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Thermal properties and flammability of polylactide nanocomposites with aluminum trihydrate and organoclay

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ABSTRACT

Biodegradable polylactide (PLA) nanocomposites with aluminum trihydrate (ATH) and modified montmorillonite (MMT) were prepared via direct melt compounding using a twin-screw micro extruder. The exfoliated and intercalated structures of clay in the matrix were observed by TEM and XRD. The thermal oxidative degradation temperature and activation energy of the PLA/ATH/MMT nanocomposite determined by thermogravimetric analysis are higher than that without addition of ATH and organoclay. The incorporation of layered silicates into the PLA/ATH composite results in further stabilization throughout the degradation step. The V-0 rating (UL94 V) of the PLA nanocomposite has been achieved, and the melt dripping was reduced during combustion. Results showed that high loading of the conventional flame retardant ATH yielded brittle PLA composites; however, replacing a portion of the ATH with modified MMT in the PLA matrix improved this result.

1. Introduction

Polylactide (PLA) is one of the most promising and important biodegradable polymers that can be used as an alternative to petroleum-based commodity polymers because it can be produced from renewable resources at relatively low cost and large production volume (Ajioka, Enomoto, Suzuki, & Yamaguchi, 1955; Auras, Harte, & Selke, 2004; Fukushima, Murariu, Camino, & Dubois, 2010; Ke et al., 2010; Kumar, Mohanty, Nayak, & Parvaiz, 2010; Madhavan Nampoothiri, Nair, & John, 2010; Zhang, Wu, & Qiu, 2010). Therefore, PLA has found widespread use, such as in biomedical materials, packaging, bags, films and fibers. However, PLA is highly combustible, which limits its application in electronic or electrical materials. Several researchers have reported that conventional or novel intumescent flame retardants were blended with PLA to improve the flame retardancy and anti-dripping performance of PLA during burning (Bourbigot et al., 2008; Murariu et al., 2010; Reti, Casetta, Duquesne, Bourbigot, & Delobel, 2008; Zhan, Song, Nie, & Hu, 2009).

Over the past decade, incorporating nanoscale fillers into polymer composites at typically low loads of 1–5 wt% has been extensively studied to enhance not only their mechanical properties and gas barrier performance but also to improve thermal properties and to reduce flammability (Bartholmai & Schartel, 2004; Beyer, 2003; Gilman, 1999; Gilman et al., 2000; Kiliaris, Papaspyrides, & Pfaendner, 2008; Wu, Wu, Wu, & Zhang, 2006). Among these fillers, polymer/layered silicate (PLS) nanocomposites have attracted great interest due to the low cost of clays and amenability to a variety of manufacturing processes. Polymer/clay nanocomposites synthesized without an additional flame retardant exhibited a lower heat release rate (HRR), including peak HRR, than that of the neat polymers during forced combustion tests via a cone calorimeter (Kashiwagi et al., 2003; Morgan, 2006). However, the total heat release remained unchanged. During the combustion, the clay in the polymer matrix collapsed to form a clay-rich barrier, which resulted in a slow burning but not extinguishment. Most PLS nanocomposites cannot meet the regulatory tests without further modification. Consequently, combining PLS nanocomposites with other flame retardants is an attractive solution to enhance the thermal stability and flame retardant properties.

Ethylene vinyl acetate (EVA) nanocomposites at lower aluminum trihydrate (ATH) loading exhibit superior mechanical and flame retardant properties than conventional ATH-filled EVA (Gilman et al., 2000). Another approach is to combine a phosphate flame retardant additive with an organoclay and polystyrene by a mass polymerization process to produce a PLS nanocomposite, which showed a reduction in both the HRR peak and total heat released via cone calorimetry (Chigwada & Wilkie, 2003). Furthermore, PLA-based nanocomposites can be prepared using two

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different nano fillers: expanded graphite and organically modified montmorillonite via melt compounding (Fukushima et al., 2010). Improvements in thermal and mechanical properties of PLA were obtained in the presence of both nanoparticles and were attributed to the good dispersion and to the co-reinforcement effect. We also found that adding the nanodispersed layered silicate and ATH flame retardant to the EVA/LLDPE blend produces a synergistic effect on the flame retardancy and smoke-suppressing ability of the composite (Chuang et al., 2004). Accordingly, integration of the conventional flame retardant ATH and layered silicate into the PLA matrix is expected to improve the thermal and/or mechanical properties of the PLA composite.

In this study, polylactide (PLA) composites with aluminum hydroxide (ATH) and modified montmorillonite (Cloisite 30B) were prepared via direct melt compounding in a twin-screw micro extruder. The morphology, thermal degradation, and mechanical properties of the PLA/ATH/MMT composites were investigated by XRD, TEM, TGA and tensile testing. Furthermore, the fire retardant properties were observed by a vertical burning UL94 test and cone calorimetry. The effects of different compositions of conventional retardant and modified MMT on the thermal and mechanical properties of the nanocomposites will be discussed.

2. Experimental

2.1. Materials

Polylactide (PLA, PLA2002D^{TM}) was purchased from NatureWorks LLC. Aluminum trihydrate (ATH, H-42M grade) with an average particle size of about 1.1 μm was obtained from Showa Denko Co. Ltd., Japan. Modified montmorillonite clay with methyl tallow bis(2-hydroxyethyl) ammonium (Cloisite 30B) was purchased from Southern Clay Products Inc. The PLA, ATH and Cloisite 30B were dried overnight at 90 °C under vacuum before compounding.

2.2. Sample preparation

Polylactide composites synthesized from ATH and modified montmorillonite (Cloisite 30B) were melt compounded in a twin-screw micro extruder (MiniLab HAAKE Rheomex CTW5, L/D = 12:1) at 120 rpm for 6 min under 160 °C. The three sample groups Ax, Bx, and Cx correspond to the PLA composites having 30, 40 and 50 wt% of fillers, respectively, in which the “x” indicates the weight percentage of the ATH, and the remaining is the weight fraction of Cloisite 30B. For example, sample A27 denotes the composite of PLA with addition of 27 wt% ATH and 3 wt% Cloisite 30B.

2.3. Analysis

X-ray diffraction spectra (XRD) were obtained using a diffractometer (PANalytical X’Pert PRO) with Cu radiation ($\lambda = 0.154$ nm). The morphology of the clay in the composite was observed with a JEOL transmission electron microscope at 200 kV (model JEM2010). Thermal degradation behavior of the PLA nanocomposite was observed using a thermogravimetric analyzer (TGAQ-50). Experiments were carried out on samples of about 10 mg under air flow (90 mL/min) at a heating rate of 20 °C/min.

Limiting oxygen indices (LOI) of the composites were determined using a Suga test apparatus (model: ON-1). A cone calorimeter (Atlas Cone 2) was used to evaluate the flammability of the composites (size: 100 mm × 100 mm × 6 mm) at 50 kW/m^2 incident heat flux. The UL-94 vertical test was performed according to the ASTM D3801 testing procedure (sample size: 120 mm × 13 mm × 3 mm). According to ASTM D638 method, mechanical tensile properties of the composites were measured by a tensile tester (Tensometer 10, Monsanto Co.) at an extension rate of 5 mm/min under room temperature.

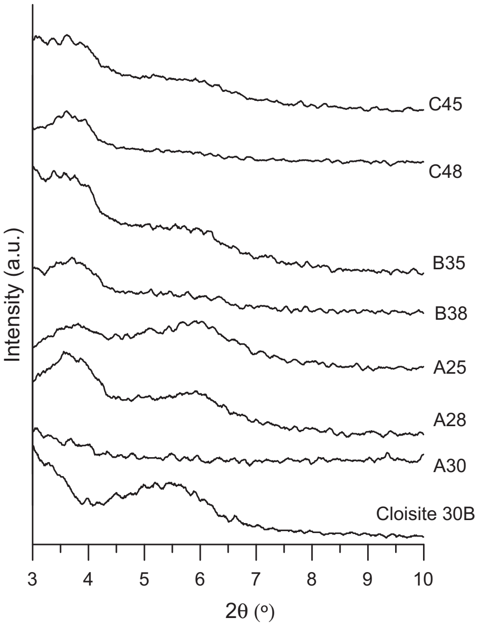

Fig. 1. XRD patterns of PLA, ATH, modified MMT and PLA composites.

3. Results and discussion

3.1. Morphology

The interlayer distance between silicate layers can be observed from the basal reflection of the X-ray diffraction curve (Pluta, 2006; Pluta, Galeski, Alexandre, Paul, & Dubois, 2002). Fig. 1 shows the X-ray diffraction patterns of the modified MMT (Cloisite 30B) and composites from group A. Both the PLA and ATH give a flat cure in the 3–10° range of the XRD. The modified clay, Cloisite 30B, exhibits a diffraction peak at about 5.3° corresponding to the basal reflection (0 0 1) and *d*-spacing of about 1.7 nm. With the addition of 28 wt% aluminum trihydrate and 2 wt% Cloisite 30B (sample A28), a peak at the lower angle of 3.3° is observed, which is attributed to the intercalated nanostructures that have a 2.7 nm interlayer distance. There is another peak at the higher angle of about 5.7°, which corresponds to a 1.5 nm *d*-spacing and implies that a partial re-aggregation of MMT platelets occurred during the processing.

Increasing the ATH content results in broad peaks near 3.3°, which indicate intercalated or exfoliated nanocomposite structures. Moreover, the re-aggregation phenomena seem to be reduced or eliminated, as shown in Fig. 1. In other words, the presence of ATH may facilitate the melt intercalation of PLA into the organically modified MMT during compounding in the twin-screw extruder. The morphology of the composite was further observed by the TEM. In Fig. 2, the larger dark image shows the crushed ATH and that the modified MMT was well dispersed in the PLA matrix. In the high-magnification TEM picture of sample B35, there are several intercalated tactoids composed of a number of lamellae with *d*-spacing higher than 3 nm, and individual MMT sheets are clearly observed. This result implies that the structure of the PLA/ATH/MMT nanocomposite is exfoliated–intercalated, which verifies the result obtained from the XRD pattern.

3.2. Thermal degradation

The thermal properties of the PLA composites were investigated by TGA in an air atmosphere. Fig. 3 shows the thermal degradation

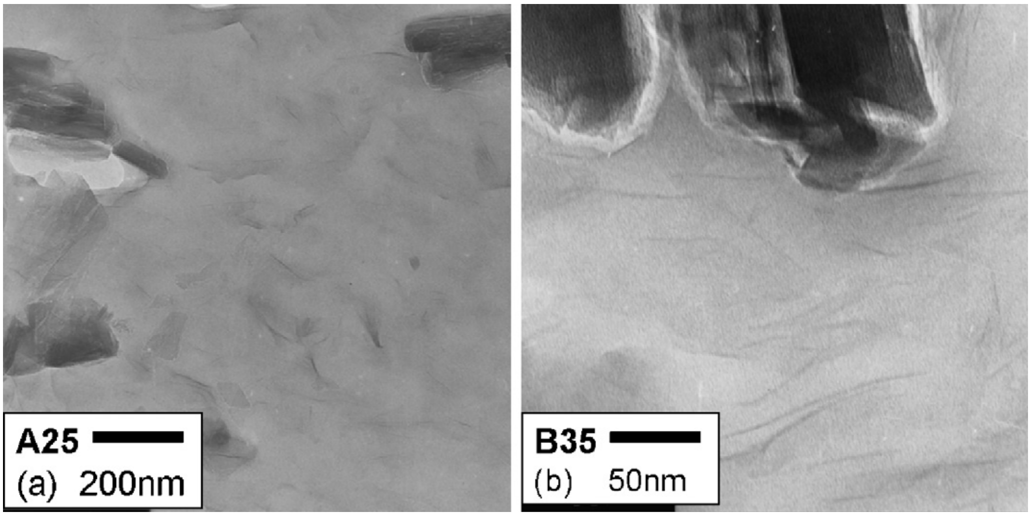

Fig. 2. TEM of PLA nanocomposites.

properties of the composites determined by TGA. The temperatures of the 5% loss (T_d) and the maximum thermal degradation rate of aluminum trihydrate are 250 °C and 280 °C, respectively. The main thermal decomposition of the unmodified PLA occurred at about 371 °C and was reduced to about 320 °C with the addition of 40 wt% ATH (sample B40). This drop is due to the lower dehydration temperature, 250–320 °C, of the ATH filler. However, the char yield at 650 °C increases with the ATH content. Adding a small amount of MMT raises the thermal stability of the PLA by about 10–15 °C, due to the barrier effect of the clay layers that happens during polymer combustion (Fukushima et al., 2010). Therefore, as shown in Fig. 3, the thermo-oxidative degradation temperature of the PLA composite was improved by substituting Cloisite 30B for a portion of the ATH. For example, the temperature at the maximum decomposition rate, T_{max}, of the PLA/ATH composite containing 40 wt% of ATH (sample B40) is 321 °C. This value increased to 337 °C at 5% MMT and 35% ATH (B35). Incorporation of layered silicates, MMT, into the PLA/ATH composite yields further stabilization throughout the degradation step.

The thermo-oxidative degradation activation energies of PLA composites containing 50 wt% of fillers, group C, were calculated by Ozawa and Kissinger methods according to the TGA data, which were measured under air at different heating rates: 2.5, 5, 10, 15, and 20 °C/min (Kissinger, 1957; Ozawa, 1965). The results are listed in Table 1. The degradation activation energy of PLA is 132 kJ/mol by the Ozawa method, which increases to 146 kJ/mol with the addition of 50% ATH. This reduction in thermal decomposition at higher ATH content is due to heat absorption from the liberated water and refractory aluminum oxide acting as a protecting layer on the substrate surface (Almeida Pinto, Visconte, Gallo, & Nunes, 2000; Thirumal, Singha, Khastgir, Manjunath, & Naik, 2010). Moreover, the barrier effect of layered silicates on volatiles in the nanocomposites could retard the thermal oxidative degradation; thus, with the addition of a certain amount of MMT in the PLA/ATH composite, the degradation activation energy increases.

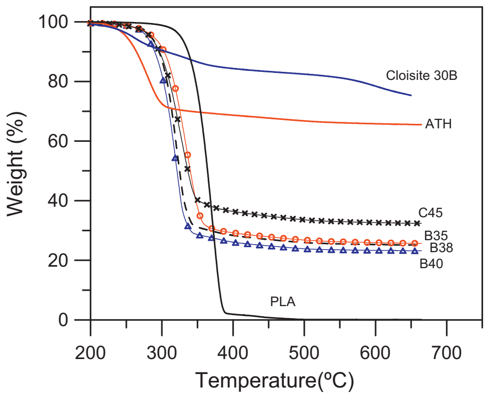

Fig. 3. Weight loss curves of PLA, ATH, modified MMT and PLA nanocomposites at different ATH and MMT loading.

3.3. Flammability properties

The limiting oxygen index (LOI) values of PLA and composites with aluminum trihydrate or Cloisite 30B are given in Table 2. The LOI of the neat PLA is 20.5. This value increased to 28.5, 30, and 36 with the addition of 30, 40 and 50 wt% of ATH, respectively. Incorporating layered silicates into the PLA/ATH composites (group A or B) resulted in an LOI that was lower or equal to the initial value. However, for composites with a higher fraction of ATH, such as group C, increases in LOI were observed. For example, the sample containing 50% ATH had an LOI of 36, but nanocomposite C45, which had 5% MMT substituted for ATH, had an LOI of 42. It is believed that when burning nanocomposites having low contents of ATH, the layered clay in the nanocomposite is unable to integrate well with ATH to form a rigid insulation layer on the ablating surface and possibly drips away with the melting material; thus, the addition of MMT is unable to improve the LOI of PLA composites. At high fractions of ATH, the MMT could be integrated with another filler ATH to produce a solid insulation barrier during combustion, increasing the LOI value. The results suggest that the addition of modified MMT creates a synergistic effect with the conventional flame retardants in the PLA composite.

Table 1
Thermo-oxidative degradation activation energy of PLA/ATH/MMT composites.

Sample	Ozawa method (kJ/mol)	Kissinger method (kJ/mol)
PLA	131.5	133.7
C50	146.1	150.0
C49	152.6	155.0
C48	150.2	153.0
C47	146.0	152.8
C46	139.0	148.6
C45	141.7	152.3

Table 2
Flame retardant properties of the PLA composites.

Sample	LOI (%)	UL-94	Total flaming combustion of all five specimens (s)	Flame dripping	Cotton ignited
PLA	20.5	Fail	>250*	Yes	Yes
A30	28.5	V-2	31	Yes	Yes
A29	27.0	V-2	35	Yes	Yes
A28	27.5	V-2	92	Yes	Yes
A27	26.0	V-2	95	Yes	Yes
A26	27.0	Fail	307	Yes	Yes
A25	27.0	Fail	941*	Yes	Yes
B40	30.0	V-0	11	Yes	No
B39	30.5	V-0	16	Yes	No
B38	31.0	V-2	155	Yes	Yes
B37	30.0	V-2	162	Yes	Yes
B36	30.0	V-2	107	Yes	Yes
B35	30.0	Fail	537*	No	No
C50	36.0	V-0	15	Yes	No
C49	36.0	V-0	22	Yes	No
C48	37.0	V-0	16	Yes	No
C47	37.0	V-0	46	Yes	No
C46	41.5	V-0	41	Yes	No
C45	42.0	V-0	33	No	No

Fail: no rating of UL-94 tests.
* Flaming or glowing combustion up to the holding clamp.

The UL94 flammability rating serves as an indication of polymer acceptability for use as a device component. The results of UL94 for vertical burn are listed in Table 2. The unfilled PLA was highly flammable according to the test, exhibiting burning with a flame present or glowing combustion up to the holding clamp. Moreover, the cotton indicator was ignited by melt drips. When PLA was combined with 30% ATH (composite A30) the burning stopped within 10 s, but the drips still ignited the cotton. This result is classified as a V-2 rating. At higher ATH content (B40 and C50 as examples), the burning time lessened, and ignition of the cotton indicator was avoided; thus, the classification was upgraded to a V-0 rating. Adding the substitutive filler Cloisite 30B resulted in a longer burning time, which failed the UL94 tests as shown in the cases A25 and B35. If the ATH loading was lower than about 39 wt%, there was no compact insulator formed on the burning surface, and the flame could not be retarded effectively. However, the melt dripping could be reduced by adding the MMT substitute, and no dripping occurred at 5% Cloisite 30B and 45% ATH. These results suggest that a PLA/ATH/MMT nanocomposite having a U94 V-0 rating without dripping can be achieved via melting compounding using a twin-screw extruder.

The cone calorimeter is a very effective bench-scale tool used to study the flammability properties of materials and the heat release rate (HRR). The HRR, and especially the peak HRR, have been found to be helpful in evaluating fire safety. The ignition time of the unmodified PLA is about 58 s, and the peak HRR and heat flux are 629 and 259 kW/m^2, respectively, as shown in Fig. 4 and Table 3. The results indicate that the conventional retardant aluminum trihydrate has a significant effect on the PLA composite. For the composite containing 50 wt% ATH (sample C50), the ignition time was delayed to 163 s, and the peak and average HRRs were reduced to 316 and 90 kW/m^2, respectively. Adding Cloisite 30B substitutive filler into the PLA composite neither retarded the ignition time nor decreased the heat flux, but it did reduce the peak HRR.

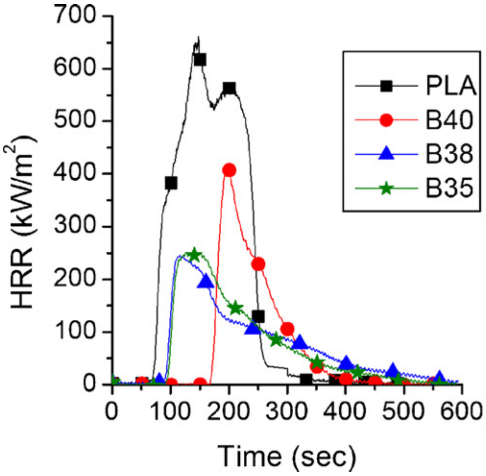

Fig. 4. Heat release rate curves of PLA and composites B40, B38 and B35.

Table 3
Flammability properties of PLA composites determined by the cone calorimeter.

Sample	Time to ignition (s)	Peak HRR (kW/m^2)	Av. HRR (kW/m^2)	Av. HOC (MJ/kg)
PLA	58	628.5	259.2	23.1
A30	75	443.8	156.6	21.7
A28	60	327.4	128.3	19.0
A25	58	283.8	125.9	18.1
B40	142	411.8	117.4	17.4
B38	62	246.3	102.0	10.2
B35	65	252.0	121.6	18.2
C50	163	316.4	90.2	14.0
C48	55	230.4	101.1	16.7
C45	64	221.5	103.3	16.9

Table 4
Mechanical properties of PLA/ATH/MMT composites.

Sample	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Pure PLA	3.69 (±0.05)	55.2 (±3.07)	9.98 (±0.52)
A30	4.42 (±0.20)	55.3 (±1.35)	6.76 (±0.33)
A29	4.65 (±0.07)	52.5 (±2.25)	6.06 (±0.28)
A28	4.71 (±0.05)	56.5 (±3.34)	6.53 (±0.32)
A27	4.93 (±0.23)	51.5 (±3.36)	5.61 (±0.37)
A26	4.69 (±0.19)	49.3 (±8.98)	5.75 (±0.94)
A25	4.55 (±0.19)	45.0 (±9.42)	5.31 (±0.98)
B40	4.51 (±0.38)	44.9 (±0.67)	5.78 (±0.30)
B39	4.65 (±0.50)	47.4 (±2.59)	5.67 (±0.42)
B38	5.02 (±0.37)	44.4 (±3.61)	5.24 (±0.12)
B37	5.01 (±0.05)	52.4 (±1.29)	5.81 (±0.25)
B36	5.50 (±0.09)	44.6 (±5.45)	4.49 (±0.43)
B35	4.99 (±0.25)	43.8 (±1.97)	4.63 (±0.25)
C50	4.19 (±0.34)	32.0 (±2.09)	3.07 (±0.27)
C49	5.21 (±0.58)	46.0 (±5.51)	4.95 (±0.35)
C48	5.60 (±0.42)	41.4 (±7.39)	4.34 (±0.36)
C47	4.72 (±0.06)	35.6 (±0.31)	3.50 (±0.11)
C46	4.27 (±0.35)	34.8 (±3.01)	4.10 (±0.23)
C45	3.24 (±0.21)	36.9 (±1.35)	4.68 (±0.22)

3.4. Mechanical properties

The mechanical tensile properties of PLA/ATH/MMT composites are summarized in Table 4. The tensile modulus of the unmodified PLA is 3.7 GPa, the tensile strength is 55.2 MPa, and the elongation at break is 10%. Most of the tensile moduli of composites were increased by the addition of aluminum trihydrate. The composite B40 has 40 wt% ATH, which increased the modulus to 4.5 GPa, but the strength and break elongation declined to 45 MPa and 5.8%, respectively. The sample exhibited a loss in mechanical strength and became brittle at higher ATH loading. It is expected that the addition of layered silicates will increase the mechanical modulus and strength. As shown in the Table 4, when the modified MMT Cloisite 30B was added to replace a portion of the fillers at a certain composition, the mechanical properties improved. For example, by adding 3% MMT, the tensile modulus of composite B37 rose to 5 GPa, and its tensile strength became 52.4 MPa, which is a 17% increase compared to sample B40.

4. Conclusion

The polylactide (PLA) nanocomposites with exfoliated and intercalated structures of montmorillonite (MMT) in the polymer matrix have been successfully prepared by direct melt compounding with aluminum trihydrate (ATH) using a twin-screw micro extruder. Incorporation of modified layered silicates into PLA/ATH composites result in further thermo-oxidative stabilization throughout the degradation step. The thermal degradation activation energy can be increased with the addition of MMT and ATH. It is hypothesized that during the UL94 test, the added layered silicates and the high ATH content in PLA are integrated to form a compact insulator on the burning surface, reducing the melt dripping. It was found that at high contents of the conventional flame retardant ATH, the PLA composite becomes brittle, but this can be improved by adding modified MMT to replace a portion of ATH in the PLA matrix.

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