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

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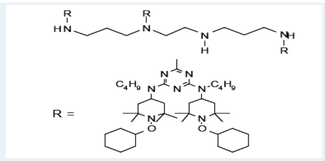
This article describes studies on the thermal behavior and flame retardant properties of polylactide (PLA) composites with halogen-free flame retardant expandable graphite (GR). The heat release rate (HRR) and total heat release (THR) were used to evaluate the flammability by cone. Vertical burning test (UL-94) was also successfully passed revealing non-dripping and char formation. Ignition oxygen index (IOI) and burning rate (BR) was used studied composites combustion rate in the LOI test. Monomeric N-alkoxy hindered amine (NOR116) was also discussed as the flame retardant synergist in the PLA/GR composites.

Materials

The Poly(lactic acid), 3051D- (PLA) was supplied by Nature Works (USA). Flamestab NOR 116 a flame retardant and flame retardant synergist in polyolefin applications was supplied by Ciba specialty chemical.

Sample	Formula
Flamestab NOR 116 (Fl)	

Material processing

The composites were prepared via melt-processing using a leistritz co-rotating twin screw extruder (d=18 mm, l/d=40). Flow with 4.0 kg/h, speed with 150 rpm were used。 The residence time was about 50s.The samples were prepared by direct addition of the different nanofillers. Composition were listed below

Samples	PLA	GR	FI
	%wt	%wt	%wt
PLA	100.0	-	-
PLA1FI	99.0	-	1.0
PLA1GR	99.0	1.0	-
PLA2.5GR	97.5	2.5	-
PLA5GR	95.0	5	-
PLA10GR	90.0	10.0	-
PLA1GR1FI	98.0	1.0	1.0

The flame retardant properties of PLA composites

The oxygen index (OI) is the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports candle-like combustion of a specimen. The ignition and burning time is considerable at the determination of the oxygen index. For more detailed evaluation of fire behavior, the measurements of IOI (ignition oxygen index) and increase of BR (burning rate) with OC (ΔBR) are as to complement each other*. The presence of small amount of expandable graphite additives slightly increases values of both IOI and OI in PLA/graphite composites compared with pure PLA. General, the low value OI is not good for the flame retardancy, in fact only PLA/5GR can pass UL-94 rating V-0. In accordance with a low combustion rate of 0.84 and slightly high IOI. The charring without cracking on the top of stick was also observed. The other system on the list with UL-94 rating V-2 is due to lower IOI and more fast combustion rate. For example, the system of 2.5 GR, IOI is 25 and ΔBR is 0.94, while the system of 1GR, IOI is 23.5 and ΔBR is 1.46, and there are charring and dripping on the side of the stick. For the pure PLA a total combustion and dripping behavior from the stick was observed, the combustion rate (1.7) is larger than any other system on the list. This results show that ignition oxygen index and combustion rate is also beneficial for the evaluation of the flame retardancy.

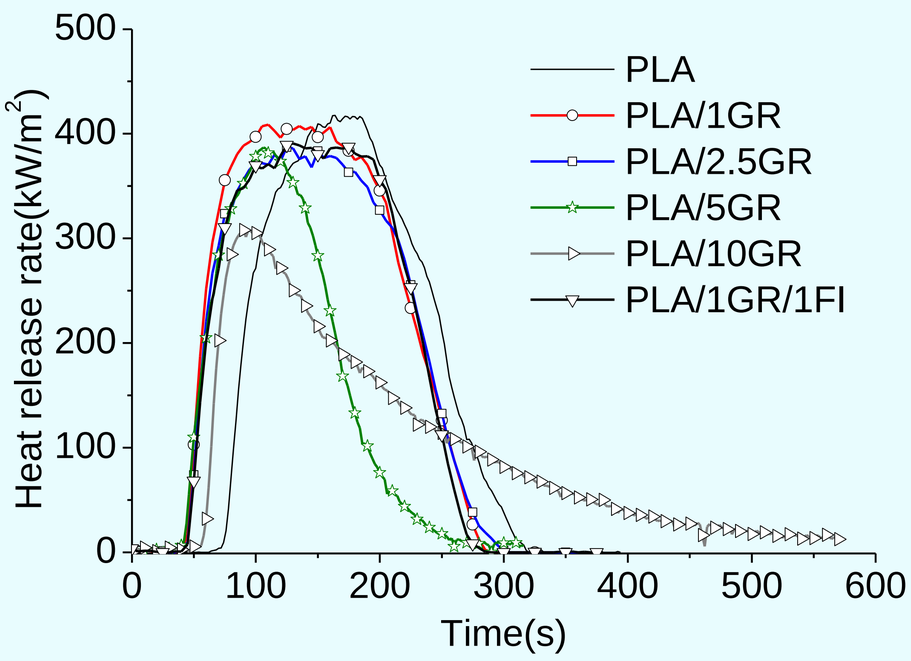
Sample	IOI	LOI	BOI	ΔBR	UL-94V
	%vol	%vol	%vol	[mm/(s OC%)]	
PLA	**20.9**	**23**	**21.3**	**1.7**	**NC**
PLA1GR	**23.3**	**23.3**	**22.2**	**1.41**	**V2**
PLA2.5GR	**25**	**25**	**23**	**0.94**	**V2**
PLA5GR	**24.5**	**24.5**	**22.5**	**0.86**	**V0**
PLA10GR	**-**	**-**	**-**	**-**	**V0**
PLA1GR1FI	**23**	**23**	**21.6**	**0.81**	**V2**

* Camino, G.; Costa, L.; Casorati, E.; Bertelli, G.; Locatelli, R. The oxygen index method in fire retardance studies of polymeric materials *Journal of Applied Polymer Science*. **1988**, *35*, 1863-1876.

Forced combustion

The cone calorimeter based on the oxygen consumption principle has been extensively used to evaluate the flammability of materials because its results correlates well with those obtained from large-scale fire tests and can be used to predict the combustion behaviors of materials in real fires. The heat release rate (HRR) and especially the peak of HRR, has been found to be the most important parameter to evaluate fire safety. The peak HRR and HRR of PLA composites decrease with increasing graphite content. Compared to pure PLA, the peak HRR of composites 5wt% and 10 wt% graphite shows a decrease with reduction of peak HRR about 10% and 28%. Meanwhile, the total heat released also distinct decreases of 33% and 20% respectively, while the loading amount of graphite less than 5wt%, the HRR, Peak HRR and THR do not significant decrease compared with the pure PLA. The flame retardant capability of graphite is thus relative to the amount of graphite. These results indicate that it is necessary a complete coverage of PLA by graphite to reduce small molecular volatile and suppress smoke production effectively when graphite loading over 2.5wt%. Meanwhile, it prevents the heat release by promoting char formation. The char layer may act as an insulator and mass transport barrier which slows the escape of the generated volatile products and oxygen diffusion, then slow down heat and mass transfer between the gas and condensed phase, which prevents the underlying polymeric substrate from further attack of heating which are accordant with the results of UL-94 test.

Sample	TTI	THE	HRRAve	pkHRR	EHC	TSR
	(s)	(MJ/m²)	(kW/m²)	(kW/m2)	(MJ/kg)	(m²/m²)
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



The flame retardant properties of PLA composites

PLA/expandable graphite composites have been produced by melt-blending. Expandable graphite amount improves the flame retardancy 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.