Intumescent Polylactide: A Nonflammable Material

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ABSTRACT: In this article, we examine intumescent polylactide, which exhibits a nonburning behavior upon heating. The combination of melamine and ammonium polyphosphate incorporated in the polylactide allowed us to obtain an intumescent char and low flammability. The incorporation of an additional ingredient such as organo-modified montmorillonite Cloisite 30B or multiwall carbon nanotubes demonstrated varying effects on the material's reaction to fire, i.e., a large synergistic effect was observed when Cloisite 30B was used, whereas it was antagonistic when multiwall carbon nanotubes were used. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3860–3865, 2009

Key words: polylactide; melamine; ammonium polyphosphate; montmorillonite; multiwall; carbon nanotubes; intumescence

INTRODUCTION

An overview of the literature reveals that only a few authors have reported on the flame-retardant properties of biopolymers and biocomposites.[1,2] Because aliphatic polyesters, particularly polylactide (PLA), deserve attention in the area of environmentally degradable polymer materials,[3] in this work we focus on this biopolymer. The flame retardancy of PLA was studied by Kimura and Horikoshi[4] in 2005. They suggested formulations with conventional flame retardants (metal hydroxides) at high loading (about 60 wt %), exhibiting V-2 ranking at the UL-94 test. More recently our laboratory published studies on flame-retardant PLA by the use of conventional flame retardants (phosphate and phosphinate) at relatively low loading or nanoparticles (organomodified montmorillonite) exhibiting low flammability.[5–7]

The goal of this work was to achieve a low flammability of PLA at acceptable loading (up to 30 wt %) with the use of an intumescent system (intumescence means the development of an insulative, expanded charred coating at the surface of the polymer upon heating[8]) containing nanoparticles as potential synergist. The first part will be devoted to an optimized intumescent system. An intumescent flame retardant system usually is composed of three components: an acid source, a carbonization agent (or char forming agent), and a blowing agent.[9,10] Our system is composed of ammonium polyphosphate (APP) as the acid source, of melamine as a blowing agent, and of the polymer itself, i.e., PLA as carbonization agent. We demonstrated that polymer can be used in some cases as a char-forming agent.[11,12] In the second part, we will focus on the potential synergistic effect afforded by nanoparticles,[8] i.e., multiwall carbon nanotubes (MWCNTs)[6] and organomodified montmorillonite cloisite 30B (C30B) because we have found that nanoparticles in association with intumescents can act as synergists.[6,13,14]

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EXPERIMENTAL

Materials and preparation of the nanocomposites

PLA (number average molar mass = 74,500 g/mol, residual monomer content = 0.18%, D-isomer content = 4.3%, melt flow index [190°C, 2.16 kg] = 6.61 g/10 min and density: 1.25 g/cm^3) was supplied by NatureWorks (Minnetonka, MN) and dried overnight at 110°C before use.

For flame retardants (FRs), APP (Exolit AP 422, soluble fraction in water <1 wt %) in powder was supplied by Clariant (Charlotte, NC). Melamine (99%) was obtained from Sigma-Aldrich (St. Louis, MO). For nanoparticles, the starting material, sodium-MMT, was commercially modified by the use of methyl, tallow, bis-2-hydroxyethyl, and quaternary ammonium chloride (Cloisite 30B). Carbone nanotubes are multiwall carbon nanotubes (MWNTs) supplied by Nanocyl (Nanocyl-7000 at 90% purity; Nanocyl, Sambreville, Belgium). The FRs and nanoparticles were dried 24 h at 80°C before use.

TABLE I
Composition and Name of the Formulations PLA/Melamine/APP at 30 wt % Loading

PLA (wt %)	FR loading (wt %)	Melamine (wt %)	APP (wt %)	Formulation name
70	30	25.00	5.00	PLAMel25APP5
70	30	15.00	15.00	PLAMel15APP15
70	30	5.00	25.00	PLAMel5APP25

Sample preparation

For PLA/FR, PLA was mixed with FRs (10–30 wt % loading) at 185°C by use of a Brabender laboratory E350 mixer measuring head (roller blades, constant shear rate of 50 rpm) for 10 min. For PLA/FR/nanoparticles, PLA was melt-mixed with the nanoparticles and the FRs by use of the same protocol as described previously. The loading of nanoparticles varies from (0.33–1.00% wt % with constant loading in FR/nanoparticles from 10 to 30 wt %, respectively).

Fire testing

The Limited Oxygen Index (LOI; i.e., minimum oxygen concentration to support candle-like combustion of plastics) was measured with a Fire Testing Technology instrument on sheets (100 × 10 × 3 mm^3) according to the standard "oxygen index" test (ISO4589). It measures the minimum concentration of oxygen in a nitrogen/oxygen mixture required to just support combustion of a test sample under specified test conditions in a vertical position (the top of the test sample is ignited with a burner).

UL-94 classification was obtained on sheets (127 × 12.7 × 3.2 mm^3) according to the conditions of the standard test (ASTM D 3801), ie, in a vertical position (the bottom of the sample is ignited with a burner). This test provides only a qualitative classification of the samples (V-0, V-1, and V-2 labeled samples).

The Fire Testing Technology Mass Loss Calorimeter was used to perform measurements on samples following the procedure defined in ASTM E 906. Our procedure involved exposing specimens measuring 100 mm × 100 mm × 3 mm in horizontal orientation. External heat flux of 35 kW/m^2 was used for running the experiments. This flux corresponds to common heat flux in a mild fire scenario. When measured at 35 kW/m^2, heat release rate (HRR) is reproducible to within ±10%. The data reported in this article are the average of three replicated experiments.

Thermal analysis

Thermogravimetric analyses were conducted at heating rate 10°C/min in synthetic air (air liquid grade; flow rate = 75 mL/min) using a Setaram TGA 92. In each case, samples (10 mg) were positioned in open vitreous silica pans with gold foil. The precision on the temperature measurements is ±1.5°C in the temperature range of 50–800°C.

Interactions between the compounds of a mixture can be revealed by comparing the experimental TG curve with a "theoretical" TG curve (W_{theo}), calculated as a linear combination of the TG curves of the mixture ingredients weighted by their contents:

$$W_{\text{theo}}(T) = \sum_{i=1}^{n} x_i W_i(T)$$

where x_i is the content of compound I and W_i is the TG curve of the compound i.

To determine the potential interactions between the two components and their further effects on the thermal stability of the systems, the curves of weight differences between experimental and theoretical TG curves were computed as follows:

$$\Delta W(T) = W_{\text{exp}}(T) - W_{\text{theo}}(T)$$

where $\Delta W(T)$ is the curve of weight difference and $W_{\text{exp}}(T)$ is the experimental TG curve of the formulation.

RESULTS AND DISCUSSION

The aim of this study was to create PLA with very high fire-retardant properties. It is well known that

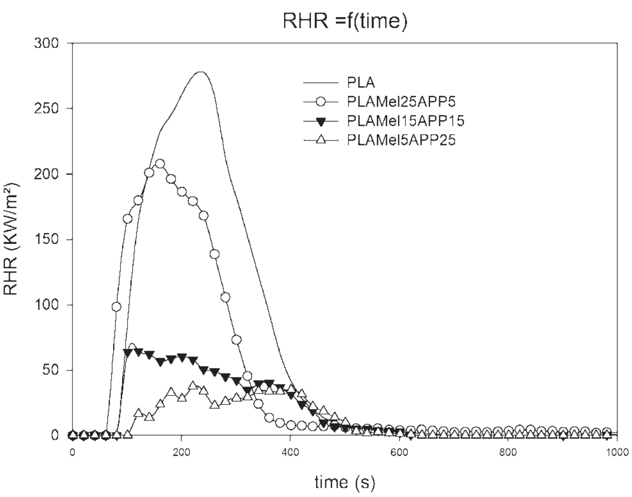

Figure 1 RHR curves as a function of time of PLA loaded at 30 wt % in melamine and APP at different ratios compared with virgin PLA.

TABLE II
Composition and Name of the Formulations PLA/Melamine/APP/MWNT or Cloisite 30B at 30 wt % Loading

PLA (wt %)	FR loading (wt %)	Melamine (wt %)	APP (wt %)	Cloisite 30B (wt %)	MWNT (wt %)	Formulation name
70	30	24.17	4.83	0.00	1.00	PLAMel25APP5MWNT
70	30	14.50	14.50	0.00	1.00	PLAMel15APP15MWNT
70	30	4.83	24.17	0.00	1.00	PLAMel5APP25MWNT
70	30	24.17	4.83	1.00	0.00	PLAMel25APP5C30B
70	30	14.50	14.50	1.00	0.00	PLAMel15APP15C30B
70	30	4.83	24.17	1.00	0.00	PLAMel5APP25C30B

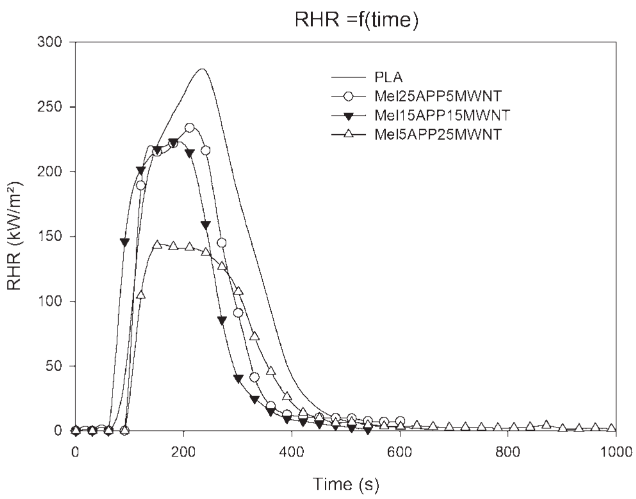

Figure 2 RHR curves as a function of time of PLA/melamine/APP/MWNT loaded at 30 wt % with different ratios of melamine and APP compared with virgin PLA.

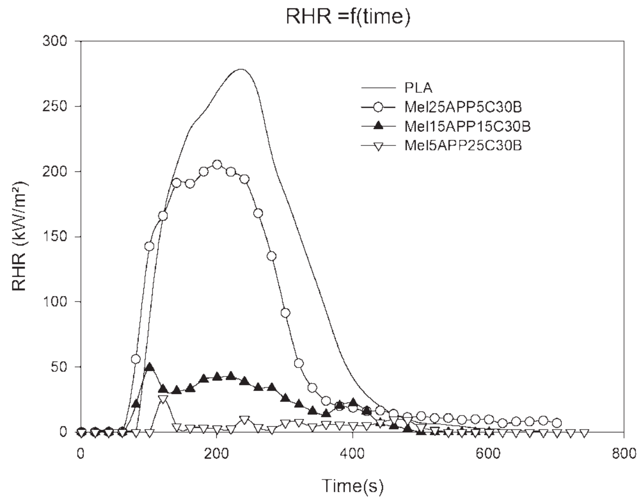

Figure 3 RHR curves as a function of time of PLA/melamine/APP/C30B loaded at 30 wt % with different ratios of melamine and APP compared with virgin PLA.

the usual loading for intumescent additives is 30 wt %. First, we developed a PLA/FR composite containing melamine and APP as intumescent ingredients, and we tested three different ratios, i.e., 5 : 1, 1 : 1, and 1 : 5, respectively (Table I).

The rate of heat release at 35 kW/m^2 was measured by mass loss calorimetry (Fig. 1). For all the formulations we observed an intumescent char and in all cases the addition of melamine and APP at 30 wt % decreased the peak of the rate of heat released (pRHR) compared with the neat PLA. The strongest reduction was observed in the case of PLAMel5APP25 (ratio 5 : 1) because pRHR decreased by 87%. Regarding the total of heat released (THR), the PLAMel5APP25 composite also exhibited the strongest and most noticeable reduction in THR (10.7 MJ/m^2) compared with neat PLA (58.4 MJ/m^2). We should emphasize that this material delays the time to ignition (TTI); the neat PLA began to burn at 85 s whereas PLAMel5APP25 shows a TTI at 109 s.

We then investigated the use of nanoparticles as potential synergist in our formulations. Our previous work has shown large synergistic effects when incorporated in intumescents.[6,13,14] To keep the same amount of FR, the nanoparticles were added at 1 wt % loading by substitution of the FR and, as performed previously, the three ratios 1 : 5; 1 : 1; and 5 : 1 were tested (Table II).

The first nanoparticles tested were MWNT. The mass loss calorimeter curves (Fig. 2) show that the MWNT produces an antagonistic effect. Indeed, the pRHRs related to each formulation containing

TABLE III
Composition and Name of the Formulations PLA/Melamine/APP/ Cloisite 30B or MWNT at 10 wt % Loading

PLA (wt %)	FR loading (wt %)	Melamine (wt %)	APP (wt %)	Cloisite 30B (wt %)	MWNT (wt %)	Formulation name
90	10	1.59	8.07	0.00	0.00	PLAMel2APP8
90	10	1.59	8.07	0.33	0.00	PLAMel2APP8C30B
90	10	1.59	8.07	0.00	0.33	PLAMel2APP8MWNT

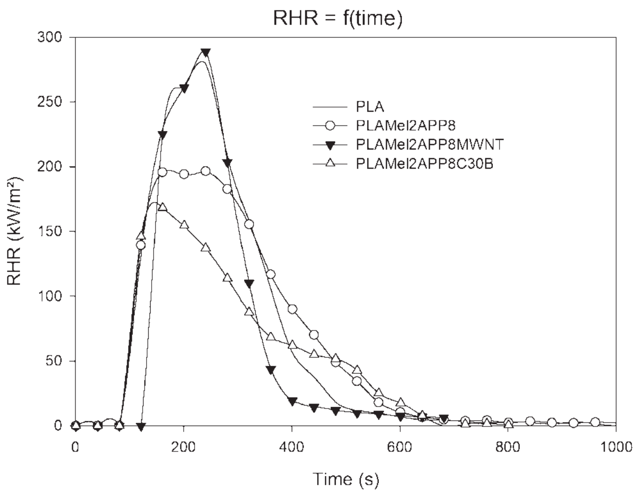

Figure 4 RHR curves as a function of time of PLA/melamine/APP with and without MWNT or C30B loaded at 10 wt % with a ratio 1 : 1 of melamine and APP compared with virgin PLA.

MWNT were worse than those without MWNT (Fig. 1).

The second nanoparticles tested were Cloisite 30B (Table II). The RHR curves (Fig. 3) exhibit an extraordinary reduction of pRHR for the formulation PLAMel5APP25C30B: pRHR was decreased by 90% in comparison with the neat PLA, whereas the formulation PLAMel25APP5C30B did not show any difference with that without Cloisite and, for the formulation PLAMel15APP15C30B, the pRHR was only slightly decreased. Moreover, a large decrease of the THR also was observed, the THR of virgin PLA was 58.4 MJ/m^2, whereas it was only 2.5 MJ/m^2 for PLAMel5APP25C30B: this material exhibits a real nonburning behavior. TTI also was delayed; the incorporation of C30B did affect delay obtained without C30B: TTI was 109 s and 111 s for PLAMel5APP25 and PLAMel5APP25C30B, respectively.

It is noteworthy that similar results were observed at 20 wt % loading (not shown) and at 10 wt % loading (Table III, Fig. 4). The formulation with melamine and APP at 10% loading showed a 30% reduction of pRHR, whereas the reduction was 48% with C30B. On the contrary, the incorporation of MWNT instead of C30B did not provide any reduction of the pRHR: the FR formulation exhibited the same behavior as that of the neat PLA, confirming the antagonistic effect already observed at 30 wt % loading. Regarding THR, the best result was obtained with C30B: the THR of the formulation PLAMel2APP8C30B was 49 MJ/m^2, whereas it was 58.2 and 58.4 MJ/m^2 for PLAMel2APP8 and neat PLA, respectively. These results permit us to conclude that C30B is a real synergist for intumescent PLA.

LOI and UL-94 tests also were performed (Tables IV–VI). The results show that (1) the combination of melamine and APP in PLA provides high LOI values and V-0 classification can be achieved; (2) the right ratio of melamine/APP is essential because the best results are always reached with the ratio 1 : 5; (3) the incorporation of C30B permits in all the cases an increase of LOI values; and (4) the incorporation of MWNT always provides an antagonistic effect, decreasing LOI and UL-94 classification (except at 30 wt % loading for the ratio 1 : 5 [wt/wt] melamine/APP).

Regarding these results, we have investigated the role of nanoparticles by thermogravimetry. The TGA curves of the pure products of the formulations are depicted in Figure 5. The PLA begins to decompose at 230°C[15,16] and melamine at 180°C. Both are decomposed in one step with no residue left at the

TABLE IV
LOI and UL-94 Ranking of Neat PLA and PLA/Melamine/AP422 with and without C30B or MWNT at 30 wt % Loading

Ratio of melamine/APP	Formulation name	LOI (vol %)	UL-94
	PLA	20	NC
5/1	PLAMel25APP5	33	V-0
	PLAMel25APP5C30B	38	V-0
	PLAMel25APP5MWNT	24	NC
1/1	PLAMel15APP15	40	V-0
	PLAMel15APP15C30B	42	V-0
	PLAMel15APP15MWNT	30	NC
1/5	PLAMel5APP25	46	V-0
	PLAMel5APP25C30B	52	V-0
	PLAMel5APP25MWNT	32	V-0

TABLE V
LOI and UL-94 Ranking of PLA/Melamine/AP422 with and without C30B or MWNT at 10 wt % Loading

Formulation name	LOI (vol %)	UL-94
PLAMel2APP8	33	V-0
PLAMel2APP8C30B	35	V-0
PLAMel2APP8MWNT	24	NC

TABLE VI
Afterflame Time After First Flame Application (t_1) and Afterflame Time After Second Flame Application (t_2) Measured for UL-94 Test for Formulations (with a Ratio of Melamine/APP 1 to 5) Loaded at 10 and 30% wt % FR

Loading (wt %)	Formulation name	Extinction time (s)		UL-94
		t_1	t_2	
10	PLAMel2APP8	2–4	3–5	V-0
10	PLAMel2APP8C30B	1–5	2–4	V-0
10	PLAMel2APP8MWNT	26–32	29–35	NC
30	PLAMel5APP25	0–3	1–3	V-0
30	PLAMel5APP25C30B	0	0	V-0
30	PLAMel5APP25MWNT	2–5	2–4	V-0

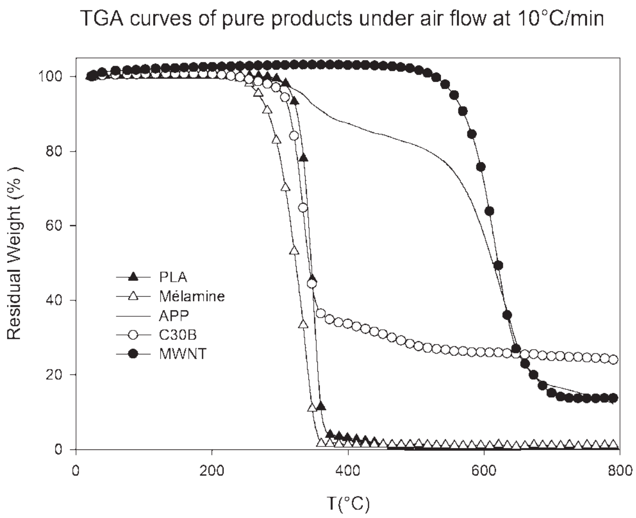

Figure 5 TGA curves of pure compounds of the studied formulations.

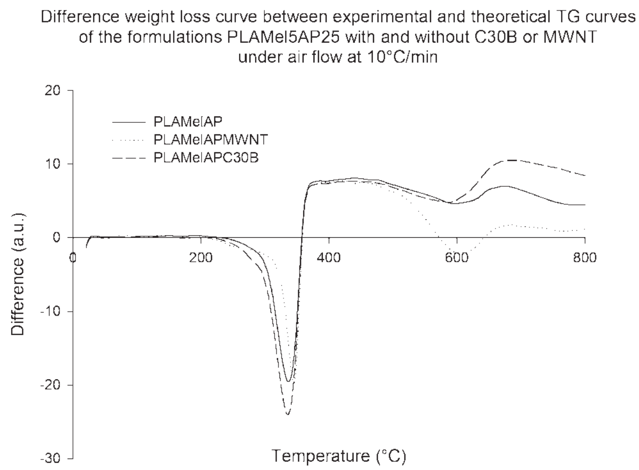

Figure 7 Difference weight loss curve between experimental and theoretical TG curves of PLA/melamine/APP with and without MWNT or C30B.

end of the experiment, i.e., 800°C. Decomposition of C30B is well known and documented[17–20] its proceed in three steps: the first one before 100°C and the second and third one at 200°C and 400°C, respectively, with 23% of residual weight. MWNTs are decomposed at greater temperatures, i.e., 500°C also in one step, leading to a 14% residue. APP is decomposed in two steps, at 200 and 460°C, with 11% of residue. Its degradation is well known. When heated, it eliminates ammonia and water, and the final product of degradation is characterized by a cross-linked P···O···P structure.[21]

The TGA curves obtained for the formulations containing melamine and APP at ratio 1 : 5 with or without nanoparticles (Fig. 6) show that all the formulations decomposed in two steps: (1) the first step yields the formation of transient char which (2) is degraded via oxidative reaction. Those curves are similar up to 500°C, i.e., before the degradation of the transient char. At greater temperatures, C30B limits the degradation of the char whereas MWNT accelerates this degradation. At 800°C, the final residues are of 12, 8, and 5 wt % for PLA/melamine/APP with C30B, PLA/melamine/APP without nanoparticles, and PLA/melamine/APP with MWNT, respectively.

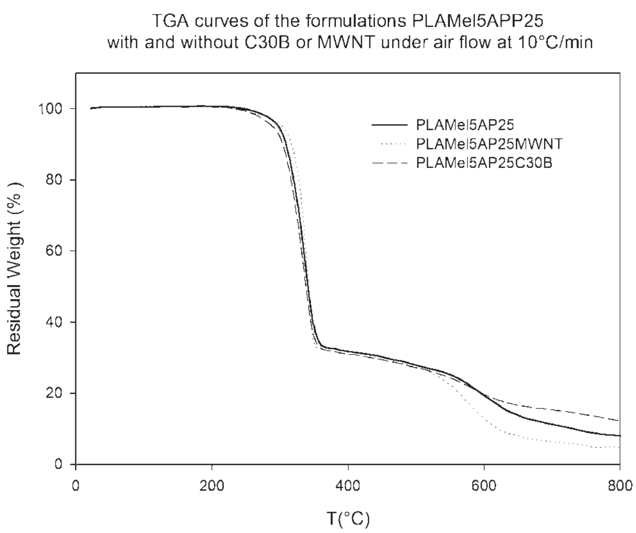

Figure 6 TGA curves of formulations PLA/Melamine/APP with and without MWNT or C30B.

The difference of weight loss curves (Fig. 7) exhibit the same behavior for the three formulations until 460°C, starting with negative interactions (destabilization zone) which are similar between 200 and 360°C. These are immediately followed by positive interactions (stabilization area), which end at 460°C for the formulation containing MWNT whereas, without nanoparticles (PLAMelAPP), this positive region is maintained up to 800°C. The addition of C30B (PLAMelAPPC30B) permits one to obtain an increase of stabilization area. Those results prove the role of the nanoparticles in PLA/melamine/APP formulations, which can stabilize or destabilize the intumescent char. C30B acts as a reinforcing agent of the intumescent coating permitting to increase its efficiency while MWNT acts in the opposite way.

CONCLUSIONS

In this study, we prepared a PLA exhibiting very low flammability via intumescent behavior. It is the first work reporting such fire-retardant behavior of PLA at low loading. Using a combination of melamine and APP as intumescent ingredient, we showed that the best ratio was 1 : 5. A large synergistic effect was observed when a small amount of organoclay C30B was used. At 30 wt % extremely high LOI values were measured (up to 52 vol %), and a V-0 rating was achieved. pRHR is extremely low and was decreased by 90% compared with virgin PLA. At lower loading (10 and 20 wt %), the intumescent PLA still exhibited very low flammability. In conclusion, it offers an exceptional way to make a biopolymer exhibiting nonburning behavior.

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