FLAME RETARDANT AND THERMAL BEHAVIOUR OF THE PLA/EXPANDABLE GRAPHITE COMPOSITES

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Abstract - The thermal behaviour and flame retardant properties of polylactide (PLA) composites with expandable graphite (GR) an halogen-free flame retardant were studied. The presence of expandable graphite amount improves the flame retardance and thermal stability of PLA composites. The vertical burning test was successfully passed revealing non-dripping and char formation for PLA composites with expandable graphite amount equal and higher than 5wt%. The presence of hindered amine can increase thermal stability and decrease of the heat release rate as a flame retardant synergist in PLA/expandable graphite.

Introduction: The physical and mechanical properties of PLA make it a good candidate as replacement for petrochemical thermoplastics in several application areas. The properties profile of commercial PLA is in some aspects similar to synthetic thermoplastics (mechanical strength, elastic recovery and heat sealability), while it shares other properties with bio-based polymers (biodegradability, dye-ability, barrier characteristics). According to two major companies producing PLA, namely Nature Works and PURAC, about the substitution potential for PLA, they agree on the potential for PLA or PLA components to partially replace low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyamide (PA), polystyrene (PS) and polyethylene terephtalate (PET), as well as seeing possibilities for PLA to substitute for polymethylmethacrylate (PMMA). Even if PLA is primarily used in packaging and the textile sector today, its expected market should be rapidly extended to transportation and electrical and electronic equipment (E&E) sectors. Thus it can be clearly seen that flame retarding PLA is (or will be) becoming an issue for this polymer.
Expandable graphite combining with the other addictives have excellent fireproofing properties so that the blends burn slowly and smoothly accompanied with the significant decrease of heat release rate and effective heat of combustion values. As far as we know, however, no much study on the effect of expanded graphite in blend with PLA has been reported so far in literature, this work is mainly devoted to an investigation of the combustion characterization and thermal stability of expandable graphite in PLA blends using cone calorimeter test, thermogravimetric analysis, IOI and UL-94 test. The main purpose of the present work is to investigate the effect of expandable graphite alone on the PLA materials so that it helps to develop better free halogen flame retardant PLA materials combined with the low price and possibility for the industry application.
Experimental: Poly(L-lactic acid) "NatureWorks® PLA Polymer 3051D", was obtained from Natureworks. Flamestab NOR 116 (F1), an oligomeric N-alkoxy hindered amine which acts as a flame retardant in polyolefin applications was supplied by Ciba Specialty Chemicals. Expandable Graphite with a typical size of 300 micrometer (GR) was used. The amount and the type of the different additives were indicated in Table 1.

Table 1. - Composition of the different samples and TGA analyses

Samples	**PLA**	**GR**	**Fl**	**Under N_2**		**Under Air**	
Name	%wt	%wt	%wt	$T_{10\%}$(°C)	T_{max}(°C)	$T_{10\%}$(°C)	T_{max}(°C)
PLA	100.0	-	-	338	368	323	353
PLA1FI	99.0	-	1.0	332	364	329	355
PLA1GR	99.0	1.0	-	337	364	331	359
PLA2.5GR	97.5	2.5	-	344	370	326	345
PLA5GR	95.0	5.0	-	333	356	331	364
PLA10GR	90.0	10.0	-	323	364	335	365
PLA1GR1FI	98.0	1.0	1.0	331	364	334	369

Results and Discussion: The PLA matrix degradation is scarcely influenced by the presence of oxygen (Table 1). For the PLA with expandable graphite composites, the TGA results of adding 1 %wt, 2.5 %wt of GR and 1 %wt FI to the PLA, are similar to the pure PLA whether in the nitrogen or the air, but at added higher loading for example 5 %wt and 10 %wt of GR or blend of 1 %wt GR 1 %wt FI in the air, there is an increase of pyrolysis temperature about 11-16 °C. This behaviour may be attributed to the higher thermal stability of expandable graphite. The HRR and THR curves of PLA composites with different graphite content, the corresponding combustion data are presented in Table 2.

Table 2. - Cone calorimeter data of PLA and its composites

Sample	TTI (s)	THE (MJ/m^2)	HRRAve (kW/m^2)	Pk HRR (kW/m^2)	EHC (MJ/kg	TSR (m^2/m^2)
PLA	64	64	254	426	18	69
PLA /1FI	67	62	242	403	17	56
PLA/1GR	44	70	267	409	18	77
PLA/2.5GR	42	67	253	396	18	73
PLA/5GR	43	44	201	378	18	36
PLA /10GR	60	52	126	307	17	32
PLA/1GR/1FI	43	66	260	396	18	58

Notes: TTI(Time to ignition);THR(Total heat release);HRRAve(Average Heat release rate); PkHRR(peak heat release rate);EHC(Effective heat of combustion); TSR(Total smoke release)

The peak HRR and HRR of PLA composites decrease with increasing graphite content. The flame retardant capability of graphite is thus strictly linked to the amount. When Fl is added to PLA/expandable graphite the Peak HRR and TSR decrease from 426 of pure PLA down to 398 of the Peak HRR and 69 to the 58 of TSR, respectively. UL-94 test is widely used to evaluate flame retardant properties of materials and to screen flame retardant formulations. Pure PLA burn completely with flaming droplets, changes in burning behaviour was observed for composites with 5wt% and 10wt% GR. Those two composites are self-extinguished and passed the UL-94 V-0 test. It means the formation of an intumescent structure which protects the PLA and stops the combustion of the sample. However, the composites with GR content less than 5wt% only pass UL-94 V-2 test. It shows that the low amount of graphite is not enough to form stable char layer, so the flame retardant effect of the graphite is relative to the amount of the graphite.
The oxygen index test is recognized as another useful tool for mechanistic studies of fire retardance in polymeric materials. The oxygen index (OI), which is the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports candle-like combustion of a specimen, can indeed be measured with a relative standard deviation below 10% as shown by interlaboratory testing (ASTM D 2863).The ignition and burning time is considerable at the determination of the oxygen index. For more detailed evaluation of fire behaviour, the measurements of IOI (ignition oxygen index) and increase of BR(burning rate) with OC (ΔBR) are as to complement each other [1]. The presence of small amount of expandable graphite additives slightly increases values of both OI and LOI in PLA/graphite composites compared with pure PLA.

Table 3. UL-94 and LOI results of PLA and its composites

Sample	OI	LOI	BOI	ΔBR [mm/(s OC%)]	UL-94 Classification
PLA	23	23	21.3	1.7	NC
PLA1GR	23.3	23.3	22.2	1.41	V2
PLA2.5GR	25	25	23	0.94	V2
PLA5GR	24.5	24.5	22.5	0.86	V0
PLA10GR	-	-	-	-	V0
PLA1GR1FI	23	23	21.6	0.81	V2

aSQTt= transition self-quenching time from unstable to stable burning; OI=Oxygen index; IOI=ignition oxygen index; BOI= burning oxygen index; ΔBR= incremental ratio burning rate/oxygen concentration.

Conclusions: PLA/expandable graphite composites have been produced by melt-blending. Expandable graphite amount improves the flame retardance and thermal stability of PLA composites when the loading of expandable graphite is larger than 5 wt%. The vertical burning test was successfully passed revealing non-dripping and char formation for PLA composites with expandable graphite amount equal and higher than 5wt%. The monomeric N-alkoxy hindered amine (NOR116), can increase thermal stability and decrease of the heat release rate as a flame retardant synergist in PLA/expandable graphite.

References

1. Camino G., Costa L. et al. Journal of applied polymer science, 1988; 35: 1863-1876