

Investigation of the effect of inorganic smart fillers and expanded graphite on the flame retardancy of polyisocyanurate insulation foam

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ABSTRACT

Use of highly insulating polyisocyanurate (PIR) based insulation materials enhanced with eco-friendly lamellar inorganic fillers contributes to meeting energy performance requirements, environmental challenges and cost reduction without undue compromise of the overall building fire safety. This work aims to assess the fire behaviour of PIR foams enhanced with lamellar inorganic smart fillers, namely Layered Double Hydroxides (LDHs), Expandable Graphite (EG) and Ammonium Polyphosphate (APP). The morphology of the foam structure was firstly studied using Optical Microscopy and Field Emission Scanning Electron Microscope and subsequently the fire reaction properties and thermal stability of foam samples enhanced with different types of lamellar inorganic smart fillers were evaluated using cone calorimeter (CC) and thermogravimetric analysis (TGA). TGA results indicated that thermal decomposition of the neat PIR samples occurs in two distinct stages associated with the degradation of the urethane-urea linkages of the hard segment, releasing low calorific capacity products and the degradation of polyol derived products with higher calorific capacity than those derived from isocyanate. The initial degradation temperature of PIR-layered filler samples decreases compared with neat PIR foam, indicating that incorporation of flame retardants decelerates the degradation of PIR foam and as a result decreases the thermal stability of PIR foam. The cone calorimeter data showed that the effects of LDH alone has limited effect on reducing the heat release rate (HRR) or smoke production rate (SPR) as it is only act in the solid phase. With the addition of EG or EG+APP, HRR is further decreased owing to the increased char strength as well as the release of non-combustible gases, and simultaneously effectively suppress smoke and gases during the combustion process.

KEYWORDS: polyisocyanurate insulation, layer doubled hydroxides, expanded graphite, ammonium polyphosphate, fire performance, thermogravimetric analysis, cone calorimeter analysis.

INTRODUCTION

Modern day energy codes are driving the design and multi-layered configuration of exterior wall systems with significant emphasis on achieving high-performance insulation towards improving energy performance of building envelopes. Insulation in walls may comprise of either non-combustible materials such as fiberglass or mineral wool, or frequently encountered a wide range of highly insulating combustible foam plastic materials. Most commonly used insulation materials include polymers such as extruded polystyrene, expanded polystyrene, polyurethane foam (PUF) and polyisocyanurate (PIR) with or without flame retardants [1]. Appropriate use of the above materials requires that they meet energy performance requirements, environmental challenges and cost reduction without undue compromise of the overall building fire safety. Numerous studies [e.g., 1-3] have established that thermal decomposition of polymeric foams, in both inert and oxygen atmospheres, is a complex process consisting of numerous decomposition pathways that strongly

depend on the reactivity of organic compounds employed in its synthesis. PIR foams are part of the polyurethane (PUR) rigid foam family and their main characteristic is that they contain a high percentage of cyclic isocyanurate chemical linkages and use of polyester polyol instead of the standard polyether polyol used in PUR's. PIR are based on the reaction of polycyclotrimerization of diisocyanates or isocyanate terminated prepolymers to form triazine-trione ring structured isocyanurate rings [4] that, from the thermodynamic point of view, are more thermally stable than urethane bonds found in PUR foams as it dissociates at approximately 200°C as opposed to 350°C for polyisocyanurates [5].

To improve the flammability of polymer-based insulation materials, various fire retardants can be used. The substitution of commonly used halogen-based flame retardants in polymers for eco-friendly second-generation “greener” ones such as mineral fillers like Layered Double Hydroxides (LDHs) or zirconium phosphate nanocomposites [2, 3], is currently of great interest for increasing flame retardancy, thermal stability and smoke suppression by avoiding the release of corrosive and toxic volatile compounds from combustion [6]. LDHs consist of synthetic layered compounds containing positively charged metal hydroxide layers with charge balancing anions located in between. More specifically, LDHs are described by the generic formula $[M^{II}_{1-x}M^{III}_x(OH)_2](A^{n-})_{x/n} \cdot yH_2O$, where M^{II} is the divalent cation, M^{III} is the trivalent cation, A is the interlayer anion with n- charge, x is the $[M^{III}/(M^{II}+M^{III})]$ metal molar ratio, generally confined between 0.2 - 0.4 and y is the mol of water in the interlayer region [7]. LDHs may be formed with all divalent and trivalent metal ions including transition metals, able to do an octahedral coordination with the OH hydroxyl groups and are classified as members of the magnesium aluminum hydroxy carbonate hydroxalcite ($MgAlCO_3$) supergroup [8].

The increased fire retardancy by LDHs is observed in both gaseous and solid phases as they develop non-flammable gases diluting flammable gases and promoting surface charring. Their main mechanism during thermal degradation is the release of water and carbon dioxide, diluting combustion gases, and reducing endothermic decomposition of metal hydroxides. Specifically, this latter inorganic-reinforced carbonaceous residue thermally protects the underlying polymer as the formation of this residue and slows down the combustion process of PUF [2, 6]. At elevated temperatures, LDHs have been shown to release water and go through endothermic decomposition. Different authors have recently studied several types and contents of LDH in polymeric-based insulation materials [2, 3]. Despite their effectiveness, LDHs have until now limited commercial success as fire retardants because of their difficulty to disperse and distribute uniformly in polymers, which limits their effectiveness [2]. Whilst most available studies [2, 3, 6] concern the fire retardancy effects of LDHs in on PUF, a recent study [9] investigated the potential synergistic effect between organically modified nanoclay LDH and flame retardants on PIR nanocomposites.

Recent studies also revealed that (i) the fire behaviour of PIR [10] and PUR [11] foams improve when modified with high Expandable Graphite (EG) contents and (ii) the addition of Ammonium Polyphosphate (APP) can further improve total fire behaviour while enhancing residue formation. EG is a graphite intercalation compound with a special layered structure of graphite that is found to expand when exposed to heat, to up to 100 times, forming a huge insulation layer that enhances the fire resistance of the PIR [10]. This formed char layer is characterised by the presence of “worms” that are derived during its expansion which is attributed to a redox process between H_2SO_4 , intercalated between graphite layers and the graphite itself, producing CO_2 , H_2O and SO_2 [12,13]. APP has a polyphosphate chain structure and high molecular weight and its efficacy is attributed to the increased char formation by a condensed phase reaction [10]. The phosphoric acid generated from APP has good synergistic effect with EG towards improving the char morphology [12].

The aim of the current work is to assess the fire behaviour and potential synergistic effects of lamellar inorganic smart fillers, including LDH, EG and APP, on the flame retardancy of PIR foams. The morphology of the foam structure was studied using Optical Microscopy and Field Emission Scanning Electron Microscope (FE-SEM) and the fire reaction properties and thermal stability of foam samples

enhanced with different types of lamellar inorganic smart fillers were evaluated using cone calorimeter (CC) and thermogravimetric (TGA) analysis.

EXPERIMENTAL INVESTIGATION

Materials

The PIR samples having a constant isocyanate index (NCO/OH) of 3.0 were produced at Selena Lab by high pressure impingement mixing type of foam machinery, operating at constant processing parameters. The initial premixing of the main components of the polyol blend including polyol, catalysts, stabilizer and methylal blowing agent, of all samples was performed for 2-3 min at 1500 rpm. This polyol mix was then mixed with the fillers for 5 min at 2500 rpm. The required amount of isocyanate, methylene diphenyl diisocyanate (MDI), was finally poured into the mixture and stirring was continued for 10 s at the same speed. The average density of the PIR is about 45 kg/m³.

All the fillers, i.e., Layered Double Hydroxides containing MgAlCO₃ (LDH), Expanded Graphite (EG) and Ammonium Polyphosphate (APP) were produced at Prolabin and Tefarm SRL. The final formulations were prepared at Selena Lab. In total, five formulations were examined, namely neat PIR, PIR-2%LDH, PIR-2%LDH+5.1%EG, PIR-2%LDH+5.1%EG+3.6%APP1 (APP with high degree of polymerisation) and PIR-2%LDH+5.1%EG+3.6%APP2 (APP with low degree of polymerisation). The loadings specified are in % wt. The sample sizes in the cone calorimeter tests are 100 mm x 100 mm x 24mm whereas powders were used in TGA.

Test methods

Optical Microscopy at 500 μm was used for the morphological evaluation of the foam structure. Images and fluorescence photos were collected using the Avio Zoom V16 Zeiss Stereo and Zoom Microscope. Cellular structure of the samples was further evaluated using a LEO 1525 FE-SEM (Field Emission Scanning Electron Microscope) at 100 μm to provide elemental identification and quantitative composition information.

The thermal stability was evaluated under Air (reactive) and N₂ (inert gas) using a Mettler Toledo TGA apparatus. About 10 mg foam sample was placed in an alumina pan with no lid. The heating rate was 20°C/min with a maximum temperature of 1000 °C. The gas flow rate is 150 ml/min. The following parameters were determined: initial degradation temperature, $T_{5\%}$ (temperature at 5% weight loss), the weight, W , at the maximum weight loss rate and corresponding maximum temperature, T_{max} , for each degradation step and char residue at 1000°C.

Cone calorimeter (CC) tests were performed with a Dark Star Research Ltd (UK) apparatus according to the ISO 5660-1 [14]. The samples were horizontally placed in a 106 mm x 106 mm x 26 mm stainless steel metal holder. The interior surface was insulated with 2 sheets of 3 mm high temperature vitreous wool Insulfrax® Paper, with a nominal density of 150 kg/m³ and conductivity 0.098 W/mK at 400°C, coated with 0.07 mm AT502 30 Micron aluminium foil tape, Category 1 according to BS 476 Part 6 and 7 [15, 16]. All samples were conditioned before testing according to ISO 554 [17] at 23°C \pm 2°C at 50% \pm 5% relative humidity. At least two repeatability tests were performed for each specimen tested. The heat flux used was 50kW/m². For each formulation, at least three tests were conducted to ensure good repeatability. Experimental results include time to ignition (TTI), heat release rate (HRR), total heat released (THR), peak HRR (p-HRR), average heat of combustion (Av-HOC), smoke production rate (SPR), and smoke and CO yield. The unexposed surface temperature was measured using a 1 mm type-K shielded thermocouple.

Additionally, two digital cameras were positioned facing the front or sideways of the test apparatus to record observations regarding specimen burning behaviours and smoke colour. The uncertainty of the measurements complied to ISO 5660 [14]. The holder seemed adequate to support the edges of the

samples in the initial burning stages and thus no additional retainer framing has been used to prevent samples deformation. In several samples, a significant glowing was observed after flameout.

RESULTS AND DISCUSSION

Optical Microscopy and FE-SEM

A morphological evaluation, in terms of regular and cellular structure, of the tested samples has been performed by optical microscopy and FE-SEM, as depicted in Figs. 1 and 2 respectively for selected formulations. Figure 1 shows that LDH does not significantly alter the morphology of the PIR sample. The FE-SEM results indicate that the average cell diameter of neat PIR, PIR-2%LDH, PIR-2%LDH+5.1%EG, PIR-2%LDH+5.1%EG+3.6%APP1 and PIR-2%LDH+5.1%EG+3.6%APP2 samples is respectively 390, 312, 192, 142 and 271 μm . There is a slight decrease in the average cell diameter with fillers but cellular morphology with the addition of fillers has not been substantially changed in comparison with PIR samples.

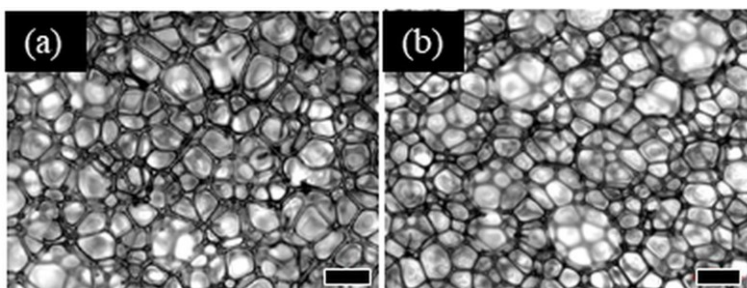


Fig. 1. Morphological evaluation using optical microscopy (black scale bar indicates 500 μm) of pure PIR (a) and PIR-2%LDH (b).

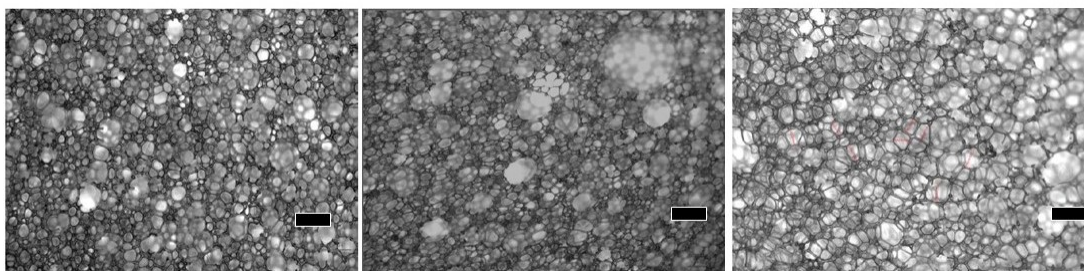


Fig. 2. Morphological evaluation using SEM (black scale bar indicates 500 μm) of PIR-2%LDH+5.1%EG (a), PIR-2%LDH+5.1%EG+3.6%APP1 (b), PIR-2%LDH+5.1%EG+3.6%APP2 (c).

Thermogravimetric analysis (TGA)

Figures 3 and 4 present the weight loss and weight loss rate of all formulations under N_2 and Air atmospheres respectively with the results summarised in Table 1. TGA analysis reveals that the initial degradation temperature of PIR-layered filler samples decreases compared with the neat PIR foam, indicating that incorporation of flame retardants decelerates the degradation of PIR foam and as a result decreases the thermal stability of the PIR foam. It can also be observed that the degradation of

all PIR foams without APP in both atmospheres occurs in two steps associated with the degradation of the urethane-urea linkages of the hard segment, releasing low calorific capacity products and the degradation of polyol derived products with higher calorific capacity than those derived from isocyanate. With the addition of APP, an additional degradation step was observed at around 530°C associated with the degradation of APP.

The initial degradation temperature, $T_{5\%}$, is 258°C for pure PIR. It can be seen from Table 1 that $T_{5\%}$ decreases with the addition of LDH compared with net PIR foam, indicating that incorporation of flame retardants accelerates the degradation of PIR foam and as a result decreases the thermal stability of PIR foam higher temperature range. But this is not the cases for EG-containing formulations (w/wo APP) indicating that EG degrades at lower temperatures.

The first pyrolysis step takes place from 200 to 400°C is identified as the main mass loss step in accordance to bibliography [18, 19]. The temperature at the maximum degradation rate, $T_{max,1}$, is slightly decreased with the LDH filler, whereas it is substantially decreased with the incorporation of EG or EG with APP. This first step is related to the degradation of the urethane-urea linkages of the hard segment [19], releasing low calorific capacity products; residue weight values of this first reaction are denoted as W_1 .

The second stage of decomposition corresponds to the degradation of polyol derived products with higher calorific capacity than those derived from isocyanate [3] and lower residue weight, W_2 . The second degradation step of the pure PIR foam takes place between 400 and 600°C, and the maximum rate degradation temperature, $T_{max,2}$, is 457°C with the final char residue 25.4% of the initial mass. With the addition of EG, the temperatures are generally decreased due to degradation of the fillers at lower temperature. Increasing filler content results in increased char formation.

The former decrease is more substantial with the addition of EG and APP. Samples PIR+2%LDH+5.1%EG+3.6%APP1 and PIR+2%LDH+5.1%EG+3.6%APP2 final residue is above 37% in both atmospheres. All the above results indicate that the addition of APP to PIR decreases the thermal stability of PIR at the first stage and decreases the thermal stability at the second stage. From 500°C, the amount of residue is always higher than 25% suggesting that the potential synergistic effect of APP on the formation of thermally stable material is better than the incorporation of plain EG and LDH.

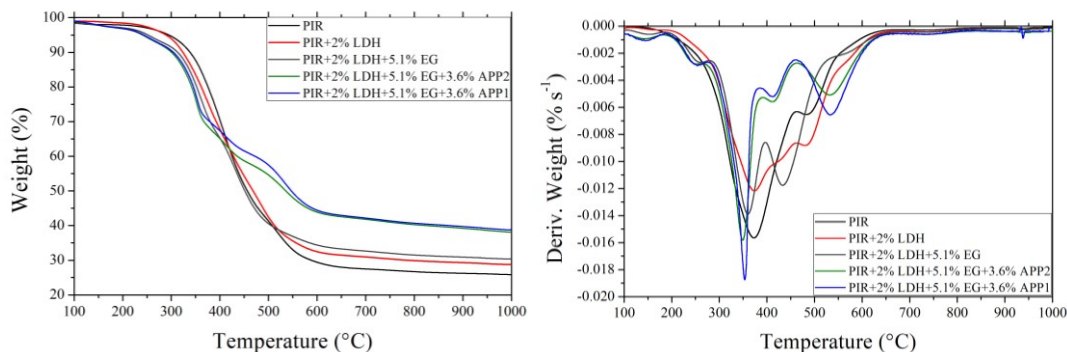


Fig. 3. TG (left) and DTG (right) of all the formulations in N_2 atmosphere.

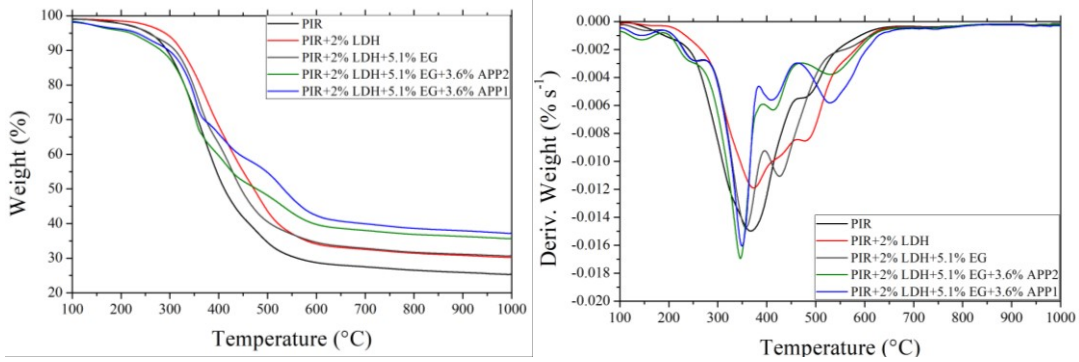


Fig. 4. TG (left) and DTG (right) of all the formulations in air atmosphere.

Table 1. TG/DTG results of all formulations.

Samples	Gas	$T_{5\%}$ [°C]	Stage 1		Stage 2		Stage 3		Residue 1000°C [%]
			$T_{max,1}$ [°C]	W_1 [%]	$T_{max,2}$ [°C]	W_2 [%]	$T_{max,3}$ [°C]	W_3 [%]	
PIR		295	373	80.8	480	44.7	-	-	25.9
PIR+2%LDH		289	374	76.0	511	40.3	-	-	28.7
PIR+2%LDH+5.1%EG	N ₂	251	360	76.9	416	61.1	-	-	30.3
PIR+2%LDH+5.1%EG+3.6%APP1		241	349	78.5	435	62.8	534	52.2	38.8
PIR+2%LDH+5.1%EG+3.6%APP2		241	349	77.0	425	61.3	534	50.2	38.2
PIR		258	372	64.1	457	40.7	-	-	25.4
PIR+2%LDH		290	370	77.5	446	55.9	-	-	30.3
PIR+2%LDH+5.1%EG	Air	255	357	76.4	429	54.7	-	-	30.7
PIR+2%LDH+5.1%EG+3.6%APP1		219	349	71.8	421	62.6	538	49.1	37.2
PIR+2%LDH+5.1%EG+3.6%APP2		232	349	77.3	416	56.9	538	44.3	35.7

Cone Calorimeter analysis

Figure 5 shows comparisons of the HRR and SPR histories of all formulations. It is worth noting that all formulations ignited almost immediately after being exposed to the heater due to its low density and high flammability. Neat PIR has the highest HRR and SPR as expected. Fissures were observed on the final char residue at the end of the test along with detachment and exfoliation of the upper layer surface as highlighted in Table 6. The trends of SPR are similar to those of HRR, and consequently we will focus our discussions in this section on the HRR.

With the addition of LDH alone, there is a small decrease in the first peak HRR with a more substantial reduction in the second peak HRR. The char also appears stronger than that of the neat PIR. With a further inclusion of EG, the HRR is reduced further, however, it is interesting to note that APP1 has limited effect on the HRR whereas PIR-2%LDH+5.1%EG+3.6%APP2 achieves the lowest HRR and SPR, likely because of the increased strength of the char layer as shown in Table 6, which provides an effective barrier against heat and oxygen, release non-combustible gases, and simultaneously effectively suppress smoke and gases during combustion process.

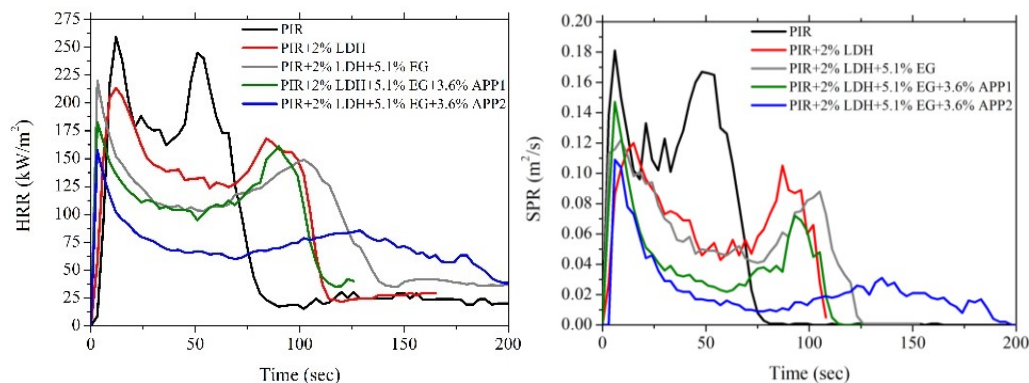


Fig. 5. Comparisons of HRR (left) and SPR (right) of all formulations.

The present results also demonstrated that the degree of polymerisation has a very important effect on the fire performance of the composites as shown in both Figs. 5, 6 and Table 2. Another important finding is that LDH decreases smoke and CO yields compared to neat PIR. Improved fire behaviour when EG and APP2 fillers are used, is evident as the flame-retardant properties of PIR+2%LDH+5.1%EG+3.6%APP2 sample are improved significantly. Both the p-HRR and Av-HOC are decreased with additions of fillers. The fact that EG or EG + APP has considerably lower values of heat of combustion than PIR or PIR+2%LDH confirms that they act also in the gaseous phase in suppression combustion. One other important observation is that all the fillers have either similar or lower smoke or CO yields compared to neat PIR, highlighting one of their main advantages of these type of fire retardants in comparison with halogenated fire retardants.

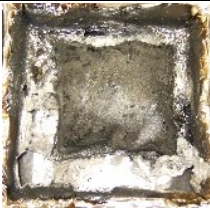

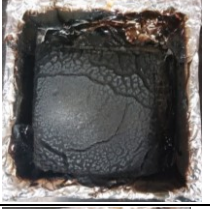
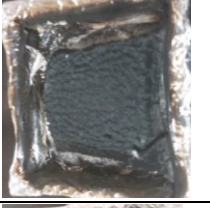

Table 2. Summary of cone calorimeter results at 50kW/m².

Samples	THR [MJ/m ²]	p-HRR [kW/m ²]	Av-HOC [MJ/kg]	Smoke yield [-]	CO yield [-]
PIR	17.85	259.1	49.7	0.0980	0.1130
PIR+2%LDH	17.15	213.4	32.1	0.0690	0.0400
PIR+2%LDH+5.1%EG	16.76	207.5	20.9	0.0734	0.0305
PIR+2%LDH+5.1%EG+3.6%APP1	13.66	183.0	22.5	0.0907	0.0553
PIR+2%LDH+5.1%EG+3.6%APP2	15.03	157.9	23.1	0.0484	0.0383

Table 3 presents the char residue of all samples after the tests. As can be seen in the figure, the presence of fillers promotes the formation of a more rigid and hardened residual char layer. For pure PIR sample, the char was brittle and non-uniformly distributed. In addition, detachment and exfoliation of the upper layer surface was also observed.

A very distinction in appearance was observed in the residual char from PIR+2%LDH+5.1%EG+3.6%APP1 and PIR+2%LDH+5.1%EG+3.6%APP2, which were intact and spongy. Clearly, the strength and integrity of the char plays a very important role in reducing the burning rate/heat release rate for meso- to large-scale samples, in which internal heat and mass transfer becomes important, as opposed to the mg samples used in TGA.

Table 3. Residual char digital photos of all PIR samples after the CC testing at 50 kW/m².

Samples	Char Residue	Observations
PIR		<ul style="list-style-type: none"> • Fissures at the char • Black smoke during combustion • Detachment and exfoliation of upper layer surface
PIR+2%LDH		<ul style="list-style-type: none"> • Considerable combustion • White sooty smoke before ignition • Deformation and expansion of the sample
PIR+2%LDH+5.1%EG		<ul style="list-style-type: none"> • Considerable combustion • White sooty smoke before ignition • Deformation and expansion of the sample
PIR+2%LDH+5.1%EG +3.6%APP1		<ul style="list-style-type: none"> • Complete combustion • White sooty smoke before ignition • Deformation and expansion of the sample
PIR+2%LDH+5.1%EG +3.6%APP2		<ul style="list-style-type: none"> • Complete combustion • White sooty smoke before ignition • Deformation and expansion of the sample

The abovementioned results are verified by the temporal evolution of the unexposed surface temperature of all formulations as depicted in Fig. 6 for all formulations. The unexposed surface temperature rise is slower with the inclusion of LDH and significantly slower with the inclusion of EG and EG +APP. The improved fire behaviour and potential synergistic effect of EG and APP2 is more pronounced in PIR+2%LDH+5.1%EG+3.6%APP2 as the formed char quality is increased. A decreased thermal degradation was observed for samples PIR+2%LDH+5.1%EG+3.6%APP1 and PIR+2%LDH+5.1%EG+3.6%APP2, as the temperature achieved a maximum value at nearly 700°C delayed by more than 2 mins. The unexposed surface temperature was found strongly dependant on the deformation during combustion as the thermocouple tip is attached to the centre of the sample holder in direct contact with the unexposed surface. Those deformations are more intense in plain PIR and PIR+2%LDH samples, as depicted in Table 3, and though they could be reduced with the use of

a grid it was avoided by the authors as that would mean changing the material's properties and fire response.

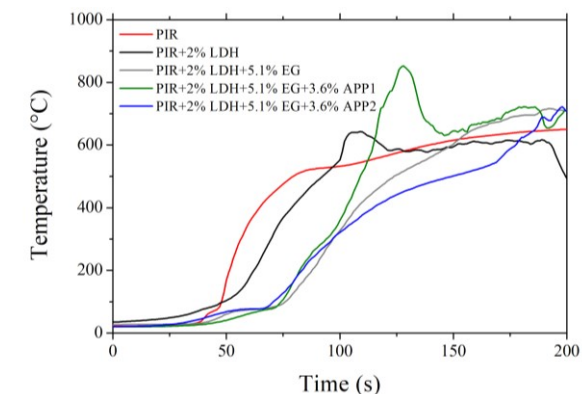


Fig. 6. Unexposed surface temperature of all formulations.

CONCLUSIONS

Fire reaction properties and thermal stability of PIR form with smart fillers including Layered Double Hydroxides (LDHs), Expandable Graphite (EG) and Ammonium Polyphosphate (APP) were evaluated using TGA and cone calorimeter (CC). Optical Microscopy and FE-SEM (Field Emission Scanning Electron Microscope) measurements were performed for the samples, which verified that the fillers were exfoliated in the PIR samples.

It was found that all fillers promote the formation of a reinforced char layer providing an effective barrier against heat and oxygen. The effects of LDH alone has limited effect on reducing the HRR or SPR as it only acts in the solid phase as the total heat release of PIR+2%LDH is the same as that of the neat PIR. With the addition of EG or EG+APP, the HRR is further decreased owing to the increased char strength as well as the release of non-combustible gases, which effectively suppress smoke and gases during the combustion process. The best performance was achieved by PIR+2%LDH+5.1%EG+3.6%APP2 that resulted in higher char residue, decreased p-HRR values, and decreased smoke generation and CO production. This result also confirms that the degree of polymerisation of fire retardants is also significant in its fire performance.

Further coupled TGA-FTIR analysis at different heating rates under both oxygen and inert atmospheres will be further conducted. Degradation products will be identified, and information will be used to derive a kinetic model to simulate the pyrolysis degradation mechanism of PIR-layered filler foams. Additional combinations of different layered fillers will be investigated in the future to further tune the fire resistance properties of PIR nanocomposites.

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