including cellulosic and hydrocarbon coatings) are currently being performed and will be completed within 2 months. The goal is to identify potential differences in terms of recorded steel temperatures or char characteristics and further explain what mechanisms might cause these differences.

Acknowledgement: The authors would like to thank Hempel Spain for supplying the coated samples and for making it possible to run industrial furnace tests and to Hempel foundation for the financial support.

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P39- RECYCLING BROMINE AND ANTIMONY FROM ACRYLONITRILE BUTADIENE STYRENE (WASTE PLASTICS CONTAINING BROMINATED FLAME RETARDANTS).

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Main message: A large proportion of engineered plastics is diverted to landfills because of the presence of flame retardants and the absence of a proper recycling method. This work develops a pyrolysis process that deploys calcium hydroxide as a bromine-fixation agent. Calcium hydroxide shows its robustness by fixing a maximum of 88 % of total bromine and simultaneously traps antimony. The formation of valuable calcium bromide reflects the utility of this method for recycling brominated plastics.

Keywords: Pyrolysis, Decabromodiphenyl ethane, E-waste, Brominated flame retardants, Catalytic effect.

Introduction

WEEE plastics often contain additives that hinder recycling and there is a critical need for new reclamation technologies. Plastics using brominated flame retardants contain Br, Sb, and monomers that if recovered can be repurposed to make valuable new products. From this perspective, the present study investigates the mechanism of the BFR debromination under controlled conditions, in the presence of Sb_2O_3 and $Ca(OH)_2$, to develop a viable process for recycling plastics containing BFR and Sb_2O_3.

Experimental

The experimental equipment comprised a simultaneous thermogravimetric apparatus and differential scanning calorimeter (TGA-DSC) for determining the debromination kinetics of decabromodiphenyl ethane (DBDPE) with and without antimony trioxide and calcium hydroxide. The TGA-DSC also produced the solid residue used for quantitative experiments and characterisation. DBDPE constitutes the most common brominated flame retardant used presently in electronic and electrical equipment [1]. The sample sizes were ≈ 5.5 mg for kinetics and 100 mg for other analyses. The flow rate of the argon carrier gas amounted to 50 mL min^{-1}, with the temperature ramp set from 5 – 20 K min^{-1} for kinetics and 10 K min^{-1} for other reactions. We characterised the char by powder x-ray diffraction (PXRD), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscope (TEM), attenuated total reflectance (ATR), electron probe microanalysis (EPMA) and vibrational spectroscopy (IR and Raman).

Results and Discussion

DBDPE undergoes two successive mass loss stages of ≈ 82 % and ≈ 15 % at the temperature ranges of 350 – 500 °C and 500 – 715 °C, respectively. The initial mass loss occurs after melting and is associated with the decomposition and evaporation of the BFR. Kinetics of the pyrolysis of DBDPE comprise two consecutive processes characterised by activation energies of approximately 150 kJ mol^{-1}. Sb_2O_3 transforms the two-stage decomposition into three stages and increases the activation energy within conversions of 0.4 to 0.6, reflecting the formation of strong Sb-O-Br bonds. XRD results indicate the presence of antimony bromides and oxybromides at 500 °C as a result of char formation [2]. The presence of antimony induces the formation of anthracene indicating removal of Br by Sb-mediated coupling reaction. This occurs whether or not calcium hydroxide is present in the system. The application of calcium hydroxide to the brominated flame retardants transforms the degradation process to one stage associated with 35 % loss of the reacting material between 350 to 500 °C. This fast comportment is followed by a slow loss of 10 % mass from 500 to 800 °C. Calcium hydroxide readily decomposes BFR forming $CaBr_2.6H_2O$ and mixed salts with antimony. Calcium hydroxide almost completely removes bromine (88 %, Figure 1) from the BFR, which indicates that only minor modifications are necessary for complete removal e.g., increased quantity of calcium hydroxide. Electron probe microanalysis reveals strong correlations between antimony and calcium at 800 °C. The results indicate the versatility of calcium hydroxide in fixing Br and Sb and will foster a deeper understanding into the processes that take place when the plastic polymer is incorporated.

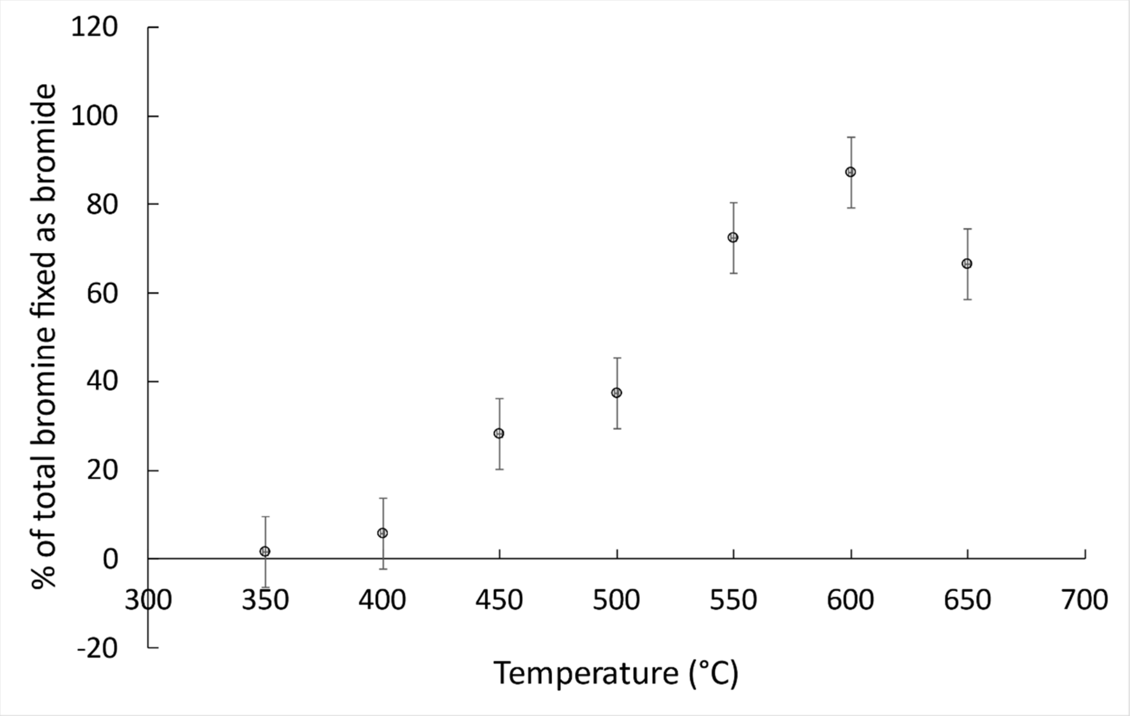

FIGURE 1. Percentage of total bromine in feed fixed by calcium hydroxide after pyrolysis to the respective temperatures.

Acknowledgement: Australian Commonwealth Government and the American Chemistry Council funded this work.

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P40- Catalyst Effects on Recyclability and Flame-retardancy of Functional Carboxylic Acid Cured Epoxy Thermosets

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Main message: In the last years, the development of polymers based on covalent adaptable networks has gained great relevance as a bridge between the malleable thermoplastic and mechanically stable thermosets. The main interesting feature of this class of polymers is the dynamic exchangeable bonds embedded in the network; it makes them resemble the structure of a thermoset with the flowing ability under certain stimuli, e.g., heat. Carboxylic/phosphate-ester bonds are of great interest to build such recyclable thermosets. Transesterification reactions can be used to promote bond exchanges for recycling and reprocessing of these materials. In this context, catalyst is required to realize transesterification, e.g., zinc acetate or organic base. In our work, we are investigating the effect of the solid acid type heterogeneous nanocatalysts for the transesterification based recyclability and material decomposition properties.

More in details, three kinds of catalysts have been properly synthetized and will be incorporated in the polymer matrix: binary oxide SiO_2-Nb_2O_5, SiO_2-P_2O_5 and ternary oxide Si-Nb-P. Based on previous results, the ternary oxide, Si-Nb-P, showed extraordinarily improvement on phosphorous incorporated polyester thermoset, more specifically the fire behavior, especially promoting the char formation.

The coming step will be the developing of few polyester thermosets, while examining the effect of the three above-mentioned catalysts.

Keywords: covalent adaptable networks, carboxylic/phosphate-ester bonds, transesterification reaction, recycling and reprocessing, oxide catalysts

Introduction

Common knowledge is that synthetic polymers have become progressively more important in our society, and, at the same time, plastic wastes continue to grow with increasing population and economic growth. Therefore, it is a constant challenge the research for recycling properties and sustainable societal development. The emergence of dynamic covalent polymer networks, which retain the benefits of thermosets yet can be reprocessed like thermoplastics, is starting to change the game. The so-called, "vitrimer", as proposed by Leibler and co- workers in 2011, for instance, are a reprocessable thermosets based on dynamic bond exchange via the associative mechanism. Transesterification reaction is one of the most reported designs for vitrimer preparation. Ester based vitrimers can thus be prepared by designing networks bearing ester bonds and OH groups with addition of a trans-esterification catalyst, a fundamental trigger for the dynamic reaction [1]. A significant advantage of these designs is the tunability of bond exchange activation temperature and bond-exchange rate by varying the type and fraction of trans-esterification catalysts [2]. They demonstrated that, in the presence of a suitable catalyst, an epoxy/anhydride network with ample hydroxyester moieties could be reprocessed via a dynamic transesterification reaction [3]. In such a network, an ester bond could be broken only if a new one was formed simultaneously. This resulted in a constant cross-link density at any reprocessing temperature.

Moreover, recycling is not the only angle from which polymers need to be evaluated. Flammability too is a key aspect influencing their performance. In a material that itself is intrinsically flammable and carry a large fire load, among additives, flame retardants (FR) represent a significant group whose use is crucial in many sectors where fire safety is a major issue (building, transportation, electronics) [4]. In the recent period, the development of green additives for polymers requires even greater importance. Thus, leading to the formulation of effective phosphorus-based flame retardants, as an alternative to halogen-based ones, to improve safety and reduce the environmental and toxicological concerns. Phosphorus-containing flame retardants possess excellent properties such as low smoke emission, low toxicity, and formation a stable carbonized layer after burning.

The mechanism according to which these FRs acts is promoting the dehydration of a matrix into char and capturing free radicals, in the respectively condensed and the gas phase. The char layer plays a role of “shielding blanket” that isolates the exchange of oxygen and heat [5].

To be noticed is the further development to solve problems related to the treatment of flame retardants as additives, among which phase segregation and opacity of the material. The solution can be in the passage from additive to reactive approach. In this latter case, flame retardant species are covalently bonded to the polymer chain what inhibits their mobility within the polymer network and maintains their efficiency over the time.Indeed, at equivalent phosphorus content, the reactive approach was shown to promote a higher char yield and a stronger reduction of the heat release.

The functional polyester thermosets were synthesized as Fig. 1, with molevular ratio as listed in Table 1.

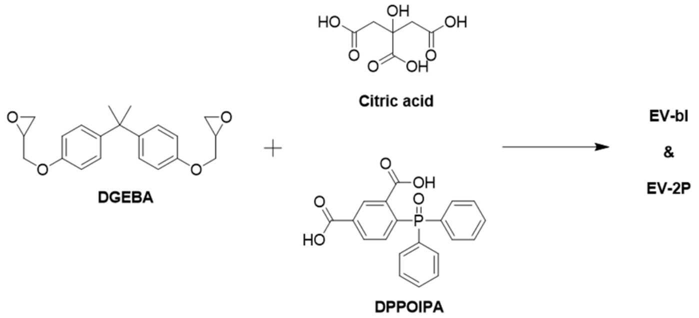

FIGURE 1. Schematic synthetic pathway of (a) EV-bl and (b) EV-2P using ternary oxide Nb_2O_5-P_2O_5-SiO_2 as the transesterification catalyst for later stages.

TABLE 1. Formulation of EV-bl and EV-2P.

Thermosets	**Bisphenol A diglycidyl ether (DGEBA)**	**Citric acid**	**DPPOIPA**	**NbP@SiO₂**
EV-bl	1	0.67	0	10 wt%
EV-2P	1	0.4	0.4	10 wt%

*Starting materials are in molecular ratio.

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P41- Novel techniques for the prediction of the fire hazard of polyisocyanurate insulation foams.

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Main message: A novel methodology has been developed using diamond-attenuated Total Reflectance Fourier Transform Infrared spectroscopy (d-ATR-FTIR). The method quantifies the isocyanurate to urethane ratio with a PIR structure. The quantified ratio was then used to predict the materials flammability and smoke toxicity. The ratio showed good correlation to the samples Peak heat release rate measured using Cone Calorimetry, providing a potential tool to predict the fire behaviour of PIR foams prior to mass production as a means of pre-fire regulation testing. The ratio also showed excellent correlation to HCN yields measured using the Steady State Tube Furnace, providing a potential tool for smoke toxicity predictions for PIR foams.

Keywords: Flammability prediction, isocyanurate to uretnane ratio, smoke toxicity prediction.

Introduction

Polyurethanes are thermosetting polymeric materials synthesized by the addition of a polyisocyanate with a polyalcohol. By varying the ratio of polyol to isocyanate in polyurethane formulations, polyisocyanurate foams are created[1]. The presence of the polyisocyanurate ring structure reduces the tendency to release volatile and flammable isocyanates and increases the materials charring properties due to the increased bond strength in the ring structure in comparison to the polyurethane structure, naturally improving the materials reaction-to-fire behavior[1]. The lower the ratio of isocyanurate to urethane, the more flammable the material becomes. As the polyisocyanurate content within a PIR has a direct effect on the material's overall flammability, a means of quantifying the content of polyisocyanurate content has potential to predict the overall materials flammability.

Experimental

Cone calorimetry was used to quantify the flammability of a series of randomly selected PIR's. Samples were cut into a 100 x 100 mm^2 square. The sample was then wrapped in aluminium foil with the surface exposed and placed onto a steel sample holder with no upper retaining frame. The sample was weighed and placed on the load cell of the cone calorimeter. Samples were subjected to a heat flux of 35 kW m^{-2}. Measurements were recorded from time to ignition to the when flaming ceased within the material with all samples being run duplicate.

The steady state tube furnace (SSTF) (ISO TS 19700) was used to generate fire effluent for smoke toxicity analysis for the samples used.

The ratio of isocyanurate to urethane was measured using a novel method using diamond Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (d-ATR-FTIR). Cubic samples of mass 0.05g were cut from their foam specimens and placed into a KBr pellet press and subjected to pressures of 700 M N m^{-2} for a period of 2 minutes. This created a smooth, flat circular disk eliminating potential inconsistencies in density and removing any bubbles present in the foam structure.

Within the d-ATR-FTIR spectra, two peaks were monitored in each scan: 1220 cm^{-1} , corresponding to the Amide II peak used to identify urethane, and 1408 cm^{-1} corresponding to the isocyanurate peak used to identify ring formation.
The area of the two peaks were taken from the spectra and used to calculate a ratio of isocyanurate to urethane within the sample. Each scan from the sample produced an identical spectrum, with values within ±0.01% of each other.

Results and Discussion

The isocyanurate to urethane index of each sample was measured and plotted against the peak heat release rate for each material, seen in Figure 1. The isocyanate to urethane index shows a general negative trend whereby an increased isocyanurate to urethane index showed a decrease in peak heat release rate. As the index increases, the increased presence of the ring structure in the PIR means that more heat is required to break down the bonds present, meaning a lower peak of heat release rate is observed.
A series of further randomly selected PIR's isocyanurate to urethane indexes were then compared to yields of HCN generated from the SSTF at 825 ◦C under-ventilated conditions correlating to post-flashover fire scenario, shown in Figure 2. The data showed excellent correlation, whereby an increase in isocyanurate to urethane index resulted in an increase in HCN yield. An observable link has been established between the isocyanurate to urethane index within a PIR sample and the peak heat release produced during cone calorimetric testing whereby an increase in isocyanurate to urethane index correlates to a decrease in peak heat release.

A strong link has also been established between the isocyanurate to urethane index in a sample and the HCN production during combustion in post-flashover conditions, whereby an increasing isocyanurate to urethane index corresponds to a higher production of HCN. This newly developed method could be used as a tool to predict both the fire toxicity and fire behavior of PIR foams prior to mass production as a means of pre-fire regulation testing. The method is both cheap and easy to use and holds the potential to save millions of pounds spent on fire testing as the method could provide an indication to the materials ability to pass regulation testing without the cost of testing the material a number of times with little indication as to if it will pass or not.

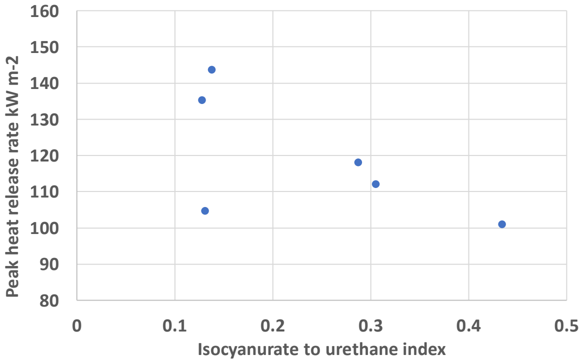

FIGURE 1. : Isocyanurate to urethane index vs Peak heat release rate measured using cone calorimetry, tested at 35 kW in frame.

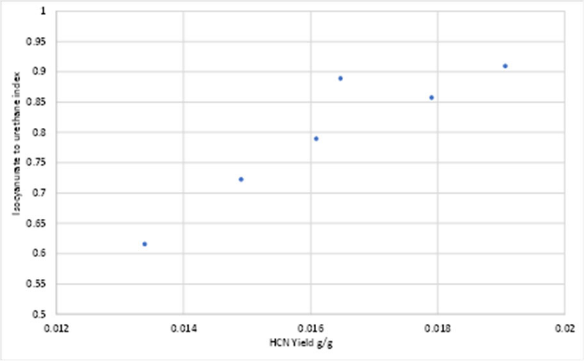

Figure 2: Isocyanurate to urethane index vs Hydrogen cyanide yield obtained from conducting tests using the ISO/TS Steady State Tube Furnace at 825◦C under-ventilated conditions.

Acknowledgement: No external funding was received.

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P42- DESIGN, CONSTRUCTION AND VALIDATION OF A SIMPLE, LOW-COST PHI-METER

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Main message:
A phi meter allows the ventilation condition of a fire to be monitored by analysis of the smoke. The toxic product yield of the main asphyxiants has been shown to depend on the ventilation[1]. This study designed and constructed a fully functioning, low cost portable phi meter for use in large-scale testing, with a full optimisation and validation of the apparatus.

Keywords: Phi meter, fire stages, fire characterization, equivalence ratio, smoke toxicity.

Introduction

The equivalence ratio is a means of expressing the fuel-to-air ratio, or ventilation condition which can be used to characterize fires. The use of a phi meter allows for definition of equivalence ratio during a fire test[2]. It has previously been used in large-scale fire tests to determine the fire condition during experimentation[3]. A direct equivalence ratio measurement allows more understanding of the fire stage during the experiment, which is of particular use for large-scale tests. The equivalence ratio is the best means for comparing bench to large-scale toxicity data as the combustion condition is known. The ability to monitor and quantify the equivalence ratio during fire tests is therefore desirable. Pervious phi meter designs used large furnaces with expensive catalysts and required the use of oxygen gas canisters. To improve the portability and safety of the new design, the phi meter constructed in this research used air. This decision was based on experimental data conducted using the secondary oxidizer on the ISO/TS 19700 steady state tube furnace (SSTF).

Experimental

A combustor similar to that used in the microscale combustion calorimeter (MCC) was used for the phi meter. The phi meter was initially ran with 50 cm^3 fresh air and 50 cm^3 of fire effluent per minute, with a maximum total flow rate of 100 cm^3 min^{-1}. Due to the extremely low flow rates required, specialist mass flow controllers and pumps were required. The furnace component of the phi meter was designed with engineers and constructed by Concept Equipment. The gas analysis system created was placed in a small box for improved portability. The schematic design of the analysis system is shown in Figure 1. The flow in the mass flow controllers was set and controlled by a program written on a Raspberry Pi 3B+. The constructed equipment was optimized using the MCC to find the optimal operational temperature. An NDIR was connected to the exhaust line monitor CO and CO_2 yields at the subsequent temperatures. The final operating temperature of the phi meter was chosen to be 900 C. It was then validated using the SSTF by testing the equipment at pre set equivalence ratios using a range of materials.

Results and Discussion

The validation of the phi meter using the SSTF set to specific fire conditions, showing a comparison between the set test value, value measured by the SSTF and the value measured by the phi meter is shown in Table 1. On each occasion, the phi meter measured the equivalence ratio in a close proximity to both the set test value and the measured value of the SSTF. The data shows that the phi meter was fully optimized and validated prior to its use in tests without a defined equivalence ratio.

The phi meter was successful in monitoring the equivalence ratio during burning experiments. It was able to detect the different fire stages reached during 3 different 'pre-set' ventilation conditions.

The new design of the phi meter was able to successfully demonstrate its validity and use for equivalence ratio monitoring, both on a bench and large-scale. The equipment is portable, safe for use in large-scale testing, and low cost as it does not require the use of expensive catalysts. The new re-designed phi meter is a reduced cost and portable version of the original designs, which will allow for greater affordability, and hence more widespread use.

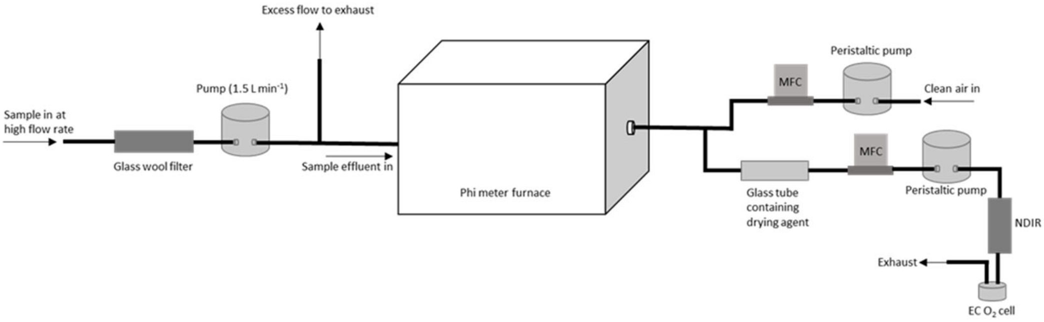

Figure 1. Schematic diagram of the design of a new, low-cost phi meter constructed in this study.

Table 1. Validation of the phi meter using PMMA tested in the SSTF at set equivalence ratios set for well-ventilated and under-ventilated flaming at 650 °C and 850 °C using a 1:1 ratio of fire effluent to fresh air in the phi meter, showing the aimed condition, the condition measured using the SSTF apparatus and the measurement taken using the phi meter.

	Equivalence ratio		
Temperature and ventilation condition	**Target value**	**Measured using SSTF**	**Measured using phi meter**
650 °C Well-ventilated (fire stage 2a)	0.5	0.35	0.40
650 °C under-ventilated (fire stage 3a)	1.5	1.40	1.45
825 °C under-ventilated (stage 3b)	1.5	1.45	1.47

Acknowledgement: We thank Fire Safe Europe for provision of a studentship, and Concept Equipment, UK for help and advice with the design.

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P43- Sustainable egg white/lignin nanocoating for flame retardant cotton

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Main message: To develop a sustainable, cheap, and efficient flame-retardant cotton treatment, a lignin-based multilayer nanocoating comprised of magnesium lignosulfonate (L), egg white protein (EWP), and monoammonium phosphate (MAP) was deposited on cotton using the layer-by-layer (LbL) assembly. A five-bilayers of 0.5% EWP_3/(1% L-10% MAP)$_{4.2}$ adds only 6.7 % weight and imparts self-extinguishing behavior to cotton on a vertical flame test (VFT).

Keywords: cotton, layer-by-layer assembly, lignin, egg white proteins, monnoamonim phosphate.

Introduction

In previous work, an intumescent system composed of chitosan and lignin was applied to cotton via the LbL assembly [1]. Five bilayers of it make cotton self-extinguishing. Even though chitosan is a very effective intumescent chemical, its price, and low solubility in a wide pH range make it inconvenient for industrial applications. In this work, egg white is used as an alternative to chitosan because it is cheaper, easier to prepare, and has components characteristic of an intumescent system.

Experimental

The coating was deposited on desized and scoured cotton woven fabric (175 g/m^2), purchased from Alkaloid AD Berovo, North Macedonia. Magnesium lignosulfonate (L) powder was supplied from Borregaard AS (Sarpsborg, Norway). CH, with a molecular weight of 190,000-310,000 g/mol, was purchased from Carbosynth limited (Compton, Berkshire, UK). Egg white protein (EWP) was purchased from P.I.C. Co. DOOEL (Skopje, North Macedonia). MAP, hydrochloric acid 37% (HCl), and sodium hydroxide pellets (NaOH) were purchased from Sigma-Aldrich (Milwaukee, WI). The LbL deposition and the preparation of 0.5% EWP_3 and (1% L-10% MAP)$_{4.2}$ solutions were performed as reported in the previous work [1]. Three samples for each LbL recipe were vertical flame tested following the ASTM D 6413 standard. The combustion behavior was tested with a micro cone calorimeter (MCC) according to ASTM D 7309, using an MCC-2 instrument (Govmark, Farmingdale, NY).

Results and Discussion

Images of the cotton samples coated with 5 BL 0.5% EWP_3/(1% L-10% MAP)$_{4.2}$ presented in Fig. 1 show self-extinguishing behavior on VFT. Although the sample coated with the EWP-containing recipe has a lower weight gain after LbL (6.7%), it still behaves similarly on VFT as the sample coated with the CH-containing recipe (Fig. 1 and Table 1).

The results obtained from MCC also show similar trends for both samples. They both have a 60% reduction in the peak heat release rate (pKHRR) and a 27% lower temperature of the peak heat release rate (T_{pkHRR}). The sample coated with the EWP-containing recipe releases approximately 59% less total heat (THR), while the one with the CH-containing recipe has a THR reduction of 65% relative to uncoated cotton. The fire growth capacity (FGC), which shows the potential of the material to ignite and grow in fire intensity once ignited, is reduced by more than 81% when cotton is deposited with 5 BL of 0.5% EWP_3/(1% L-10% MAP)$_{4.2}$ or 5 BL 0.5% CH_3/(1% L-10% MAP)$_{4.2}$.

These results can be attributed to the chemical composition of the proteins present in the egg white. These proteins are rich in various amino acids, including the sulfur-containing cysteine amino acid [2] and phosphorus-containing ovalbumin (the primary protein present in the egg white) [3]. EWP, in addition to being a carbon donor, contains phosphorus that catalyzes the formation of the charred layer and nitrogen and sulfur that are released in the form of gases that expand the volume of the charred layer. Therefore egg white proteins have great potential to be used in intumescent systems as an alternative to chitosan.

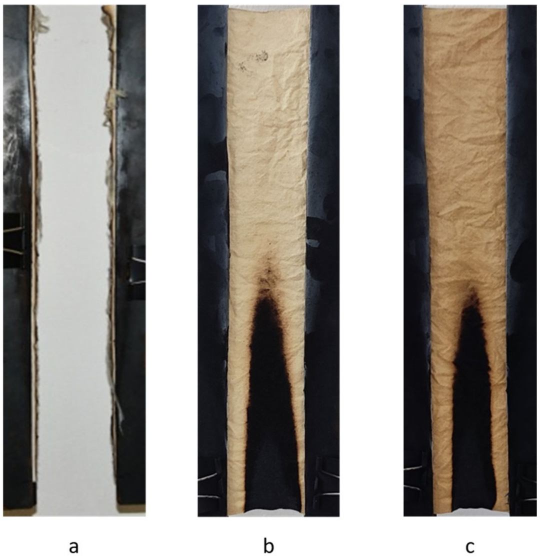

FIGURE 1. Pictures from VFT of a) uncoated cotton, and LBL-coated cotton with: b) 5 BL 0.5% $EWP_3/(1\%\ L\text{-}10\%\ MAP)_{4.2}$, c) 5 BL 0.5% $CH_3/(1\%\ L\text{-}10\%\ MAP)_{4.2}$.

TABLE 1. Results obtained from VFT and MCC for uncoated and LbL-coated cotton.

Recipe	BL	Weight gain after LbL [%]	Char length [cm]	Residual weight [%]	pkHRR [W/g]	T_{pkHRR} [°C]	THR [kJ/g]	FGC [J/g-K]
Uncoated cotton	/	/	/	0	271.6	387.3	12.3	210.0
EWP/(L-MAP)	5	6.7	12.9	91.6	108.5	283.1	5.0	38.9
CH/(L-MAP)	5	10.0	12.9	92.7	107.6	282.4	4.3	38.9

Acknowledgement: The authors would like to thank the NATO Science for Peace and Security (SPS) program for their funding through the G5905 (MULProTex) project.

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P44- Quantitative characterization of FR dispersion by X-ray computed tomography and its influence on FR performance

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Main message

Thermoplastic polypropylene (PP) offers unique properties including mechanical performance, chemical resistance and ease of processing, and finds many applications in the building and construction, automotive and transportation, consumer electronics and healthcare industries. However, due to the hydrocarbon-based nature of polymers, the predisposition to combustion is a challenge, and flame retardant (FR) properties are strictly required. In addition, many halogen-based FRs are being phased out, SABIC is exploring innovative strategies to combine phosphorus-based FRs with polypropylene with an enhanced FR performance.

Keywords: Thermoplastics, Polypropylene (PP), Flame Retardant, Dispersion, Computed Tomography

Introduction

The combination of different FR additives shows promising results as the characteristic synergistic effect can promote the formation of a char by intumescent mechanisms [1]. The occurrence of a synergistic effect is influenced by many factors, in particular the dispersion of the FR additives [2, 3]. Depending on the geometry, the surface chemistry of the FR particles and their interaction with the polymer matrix, the FR particles can be well dispersed or heterogeneously distributed. The dispersion efficiency also strongly depends on compounding/processing conditions [4]. Conventional methods to evaluate the dispersion quality of fillers are mostly based on electron microscopy [5]. However, those are based on 2D projections, and do not necessary represent the volume information. On the other hand, micro-computed tomography (µCT) is a non-destructive method that can obtain 3D information on the internal microstructure of a sample, and can be used to quantitatively assess the filler dispersion or aggregation [6, 7].

Experimental

Polypropylene (PP) samples containing nitrogen-phosphorus based FR additives were produced to assess the influence of processing conditions (screw speed, screw design, throughput, melt temperature) on FR particle dispersion and subsequent FR performance. Two series of samples are investigated: (1) a FR-PP grade extruded with different screw designs, throughput and melt temperature, and (2) a FR-PP grade combining different FR additives produced with different throughput or melt temperature. An overview of the samples series is provided in Table 1.

The morphology of the polymer systems is characterized by using a Bruker SKYSCAN 2214 µCT. After reconstruction via the NRecon software, the images are post-processed and analyzed with the help of the 3D.SUITE Software. The dispersion of FR particles is evaluated by measuring the particle size distribution, which provides quantitative information on the level of aggregation. The FR performance of the materials is characterized by performing UL-94 fire testing.

Results and Discussion

In the first series of samples, the level of aggregation of the FR particles is limited (Figure 1A), with a volume average diameter of typically 10µm (Figure 1B). However, statistical analysis shows that a better dispersion is achieved in sample 1c, which yields a UL-94 rating V-0 at a thickness of 1.6 mm. No statistical difference is observed in the dispersion of the FR particles in the respective pellets or molded parts. In the second series of samples, the level of aggregation is much higher (Figure 2A), with a diameter larger than 13 µm, showing more substantial differences depending on the processing conditions (Figure 2B). Statistical analysis shows that sample 2c presents a better dispersion as compared to the other two samples, as well as a better FR performance.

The level of aggregation of FR particles has been characterized quantitatively by µCT. The dispersion of the particles depends on the processing conditions and the FR package. A strong correlation between dispersion and FR performance is observed.

Table 1. Overview of the conditions used to produce the samples and summary of the results

	Screw	RPM	Temperature [°C]	FR rating	FR particles diameter [µm]
Sample 1a	A	530	260	V-1	10.18
Sample 1b	B	300	215	V-1	10.18
Sample 1c	B	530	260	V-0	9.84
Sample 2a	C	100	230	(*)	20.6
Sample 2b	C	100	280	(*)	16.9
Sample 2c	C	300	230	V-0	13.2

(*) No rating could be assigned as the sample failed the UL-94 test

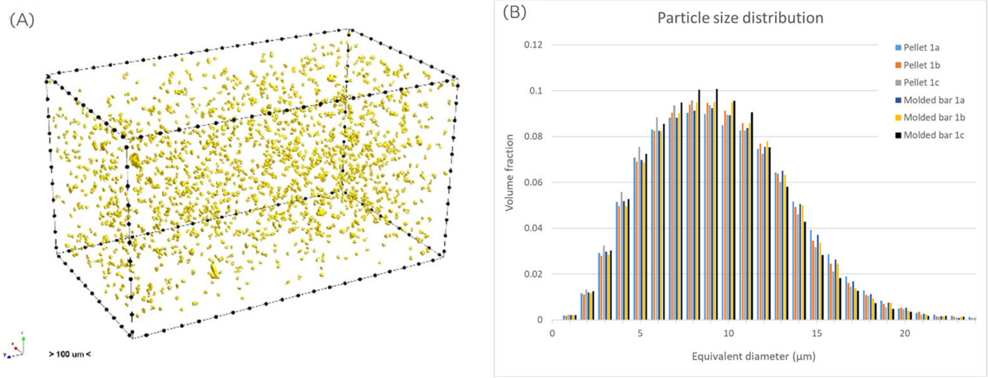

FIGURE 1. (A) 3D representation of the FR particles in the molded bar 1c, showing particles with a diameter larger than 15 µm. (B) Particle size distribution of the FR in pellets and molded bar samples.

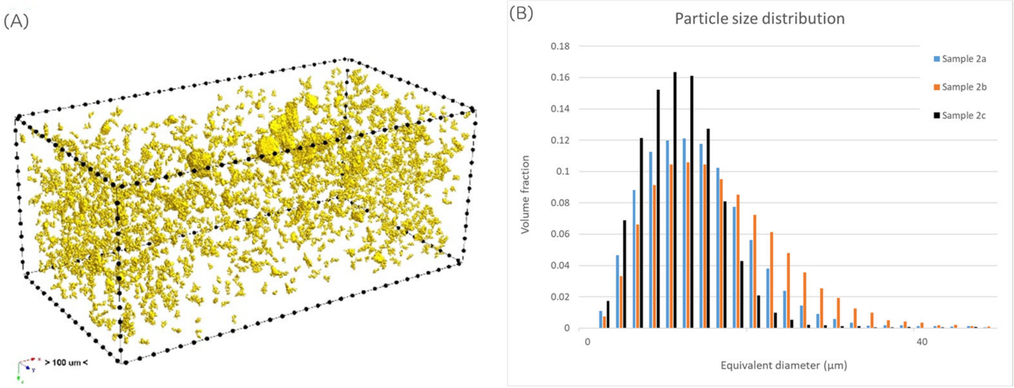

FIGURE 2. (A) 3D representation of the FR particles in the molded bar 2a, showing particles with a diameter larger than 25 µm. (B) Particle size distribution of the FR in samples 2a, 2b and 2c.

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P45- COMBINED EFFECT OF SOLID AND GAS PHASE FLAME RETARDANTS IN EPOXY GELCOATS FOR CARBON FIBRE-REINFORCED EPOXY COMPOSITES

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Main message: Gelcoats, commonly used in the automotive, railway and aerospace industries, have the primary function of providing aesthetic appearance and mechanical protection to composite parts but can also be complemented by secondary properties such as flame retardancy. The main aim of our work was to find an optimal ratio of ammonium polyphosphate (APP) and resorcinol bis(diphenyl phosphate) (RDP) to provide flame retardancy and flexibility of epoxy gelcoats on carbon fibre- reinforced epoxy composites.

Keywords: multifunctional gelcoat, flame retardant, combined mode of action, fibre-reinforced epoxy composites, transportation industry

Introduction

Epoxy gelcoats are often brittle; thus, they can easily detach from the composite surface [1]. In our previous work [2], we developed flame retarded epoxy gelcoats with APP, which were efficient but brittle and not sprayable without a diluent. Our hypothesis was that an appropriate combination of APP and liquid, low-viscosity RDP could provide sprayability without a diluent and synergistic flame retardant effects via their combined solid and gas phase mechanism [3].

Experimental

We prepared flame retardant gelcoats based on commercially available epoxy gelcoats using APP and RDP with an overall 10% phosphorus (P) content. The thermal behaviour of the matrices was characterised by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The viscosity of the gelcoats was investigated by parallel plate rheology, while we characterized the fire performance with LOI, UL-94 and mass loss calorimetry tests. The best-performing gelcoats were applied on carbon fibre-reinforced epoxy composites via spraying, and their fire performance and the interfacial strength between the laminate and the gelcoat were characterised.

Results and Discussion

Mixed gelcoat compositions were made with 10% overall P content with the following compositions: 5%P APP + 5%P RDP; 6%P APP + 4%P RDP; 7%P APP + 3%P RDP; 8%P APP + 2%P RDP; 9%P APP + 1%P RDP. These combinations were compared to the reference gelcoat and its flame retarded version containing 10%P APP.

The reference gelcoat was developed for application by brushing, and the addition of APP further increased the viscosity, making the gelcoat unsuitable for spraying without a diluent. We found that the compositions containing 6%P APP + 4%P RDP and 7%P APP + 3%P RDP are still sprayable without diluting. This is advantageous because of better reproducibility, and spraying also results in a more compact gelcoat microstructure and consequent lower heat release rate than brushing [4, 5]. All compositions reached the self-extinguishing V-0 classification during the UL-94 tests, and their LOI reached even 65 V/V%. According to these gelcoat results, we applied the two best-performing mixed compositions (6%P APP + 4% P RDP, 7%P APP + 3%P RDP), the reference and the gelcoat containing 10%P APP only on reference pentaerythritol (PER) based composites. These mixed compositions not only reduced the peak heat release rate (pHRR) and the time to the pHRR (Fig. 1.)

compared to the PER-based reference composite and the composite coated with reference SG715 gelcoat without flame retardant, but they also provided sprayability, flexibility, appropriate hardness and good adhesion to the composite substrate.

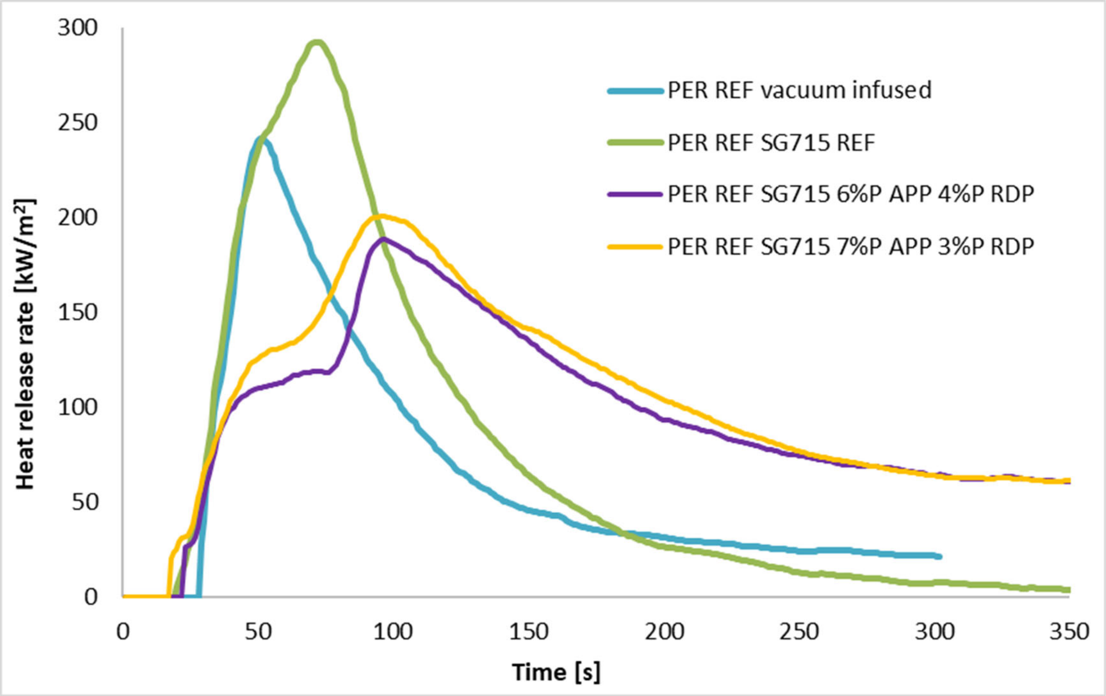

FIGURE 1. The heat release rate of the pentaerythritol (PER) based reference and flame retarded composites coated with ammonium polyphosphate (APP) and resorcinol bis(diphenyl phosphate) (RDP) containing epoxy gelcoats

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P46- NOVEL BIO-BASED PHOSPHORUS FLAME RETARDANT FOR POLY(LACTIC ACID)

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Main message: Novel bio-based phosphorus compound, derived from naturally sourced coumarin, is used as additive during PLA's manufacturing process to improve fire retardant properties in a one-step process. Incorporation of 10% wt. of the additive improves the thermo-oxidative stability and an LOI of 26 % is achieved.

Keywords: PLA, Bio-based, Phosphorus additive, Reactive extrusion, Fire retardancy

Introduction

Poly(lactic acid) (PLA) is an aliphatic polyester which derives from lactic acid. The interest for this bioplastic has increased in the last decade, as search for alternatives to oil-based plastics such as poly(ethylene) (PE) and poly(styrene) (PS), becoming compelling [1]. Not only, PLA has mechanical properties, which compete with these traditional polymers such as the tensile modulus [2], in addition, PLA is a bio-based, bio-compostable and bio-compatible polymer which bio-degrades back in lactic acid which is non-toxic. However, like most polyesters, PLA is also highly flammable preventing its widespread use in fire-safe applications such as in the automotive and electrical sector. In this work, we present a novel bio-based, halogen-free phosphorus FR [3] additive that added during the polymerization, grants in a one-step process, flame resistant PLA.

Experimental

PLA was synthesized via ring-opening polymerization (ROP) ((*L*)-lactide monomer, Tin(II) 2-ethylhexanoate catalyst were purchased from Sigma Aldrich) via reactive extrusion (REX) in a twin-screw extruder at 185 °C [4]. The phosphorus additive was added at a specific time during the polymerization process in order to mix thoroughly with the polymer melt. The fire properties were assessed using limiting oxygen index (LOI) measurements on hot pressed 6x1x0.1 cm^3 samples. Thermo-oxidative stability was assessed through molecular weight measurements after each processing step (from the extruded polymer, grinding, to hot pressing). Gel permeation chromatography (GPC) measurements were performed on around 2–4 mg of material, which were dissolved in 1 mL of hexafluoro-2-propanol (HFIP). The solution was injected, through the auto sampler, in a 1260 Infinity II High Temperature GPC System (Agilent Technologies, USA) equipped with a triple detector (refractive index detector, viscometer and light scattering detector). Measurements were performed with two Agilent PL Polypore (5 μm particle size) column (Agilent Technologies, USA) in series, after calibration with PS standards. The measurement conditions are the following: column temperature of 30 °C, flow of 1 $mL\cdot min^{-1}$ of HFIP with as the solvent, and injection volume of 100 μL.

Results and Discussion

Based on the LOI tests, it is shown that the incorporation of 10 % wt. of the phosphorus additive enhances the flame retardancy to 26% compared to the blank PLA, which has an LOI of 19% (in accordance to the literature values)[5]. The GPC measurements (Table 1) show that, the incorporation of the additive has an influence on the thermo-oxidative stability as seen by TGA results (not shown here) and the reduced molecular weight loss compared to blank PLA.
All of the results will be fully detailed in the communication.
Graphical abstract of the work (see Figure 1).

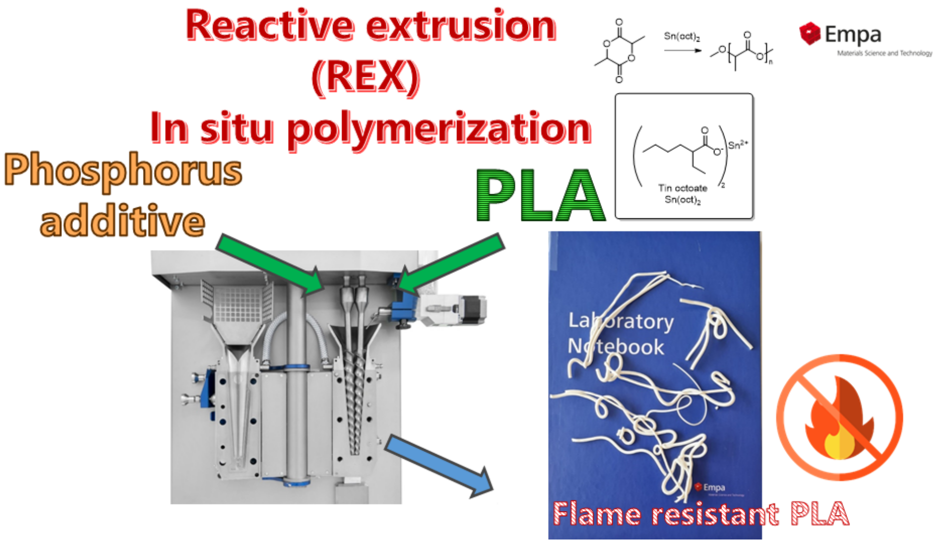

FIGURE 1. Graphical abstract of the *in situ* REX manufacturing process of flame resistant PLA with phosphorus FR

TABLE 1. Molecular weight average (M_w) comparison of the two PLA samples selected[1]

Polymer type	Sample Name	Average $M_w(\frac{g}{mol})$	Dispersity (*Đ*)
Blank PLA	Milled	105817	1.6
	Milled dried	111012	1.6
	Square plate	60496	1.6
	Round plate	60496	1.6
PLA + phosphorus additive	Milled	86886	1.6
	Milled dried	76774	1.6

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[1] Average was calculated on two GPC measurements of the same sample

	Square plate	56322	1.6
	Round plate	64981	1.6

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P47- TRANSFER OF THE MODES OF ACTION FROM POLYMER MATERIALS TO GLASS- FIBER-REINFORCED PLASTICS: FLAME RETARDANCY – FIRE RESISTANCE – POST-FIRE MECHANICS

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Main message: Fire resistance of fiber-reinforced polymers (FRPs) has been an important area of research for many years since FRPs are mainly used in the transportation and construction sectors. This study presents the fire behavior, and mechanical performance between the flame retarded pure epoxy resin and flame retarded glass-fiber composites before, during, and after a fire event. This enables a deeper understanding of the transferability of flame retardants on composite materials.

Keywords: glass-fiber reinforced polymer, flame retardancy, fire behavior, flammability, modes of action.

Introduction

FRPs are used mainly as structural components in ship and aircraft construction due to their exceptional mechanical properties. There has been significant research on flame retardants for pure epoxy resins. There have also been attempts to investigate the influence of flame retardants in fiber- reinforced composites. However, systematic studies on the transfer of flame retardants to FRPs are limited. Therefore, it is imperative to compare the fire behavior between the pure epoxy resin and FRPs.

Experimental

The processability of the epoxy resin DGEBA (DER-331) containing two flame retardants (ammonium polyphosphate (APP) and melamine polyphosphate (MPP)) was optimized using rheometric analysis to ensure that the viscosity remained below 50.000 mPa at 120 °C for prepreg production on a pilot scale setup. The processing parameters for resin and laminate curing were optimized based on rheology and DSC data to produce GFRP laminates of size 220 mm x 300 mm (length x width) in a pressurized autoclave with unidirectional (UD) non-woven glass fibers with an aerial weight of 640 gm^{-2}.

For the cone calorimeter, samples with a sample size of 100 mm x 100 mm x 4 mm (length x width x thickness) were measured in accordance with ISO 5660 in a horizontal position with an external heat flux of 50 kWm^{-2}. The thermal decomposition was determined by thermogravimetry using a TGA/SDTA 851. TGA coupled with a Fourier-transform infrared (FTIR) spectrometer was used for the evolved gas analysis. A sample with a mass of 10 mg was measured at a heating rate of 10 $Kmin^{-1}$ under nitrogen.

The flammability was determined by the oxygen index (LOI) following ISO 4589 with a sample size of 130 mm x 6.5 mm x 3 mm (length x width x thickness), and by UL-94 following IEC 60695-11-10 with a sample size of 125 mm x 13 mm x 3mm (length x width x thickness). For the investigation of the post- fire mechanics, samples with a sample size of 100 mm x 100 mm x 4 mm (length x width x thickness) were flamed at a heating rate of

30 kWm^{-2} for 7 minutes.

Results and Discussion

The modes of action, flame inhibition and char enhancement, and fire behavior of pure epoxy resins and FRPs with the flame retardants APP and MPP were investigated using a cone calorimeter. With this method, it is possible to investigate the heat release rate (HRR) and the total heat release (THR) vs. time. The HRR and THR of the flame retarded epoxy resins without glass fiber and flame retarded epoxy resins with glass fiber are compared in Figure 1.1. The presence of glass fiber reduced the HRR and the THR, thus the specimens with glass fiber maintained structural integrity for a longer time. The post-fire residue of the flame retarded epoxy resins with and without glass fibers from the cone measurements is compared in Figure 1.2. The residue with fiber-reinforced composite showed an accumulation of glass fiber and no carbonaceous residue, thus proving a worse char enhancement than the samples without glass fiber.

The pyrolysis of the epoxy resin with and without glass fibers was investigated using the TGA-FTIR. The addition of glass fiber led to an increase in both $T_{5wt.-\%}$ and T_{max} as well as a lower mass loss when the glass fiber was added to the epoxy resin. The reduction in mass loss results from the average glass fiber weight of 76 wt.-% in all the samples which acts as an inert filler. This results in an average mass loss of 14%, while the samples without glass fiber can have up to 80% mass loss.

The results for flammability in terms of UL94 and LOI show a significant difference between the epoxy with and without glass fiber. Samples without glass fiber yielded an average LOI of 25%, while samples with glass fiber yielded an average LOI of 38%. The UL94 classification was HB for almost all the samples due to long burning times and a wicking effect. Samples burnt at a heat flux of 30 kWm^{-2} showed an average reduction in tensile modulus, compressive strength, and toughness in comparison to the identical control samples.

The glass fibers show an enormous influence on the fire behavior and flammability of the composite materials and a change in the mechanical and rheological properties of the composite is also present. Therefore, it is imperative to investigate, understand and compare the fire behavior, flammability, and pre-and post-fire mechanics between the flame retarded composite material and the flame retarded neat epoxy resin to meet the demanding requirements for the transport and construction sector.

Acknowledgments

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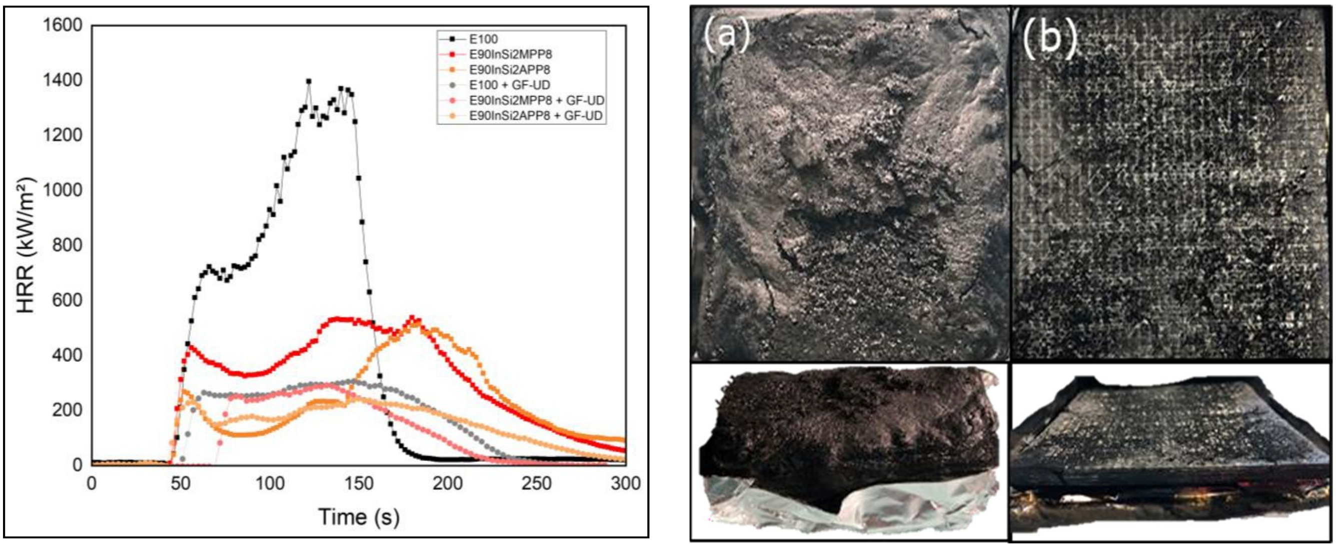

FIGURE 1. 1. Heat release rate (HRR) and total heat release (THR) vs. time of the flame retardant epoxy resin (■) without and (●) with glass fiber. 2. Comparison of the fire residue of DGEBA + 2% Inorganic silicate + 8% MPP (a) without and (b) with glass fibers.

P48- FIRE RETARDANT BASALT FIBER-REINFORCED POLYMER COMPOSITES

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Main message:

The overview of the literature reveals that there is a lack of comprehensive research on alternative fiber-reinforced polymers. In this present study, we have investigated the fire resistance of basalt fiber polymer composites (BFRP). Different forms of basalt fiber reinforcement (plain woven fabric, chopped strands, milled fibers) was used with an epoxy polymer matrix. The fire resistance of the produced composite materials was evaluated by horizontal burning test and mass loss cone calorimetry.

Keywords: basalt fiber, composites, mass loss cone calorimetry

Introduction

Inorganic basalt fibers are produced from natural, sustainable sources and obtain comparable mechanical performance to commercial glass fibers [1,2]. Basalt fibers possess higher thermal stability than glass fibers and have high chemical resistance due to the chemical structure originating from the volcanic gabbro. These favorable properties and moderate cost make BFRP composites an attractive group of structural materials for application in power, civil-construction and transport industries [3,4].

Experimental

Three different types of basalt fiber reinforcements were used in our experiments: milled fibers (Basaltex, Belgium, average fiber length: 108.57±57.09 µm), chopped fibers (Kamenny Vek, Russia, nominal fiber length: 12.7 mm), and plain-woven basalt fabrics (Kamenny Vek, Russia, areal density: 210 gsm). A common laminating epoxy system of component A-IPOX MR 3010 modified bisphenol A/F resin and component B-IPOX MH 3124 modified cycloaliphatic amine hardener (Ipox Chemicals GmbH, Germany) with mixing ration of 100:33 by mass, was used as polymer matrix. In the case of milled and chopped basalt fibers 10; 20; 30 m/m% fiber content was maintained, and dispersion of fibers was measured on five samples per material selected from different places of the plates. The short fibers were well dispersed as the standard deviation of the measured fiber content was below 0.5 m/m%.

Fiber distribution and interlaminar properties of hybrid laminates are compared with the plain-woven reinforced specimens by short beam shear tests and optical microscopy. The fire behavior of the materials was investigated by UL-94 horizontal burning tests and mass loss cone calorimetry.

Results and Discussion

Previously, the mechanical, thermo-mechanical and thermal shielding properties of the BFRP composites was investigated [5]. Fabric reinforced BFRP specimens achieved a flexural modulus of 15.54 GPa and strength of 336.40 MPa. Higher fiber content in hybrid laminates decreased the linear burning rate by 8%, and the maximum surface temperature was approximately 80 °C lower after jet fire impingement compared to woven reinforcement structure.

UL-94 horizontal burning test results show that the BFRP composites are rated HB according to the standard, but the linear burning rate of the different reinforcements varied significantly. Lower burning rates were achieved at higher fiber content. Highest flame spread was examined at the woven textile reinforced specimens due to the so-called candle-wick effect. The presence of milled fibers in hybrid laminates decreased the burning rate by up to 19%. The mass loss cone calorimetry test show that the total heat release rate (THR) of the specimens decreased with the increasing fiber content.

Acknowledgement: The research reported in this paper is part of Project No. BME-NVA-02, implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021 funding scheme. This research was also supported by the National Research, Development and Innovation Office (NKFIH FK 142517) and by the ÚNKP-22-5-BME-309 New National Excellence Program of The Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund. P. T-B. is thankful for the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (BO/00658/21/6).

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P49- Laboratory-scale instrumented bench for the evaluation of fire resistant systems

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Main message: Fire tests are required to evaluate materials in many sectors such as transportation, aeronautics, building, aerospace... However, fire testing is time-consuming and expensive (material, organization). It is therefore difficult to use it for the development a new concepts responding to a specific fire scenario[1]. Bench scale tests are developed and presented to provide innovative approach for developing new fire resistant systems.

Keywords: fire protection, scale reduction, infrared thermography, instrumentation

Introduction

For many years now, laboratories have been developing bench-scale fire tests to meet the growing need of industrial sector, reducing time and cost for new concept development. Moreover, the reduction of scale brings an important advantage allowing to study the phenomena involved to understand and optimize the systems. To do this, all the tests are or can be instrumented to characterize the fire behavior of the material in a specific fire scenario. Different instrumentation can be used during the tests such as infrared camera filtered or multispectral camera (Figure 1), high-speed camera, thermocouple (Figure 2), bi-chromatic pyrometer, gas analyzer. This instrumentation permits to observe and/or to characterize as examples intumescence, thermal barrier, cracking, erosion and so forth.

To address the issue of developing new materials with improved fire resistance, this paper aims to examine four fire scenarios and present the bench scale test developed to mimic the associated scenario.

Fire scenario at reduced scale

The fire performance of passive protection materials used for petroleum, petrochemical and gas plants for onshore and offshore installations have a critical issue because they must protect the structure in the case of a jet of flame caused by a hydrocarbon or gas leak (strong erosive jet associated to heat flux as high as 400 kW/m²). The bench scale test developed in the lab is the result of a collaboration with an industrial and a certification laboratory[2] according to ISO 22899-1:2007 Determination of the resistance to jet fires of passive fire protection materials (figure 3). It was shown that the bench is highly predictive and permits the development of new systems.

Fire safety in the railway is important to save lives in the event of an accident. The evaluation a material's ability to withstand a fire spreading along its surface is essential. For help the railway sector, a new bench scale test mimic the ISO standard 5658-2[3] allowing deveolpment of new concepts meeting the specifications described in the standard EN 45545-2.

The deployment of electric vehicles (EVs) in recent years has highlighted the fire risk of lithium-ion traction battery pack. Two scenarios are considered, the first one is the EV undergoing a pool fire under fire and the second one is an internal failure of the battery box involving a thermal runaway and then fire. To mimic those scenarios, the lab made a new test procedure based on GB/T 31467.3 for validating fire protective systems for lithium-ion traction battery pack.

The future brings us to the conquest of space. Fire safety during missions or commercial flights will be decisive. Based on the specific scenario of the space environment[4], the original bench scale test explores a fire scenario in oxygen-rich atmosphere (spacecraft for long term mission will be in atmosphere of 35% O_2 to reduce the total pressure). Hence it will create new hazards in case of fire. This test allows to follow heat release rate, gas and smoke production and then to develop new fire retarded materials

Conclusion

The bench scale tests, developed in the lab permits to successfully mimic various fire scenarios. Those tests allow to predict fire comportment of material during specific fire scenario test. Instrumented bench-scale tests developed in the lab will be presented and fully commented in the poster

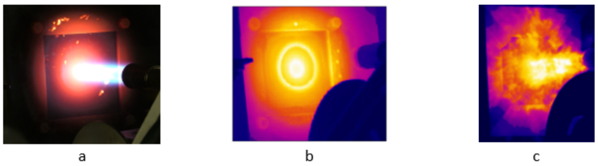

FIGURE 1. Specific instrumentation of bench with camera : a video camera, b Infrared camera with filter through the flame, c Infrared camera with filter of flame contour.

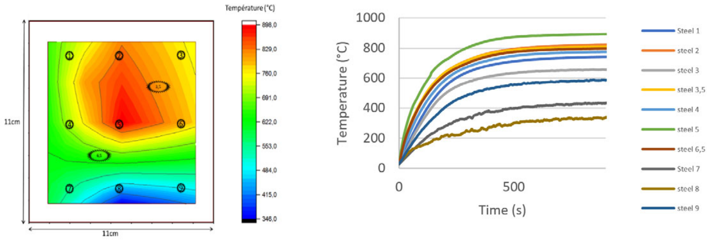

FIGURE 2. Temperature cartography obtained with thermocouple, on the backside of steel plate (10mm) on jet fire bench scale test.

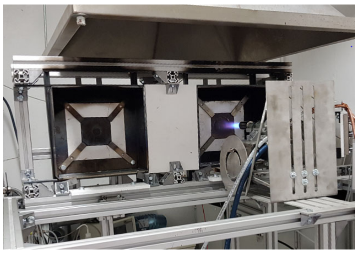

FIGURE 3. Extreme fire scenario at the lab scale according to Determination of the resistance to jet fires of passive fire protection materials to ISO 22899-1:2007

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P50- A new strategy to prepare fully bio-based Poly(lactic acid) composite with high flame retardancy, long service life and rapid degradation

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Main message: In this study, chitosan microspheres (CHTM) were first synthesized by the inverse emulsion cross-linking method and coated with phytic acid (PA) via a self-assembly reaction to produce PA@CHTM microspheres. PA@CHTM can simultaneously improve the mechanical properties, flame retardancy and UV-blocking properties of poly(lactic acid) (PLA), while accelerating the degradation of PLA in soil.

Keywords: Poly (lactic acid), sustainable, flame retardant, UV resistance, degradation in soil.

Introduction

As a fully degradable plastic, PLA is widely used in transportation, packaging, electronic packaging and many other applications. But PLA is highly flammable, with an LOI value of only 19%, and does not pass the vertical combustion rating. In addition, PLA is extremely sensitive to UV light, which significantly limits its use in outdoor environments. Most importantly, the natural degradation of PLA in the soil is prolonged, even taking decades, and artificial composting for degradation is labor-intensive. Based on these issues, preparing a multifunctional biodegradable PLA composite is of particular urgency.

Experimental

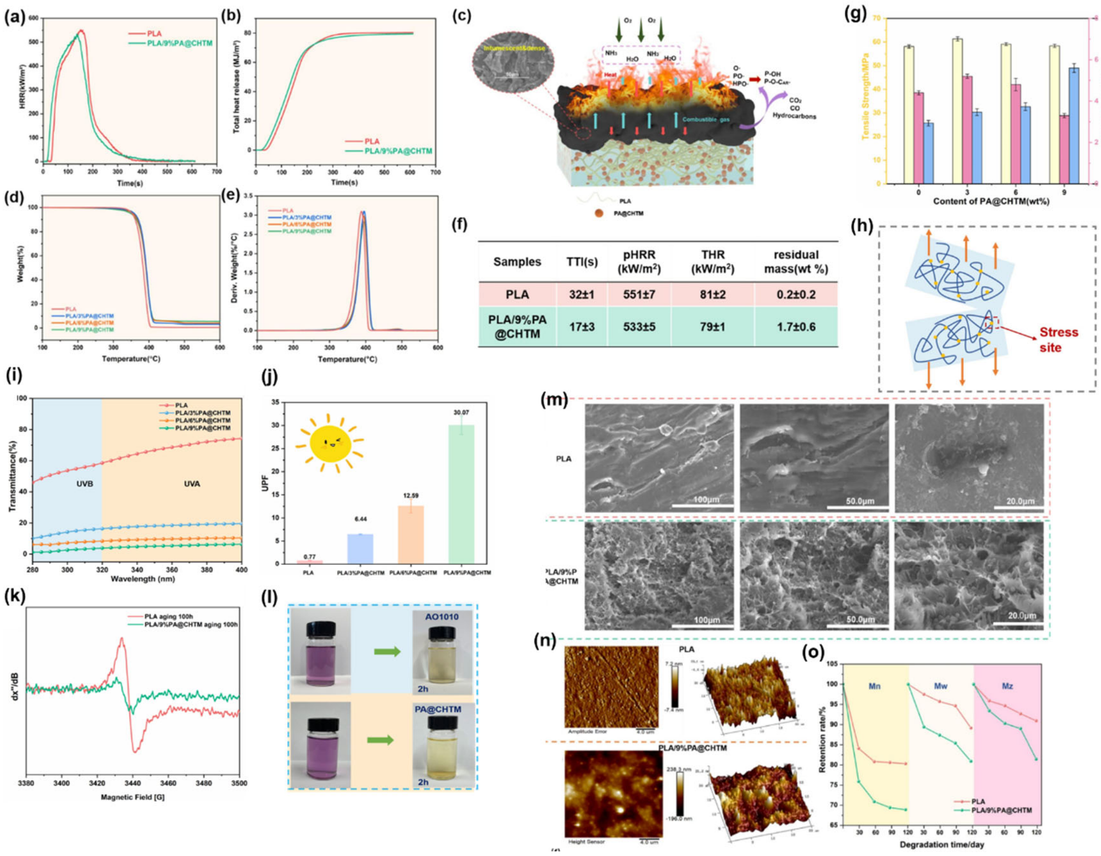
Firstly, Chitosan microspheres (CHTM) were synthesized by inverse emulsion polymerization of chitosan and glutaraldehyde. Then, a core-shell structure of micron-sized particles (PA@CHTM) was obtained by layer-by-layer self-assembly with phytic acid. Afterward, through melt blending PLA with additives, the multifunctional polymeric material was successfully prepared.

Results and Discussion

In this study, it was found that the introduction of PA@CHTM microspheres improved the thermal stability of PLA and enhanced its char formation during combustion, which helped to inhibit heat release (Figure 1(a)-(f)). In the presence of 9wt% PA@CHTM, the LOI value of the PLA sample was increased from 18.2% to 29.6%, reaching a V-0 rate in UL-94 testing. In addition, It can be seen from Figure 1(g)-(h) that the PA@CHTM microspheres were well dispersed in the PLA matrix, improving the rigidity of PLA while maintaining the tensile strength of the composite.

As exhibited in Figure 1(i)-(l), the introduction of PA@CHTM significantly improved the UV resistance of PLA. UV-VIS spectra showed a noticeable decrease in the UV transmittance and a nearly 30 times increase in the ultraviolet protection factor compared to pure PLA, which reached an ideal level. As for PLA and PLA composites irradiated at 500 W/m^2 UVA for 100 h, Figure 1(k) presented that the radicals on the surface of PLA/PA@CHTM were significantly less than PLA due to the excellent quenching ability of the PA@CHTM microspheres. The DPPH free radical indicator test showed that the free radical quenching ability of PA@CHTM was similar to that of the commercial antioxidant AO1010, allowing the microspheres to provide reasonable protection against UV catalytic degradation of PLA and prolong the life of the polymer.

Furthermore, the PLA and its composites were buried in natural soil for 30, 60, 90 and 120 days to observe the degradation process (Figure 1(m)-(o)). The GPC results showed that introducing PA@CHTM can significantly accelerate the degradation rate of PLA. After 120 days of burial, the number average molecular weight (Mn) was only 67% of the original, which was remarkably less than the 83% of pure PLA. The SEM images suggested that the PLA/9% PA@CHTM sample was severely degraded, with erosion and the appearance of continuous filaments on the surface. The reason for that was, on the one hand, the presence of PA@CHTM encouraged the accumulation of moisture around the PLA matrix; on the other hand, PA@CHTM, as a natural extract, was a good source of nutrients for microbial proliferation and accelerated the microbial erosion of PLA[1,2].



(f)

Samples	TTI(s)	pHRR (kW/m²)	THR (kW/m²)	residual mass(wt %)
PLA	32±1	551±7	81±2	0.2±0.2
PLA/9%PA @CHTM	17±3	533±5	79±1	1.7±0.6

FIGURE 1. HRR (a), THR (b) curves of PLA composites; possible flame retardancy mechanism of PLA/9%PA@CHTM (c); TG (d) and DTG (e) curves of PLA composites in N_2 flow; Key data of CONE tests for PLA samples (f); mechanical properties of PLA and its composite materials (g,h); the UVA and UVB transmittance curves (i), the ultraviolet protection factor (j), EPR spectra of PLA composites irradiated UVA for 100h (k), photographs of DPPH/ethanol solution for antioxidants, and PA@CHTM after 2h immersion (l); SEM and AFM images of PLA composites (m,n) buried in the soil after 120 days; retention rate of molecular weight for PLA and PLA/9%PA@CHTM (o).

Acknowledgement:

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P51- FIRE RESISTANT COMPOSITE MATERIALS FOR STRUCTURAL APPLICATION

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Abstract:

The National Composites Centre (NCC) is an independent, open-access technology centre delivering world-class research and development of composites. As part of the UK's Catapult innovation network, we offer our partners access to the latest technology, provide technical expertise and the business support they need to overcome barriers to innovation and accelerate their growth.

Our vision is to bring together the best mind and the best technologies to solve some of the world's most complex engineering challenges. We do this by digitally optimising composites design and manufacturing to create sustainable products; by building supply chains to deliver productivity and growth.

Growth in the use of composites has reached a level where they are now challenging the use of traditional materials. The drive to reduce the cost and increase the quality and structural performance of composites together with the emerging developments in polymer composites is the key factor supporting the increased use of FRP materials in various sectors such as aerospace, automobile, defence, marine and construction.

A major disadvantage of many composite material is poor performance in fire. When composites are exposed to heat the organics decomposes with the release of heat, smoke, soot and toxic volatiles. At the same time different sector demands different things from the materials. For example, trains are more concerned with smoke emission and opacity whereas planes are more concerned about heat generation, flame spread speed and structural integrity of materials.

NCC has the unique position of capturing requirements and providing solutions across many sectors. This study presents a review of widely used resin systems, the effect of fire on their material properties, as well as the use of different types of flame-retardant fillers and their compatibility with the materials and processing. Calorimeter tests have been performed to predict the fire classification of the materials to EN standards in order to screen material options at conceptual stage when developing materials solution for specific structural need with appropriate fire retardancy into it.

Keywords: Flame retardant additives, Flammability, FRP Composites

P52- DEVELOPMENT OF FULLY BIOBASED, FLAME RETARDANT EPOXY COATINGS

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Main message: Fully biobased flame retarded epoxy system was prepared using sorbitol polyglycidyl ether epoxy resin (SPE), and phytic acid (PA) was used as a reactive flame retardant (FR). Ammonium polyphosphate (APP) was added to the system to increase the charring ability of the bioepoxy resin. The flame retardancy was tested in bulk, and as 1-mm-thick coatings on steel. A LOI value of 55 was reached, and the back surface temperature reached only 350°C during the 1-hour-long measurement.

Keywords: bioepoxy, phytic acid, reactive flame retardant, coating, back surface temperature

Introduction

The high P-content (28%) of phytic acid (PA), known as inositol hexaphosphate, makes it a reasonable choice for use as a flame retardant. PA acts as an acid source and promotes the formation of a char layer when exposed to heat. Since its free P-acid functional groups are able to open the epoxy ring, it has been used as a reactive flame retardant, in other words as a P-containing crosslinker, in the production of bioepoxy resin.

Experimental

The flame retardant performance of the sorbitol polyglycidyl ether – phytic acid epoxy system, containing also ammonium polyphosphate was tested with standard LOI, UL-94 and mass loss type cone calorimeter tests. The bioepoxy compositions were applied as a 1-mm-thick coating on 1 mm steel plates. The heat barrier properties of the coatings were tested by measuring the back surface temperatures below the steel plates during a 1-hour-long cone measurement at 25 kW/m^2 heat flux.

Results and Discussion

According to the UL-94 and LOI tests, the fully bioepoxy system (having 1% P-content from the curing agent PA) reached only HB rating and an LOI of 24 V/V%. With the addition of 6% APP to the system (overall P-content 3%), the UL-94 rating reached V-0 and the LOI value increased to 39 V/V%. With 1% P more, the LOI was tremendously increased to 55 V/V%.

The results of the mass loss calorimeter tests showed significantly reduced and delayed pHRR values. With increasing APP content, the heat release of the system gradually decreases, the sample containing 9% APP (APP 3%P) reached a pHRR decreased by almost one third compared to the sample containing only phytic acid. In parallel, combustion becomes more prolonged, as illustrated by the flattening of the curves. Total heat release (THR) decreased by 39%, and the mass of post-combustion residues also increased significantly (Table 1.)

.

TABLE 1. Results of the mass loss measurement

Sample	**TTI** [s]	**pHRR** [kW/m^2]	**THR** [MJ/m^2]	**residue** [%]
SPE-PA ref.	96	287.8	25.2	9.4
APP (1%P)	95	180.2	23.8	11.3
APP (2%P)	96	153.3	21.9	17.2
APP (3%P)	100	104.7	15.4	31.4

The back surface temperature measurement showed significantly increased heat shielding of the coatings: by increasing the P-content of the system, the maxima of the detected temperatures decreased. The sample containing 4% P all together decreased the maximum from 470°C to as low as 350°C (Figure 1.)

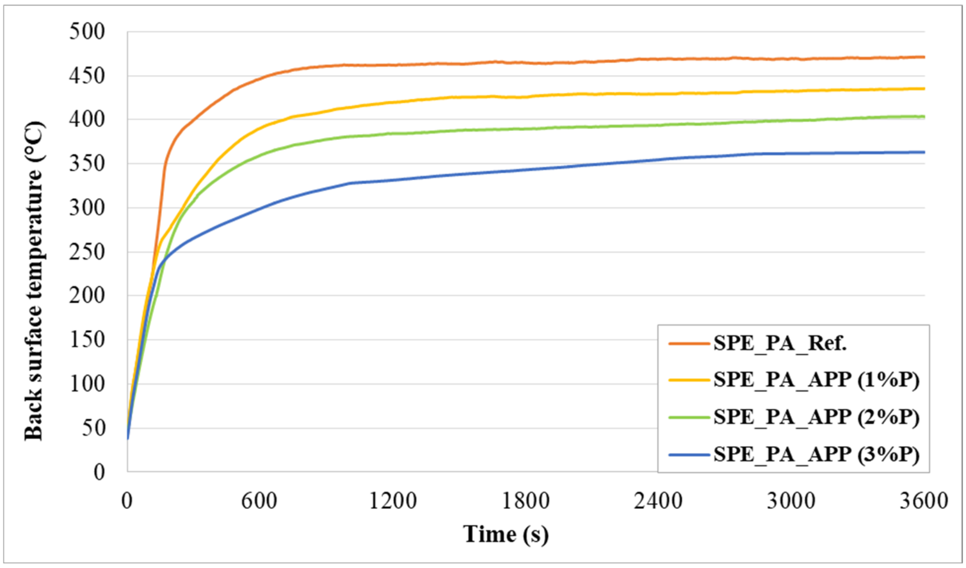

FIGURE 1. Back surface temperatures measured at 25 kW/m^2 heat flux

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P53- Thermal barrier fibrous membranes for polymeric composites

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Main message: Ceramzing nanomaterials, namely TiO_2, Al_2O_3 and ZnO were applied on aramid fibrous veils. Results have shown a significant improvement in the thermal barrier effects and reduction in thermal conductivities of the modified veils. The addition of ceramizing nanomaterials can enable these aramid veils to act as thermal barrier coatings for polymeric composites.

Keywords: Thermal barrier, nanomaterials, CFRPs, thermal conductivity

Introduction - Background

Carbon Fibre Reinforced Polymeric Composites (CFRP)s are commonly used in aerospace, owing to their significant weight saving properties over metallic structures. However, under extreme temperature and pressure, resin in CFRPs may soften and thermally decompose, leading to ignition. Surface coatings, chemical or ceramic thermal barrier coatings (TBC)s can be used to mitigate this risk. Ceramic coatings, such as Yttria-Stabilized Zirconia (YSZ), tend to have higher operating temperatures and can be effective physical barriers due to their low thermal conductivity and heat capacity values. Traditional ceramic coatings are not suitable to protect CFRPs as heat treatment of >1000°C is required to coat these traditional TBCs onto substrates, which is above the glass-transition temperature (T_g), and thermal decomposition temperatures of organic polymeric substrates and epoxy resins in CFRPs.

Ceramic nanofillers can be dispersed in a resin / binder and used as a surface coat to protect polymeric composites. Whilst these coatings have shown promising results, the nanofiller content cannot be high enough to completely covering the surface, which leaves the resinous part exposed to external heat. At high temperature, the exposed resinous component degrades and may ignite, compromising the overall thermal barrier effectiveness of the coating [1].

Instead, a novel method of applying inorganic ceramizing nanomaterials onto a high-performance substrate (coating or fibrous veil) is being researched which will negate the drawbacks mentioned above. These nanoparticles-modified fibrous veils will provide a physical barrier effect and inhibit the transfer of heat onto the CFRP substrate. Aramid was chosen as an initial candidate fibrous veil due to its high operating temperatures of up to 400°C and low thermal conductivity of ~0.025 W/mK [2]. Inorganic ceramic nanomaterials such as TiO_2, Al_2O_3 and ZnO have very low thermal conductivity as well and hence, have been selected as the initial candidate materials for incorporating into these novel TBCs.

Experimental

Sample preparation:

Non-woven aramid veil was supplied by Technical Fibre Products. This veil was then functionalised with either 2 mol. hydrochloric acid (HCl) and 20 wt% sodium hydroxide (NaOH) to introduce carboxylic reactive groups on the surface or sulfuric acid to introduce sulfonic reactive groups on the surface of aramid fibres.

The nanomaterials were then applied to the functionalised aramid veil by submerging in 5wt% Al_2O_3 or ZnO aqueous suspensions for 24 h. Samples were then dried and washed with water to remove excess nanomaterials. For TiO_2 coating, 5 wt% TiO_2 was dispersed in a solution of dopamine hydrochloride to produce a colloidal suspension. Functionalised aramid veil was then submerged in the suspension for 24 h. Reactive groups on the surface of the aramid react with the phenolic hydroxyl groups during esterification leading to a π-π reaction [3]. This process forms a thin film of polydopamine (PDA) on the surface of the aramid veil. Additionally, dopamine solution produces a PDA shell around the TiO_2 nanoparticles. Thus, *in-situ* polymerisation leads to a thin film of TiO_2 and PDA on the surface of the aramid veil.

Characterisation:
Fourier Transform – Infra Red (FTIR) spectroscopy was used to characterise chemical changes on the aramid fibre's surface due to chemical functionalisation.
Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray (EDX) was then used to study the presence and distribution of nanomaterials on the aramid surface.

Thermal properties characterisation:
Thermal conductivity (λ), a very important metric in determining the effectiveness of the nanomaterial coating on the veils, was measured using a TPS 3500 hot plate thermal conductivity system with a Kapton 7757 sensor.

Additional studies are currently ongoing, including exposure to a stead state heat source to directly measure the thermal barrier effect exhibited by these samples.

Results and discussion

Initial results on thermal conductivity (λ) are listed in Table 1. λ of uncoated aramid is 0.023 W/mK. ZnO and Al_2O_3 coated aramid samples shows a significant decrease in λ value. This shows that the additional ceramic nanomaterials provided an insulative thermal barrier effect. Additional tests are being carried out and will be presented at the conference.

TABLE 1. Thermal Conductivity at 22°C

Sample	**Thermal Conductivity [W/mK]**	**Area Specific Heat [MJ/m^3K]**
Uncoated aramid	0.023	0.247
ZnO	0.018	0.238
Al_2O_3	0.019	0.260
TiO_2 with Polydopamine	0.021	0.259

Acknowledgement: Funded by Defence Science and Technology Laboratory (Dstl), UK.

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P54- FIRE BEHAVIOR AND NUMERICAL SIMULATION OF FACADE ELEMENTS FOR BUILDINGS

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Main message: The external thermal insulation materials expand the fire propagation on the facade. An original test bench at intermediate scale is introduced to study the flame propagation on ETI samples. A series of experimental tests are then presented to understand the ignition process and to describe the thermal decomposition of materials. A numerical model is developed in COMSOL Multiphysics to study the distribution of heat flux towards the facade and the thermal insulation. Finally, proof-of-concept experiments with one commercial intumescent coating are presented for the fire protection of the facade.

Keywords: Ignition, Flame propagation, Fire test bench, Intumescent coating, Modeling.

Introduction

In Europe, the current trend is to increase buildings insulation in order to increase energy performance. Thus, the external thermal insulation (ETI) has been developed extensively. This potentially translates into an increase in the fuel mass and fire propagation on the facade because the insulation materials are generally derived from plastic (PE, EPS, PIR, etc.). Recent dramatic events, in particular the Grenfell Tower Fire [1], remind us of the importance of addressing the fire issues as a whole.

The ignition of solids is now well understood but only for simple and rather academic cases [2]. Experimental tests at small scale are recommended, for majority of the construction material, to test their reaction to fire. After its ignition, the fire spreads on the combustible. One of the key points is the heat and mass exchanges between the flame and the wall. The flame heat flux to the solid drives the temperature rise inside the material, leading to its thermal decomposition and pyrolysis. This heat flux is due to convection and radiation of the flame.

In this context, the objectives of the present paper are to understand the ignition process, to determine key parameters and properties as well as to describe the thermal decomposition process of ETI elements at small scale.

More other, a specific test bench at intermediate-scale has been developed to analyze, for ETI sample, the thermal decomposition and the flame propagation, under controlled conditions.

Experimental

At the small-scale: the thermal decomposition is investigated by TGA-FTIR and DSC. The fire reaction is studied using Cone Calorimeter. New insulation materials are developed by introducing an intumescent material. The experimental data is used to analyze material flammability, ignition and burning behavior and to characterize the kinetics of the decomposition.

At the intermediate-scale: a prototype that capitalizes on this concept by combining a plane radiant heater with a horizontal and rotational motion, in order to study the degradation and the flame propagation on ETI samples when they are thermally stressed by a controlled fire source.

Results and Discussion

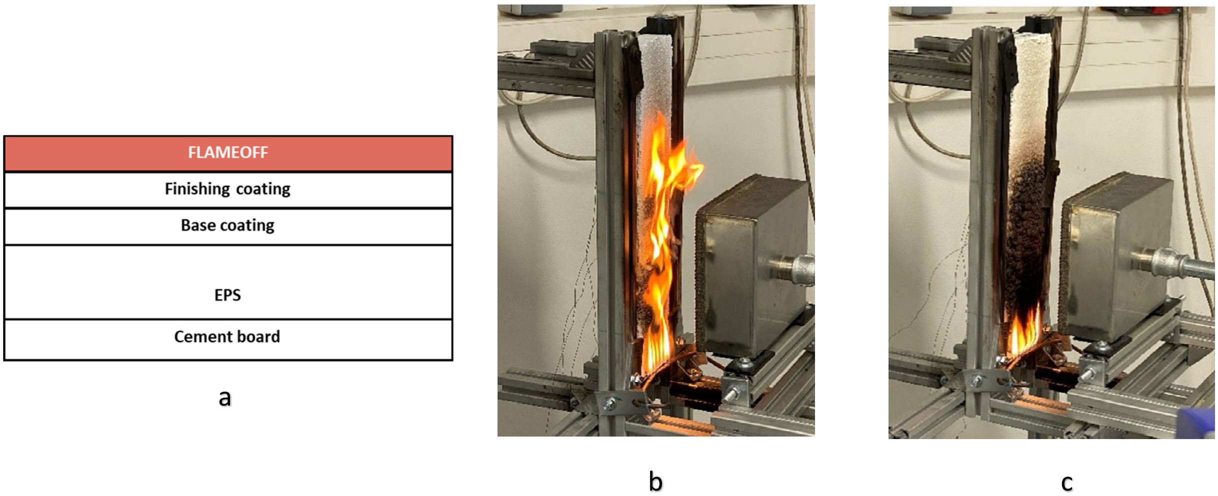

Figure 3 a) Structure of ETI, b) Original ETI and c) Intumescent coating ETI face to a plane heater at 8cm

For all intermediate-scale experiments, the test bench is shown in Figures 1b and 1c. Adjusting the inclination and distance makes it possible to expose the sample to heat flux-time curve defines in fire safety standards.

The commercial ETI structure is shown in Figure 1a. A 50cm height, 10cm width and 4cm thickness EPS is used as ETI substrate, attached to cement board. Two different 1.5mm polymer coatings are applied on the surface. For the original facade, confronting the plane heater of 46.5 kw/m^2 at 8cm, the substrate begins to pyrolysis rapidly, especially EPS, and release combustible smoke, where the ignition occurs. The flame heats upward the unburned area and induces a new pyrolysis reaction.

With a 1mm FLAMEOFF coating, when substrate is heated, a loose char layer is formed on the surface, which slows down heat transfer and prevents ignition. Most of the substrate is thus preserved.

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P55- COMBINED EFFECT OF PHOSPHOROUS-CONTAINING COMPOUNDS IN FLAME RETARDANCE OF POLYBUTYLENE SUCCINATE

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Main message:
The rise of new biobased materials to substitute the durable petrochemical thermoplastics inevitably drives the research for their flame retardance as it's a key element for their application in the industry. Polybutylene succinate (PBS) like many other biopolymers, is highly flammable, melts and drips during burning which increases the chances of flame spreading. To evaluate and improve flame retardance, it's important to identify how the flame retardant additive interacts with the polymer in the presence of fire. In our research, we aim to understand how PBS degrades during combustion and how different phosphorous-containing flame retardants exert their effect on the PBS and its degradation. The realized advantages of these flame retardants with different mechanisms are then combined to improve the flame retardancy of PBS.

Keywords: Polybutylene succinate, phosphorous flame retardants, combined mechanism

Introduction

Polymers derived from renewable resources are increasingly used in many fields due to their environmental benefits. The flame retardancy of these biobased materials is a key element for their application in the industry. Among the biobased polymers, polybutylene succinate (PBS) is gaining increasing attention as an alternative to petroleum-based plastics in recent years, however, its high flammability and the fact that it melts and drips during burning increases the chances of flame spreading [1]. To evaluate and improve flame retardance, it's important to identify how the flame retardant additive interacts with the polymer in the presence of fire.

Phosphorous-containing flame retardants are a broad and expanding class of flame retardants with different flame retardant mechanisms acting in either or both the gas and solid phase. There is a wide variety of phosphorus compounds in which the phosphorus atom can be in several oxidation states and the phosphorus content of the additives varies in a wide range. However, the phosphorus content alone does not allow us to conclude the effectiveness of the flame retardant; it depends on many factors, such as the mechanism of action, the matrix in which they are embedded, and the materials they are combined with [2].

Experimental

The PBS is loaded with commercially available phosphorous-containing flame retardants with different main mechanisms and thoroughly studied in thermal analyses, laser pyrolysis-FTIR coupled method, and combustion studies (UL94, LOI, MLC) to understand the flame retardant mechanisms. The realized advantages of these investigated flame retardants with different mechanisms are then combined to further improve the flame retardancy of PBS. Potential functionality addition on the flame retardants is considered to enhance the flame retardancy.

The main route to improve the flame retardancy of the PBS is to hinder its rapid degradation by melting and dripping which indicates rapid chain breaks during the combustion. While the intumescent flame retardants are helpful through the formation of a charred layer which prevents the diffusion of oxygen, flammable gases and heat, the gas phase-acting flame retardants achieved better impact in the initial stage of combustion, by delaying the formation of volatile flammable gases that feeds the flame. We believe that the flame retardancy of highly flammable materials lies in the combined effect of flame retardants with different mechanisms.

Acknowledgement: The project was funded by the National Research, Development and Innovation Fund of Hungary in the frame of TKP2021-NVA-02, 2019–1.3.1-KK-2019–00004 and GINOP_PLUSZ-2.1.1-21-2022-00041 projects. The research was funded by the Hungarian Scientific Research Fund, grant number FK128352.

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P56- SYNTHESIS OF SUSTAINABLE FLAME RETARDED POLYPROPYLENE BY USING WASTE MATERIAL

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Main message:
The use of a waste material as flame retardant (FR) for polypropylene (PP), i.e. flue gas desulfurization (FGD) gypsum, has been studied. FGD gypsum has been used alone or in combination with melamine cyanurate (MC) and a phosphate ester (SolDP) to find a UL94-V2 rated PP. The flame retardancy action of MC and SolDP can be, indeed, further strengthen by the presence of FGD filler.

Keywords: waste, flame retardant, gypsum, polypropylene, synergy.

Introduction

Recently, due to a growing environmental concern, in order to improve flame retardants' (FRs) sustainability, several approaches have been suggested: some of them are based on the use of FRs obtained from renewable raw materials (1), while others proposed the use of waste (2,3). Indeed, using a waste as a source of FR instead of a critical raw material will certainly increase the natural resources saving. Therefore, the aim of this work is to substitute traditional FRs with waste.

Experimental

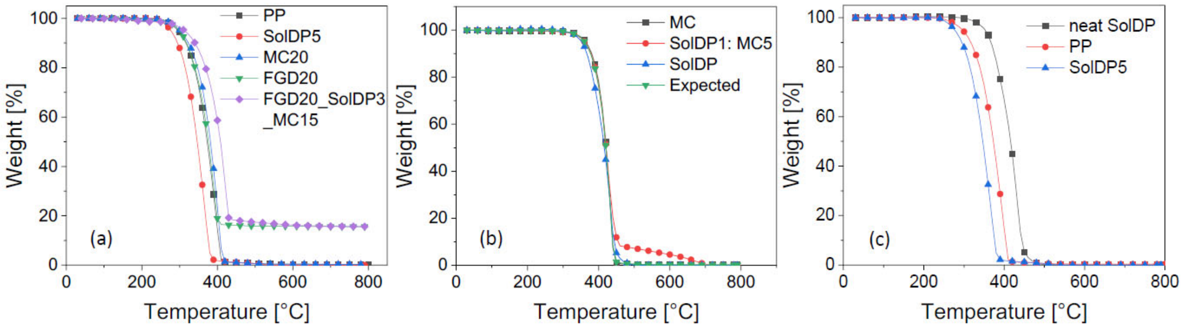
Formulations comprising different amounts of FGD (15-60%) have been prepared as well as formulations where FGD are used together with other FRs (Melamine cyanurate (MC) and an oligomeric phosphate ester called SolDP, which acts both as FR and plasticizer). For comparison, also PP filled with only MC (15-30%) and/or SolDP (5% maximum) have been studied. All formulations have been prepared by Plastograph Brabender setting the temperature at 180°C, mixing time at 10 minutes and screw speed at 50 rpm. The fire behaviour of flame retarded PP have been characterised by UL94 tests. The thermal stability of neat FRs and PP filled samples have been evaluated by thermogravimetric analysis (TGA) in order to study each additive's mechanism of action and the interactions that may occur between them. Some examples of the formulations studied are reported In Table 1.

Results and Discussion

The use of FGD as FR for PP has been studied and verified. FGD act as FR not only by releasing water of crystallization through an endothermic process, but also generating an inorganic layer at higher temperature. Thus, shielding the polymer from the flame and preventing or hindering the diffusion of oxygen toward the polymer surface, this layer protects the polymer from the ongoing degradation.

The results have also shown that the control of dripping phenomenon is essential and therefore a suitable plasticizer (SolDP), acting also as FR, shall be used in this system. Indeed, by considering the UL94 rating of FGD filled samples, it can be noted that FGD contents higher than 15wt% are able to guarantee the extinguishment of the samples after the first flame impingement. However, the FGD filler alone is not enough to reach UL94- V2 rating because of the long second extinguishment time. The apparently surprising result for the highest FGD content (60%) can be rationalized considering that such high amount raises the melt viscosity of the decomposing polymer, inhibiting its tendency to drip, which is the common mechanism that promotes extinguishment in V2-rated PP (4). The same consideration can be drawn analyzing the results obtained using MC alone or FGD-MC. The use of a plasticizer is so needed to decrease the melt viscosity, in order to favour the second self-extinguishing time by drops formation. The content of the plasticizer shall be optimized since, from one side, it favours dripping but, on the other side, it tends to decrease the heat stability of the polymeric matrix when used at high content: TGA curve of PP-5SolDP is shifted toward lower temperatures compared to that of pure PP and SolDP (Figure 1c). Furthermore, a synergy between SolDP and MC has also been revealed: TGA analysis of SolDP-MC mixture shows the presence of a higher weight residue than the expected one at temperature above 430°C (Figure 1b). Finally, a higher thermal stability has been demonstrated by TGA analysis when FGD, MC and SolDP are used together, since the curve is shifted toward higher temperatures (Figure 1a).

Summarizing, the results have demonstrated that 20wt% of FGD is the optimal content to be used together with 15wt% MC and 3wt% SolDP to get UL94-V2 PP material. The flame retardancy action of MC and SolDP can be, indeed, further strengthen by the formation of an inorganic layer formed after FGD decomposition, which is essential in guarantee the good fire reaction obtained.



Sample	PP [%]	FGD [%]	SolDP [%]	MC [%]	t1 [s]	t2 [s]	V2 Rating
FGD20	80	20	0	0	7	> 30	No
FGD60	40	60	0	0	> 30	---	No
MC15	85	0	0	15	12	> 30	No
MC30	70	0	0	30	> 30	---	No
FGD25_MC15	60	25	0	15	> 30	---	No
FGD20_SolDP5_MC15	60	20	5	15	8	8	Yes
FGD20_SolDP3_MC15	62	20	3	15	6	9	Yes
FGD20_SolDP1.5_MC15	63.5	20	1.5	15	>30	---	No

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P57- Optimization *via* artificial intelligence of intumescent coatings for wood substrates

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Main message: The development of new materials requires a large amount of experiments representing a major issue to innovate. This is particularly true for complex material formulations such as intumescent coatings that could contain a number of ingredients. Artificial Intelligence based optimization and in particular Bayesian Optimization techniques appears as efficient methods to optimize such complex systems. In this study, this method has been used as a multicriteria techniques to optimize the chemical composition of a fire protective coating for wood substrates.

Keywords: Intumescent coating, Wood, Artificial Intelligence, Bayesian Optimization

Introduction : The development of fire protective systems for wood is nowadays crucial and represents a major concern of scientists working in the field of fireproofing due to the increasing use of this material in building structures including multi-storey buildings. Among the various systems that are reported to improve the fire behavior of wood, intumescent systems represent an efficient approach. However, to find the optimal formulation of a complex systems such as intumescent coatings that could contain a number of ingredients, is not an easy task and can be time consuming. Moreover, the behavior of materials in case of fire may vary depending on the considered scenario leading to complicate the problem. In this context, Bayesian Optimization (BO) framework appeared as an efficient strategy [1,2]. The objective of this study is thus to demonstrate that BO can be used to optimize the chemical composition of an intumescent coating developed for the fire protection of wood for various fire scenario.

Experimental

Since the objective of the study is to demonstrate the interest of the approach and not to develop new intumescent systems, a well-known intumescent formulation, based on ammonium polyphosphate, dipentaerythritol and melamine has been used [3]. The formulation space and raw materials used for the preparation of the coatings are detailed in Table 1. The fire performance of white fir wood coated with intumescent coatings (230g/m²) is evaluated using three different fire testing methods. First, the fire performance of the coated wood samples exposed at an external heat flux (50 Kw/m²) is measured in both horizontal and vertical mass loss calorimeter test. Then, the flame propagation is evaluated using a lab-made small scale radiant panel test (similar to the ISO5658-2).

***Table 1** : Formulations of the coating*

Ingredients	wt min (%)	wt max (%)
Ammonium polyphosphate (APP)	20	30
Dipentaerythritol (DiPER)	5	15
Melamine	5	15
Emultex FR 728 (vinyl acetate/ VeoVa)	10	20
Titanium dioxide	0	10
Water	35	45

Results and Discussion

An artificial intelligence methodology was chosen to optimize the chemical composition of the paint, according to an active loop (Figure 1).

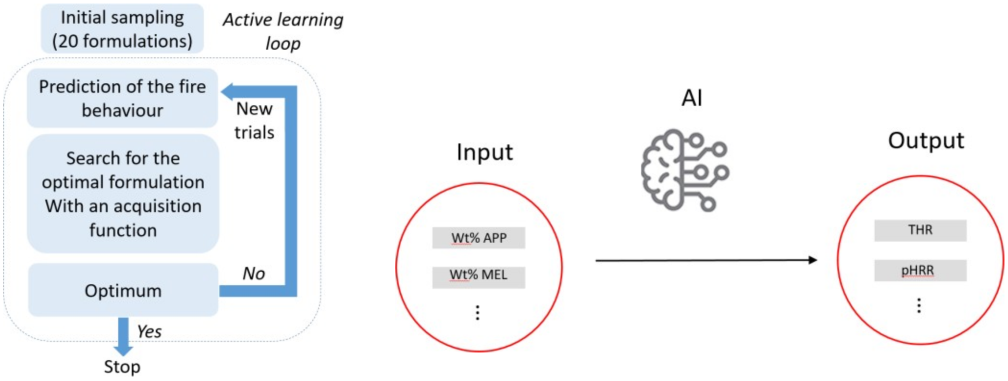

***Figure 1.** Pipeline of Experimental Design via Bayesian optimization (EDBO)*

The first step of the study consists in the set-up of a database. For that purpose, an initial sampling is made of 20 formulations chosen randomly in the formulation space reported in Table 1. The fire performance of the formulations is determined according to the three scenarios previously defined. The optimization is done on 7 parameters. Mass loss calorimeter test includes the determination of the peak of heat release rate (pHRR), total heat release (THR) (for the horizontal set- up); mass loss rate (MLR) (for the vertical set-up) and the time to ignition (ti) (for both configuration). Moreover, as mentioned before the flame propagation is measured by a small scale radiant panel test to determine the critical flux at extinction (CFE) and the virgin wood surface area. To measure this later parameter, the sample is cut and a picture is taken. A machine learning algorithm called K-means clustering is used to cluster each pixels in 2 categories: burnt wood and preserved wood (Figure 2). The virgin wood surface area is determined as the ratio between the preserved wood and the initial surface of the corss section of the panel.

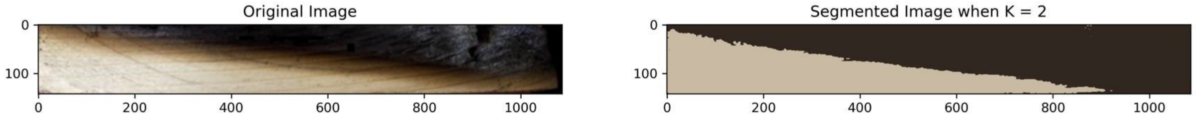

***Figure 2 :** Example of the machine learning algorithm used*

The process consists then to train a Gaussian Process regressor (GPR) with this database to predict the fire behavior according the weight percentage of each compound.

The second step of the approach consists in maximizing an acquisition function that trade off exploitation and exploration. At each iteration a new experiment is suggested by the algorithm which improve the model. This learning is done until the convergence of the system, which is given by a constant value of the acquisition function.

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P58- BIO-SOURCED INTUMESCENT NANOCOATING [1]

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Main message: Nylon–cotton fabric (NYCO), commonly used in military uniforms and workwear, presents an inherent fire risk due to its high flammability. A novel, water-based layer-by-layer assembled 15 quadlayer (QL) coating, consisting of bio-sourced chitosan (CH), phytic acid (PA), and tannic acid (TA), is applied to NYCO. This coating self-extinguishes in a vertical flame test, with only 16.6% weight added, yielding 91% residue and a 51% decrease in peak heat release rate through the synergy of TA and PA.

Keywords: flame retardant, green chemistry, nylon-cotton

Introduction

NYCO has inherent flammability risk due to a "scaffolding effect" resulting from degradation mechanisms of both cotton and nylon. The present study examines a QL flame retardant nanocoating for NYCO composed of the sustainable components CH, PA, and TA. This treatment demonstrates the potential of completely renewable flame retardants to render challenging polymers self-extinguishing and acts as an environmentally benign replacement for more cumbersome and toxic systems in current use.

Experimental

A 3.5 × 14 inch piece of NYCO was plasma treated for 5 min at low power to establish a negative surface charge using a PDC-32G Plasma Cleaner (Harrick Plasma, Ithaca, NY). The fabric was then immersed in a 5 wt% polyethylenimine (PEI) primer solution for 5 min to impart a positive surface charge. This primed fabric was then passed through DI water to rinse off loosely adhered material and manually squeezed to remove excess solution. Next, the fabric was immersed in a 4 wt% PA solution for 5 min and rinsed. The fabric was then immersed in a 1 wt% CH solution for 5 min and rinsed. The fabric was then immersed in a 4 wt% TA acid solution for 5 min followed by a rinse step. This completed the first QL. For subsequent QLs, the PEI solution was replaced with the 1 wt% CH solution and all dip times were reduced to 1 min. Solutions and rinse water were changed after depositing 1, 5, and 10 QL to avoid fouling. Once 15 QL were deposited, the fabric was dried in a 70 °C oven for 4 h. For controls, NYCO samples were coated in 30 BLs of CH/PA and CH/TA, using the same primer treatments (plasma and PEI). Characterization methods including ASTM D6413-15 12 s vertical flame test, micro-scale combustion calorimetry using method A of ASTM D7309-21a, and thermogravimetric analysis coupled with a mass spectrometer (TGA-MS) were performed to determine the flammability properties of coated NYCO. Other techniques such as scanning electron microscopy (SEM), fourier transform infrared spectroscopy, and differential scanning calorimetry (DSC) were used to gauge other coating characteristics.

Results and Discussion

A conformal 15 quadlayer coating of CH, TA, and PA was applied to nylon-cotton fabric through a layer-by-layer assembly process with controls of uncoated NYCO and 30 bilayer coated CH/PA and CH/TA NYCO. The QL coating had a weight gain of 16.6% after application, whereas the coated controls both had around 3% weight added with the bilayer (BL) coatings. Increased weight added with the QL coating is believed to be attributed to the hydrogen bonding potential of tannic acid with the combined electrostatic interaction of phytic acid with each other and chitosan. In addition, substrate color change, from beige to purple, observed with the deposition of the QL suggests chemical structural changes from the interaction between the two anionic acids, as shown in Figure 1d. Further customization and evaluation of the coating process was performed to promote hydrogen bonding potential and confirmed its effect on the weight gain and performance. SEM imaging confirmed the deposition and conformity of the QL coating, as well as the minimal deposition of the two coated controls.

Thermal and flame properties of the coated versus uncoated material were gauged through a standard 12 s VFT, in which the uncoated NYCO and bilayer coated samples burned completely (Figure 1e-g). The QL system was self-extinguishing with an average char length of 4.5 inches and an average percent reside of 91.4% (Figure 1h). SEM imaging of char from each sample showed a more smooth, voluminous char forming with the use of both tannic and phytic acid in the system, compared the web-like char of the uncoated NYCO. MCC shows that the addition of the PA BL and the QL results in an additional heat release peak forming (Figure 1i). Additional char formation occurs with the QL coating resulting in an average char yield of 30.6% (Table 1). Furthermore, the QL coating reduces the THR of NYCO by 40% and the fire growth capacity (FGC), a material's potential to ignite and perpetuate a fire, to almost half of the uncoated sample's FGC (Table 1). TGA-MS shows that the QL coating's flame retardant mechanism is heavily influenced by the presence of phytic acid, with an elevated water ratio during a heating ramp. The QL also shows the increased release of other inert gases like CO2, a byproduct of the degradation of tannic acid. In conclusion, tannic and phytic acid, in conjunction with chitosan, have a synergistic effect to help render NYCO self-extinguishing with an added benefit of being completely bio-sourced.

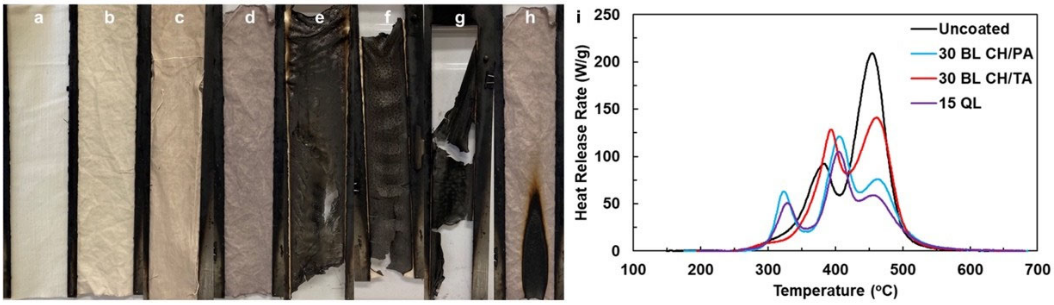

FIGURE 1. *Pre- and post-flame test images of NYCO samples: uncoated (a,e), CH/PA (b,f), CH/TA (c,g), and 15 QL (d,h). Representative plots of HRR as a function of temperature in the microscale combustion calorimeter for the various NYCO samples (i).*

TABLE 1. *MCC data for uncoated and coated NYCO samples.*

Sample	**Char Yield [%]**	**HRR Peaks [W/g]**	**THR [kJ/g]**	**FGC**
Uncoated	11.5 ± 0.2	87, 213	17.3 ± 0.3	168 ± 5
30 BL CH/PA	25.5 ± 0.1	64, 121, 77	12.5 ± 0.2	110 ± 1
30 BL CH/TA	14.9 ± 0.1	125, 141	15.7 ± 0.2	151 ± 2
15 QL	30.6 ± 0.3	50, 104, 58	10.5 ± 0.4	92 ± 3

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P59- LIQUID S-TRIAZINE PHOSPHONATE DERIVATIVES AS FLAME RETARDANTS FOR POLYURETHANE FOAMS

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Main message:

Especially for Construction applications PU rigid foams based on polyurethane and polyisocyanurate have to be flame retarded to fulfill the challenging FR standards. Beside an efficient flame-retardant effect, the flame retardants must meet many other requirements like storage stability, processability, low costs and low environmental impact. Here we report a one-step and solvent-free synthesis of symmetrical and asymmetrical substituted *s*-triazine phosphonates and preliminary investigations on their flame retardant effects on polyurethane and polyisocyanurate rigid foams.

Keywords: *s*-triazine, phosphonates, polyurethane

Introduction:

Liquid flame retardants are often used in polyurethane (PUR) and polyisocyanurate (PIR) rigid foams due to good processability. Chlorinated phosphate esters like tris(2-chloro-1-methylethyl) phosphate (TCPP) belong to the most widely used compounds. However, liquid nitrogen-rich compounds for flame retardant applications are rare.

Experimental:

For the synthesis, Schlenk technique was used with argon as inert gas. However, the reactions and purification methods can also be carried out at atmospheric conditions. The compounds were characterized by ^{1}H, ^{13}C and ^{31}P NMR, ATR-FTIR and EA. TGA measurements were performed with a TG 209 F1 from Netzsch in a nitrogen atmosphere. The heating rate was 10 K/min and the sample mass was about 5 mg.

Results and Discussion:

A Michaelis-Arbuzov reaction [1] was used to obtain symmetrical and asymmetrical substituted *s*-triazine phosphonates from alkyl phosphites and cyanuric chloride by an one-step reaction. The educt alkyl phosphite itself and the byproduct alkyl chloride was used as solvent during the reaction. No additional solvent must be used. Symmetrical substituted *s*-triazine phosphonates are obtained by a quantitative turnover of an alkyl phosphite with cyanuric chloride at a ratio of 3 to 1, as already reported in the literature [2]. We could show that asymmetrical substituted *s*-triazine phosphonates (see Figure 1) are obtained by a quantitative turnover of a mixture of two and three different alkyl phosphites with cyanuric chloride at a ratio of 2:1 to 1 and 1:1:1 to 1. NMR measurements indicate that asymmetrical substituted *s*-triazine phosphonates were obtained.

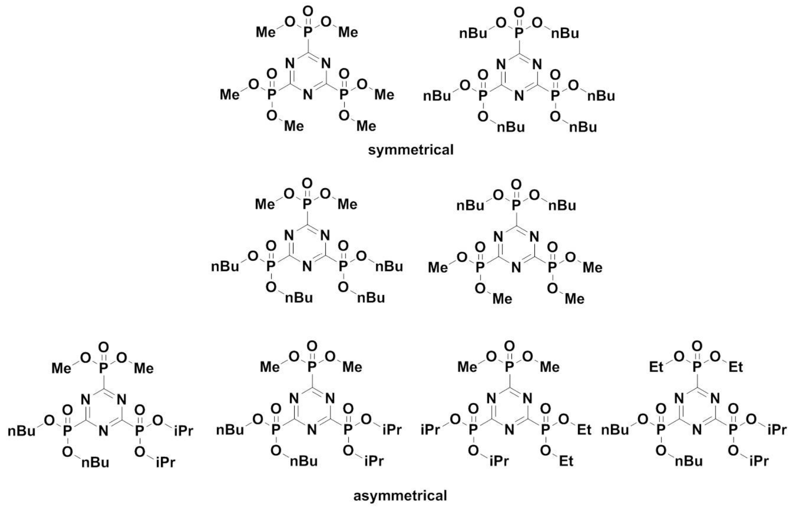

FIGURE 4. Symmetrical and asymmetrical substituted *s*-triazine phosphonates

The thermal behavior of some of the symmetrical and asymmetrical substituted *s*-triazine phosphonates is given in Table 1. By varying the phosphonate groups, the thermal degradation behavior of the *s*-triazine phosphonate and thus the starting point of flame retardant effects can be adjusted as required.

TABLE 1. TGA results of liquid s-triazine phosphonates

#	T_{onset} / °C	$T_{@98\%\ residual\ mass}$ / °C	Residue at 250 °C / %
s-Triazine(nBu)$_3$	239	215	42.9
s-Triazine(Me)(nBu)$_2$	234	170	50.7
s-Triazine(Me)(iPr)(nBu)	183	179	58.1
s-Triazine(Me)(Et)(iPr)	177	177	65.7
s-Triazine(Et)(iPr)(nBu)	194	157	54.0

Table 2 shows flame retardant test results of PUR and PIR rigid foams containing symmetrical and asymmetrical substituted *s*-triazine phosphonates. Rigid foams with 5% to 7.5% of a *s*-triazine phosphonate pass the DIN 13501 class E test

TABLE 2. Flame retardant test results of lab scale PUR and PIR rigid foams

#	FR content / %	ρ(foam) / g/L	LOI / O_2%
PUR foam	0	86	18.9 ± 0.38
PUR + *s*-Triazine(nBu)$_3$	5	91	20.8 ± 0.27
PUR + *s*-Triazine(Me)(nBu)$_2$	5	103	21.3 ± 0.27
PIR foam	0	51	21.3 ± 0.27
PIR + *s*-Triazine(nBu)$_3$	5	52	22.3 ± 0.27
PIR + *s*-Triazine(Et)(iPr)(nBu)	5	61	24.9 ± 0.38

Acknowledgement: This work was supported within the Fraunhofer and DFG transfer programme (DFG project number KR1739/35-1).

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P60- FRPData AND PyGen: BENCHMARK DATABASE FOR STUDYING POLYMER FLAME RETARDANCY AND PYROLYSIS PRODUCTS

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Main message: In this work, we first established a datasets containing about 2,000 polymer flame-retardant structures/properties, screened 361 sets of linear polycondensates, and then obtained 25,278 sets of pyrolysis products using the pyrolysis generator (PyGen). The 25278 pieces of pyrolysis products are split into 2199 sets of minimum flame-retardant primitives through the primitive generation module, and then these flame-retardant primitives are used to train to generate about 50k sets of flame-retardant structures (FRSSpace). The flame retardancy information of these polymers and FRSSpace will be a good benchmark database for studying polymer flame retardancy informatics and pyrolysis products.

Keywords: Flame-retardant performance database, combustion product database, pyrolysis product generator, flame-retardant structure space

Introduction

The research on flame-retardant modification of traditional polymers mainly follows the processes: designing the flame retardant structure, synthesizing the polymers, characterizing flame retardant properties, researching the flame-retardant mechanism, and then returning to the optimization, which is very time-consuming and laborious. Materials informatics uses massive data combined with machine learning to quickly generate new materials that meet certain standards, but the biggest challenge of polymer informatics at present is the lack of easy-to-access databases. Many polymer databases[1] have been developed for multiple studies based on polymer informatics. However, these databases performing quantitative structure-property-relationship regression tasks are not suitable for the study of polymer flame retardancy. 1) There is a lack of polymer structure and performance test data related to flame retardancy; 2) The precise design of flame-retardant structures with flame-retardant potential depends on a full understanding of the combustion process.

Therefore, we constructed a dataset of polymer pyrolysis products and flame retardant properties to help promote machine-learning research on polymer flame retardant information and experimental research on flame retardant modification. We collect about 2,000 polymer structures and their flame retardant properties (FRPData), and then use 361 of them to generate 25,278 pyrolysis products by our homemade pyrolysis products generator (PyGen) to compose the pyrolysis product dataset. To accurately design the chemical structure for flame-retardant modification, we improve the BRICS rule to generate 2199 different sets of flame-retardant "primitives" for PyGen, and then use them to train the assembly model to generate about 50,000 (50k) flame-retardant structures(FRSSpace). PyGen and FRSSpace will be future data-driven benchmark testbeds for polymer flame retardancy informatics.

Experimental

Flame retardant performance information comes from published literature and our laboratory research results. The main pyrolysis products of Py-GC/MS of 33 typical linear condensation polymers were obtained from open literature, and the pyrolysis products of different repeating units were generated by the pyrolysis generator.

The generation of PyGen is obtained from the split generator we built. The pyrolysis generator will first identify different polycondensate types, perform different pyrolysis reactions according to different polycondensate types, and generate 25278 pyrolysis products. The flame-retardant primitives are decomposed by PyGen in the primitive generation module, and these flame-retardant primitives are trained in the assembly model to generate FRSSpace.

Results and Discussion

The flame retardant performance database contains many typical homopolymeric linear polycondensates, LOI, T_g, Tm, $T_{5wt\%}$ (N_2), T_{max} (N_2), 808 effective information on the flame retardant performance of CR. The data distribution of flame retardant properties in Figure C shows that there is a linear relationship between different flame retardant properties, which provides data support for exploring the correlation of flame retardant properties.

When the polymer is heated to a certain temperature under the action of an external heat source, the weak bonds of the polymer chain begin to break, as shown in Figure A, the solid-phase chemical decomposition reaction occurs rapidly, and the decomposed flammable gas is the source of fuel for the fire. According to the different types of thermal decomposition reactions of typical linear polycondensates (Figure B), we constructed pyrolysis reaction generators. Comparing the Py-GC/MS data of 33 typical condensation polymers with the pyrolysis products obtained by the pyrolysis generator, we demonstrate that the pyrolysis products in PyGen can help researchers focus on the study of polymer pyrolysis products of interest. We converted all pyrolysis products into informative sequences with molecular fingerprints, and then visualized them in 2D space by t-SNE, as shown in Figure D. From the figure, we can see that the main pyrolysis products obtained by Py-GC/MS are completely covered by the pyrolysis products obtained by the pyrolysis generator, which has good extrapolation performance. The flame-retardant primitives are composed of the minimum flame-retardant structures similar to those in Figure E. These minimal expressions that form chemical structures are connected and trained as assembly blocks in the assembly model, and a huge chemical structure space is formed through the intelligent screening process of machine learning decision-making. As shown in Figure F, we can see that the generated flame-retardant space is uniform and has many types, which helps to study different flame-retardant researchers of flame-retardant modification systems can speed up the design of flame retardant modification efficiency.

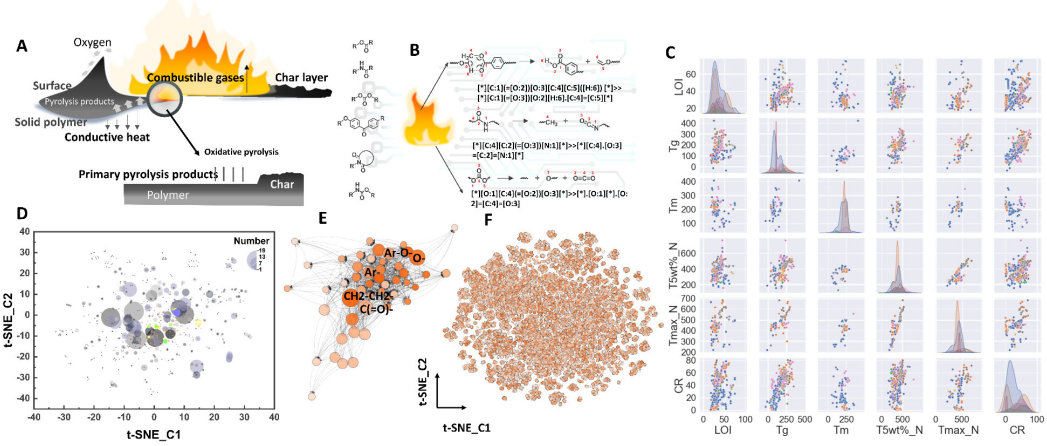

FIGURE 1. Database construction process.

Acknowledgement:

The National Science Foundation of China (51827803).

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P61- POLYMER-HYBRID NANOPARTICLES AS FLAME RETARDANTS FOR TRANSPARENT THERMOPLASTICS

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Main message: This joint project focuses on the development of halogen-free flame retardants for the application in transparent thermoplastics. Silica nanoparticles (Si-NPs) shall be equipped with flame-retardant active groups based on (organic) phosphorus and incorporated in polycarbonate (PC), polymethylmethacrylate (PMMA) and a transparent polyamide (PA) without compromising the transparency of the corresponding polymers.

Keywords: transparent thermoplastics, flame retardants, silica nanoparticles, PC, PMMA.

Introduction

Due to their low density and impact resistance, transparent thermoplastics are widely used in electronics, construction and mobility sectors.[1,2] However, most polymers are highly flammable making the use of flame retardants necessary.[3] Common halogen-free flame retardants impair mechanical properties and reduce transparency of the polymers.[4] The aim of this project is to develop a set of flame-retardant systems which conserve the mechanical and optical properties of transparent thermoplastics.

Experimental

Si-NPs with or without encapsulated hydrophilic flame-retardant reagents are synthesized via the *Stöber* process and functionalized with (polymeric) hydrophobic flame-retardant active moieties to be incorporated by extrusion into PC, PMMA and PA. The composites will be analyzed with respect to their mechanical and optical properties (tensile tests, haze & clarity measurements). Flammability tests will be performed according to UL94-V. MCC, TGA-FTIR measurements and ash analysis will give insights into the flame retardancy mechanism.

Results and Discussion

Current investigations show that by surface functionalization of silica nanoparticles with epoxy, amino and thio moieties, their compatibility with the polymer matrix of PC and PA already improves. Thus, we aim at functionalizing Si-NPs with flame-retardant active hydrophobic groups, either with low molecular weight or polymeric moieties, to enable a dispersion of the nanoparticles in transparent polymers conserving their transparency and mechanical properties. In order to enhance flame retardant efficiency, hydrophilic flame retardants or flame-retardant synergists can additionally be encapsulated into the silica nucleus during the *Stöber* process (Figure 1).

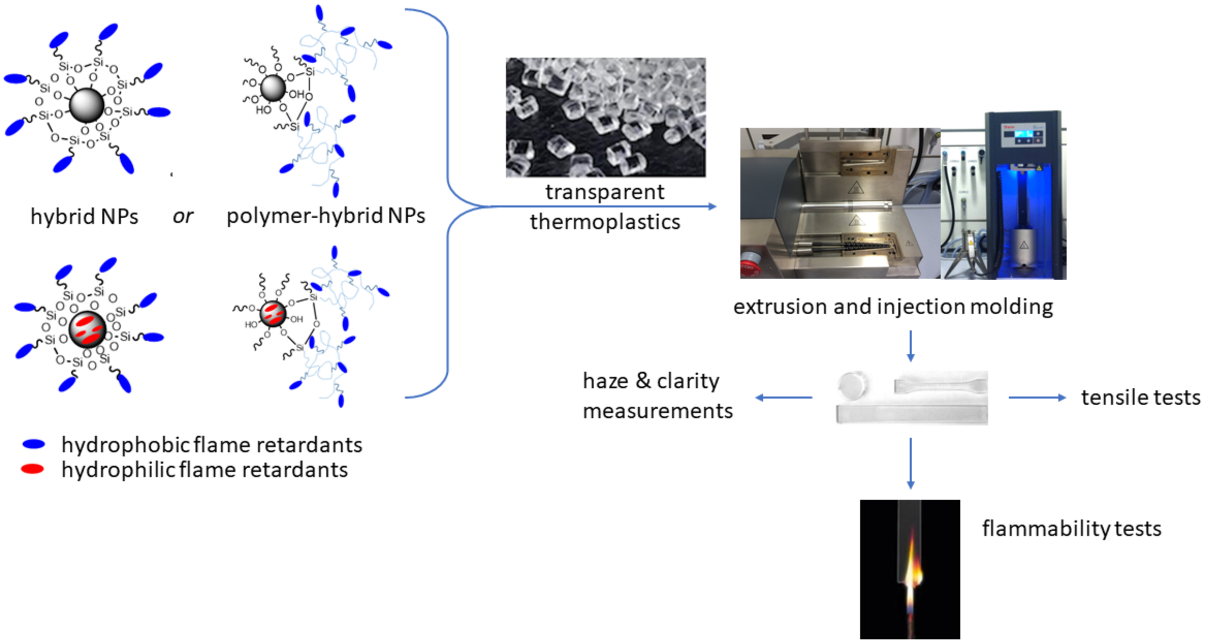

FIGURE 1. Surface-functionalized flame-retardant active silica nanoparticles with and without encapsulated hydrophilic flame retardants – processing by extrusion and injection molding with subsequent analysis.

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P62- Low heat and smoke release polycarbonate copolymer based on synergistic char-forming effect

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Main message

Polycarbonate with low heat and smoke release is highly desired in the application fields like airplane and high-speed rail. Reported herein is a novel flame-retardant strategy based on the synergistic char-forming effect between a functional monomer PPN and polysiloxane, which endowed expected low heat and smoke release to the resultant polycarbonate. The successful application of this method offers new perspectives for the preparation of flame-retardant polymers.

Keywords: polycarbonate, flame retardant, low heat and smoke release

Introduction

Polycarbonate (PC) has found wide applications in various fields due to its great overall properties, however, its flame retardancy, especially high heat and smoke release, is insufficient for applications in special fields[1, 2]. In this work, we designed and synthesized a novel flame-retardant monomer PPN and prepared the corresponding PC copolymer with the further incorporation of linear polysiloxane (BDMS). As expected, PPN and BDMS showed high flame-retardant efficiency in the condense phase, and successfully inhibited the release of heat and smoke.

Experimental

PC copolymer was synthesized by melt polycondensation. Cone calorimetry test is carried out under a heat flux of 50 kW/m^2 with sample size of 100*100*3 mm^3 according to the ISO 5660-1:2015 standard. Smoke density is tested under a heat flux of 50 kW/m^2 in the smoke density box with sample size of 75*75*3 mm^3 according to the ASTM E662-21ae1 standard.

Results and Discussion

The flame retardancy of PC-*co*-PPN-*b*-BDMS$_5$ was first investigate by UL-94 vertical burning test and limiting oxygen index (LOI) test. Pure PC exhibited certain flame retardancy, and passed the UL-94 V-2 rating and achieved a LOI value of ~26.0%. The incorporation of PPN and BDMS significantly inhibited the melt dripping behavior and improved the self-extinguishing performance of PC-*co*-PPN-*b*-BDMS$_5$, which successfully passed the UL-94 V-0 rating and achieved a high LOI value of 36.5%.

The heat and smoke release performance of PC-*co*-PPN-*b*-BDMS$_5$ was evaluated by cone calorimetry test (CCT) under a heat flux of 50 kW/m^2[3]. As shown in Figure 1 and Table 1, owing to the early decomposition of PPN and BDMS, the time to ignition (TTI) of PC-*co*-PPN-*b*-BDMS$_5$ largely decreased. As expected, the introduction of PPN significantly reduced the peak heat release rate (pHRR, Figure 1a) value of PC-*co*-PPN-*b*-BDMS$_5$, and the pHRR values of PC-*co*-PPN$_{20}$-*b*-BDMS$_5$ and PC-*co*-PPN$_{40}$-*b*-BDMS$_5$ were 334.3 and 219.6 kW/m^2, which were 65.1% and 42.8% to that of pure PC (513.0 kW/m^2). The total heat release (THR) exhibited a similar trend, where the THR values of PC-*co*-PPN$_{20}$-*b*-BDMS$_5$ and PC-*co*-PPN$_{40}$-*b*-BDMS$_5$ significantly decreased by 72.0% and 65.5% to that of pure PC, respectively. The total smoke release (TSR) of PC-*co*-PPN$_{20}$-*b*-BDMS$_5$ and PC-*co*-PPN$_{40}$-*b*-BDMS$_5$ decreased by 63.8% and 55.4% compared with pure PC respectively. Smoke density was further used to evaluate the smoke release of PC-*co*-PPN-*b*-BDMS$_5$. As shown in Figure 1d, the maximum smoke density (Ds$_{max}$) decreased from

915.5 of pure PC to 483.5 and 277.6 of PC-*co*-PPN_{20}-*b*-$BDMS_5$ and PC-*co*-PPN_{40}-*b*-$BDMS_5$, respectively. Such a low Ds_{max} was able to meet the FAR 25.853(d) standard requirement, powering the potential application of PC-*co*-PPN-*b*-$BDMS_5$ in high-end fields like airplane and high-speed rail. The flame-retardant mechanism investigation revealed that, during burning, PPN first decomposed to form a solid char layer through the rearrangement reaction which prevented the release of flammable volatiles, then BDMS formed cross-linked structures to further enhance the char layer. The synergistic effect between PPN and BDMS significantly inhibited the heat and smoke release of PC-*co*-PPN-*b*-$BDMS_5$.This work provides a novel strategy for preparing polycarbonate with high flame retardancy.

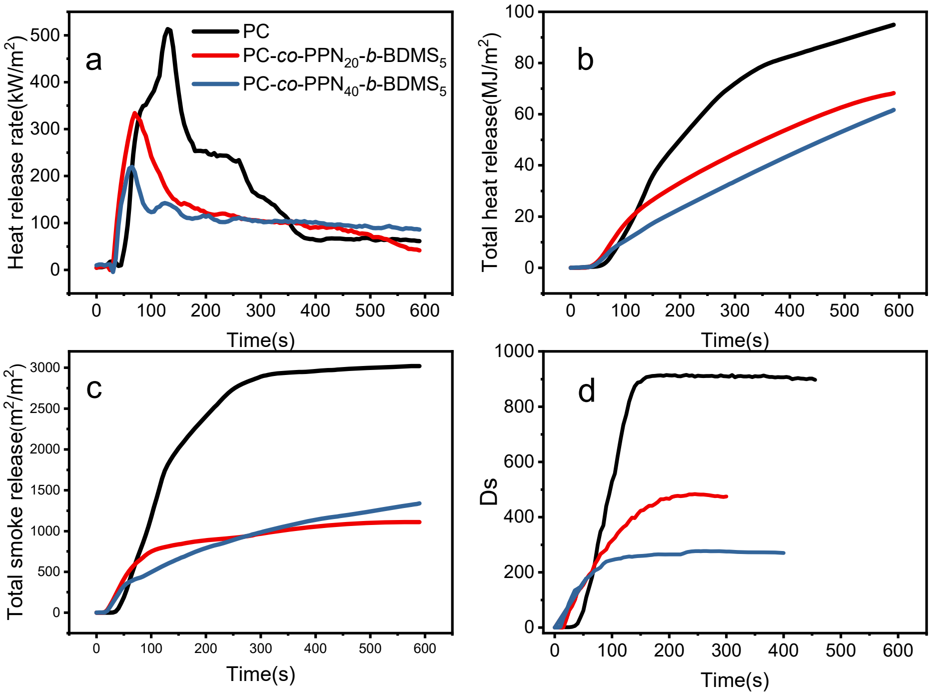

FIGURE 1. Heat release rate (a), total heat release (b), total smoke release (c) curves obtained from cone calorimetry test under a heat flux of 50 kW/m^2, and smoke density (d) curve of pure PC and PC-*co*-PPN_n-*b*-$BDMS_5$.

TABLE 1. Detailed heat and smoke release results of pure PC and PC-*co*-PPN_n-*b*-$BDMS_5$.

Sample	**TTI [s]**	**pHRR[kW/m^2]**	**THR[MJ/m^2]**	**TSR[m^2/m^2]**	**Ds_{max}**
PC	33	513.0	94.6	3032.5	915.5
PC-*co*-PPN_{20}-*b*-$BDMS_5$	17	334.2	68.1	1096.5	483.5
PC-*co*-PPN_{40}-*b*-$BDMS_5$	17	219.6	61.6	1353.1	277.6

Acknowledgment:

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P63- FIRE RESISTANCE OF NA/K BASED GEOPOLYMER CONTAINING OIL

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Main message:

Novel formulations of geopolymers containing vegetable oil are investigated as fire protective coatings for steel – The effects of geopolymer composition (Na or K metasilicate) on the thermal properties are determined - Vegetable oil is proved to improve the fire resistance of geopolymer coatings.

Keywords: Geopolymer, Metakaolin, Vegetable oil, Fire resistance, Thermal conductivity.

Introduction

Building structures made of steel may collapse under fire because of the loss of mechanical properties of steel at high temperature, hence requiring fire protection. One way to solve this issue is to use fire resistant coating materials [1]. Geopolymer (GP) binders, generally obtained by the alkali-activation of a powdered aluminosilicate source (e.g. metakaolin) with a highly alkaline aqueous solution, have been evidenced as efficient thermal barriers [2]. They are therefore good candidates as fire protective coating. As a way to improve current GP formulations, this study investigates the effect of vegetable oil incorporated in GP on the fire-resistance of the coating. To this purpose, the fire resistance and thermal parameters of different GPs are evaluated, by varying the nature of the alkali-activating solution (Na or K metasilicate) and by incorporating varying proportions of oil. Vegetable oil is chosen because it may be sourced as a locally available organic liquid waste from the food industry. Its saponification in GP is well known, but it does not affect GP setting [3].

Experimental

The raw materials used in the formulations are metakaolin powder (Argical M1000, Imerys, France), silica fume (Condensil, France), potassium metasilicate aqueous solution (Betol 5020T, Woellner, Germany), sodium metasilicate aqueous solution (Betol 39T, Woellner, Germany), potassium hydroxide pellets (purity of 99%, Sigma Aldrich), and sodium hydroxide pellets (purity of 99%, Sigma Aldrich).

Two series of GP based on potassium and sodium metasilicate solutions were prepared, while incorporating different percentage of vegetable sunflower oil (0/10/20/40wt%).

The heat conductivity is measured by the Hot Disk thermal constants analyzer (TPS2500, Sweden) from Thermoconcept (Bordeaux, France). It is based on the transient plane source method.

The burn through test [4] is used to evaluate the fire resistance of the GP coatings. It is designed to mimic the aeronautical (jet fuel) fire test defined in the ISO2685:1998 standard.

Results and Discussion

For each of the two categories of geopolymer (Na-based and K-based) with different percentages of oil, volumetric masses (density) and thermal conductivity were evaluated to explore the effects of the nature of the metasilicate solution (either based on sodium or potassium cations) and of the oil amount. An example of the results obtained is given in Figure 1. Finally, the burn through test is performed to characterize the fire resistance of the GP-oil coatings. The main results are as follows:

(i) The density measurement shows that a higher amount in oil results in a decrease in density, in agreement with the fact that the oil has a lower density than the GP (and a density lower than 1).

(ii) The values of average thermal conductivity as a function of oil mass content (Figure 1) shows that there is a decreasing linear relationship between the two. The more oil is added, the lower the thermal conductivity of the GP-oil composite. This is in good agreement with the lower thermal conductivity of oil alone, compared to GP. Also, in good agreement with the literature, K-based GP has a consistently lower thermal conductivity compared to Na-based GP, meaning that K-based GP is a better thermal insulator than Na-based GP.
(iii) For 30 minutes of burn through test (propane flame of 1100°C; heat flux of 116 kW/m^2 in the steady state – not shown),the incorporation of 20wt% oil induces a temperature reduction of 70°C at the back of the GP-coated steel plate, compared to virgin steel.

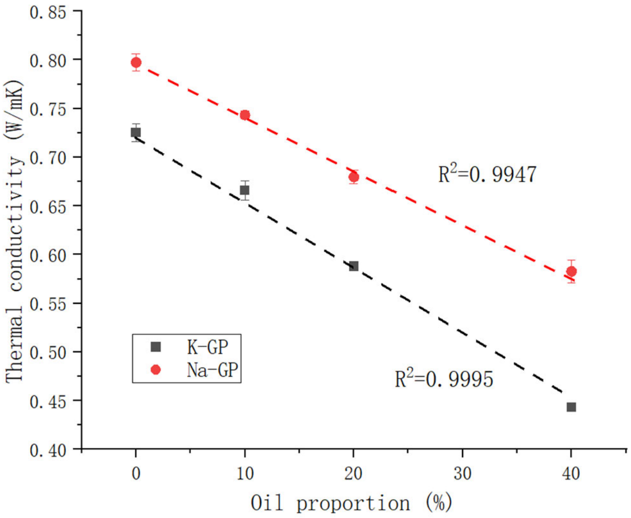

FIGURE 1. Average thermal conductivity of K-GP and Na-GP incorporated with 0/10/20/40wt% vegetable oil (3 samples per data point)

As a conclusion, GP coatings incorporated with oil can provide fire protection to steel structures to a certain extent. However, cracking occurs during the fire, which proves that such structure is fragile and needs to be improved. The results of fire resistance and associated analyses will be fully developed during the presentation.

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P64- High-performance flame-retardant polyamide 6 containing a novel phosphinamide group

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Main message:

It has been a long-sought objective to achieve both outstanding flame retardancy and excellent mechanical properties for polyamide. Herein, a novel phosphinamide-containing reactive flame retardant, named DR, was designed, synthesized, and used to fabricate a high-performance and multifunctional polycaprolactam (PA 6) copolymer (PA 6-*co*-DR). The introduction of DR brings high flame retardancy and great processability to PA 6-*co*-DR at low monomer content. More importantly, the hydrogen bond density of PA 6-*co*-DR was not influenced, therefore high mechanical strength is maintained. Taking these advantages, this strategy provided a new perspective for the design and synthesis of PA 6 with great overall performances.

Keywords: flame retardant, mechanical properties, spinnability

Introduction

Polyamide 6 is a kind of thermoplastic synthetic polymer, which has been widely used in various industrial and civil fields due to its outstanding advantages[1]. However, the aliphatic linear structure brings the high flammability of PA 6, such as the easy ignition, and the serious melt-dripping behaviors during combustion, thus severely restricting the applications in some special fields[2, 3]. Although the incorporation of phosphorus-containing groups into the molecular chain is regarded as an effective way to achieve high flame retardancy of PA 6, other properties like mechanical properties and spinnability usually deteriorate due to the disruption of intermolecular hydrogen bonding of polyamide chains[4]. Therefore, improving the overall properties of PA 6 is highly desired.

Herein, a novel functional monomer with phosphinamide group has been synthesized and incorporated into the molecular chain of PA 6. On the one hand, the phosphorus-containing groups can achieve a scavenging effect of free radicals at high temperatures, which significantly improves the flame retardancy of the resultant polyamide. On the other hand, due to the maintenance of the hydrogen bond density, the tensile strength and flexural strength of the PA 6-*co*-DR_2 were increased by 27% and 35%. In addition, the tensile strength of the resultant PA 6 fiber was also increased by 12.1%, indicating great mechanical properties and spinnability.

Experimental

PA 6-*co*-DR was synthesized through conventional melt polymerization using caprolactam, adipic acid, and DA salt as raw materials, and H_2O as the catalyst. In the first stage, the mixture was heated at 220–260 °C for the ring-opening reaction of caprolactam, then heated at the same temperature with the purge of nitrogen to remove small molecules, and finally, the pressure was reduced to conduct the polycondensation until finish.

Results and Discussion

As shown in Figure 1a, the incorporation of DR monomer effectively improves the flame-retardant properties of PA 6-*co*-DR. During the UL-94 vertical burning test, PA 6-*co*-DR_2 and PA 6-*co*-DR_3 easily achieved a V-0 rating with great self-extinguishing properties, and the melt drips of PA 6-*co*-DR were significantly suppressed. Similarly, in the LOI test, pure PA 6 is a flammable material with an LOI value of only 21%. The LOI values of PA 6-*co*-DR_1, PA 6-*co*-DR_2, and PA 6-*co*-DR_3 improved to 25.0%, 26.1%, 26.8%, respectively.

Owing to the high compatibility of the DR monomer with the PA 6 chains and the maintenance of hydrogen bond density, the mechanical performance of PA 6-*co*-DR slightly improved compared with pure PA 6. As shown in Figure 1b-c, the tensile strength and tensile modulus of the PA 6-*co*-DR_2 increased by 27% and 37%. Moreover, the flexural strength and flexural modulus of PA 6-*co*-DR_2 were as high as 113.1 MPa and 3869.0 MPa, respectively.

PA 6-*co*-DR exhibited typical shear-shinning phenomenon, indicating its great processability. More importantly, the PA 6-*co*-DR fibers were easily pulled out from a high-pressure capillary rheometer, confirming its great spinnability. As shown in Figure 1d, PA 6-*co*-DR_2 fiber showed a high tensile strength of 5.02 cN/dtex, and the elongation at break of PA 6-*co*-DR fibers gradually increased with the increase of DR content.

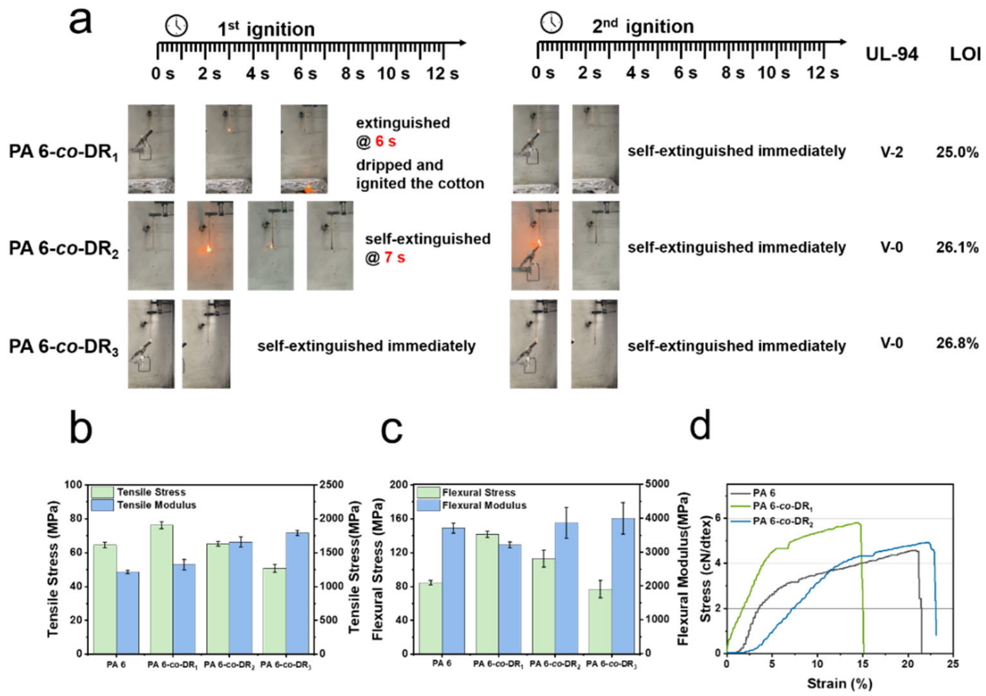

FIGURE 1. Flame retardancy and mechanical properties of pure PA 6 and PA 6-*co*-DR. (a) Combustion process during UL-94 test; (b-c) Tensile and Flexural properties; (d) Stress-strain curves of the obtained fibers.

Acknowledgement: This work was supported by the National Natural Science Foundation of China (51991351).

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P65- A STUDY OF THE INFLUENCE OF THE CHEMICAL ENVIRONMENTS OF P- AND N-CONTAINING GROUPS ON THE FIRE RETARDANCE OF POLYSTYRENE

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Main message: The primary strategies to improve the fire retardance of styrene-based polymers are largely reliant on the use of halogenated fire retardants, which are considered as hazardous to the public health and environment. Hence, many halogen-based fire retardants have already been withdrawn from the products used as construction elements in built environments. Amongst the possible halogen-free alternatives, P- and N-containing compounds have gained great attention owing to their excellent fire-retarding efficiencies and environmentally benign attributes. The current paper is focused on the chemical modification of polystyrene with P- and N-containing moieties, and the characterisation of the modified materials with regard to their thermal degradation characteristics and combustion attributes.

Keywords: Polystyrene, reactive modification, thermal stability, P-N synergism, fire retardance.

Introduction

The relative high flammability of polystyrene (PS) often restricts its wider applicability as an insulation material in the building and construction sectors [1]. In a previous study by the authors [2], several organic phosphonates were found to be effective in inhibiting the ignition propensities and suppressing the combustion of styrene-based polymers. These effects were thought to arise from both gaseous- and condensed-phase inhibitory actions of the P-bearing groups [3]. With a view to further improve the fire retardance of PS, we tried to chemically bind both phosphorus- and nitrogen-containing groups, *via* a ter-polymerization route, thus exploring possible P-N synergism [3]. The present paper specifically reports on the reactive modification of styrenic polymers with diethyl(acryloyloxymethyl) phosphonate (DEAMP), or diethyl-p-vinylbezyl phosphonate (DEpVBP), along with a N-containing compound, where N atom is in different chemical environments. Furthermore, the influence of the chemical environments of P and N atoms within the FR groups on the thermal behaviors and combustion characteristics of the modified polymers is discussed.

Experimental

The chemical structures of P- and N- containing monomers used in this study are given in Figure 1. These included: DEAMP and DEpVBP as P-containing monomers; maleimide (MI), N-methylmaleimide (MeMI), N-ethylmaleimide (EtMI), acrylamide (AM), N,N-dimethyl acrylamide (DMA) and N-isopropyl acrylamide (NIPAM), as N-bearing unsaturated compounds. The unmodified PS (used as a control sample) and the ter-polymers of styrene (St), with the above-mentioned monomers were prepared through free-radical polymerization reactions as reported previously [2]. The thermo-gravimetric analyses (TGA) were carried out on *ca.* 10 mg samples, on a Mettler Toledo TGA 2 instrument in a 25 - 800 ℃ temperature range, under both nitrogen and air atmospheres, and at a heating rate of 10℃·min^{-1}. The heat of combustion, ΔH_{comb}, (average of duplicate runs) was obtained using a Parr 6200 oxygen bomb calorimeter, and the Pyrolysis Combustion Flow Calorimetric (PCFC) measurements were conducted using a micro-scale combustion calorimeter (Fire Testing Technology Ltd.).

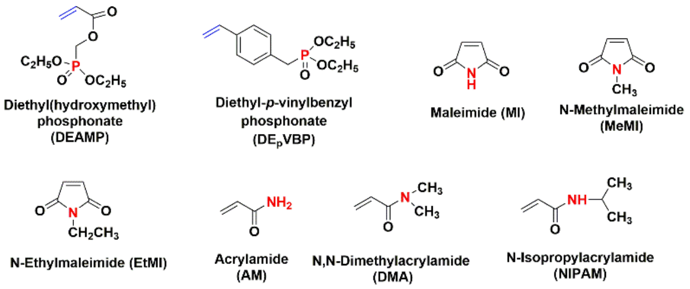

FIGURE 1. Chemical structures of P- and N- containing monomers.

Results and Discussion

Table 1 summaries relevant parameters measured using TGA, 'bomb' calorimetry and PCFC for styrenic polymers incorporating the P- (i.e., DEAMP) and different types of N-monomers. The results of DEpVBP containing materials were not included for brevity. Here, we examined the effects of two chemical environments of the N atom (i.e., as an imide and an amides) with a view to identifying the P-N synergism, if present, and also the resultant thermal stability of the ter-polymers. It is evident from Table 1 that the ter-polymerisation of St with P- and N- compounds resulted in increased levels of char formation, and lower ΔH_{comb} and reduced heat release capacity (HRC). However, the ter-polymers with built-in imide units, e.g., MI, MeMI and EtMI, exhibited a comparatively better performance than the ter-polymers with amide groups (AM, DMA, and NIPAM). For example, the HRC values for the ter-polymer with DEAMP and MI were reduced by almost 50%, whereas in the case of the ter-polymers with DEAMP and NIPAM the HRC was dropped only by 20%. These results revealed that the presence of cyclic imides, along with P-moieties, in the polymeric chains of PS tend to enhance its fire retardance to a greater degree as compared to amides. Furthermore, the alkyl substitutions of N atoms in the N-monomers showed a positive effect on the thermal stability of the modified PS. These results also indicated the beneficial effects of P- and N- containing monomeric units on the fire retardance of PS, and therefore warrant further investigation.

TABLE 1. The char residues, heats of combustion, and PCFC data of modified PS polymers

Sample	**Char residue* (wt %)**	**Char residue″ (wt %)**	**ΔH_{comb} (kJ/g)**	**HRC (J/g·K)**	**EHC (kJ/g)**
PS	0.5	0.4	40.4	753.0	36.4
Poly(St-ter-DEAMP-ter-MI)	24.3	3.6	31.3	341.0	25.8
Poly(St-ter-DEAMP-ter-MeMI)	6.9	2.6	31.7	431.6	27.3
Poly(St-ter-DEAMP-ter-EtMI)	7.5	3.1	31.5	440.3	31.4
Poly(St-ter-DEAMP-ter-AM)	8.2	2.8	33.9	617.7	34.1
Poly(St-ter-DEAMP-ter-DMA)	6.4	3.4	35.3	621.0	36.2
Poly(St-ter-DEAMP-ter-NIPAM)	7.7	1.2	35.4	590.3	34.4

Char residue*: char formed at 800℃ under N_2, Char residue″: char formed at 800℃ under air, ΔH_{comb}: Heat of combustion, HRC: Heat Release Capacity, EHC: Effective Heat of Combustion.

Acknowledgement: AB is grateful for the provision of the overseas PhD studentship from Ulster University, UK. This research was supported by the Royal Society of Chemistry (ID R19-3521).

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P66- Thermal degradation and Flammability of LIP Cigarette Paper

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Main message: The thermal degradation and flammability of ordinary area (OA) and coating band (CB) of low ignition propensity (LIP) cigarette paper were investigated. SEM results showed that it is at the whole temperature range that there are still many closely packed particles on the surface of CB. And the comparison of the evolution of their gaseous products manifested that the emission of many gas products of CB like methane, hydrocarbons, aldehydes and CO were obviously lower than those of OA. Furthermore, some evaporated species like alkanes, CO and carbonyl compounds escaped earlier than those of OA.

Keywords: Low ignition propensity; Cigarette paper; Thermal degradation; Flammability.

Introduction

In recent years, there is an increasing concern on the fire deaths and fire-related injuries caused by cigarettes throughout the world. The design of low ignition propensity (LIP) cigarette, therefore, was proposed to avoid the fire caused by cigarettes[1-2]. The most commonly recognized LIP cigarette is cigarette paper banding in which circumferential bands generally comprised of permeability reducing substances such as alginate, starch or cellulose are placed periodically along the rod[3]. However, there have been little researches on the pyrolysis and combustion of LIP cigarette paper in spite of its key determination on the self-extinguishment of a burning cigarette when not actively puffed. So the thermal degradation and flammability of LIP cigarette paper were investigated.

Experimental

The microstructures and morphologies of OA and CB of LIP cigarette paper were investigated by fourier transform infrared (FTIR) and scanning electron microscopy (SEM), respectively. Then real-time Fourier transform infrared (RT-FTIR) was employed to compare the changes of the chemical structures of CB and OA in the condensed phase, and the differences in the evolution of gaseous products of CB and OA are studied via thermogravimetric/fourier infrared spectrometry analysis (TG-FTIR). Besides, microscale combustion calorimeter (MCC) is chosen to study the difference in their combustion properties.

Results and Discussion

As shown in **FIGURE 1**, it is certainly concluded that it is at the whole temperature range that there are still many closely packed particles on the surface of CB, which endows CB with a relatively low air permeability at the smoldering state compared with OA.

The comparison of the evolution of their gaseous products (**FIGURE 1**) manifested that the emission of many gas products of CB like methane, hydrocarbons, aldehydes and CO were obviously lower than those of OA. Furthermore, some evaporated species like alkanes, CO and carbonyl compounds escaped earlier than those of OA.

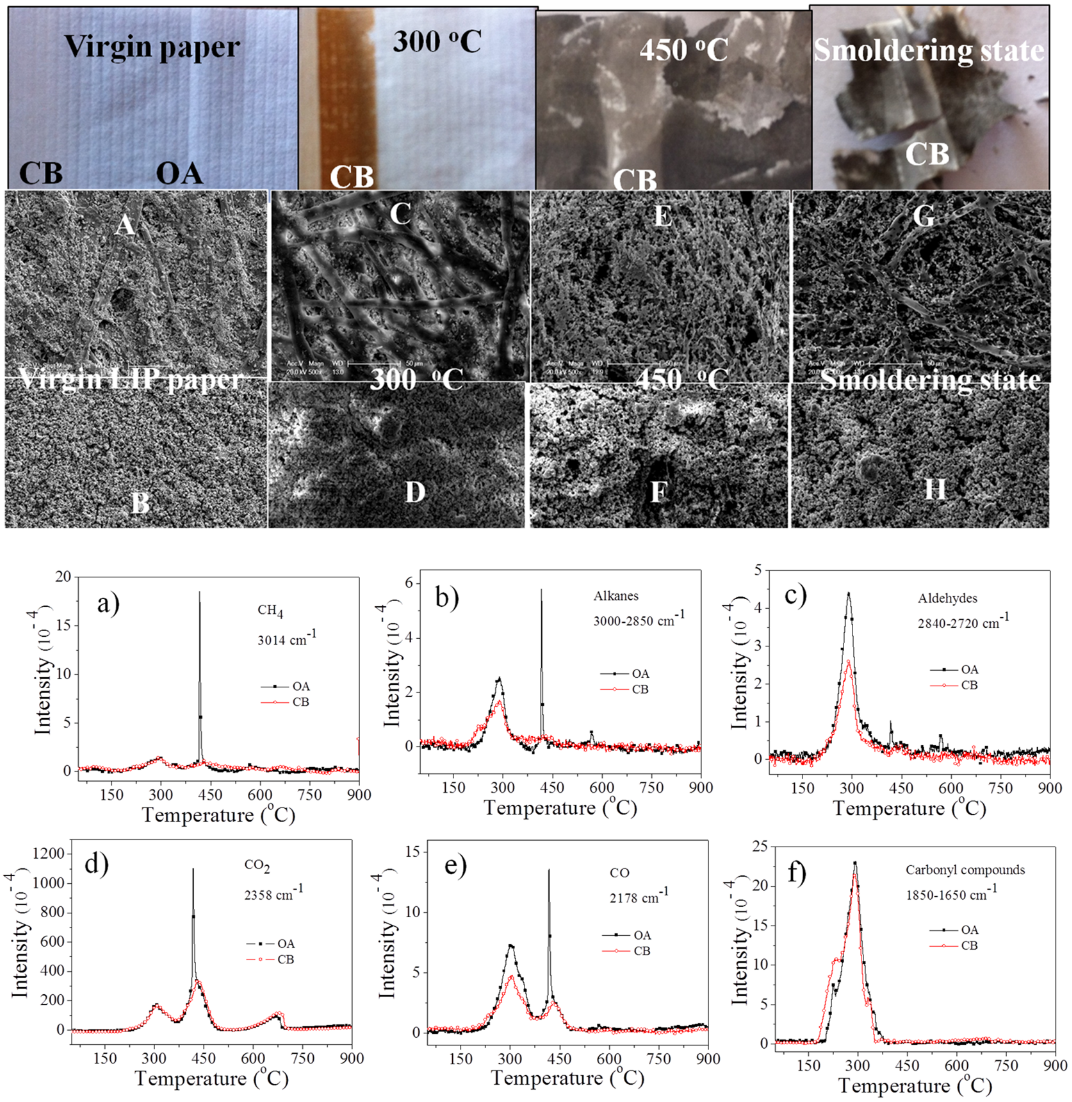

FIGURE 1. Optical photographs and SEM images of OA (A, C, E, G) and CB (B, D, F, H) of LIP cigarette paper at different conditions; IR evolution curves of various identified gaseous species for OA and CB of LIP cigarette paper.

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P67- Study on intrinsic flame-retardant vinyl ester resin and its composites with different diluents

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Main message: A vinyl ester resin monomer containing biphenyl structure was prepared from magnolol. The monomer was dissolved in styrene and methacrylic acid to obtain intrinsic flame-retardant resins SDAR and MADAR, and their fiberglass-reinforced composites GFSDAR and GFMADAR were prepared. Cone calorimeter results indicated that the total heat release and total smoke production of GFMADAR are reduced by 19.5% and 31.9% compared with those of GFSDAR due to the good wettability of MADAR on fiberglass and strong contact between its char residue and fiberglass.

Keywords: vinyl ester resin, composites, wettability, flame retardancy

Introduction

Vinyl ester resin continues to attract much attention due to its advantages of excellent chemical corrosion resistance, low viscosity, and ease of processing [1]. However, vinyl ester resin is extremely flammable. It is usually difficult to achieve good flame retardancy when the loading of flame retardant is less than 15 wt.%, which damages processing and comprehensive performance of the resin [2,3]. The preparation of intrinsic flame-retardant resin is helpful to solve this dilemma. The development of fiber reinforced polymer will help to improve the comprehensive performance of the resin.

Experimental

The reaction process of the monomer is shown in **FIGURE 1**. To obtain SDAR, the monomer (80 g) was first dissolved in styrene (20 g) at room temperature. The curing reaction was allowed to proceed for 1 h at 40 °C, for 2 h at 70 °C, for 2 h at 120 °C, and for 1 h at 160 °C. Cured MADAR samples were prepared analogously. And their fiberglass-reinforced composites GFSDAR and GFMADAR were prepared by vacuum-assisted resin transfer molding.

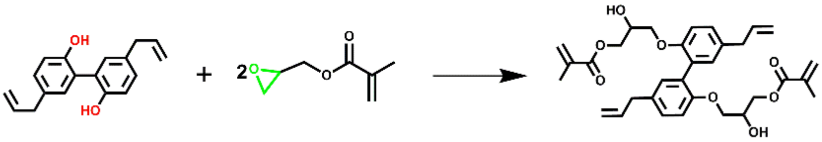

FIGURE 1. Synthetic route of the monomer

Results and Discussion

The Section microstructure of GFSDAR and GFMADAR were observed by Scanning electron microscope (SEM), as shown in FIGURE 2. In FIGURE 2A, it is observed that some fiberglass and the resin are separated on the section of GFSDAR, and some fiberglass are exposed outside of the resin. This phenomenon is not observed in the section of GFMADAR in FIGURE 2B. The fiberglass is tightly wrapped by resin, and the fiberglass bundles are tightly connected by resin. The above results show that MADAR has better wettability for fiberglass.

As shown in FIGURE 3A, the LOI values of SDAR and MADAR are 26.5% and 24% respectively, indicating that both materials exhibit intrinsic flame retardancy. The LOI values of GFSDA and GFMADAR are 30.5% and 35% respectively, which indicates that the addition of fiberglass improves the flame retardancy of the composites. Due to the good wettability of MADAR resin to fiberglass, GFMADAR shows higher LOI than GFSDAR. In addition, the combustion behavior of the material was evaluated by cone calorimeter. As shown in FIGURE 3B and 3C, the peak heat release rate (p-HRR) and total heat release (THR) of SDAR are 1112 kW/m^2 and 83.5 MJ/m^2 respectively, which are higher than the p-HRR and THR of MADAR (896 kW/m^2 and 78.0 MJ/m^2 respectively). In addition to heat release, the peak smoke release rate (p-SPR) and total smoke release (TSP) of SDAR are also higher than those of MADAR in FIGURE 3D and 3E. This is mainly due to the different pyrolysis products of the two. The addition of fiberglass significantly improved the flame retardancy of the composites. Due to the good wettability of MADAR to fiberglass, the char residue of GFMADAR after test is higher than that of GFSDAR (FIGURE 3F). Therefore, GFMADAR has better flame retardancy and smoke suppression than GFSDAR.

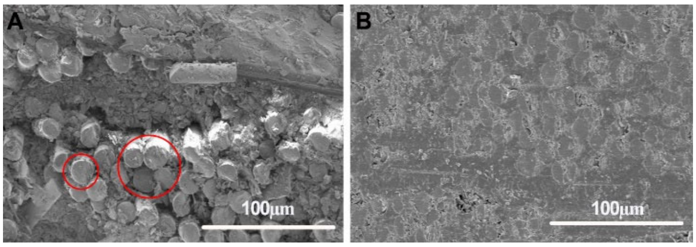

FIGURE 2. Section microstructure of GFSDAR (A) and GFMADAR (B)

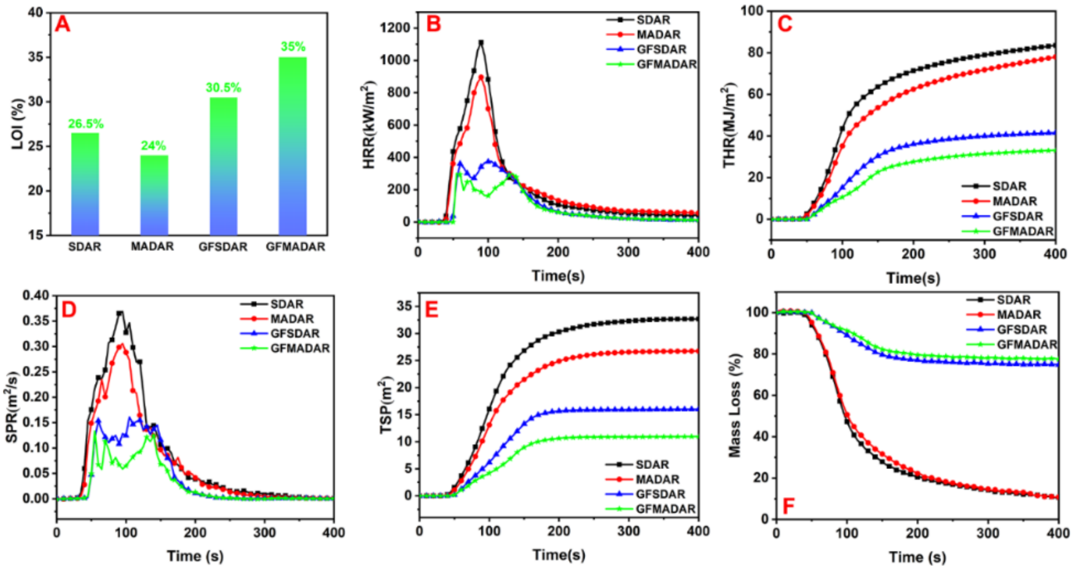

FIGURE 3. LOI (A), HRR (B), THR (C), SPR (D), TSP (E), and mass loss (F) plots of cured resins and composites

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P68- Effects of potassium nitrate and potassium citrate on pyrolysis kinetics and combustion behaviors of flue-cured tobacco

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Main message: An investigation was conducted to study how potassium nitrate (PN) and potassium citrate (PC) influenced combustion behaviors of flue-cured tobacco (FCT) in terms of combustion rate, heat release, kinetics and maximum smoking temperatures by using TGA, MCC and thermal infrared imager. Results showed that ① Pyrolysis of flue-cured tobacco consisted of 4 stages. Potassium nitrate and potassium citrate both made reaction of second stage(400-650K) easier to occur at low temperature, the third stage(650-900K) more likely to occur at high temperature and decreased the mass loss rates of these two stages and increased the total end mass. ② It could be seen from kinetic parameters that both potassium salts reduced the activation energies of pyrolysis of flue-cured tobacco, in particular potassium citrate. Both potassium nitrate and potassium citrate decreased activation reaction energy at low temperature stages (400-650K) but increased it at high temperature stages (650-900K). ③ MCC data indicated that two potassium salts broadened temperature ranges of heat release, and made combustion heat release in batches. ④ Thermal infrared imager data displayed that both potassium salts reduced maximum smoking temperatures, and that effect of potassium citrate on flue-cured tobacco was more significant.

Keywords: Potassium salts; flue-cured tobacco; TGA; pyrolysis kinetics; combustion characteristics.

Introduction

As a combustion-supporting agent, potassium salt added to tobacco can improve cigarette quality and reduce the release of harmful substances in mainstream cigarette smoke [1]. Previous studies have shown that the addition of potassium ions changes the form of tobacco combustion intermediates, thus it reduces the burning temperature of cigarettes, thereby reducing the release of harmful substances [2]. However, there are few reports on the effects of different types of potassium salts on tobacco combustion behavior from the perspective of kinetics and cigarette smoking temperature. Therefore, this paper compares the effects of potassium nitrate and potassium citrate which are commonly used in tobacco industry on the combustion behavior of flue-cured tobacco from the aspects of reaction rate, heat release, kinetics and maximum smoking temperature by using thermogravimetric analyzer, micro-combustion calorimeter and infrared thermal imager. Through this research, we can further understand the mechanism of potassium salt on tobacco combustion and provide theoretical basis for improving cigarette quality.

Experimental

Synchronous thermal analyzer was used to detect the thermal weight loss rate and calculate the kinetic parameters [3]. Micro-combustion calorimeter was used to detect the heat release characteristics [4]. Infrared thermal imager was used to monitor the combustion temperature of cigarettes [5].

Results and Discussion

The pyrolysis process of flue-cured tobacco samples can be roughly divided into four stages as Figure 1.a shown. The second and third stages contribute the most to the whole reaction and are also the focus of this study. They mainly involve depolymerization, recombination and the release and decomposition of small volatile organic compounds. The volatilization and cracking of macromolecular non-volatile components by the combustion of combustible volatile components are also involved. The addition of potassium salt makes the second stage (400~650K) of flue-cured tobacco pyrolysis easier to be carried out at the lower temperature end, which corresponds to the left shift of Peak 2. The third stage (650~900K) tends to be carried out at the higher temperature end, which corresponds to the right shift of Peak 3. At the same time, the maximum weight-loss rate of both stages is reduced.

It can be seen from Figure 1.b that the heat release of flue-cured tobacco samples is mainly divided into two stages, the first stage is between 400 and 700K, and the second stage is between 700 and 900K. The addition of potassium salt broadens the range of heat release temperature in two stages.

The introduction of potassium salt significantly affected the maximum combustion temperature of flue-cured tobacco during smoking. Specifically, both potassium nitrate and potassium citrate can reduce the maximum smoking temperature of flue-cured tobacco, and potassium citrate has the most obvious effect on flue-cured tobacco, from 883.0K to 779.5K, with a decrease of 11.7% (Table 1).

The activation energy of pyrolysis reaction of flue-cured tobacco samples is shown in Table 1. By comparison, the reaction activation energy of FCT-PN and FCT-PC both decrease at low temperature, and the decrease of FCT-PC is even greater; At high temperature, the activation energy of both reactions increase, and the increase of FCT-PN is greater.

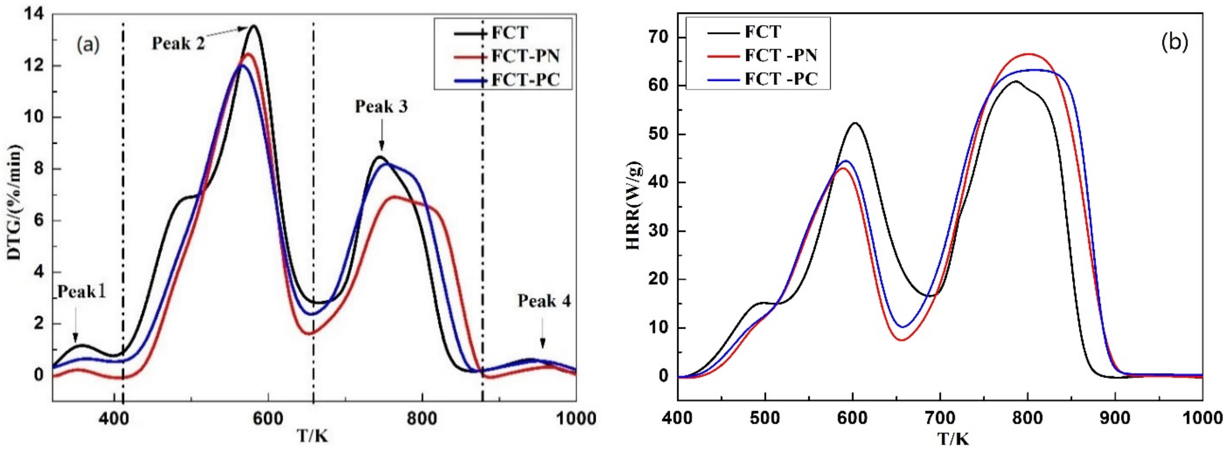

FIGURE 1. Thermal weight loss (a) and heat release characteristics (b) of flue-cured tobacco samples

TABLE 1. Pyrolysis activation energy and maximum smoking temperature of flue-cured tobaccos

Sample	**E(400-650K) [J/mol]**	**E(650-900K) [J/mol]**	**Maximum smoking temperature of cigarette [K]**
FCT	12816	11820	883.0
FCT-PN	10131	14733	847.1
FCT-PC	9787	13242	779.5

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P69- Quantitative evaluation of CO yields for the typical flue-cured tobacco under the heat-not-burn conditions using SSTF

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Main message: The quantitative evaluation of CO yields of flue-cured tobacco under the low-temperature heating conditions was investigated using a steady state tube furnace (SSTF). Then the effect of temperature, ventilation condition and elemental compositions on the CO yields was studied, respectively. There was a strikingly low CO yield of heated tobacco under a fixed ventilation condition in comparison with flaming or even smoldering tobacco, and the temperature just slightly influenced the CO yield of flue-cured tobacco under the low-temperature heating states. At 450 °C, the CO yield, with reducing air velocity, first increased fast and then tended to remain unchanged. The statistical study indicates that the ratio of potassium to sulfur (K/S) showed significant negative relationships with CO yields at the 0.01 level.

Keywords: Controlled equivalence ratio method; Carbon monoxide yield; Flue-cured tobacco; Primary elements

Introduction

Carbon monoxide (CO), as a major harmful product in cigarette smoke, causes death by binding strongly to haemoglobin, preventing the transport of oxygen from the lungs to the body. Primarily tobacco-heating cigarette (PTHC), as one of the most promising way to reduce the harm caused by tobacco use, uses a unique cigarette design to produce tobacco taste via an external heat source to heat the tobacco[1-2]. However, it is difficult to quantitatively determine the CO yields in the PTHC smoke using the present CO analysis method for the traditional cigarette, mainly due to their great differences. Recently, the appearance of the steady state tube furnace (SSTF) based on controlled equivalence ratio method succeeds in dealing with the above problems[3]. The SSTF has been used as an advantageous small-scale fire model to replicate the whole range of fire conditions, via the control of sample feed rate, temperature and airflow rate[4]. In fact, SSTF coupled to non-dispersive infrared (NDIR) analysers has been employed comprehensively to determine CO yields for a range of polymers and commercial electric cables under different fire scenarios. However, very few reports could be found related to the use of SSTF to quantitatively determine the CO yields of externally heated tobacco.

In the current work, the method for the quantitative evaluation of CO generated from the typical flue-cured tobacco under the externally heated conditions using SSTF-NDIR was established. And the influences of the heating conditions and elemental composition on the CO release were studied.

Experimental

In order to investigate the influences of temperature, primary air velocity and elemental compositions on the CO yields, three experimental programs were used accordingly. The first one: the mass of the fuel-cured tobacco leaf was 25 mg/mm, the air velocity was fixed at 3.5 L/min, and the temperature of furnace were set at 350 °C, 450 °C, 550 °C, 650 °C, 750 °C, respectively. The second one: the temperature of furnace was controlled at 450 °C, and the air velocities were kept at 14.0, 7.0, 4.7, 3.5 and 2.5 L/min, accordingly. The third one: 34 flue-cured tobacco leaves from China were chosen to be studied at 450 °C and an air velocity of 4.7 L/min, and the specimen masses were calculated on the basis of the stoichiometric ratios, the fixed air velocity and an equivalence ratio of 1.5.

Results and Discussion

As shown in FIGURE 1, there was a strikingly low CO yield of heated tobacco under a fixed air velocity in comparison with flaming or even smoldering tobacco, and the temperature just slightly influenced the CO yield of flue-cured tobacco under the low-temperature heating states. At a fixed temperature of 450 °C, the CO yield, with reducing air velocity, first increased fast and then tended to remain unchanged.

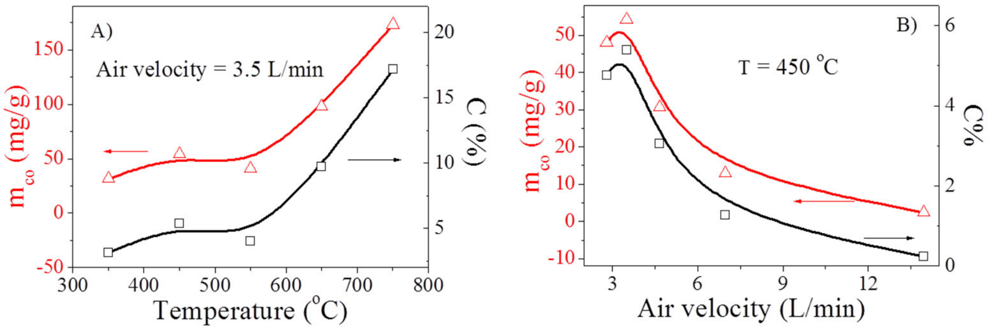

FIGURE 1. The influences of temperature and air velocity on the CO yields.

The correlation study (TABLE 1) indicates that there were no significant relationships between CO yields and the individual element except for the content of carbon and hydrogen, while the significant negative correlations of CO yields with the ratio of potassium to sulfur (K/S) at the 0.01 level appeared.

TABLE 1 Correlation analysis between elements and CO yields.

Index	C	H	O	N	K	Cl	S	K/Cl	K/S	K/N
m_{co}	0.44^*	0.59^{**}	0.29	0.10	-0.33	0.20	0.16	-0.39^*	-0.55^{**}	-0.31

*, ** Significant correlation at the 0.05 (*) or 0.01 (**) level.

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P70- PHOSPHOROUS-NITROGEN-SILICON MODIFIED GRAPHENE OXIDE AS FIRE RETARDANT MATERIAL FOR COTTON FABRIC

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Main message:

Cotton is one of the most common used natural fabric with excellent properties such as softness, comfort in contact with skin and wearability. Unfortunately, it has lower oxygen index (i.e. 18%) and ignited at lower temperature (360 – 425 °C). The fire retardancy of cotton fabric could be increase by surface modification methods. The phosphorylated amino graphene oxide fire retardant material was prepared and applied on cotton fabric using dip coating methods. The prepared fire retardant material was primary confirmed using FTIR, XRD and EDAX analysis. The thermal stability and flammability of coated cotton fabric was tested by TGA, vertical flame test and LOI test where coated fabric was found to be a better applicant as fire retardant material. The water soak test confirmed durability of coating with minor weight loss and fabric still maintain fire retardancy. This novel fire retardant coated fabric has huge potential in textile industries for developing advanced textile.

Keywords: Fire retardant, Graphene oxide, Phosphorylated amino graphene oxide, Cotton, hypophosphorous acid.

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