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Flame-retarding polylactic-acid composite formed by dual use of aluminum hydroxide and phenol resin

Yukihiro Kiuchi*, Masatoshi Iji, Tsunenori Yanagisawa, Tanaka Shukichi

Smart Energy Research Laboratories, NEC Corporation, 34, Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

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ABSTRACT

Flame retardancy of polylactic acid (PLA) was improved by dual use of aluminum hydroxide (AH) and phenol resin as safe flame retardants to allow PLA to be widely applied in durable products including electronic devices. Adding more than 50 weight-percent (wt%) of a specific AH which contains a low concentration of alkali elements sufficiently improved the flame retardancy of PLA. However, other important characteristics of the resulting PLA composites, such as flexural strength and fluidity, were decreased owing to the high concentration of AH. On the other hand, the simultaneous addition of phenol resins (including phenol novolac resin and tri-phenol methane resin) and the specific AH improved the flame retardancy of the PLA composites. This enhancement effect on flame retardancy, which was mainly due to the formation of homogeneous char layers produced by the phenol resins on the surface of the PLA composites during combustion, permitted the specific AH concentration to be reduced, thereby improving these characteristics of the composites. In particular, a high-molecular-weight phenol novolac resin (HMw PN resin) showed highly flame-retarding effect. While using phenol resins adversely affected the action of an organic crystalline nucleus agent for PLA, the use of HMw PN resin improved the problem because its concentration in the PLA composite was reduced due to its highly flame-retarding effect.

1. Introduction

Bioplastics originated from plant resources have been watched with keen interest as one of the most promising materials for preventing the continuing drain on petroleum resources and for their anchoring effect on emission of carbon dioxide. Endeavors to reduce the environmental load of products by replacing petroleum-based plastics with bioplastics have been attempted in various industrial fields. Even among bioplastics, polylactic acid (PLA) shows relatively high mechanical strength and heat resistance [1] and is produced in bulk [2]. In regard to materials for casings of durable products including electronic devices, replacing petroleum-based plastics with PLA has been attempted. Some kinds of PLA composites have already been put to practical use in products that do not require high flame retardancy, such as casing materials for a few kinds of mobile phones [3]. To apply PLA to casing materials of medium-size electronic products such as personal computers, the high flame retardancy of the PLA composites is required to prevent burning derived from these products. However, while maintaining high biomass content in the resin part of the PLA composites including flame retardants and other additives, achieving high flame retardancy of the composites has been very difficult. For example, flame-retarding polycarbonate (PC)/PLA alloy composites have already been put to practical use [4]. These alloy composites mainly consist of PC (which is originated from petroleum materials and shows high flame retardancy), PLA, and phosphorous-type flame retardants. These alloy composites contain high concentrations of the petroleum-based resin; therefore, their biomass contents are very low, i.e., under 50 weight-percent (wt %) in the resin parts (organic materials) in the composites.

We investigated how to achieve high flame retardancy of PLA composites while maintaining high biomass content in the resin parts by using a safe metal hydroxide such as aluminum hydroxide (AH) (which is one kind of soil components). The flame-retarding mechanism of AH is twofold: absorption of heat and dilution of combustible gas by generating water vapor during its decomposition [5]. AH has been used as a flame retardant for various resin compounds used in printed wiring boards [6] and covering cables [7]. Furthermore, pyrolysis of AH starts in the range of temperature from 200 to 250 °C, which is nearly equal to that of PLA. Therefore, we thought that AH is suitable for inhibiting decomposition of PLA at the beginning of combustion.

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* Corresponding author. Tel.: +81 29 850 1019; fax: +81 29 856 6137.
E-mail address: qti@da.jp.nec.com (Y. Kiuchi).

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However, to achieve high flame retardancy of PLA composites by using AH only, a high concentration of AH is needed. As a result, characteristics such as flexural strength, flexural strain, fluidity, and impact strength of the PLA composites are degraded. Thereby, to improve these characteristics by reducing the amount of AH, we have studied dual-use of AH and phenol resins as a flame-retarding aid. When heated, phenol resins containing aromatic hydrocarbons produce phenyl ethers and furan rings after the dehydrogenation by condensation of two hydroxyl groups in the resins, and then easily form char precursors with high molecular weights [8]. These chars show excellent flame retardancy [9]. Accordingly, we consider that adding phenol resin to PLA can make a flame-retarding layer mainly consisting of char over the ignited surface of the PLA composites, thereby inhibiting the combustion of the composites and aiding the flame-retarding effect by AH. In past studies, the flame retardancy of ABS was improved by dual-use of acrylonitrile-butadiene-styrene (ABS) resin and phosphorous-type flame retardant [10]. Furthermore, there is an example of dual-use of a metal hydroxide (magnesium hydroxide) and a char former (melamine) for polypropylene resin [11]. However, such a dual-use effect in the case of PLA has not been reported.

In recent studies, nanocomposite-technology was applied to improve flame retardancy of polymer [12]. However, this flame retardancy was not examined by UL94 vertical method and was only estimated by a specific radiant-heating gasification apparatus which measured mass loss rates and temperatures of a sample exposed to a fire-like heat flux in a nitrogen atmosphere (no burning). Therefore, the effect of nanocomposite to improve flame retardancy of PLA examined by UL94V method was not clear.

In this study, aiming to select an appropriate AH for attaining high flame retardancy examined by UL94 vertical method, firstly, we controlled hydrolysis of PLA by reducing alkalis contained in AH and then examined the flame retardancy and other characteristics of the PLA composites containing a specific AH with a low alkali content. Secondly, we investigated the effect of dual-use of the specific AH and phenol resins; some representative phenol resins were evaluated from the viewpoint of difference in their flame-retarding effect. In particular, we estimated the amounts of yielded chars when the phenol resins ignited and the resins' dispersibilities in PLA. Finally, we identified an issue of decrease in the action of an organic crystalline nucleus agent for PLA by adding the phenol resins, and took measures to improve it by adding a small amount of a high molecular weight of phenol novolac resin which shows highly flame-retarding effect.

2. Material and methods

2.1. Material

Polylactic-acid (PLA; product name: TE-4000; Mw: 150,000; poly-L-lactic acid = 98.6 mol%; Tm = 170 °C) manufactured by UNITIKA LTD (Japan) was used for the base material. Three kinds of aluminum hydroxides manufactured by Showa Denko K. K. (Japan) were selected as flame retardants. Two kinds (product names: H-32 and H-421) were used as conventional aluminum hydroxides. The other kind (product name: HP-350) was used as a low-alkali-content aluminum hydroxide. These three aluminum hydroxides individually contain 0.22, 0.29 or 0.04 wt% of alkali impurities in Na_2O. The average diameters of the aluminum-hydroxide particles used are 3.4, 1.0, and 3.9 μm, respectively. The phenol resins used for flame-retarding aids were manufactured by Meiwa Plastic Industries, Ltd (Japan) and listed in Table 1, which were catechol resin (C resin; product name: C-105), tri-phenol methane resin (TPM resin; product name: MEH-7500), phenol novolac resin (PN resin; product name: HF-4M; Mn = 580), phenol-*p*-xylene resin (PX resin; product name: MEH-7800), and phenol biphenylene resin (PB resin; product name: MEH-7851). Furthermore, high-molecular-weight phenol novolac resin (HMw PN resin; product name: PAPS-PN70; Mn = 2156) manufactured by Asahi Organic Chemicals (Japan) was used for a flame-retarding aid. Polytetrafluoroethylene (PTFE; product name: FA500; manufactured by Daikin Industries, Ltd. (Japan)) was used as an anti-dripping agent, to which was added 0.5 wt% of all PLA composites in this study. N,N′-ethylenebis 12-hydroxystearylamide (product name: ITOH-WAX J-530; manufactured by Itoh Oil Chemicals Co., Ltd. (Japan)) was used as an organic crystalline nucleus agent for PLA.

2.2. Blending

PLA, aluminum hydroxides, and PTFE were dried at 105 °C for 7 h before using. These dried materials were pre-blended with phenol resins. The blends were kneaded in a twin extruder (product name: S1 kneader; manufactured by Kurimoto, Ltd. (Japan)) at 190 ± 5 °C. After that, the kneaded materials were pelletized.

2.3. Injection molding

Test specimens (128 (length) by 13 (width) by 3.2 or 1.6 mm (thickness)) were prepared from the pelletized materials (pellets) by using an injection-molding machine (product name: EC20P; manufactured by TOSHIBA MACHINE CO., LTD. (Japan)). The temperature of molten pellets was 190 ± 5 °C, and that of the mold was 25 ± 5 °C. These test specimens were heated at 105 ± 5 °C for 4 h to complete the crystallization of PLA in them. Furthermore, when the crystalline nucleus agent was added to the blends, the temperature of the mold was set at 105 ± 5 °C, and the specimens were held in the mold for 60 s in order to finish the crystallization of PLA in them.

2.4. Measuring degree of crystallization

The degree of crystallization in the specimens with the crystalline nucleus agent was measured. To calculate the degree of crystallization, the enthalpy of fusion and the exothermic enthalpy (which measured by differential scanning calorimeter (DSC) 6200 manufactured by Seiko Instruments Inc. (Japan)) were used. From the following formula, the degree of crystallization was calculated from the enthalpy of fusion of infinite lamella size (namely, 93 J/g [13]), the enthalpy of fusion of the specimens, ΔHm (J/g), and crystallization enthalpy, ΔHc (J/g).

$$\text{Degree of crystallization: } x\,(\%) = 100 \times (\Delta Hm - \Delta Hc)/93$$

2.5. Flame-retarding test

Flame retardancy of the specimens with 1.6-mm thickness was estimated by UL (Underwriter Laboratories Inc. (United States)) 94 vertical-burning test. The test results were judged in the order of superior flame retardancy, namely, ratings V-0 (total flaming time of five test pieces was under 50 s, and the cotton under the dripping test pieces is not allowed to burn), V-1 (total flaming time of five test pieces was under 250 s, and the cotton under the dripping test pieces is not allowed to burn) and V-2 (total flaming time of five test pieces was under 250 s, and the cotton under the dripping test pieces is allowed to burn). In addition, anything burning over 250 s was judged as "NOT" rating in terms of flame

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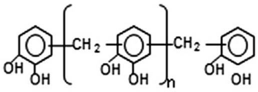
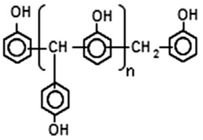
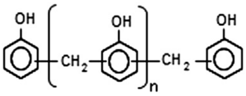
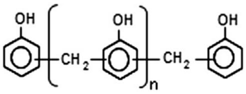
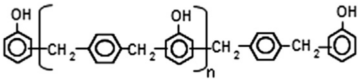
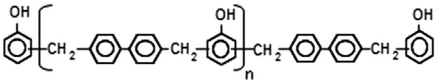
Table 1
Structures of tested phenol resins.

Phenol resin	Chemical structure	Hydroxyl equivalent	Softening temperature (°C)
Catechol resin (**C resin**)		60	106
Phenol aralkyl resin (Tri-phenol methane resin: **TPM resin**)		97	110
Phenol novolac resin (**PN resin**)		107	108
High-molecular-weight Phenol novolac resin (**HMw PN resin**)		107	155
Phenol aralkyl resin (Phenol *p*-Xylene resin: **PX resin**)		175	60
Phenol aralkyl resin (Phenol biphenylene resin: **PB resin**)		229	127

retardancy. Incidentally, as for casing materials for electronic products, high flame retardancy, namely, V-1 rating or better is demanded.

2.6. Other properties

Fluidity was estimated by using a spiral-flow mold with 1-mm thickness. The temperature of molten pellets was 190 ± 5 °C, and that of the mold was 25 ± 5 °C. The injection pressure was 118 MPa, and injection speed was 100 mm/s. Heat distortion temperatures (HDT) of the specimens with 3.2-mm thickness were measured in accordance with ISO 75-2:2004 by using an HDT testing machine (product name:TM-4126; manufactured by Ueshima Seisakusho Co., Ltd. (Japan)). These HDT tests were done in the edgewise at the pressure of 1.8 MPa at a heating rate of 2 °C/min at 100-mm span. Bending tests on the specimens with 3.2-mm thickness were done in accordance with ISO 178 by using an Instron 5567 universal testing machine manufactured by Instron (United states; cross-head speed: 1.6 mm/min; span: 50 mm). Izod impact tests on notched specimens with 3.2 mm thickness were done in accordance with ISO 180 by using a Universal Impact Tester C1, manufactured by Toyo Seiki Seisakusho, Ltd. (Japan; pendulum: 2.75 J; upswing angle: 150°). Molecular weight of PLA in terms of polystyrene was measured by gel permiation chromatography (liquid chromatograph; product name: LC-10ADvp; manufactured by SHIMADZU (Japan)) with columns for chloroform (product name: GPC-80MC, GPC-80M, GPC-8025C; manufactured by SHIMADZU). Thermo-gravimetric analysis was done by using TG/DTA 6200 (manufactured by Seiko Instruments Inc. (Japan)) at a heating rate of 10 °C/min under 0.2 l/min of N_2 gas. External appearance of ignited samples and dispersibilities of phenol resins in PLA were observed by using a light microscope (product name: DIGITAL MICROSCOPE VHX-500; manufactured by KEYENCE (Japan)).

3. Results and discussion

3.1. Flame retardancy of PLA composites with aluminum hydroxide

Aluminum hydroxide (AH) contains alkali impurities, such as sodium hydroxide (NaOH), used as a raw material in the manufacturing process of AH. These alkali impurities will accelerate the hydrolysis of PLA when it is kneaded or molded [14]. Therefore, the changes in molecular weight of PLA were investigated when it was mixed with the three kinds of AH (with different contents of alkali impurities). As shown in Fig. 1, using the AH with the lowest concentration of alkali impurities inhibited the decrease in molecular weight of PLA. The AH with the lowest alkali concentration was thus used in the following investigation on flame retardancy.

Furthermore, Fig. 1 shows that the Mn value of PLA became almost half even though the Mw did not much decrease in the presence of AH with 0.22wt% of alkali impurities in Na_2O. We consider that low molecular weights of PLA easily decomposed in the presence of AH with 0.22wt% of alkali impurities. As a result, the number of lower molecular weights of PLA increased.

The results concerning the flame retardancy of the PLA composites with the low-alkali-content AH are shown in Fig. 2. As can be seen, addition of over 49.5 wt% AH produced PLA composites with high flame retardancy (which was classed as UL94 V-1 rating). However, such a large amount of AH had negative influence on flexural strength, flexural breaking strain, impact strength, and fluidity of the PLA composites (as shown in Table 2). According to Table 2, only 5 wt% differences in the content of AH gave a profound effect on the flame retardancy of the composites (the increase from 44.5% to 49.5% changed the flame retardancy from NOT to V-1). This 5 wt% of AH gave increases in melt viscosity, endothermic energy amount and water vapor content when ignited the

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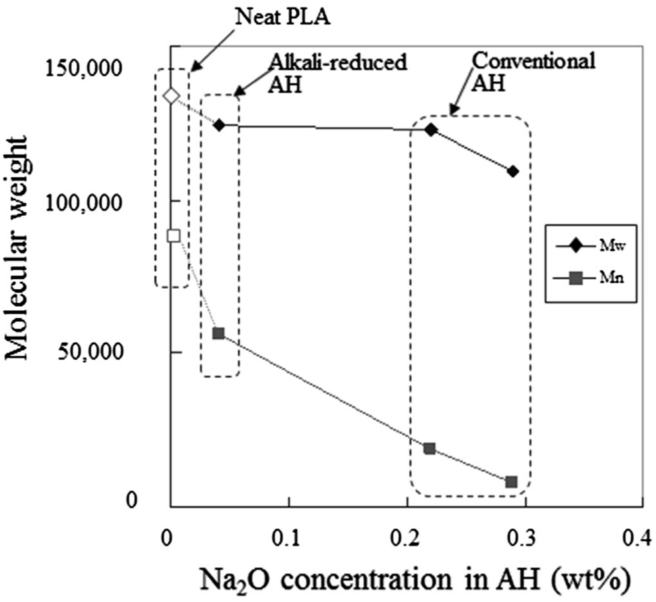

Fig. 1. Molecular weight of PLA in PLA/aluminum hydroxide (AH) composite (AH concentration in composite: 50 wt%).

composite with 49.5% of AH. It is likely that the melt viscosity, the endothermic energy amount and the water vapor content exceeded the critical point of changing the flame retardancy from NOT to V-1.

3.2. *Improving flame retardancy of PLA composites by dual use of aluminum hydroxide and phenol resins*

To prevent degradation of the properties of PLA composites when a large amount of AH is used, we investigated dual use of the low-alkali-content AH above mentioned and representative phenol resins with various structures to improve flame retardancy. As shown in Table 3, all the kinds of phenol resins tested, except phenol-*p*-xylene (PX) resin, showed flame-retarding effect. When only 44.5 wt% of AH was used, the flame retardancy of the PLA composite was insufficient ("NOT" rating). On the other hand, the dual use of the low-alkali-content AH and the phenol resins (except PX resin) improved the flame retardancy of the PLA composites, which satisfied UL 94 V-1 rating. Therefore, the amount of the low-alkali-content AH was decreased by 5 wt% compared with the use of the above AH alone. Furthermore, using PN resin and TPM resin among the phenol resins brought outstanding flame retardancy.

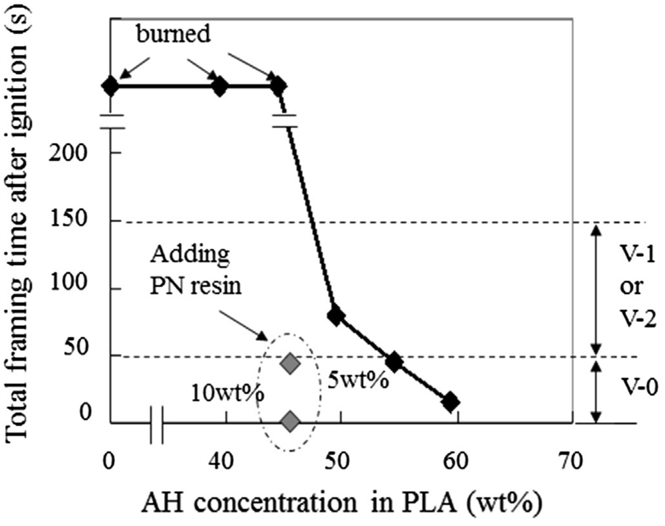

Fig. 2. Effectiveness of flame retardancy of PLA by adding AH and PN resin.

Table 2
Characteristics of PLA composites.

Characteristics	Composition (weight %)						
	PLA	100	55	50	50	45	45
	Aluminum hydroxide (AH)		44.5	49.5	44.5	49.5	44.5
	PN resin				5	5	10
	Polytetra-fluorethylene		0.5	0.5	0.5	0.5	0.5
Flame retardancy	UL94V 1.6 mmt	NOT	NOT	V-l	V-l	V-0	V-0
	Total after-flame time (s)			80	44	12	5
Mechanical properties	Flexural strength (MPa)	124	62	57	92	93	91
	Flexural modulus (GPa)	4.1	8.0	8.8	9.2	9.6	9.6
	Maximum strain (%)	3.5	1.0	0.7	1.1	1.0	1.0
Impact strength	Notch IZOD (kJ/m^2)	4.0	1.7	1.6	1.6	1.4	1.7
Fluidity	Spiral flow (L/T)	195	97	90	114	106	136
Heat resistance	HDT (1.8 MPa; °C)	66	79	91	82	84	71

Photographs of self-extinguished specimens, which were tested by UL 94 vertical burning test, are shown in Fig. 3. The PLA composite with 49.5-wt% AH formed almost no char in the burning area, while the PLA composites with both of the low-alkali-content AH and the phenol resins formed chars originated from these phenol resins. As shown in Fig. 4, the inner parts of chars were foamed by mainly volatilization of the water in AH.

To examine the flame-retarding effect of the phenol resins, thermogravimetric analysis (TGA) was performed on the phenol resins in order to compare the amounts of formed chars. As shown in Table 3 and Fig. 5, the phenol resins are arranged in descending order of the amounts of chars formed, namely, PB resin, PN resin, TPM resin, C resin, and PX resin. Before starting TGA, we expected that the PLA composites that are able to form larger amounts of chars originated from the phenol resins would show higher flame retardancy [9]. However, the flame retardancy of the PLA composite with PB resin that formed the largest amount of a char was inferior to those of PN resin, TPM resin, and C resin.

Given the above result, for improving flame retardancy by forming char, we considered that the homogeneity of char had enhancing effect on flame retardancy. Therefore, the dispersibilities of the phenol resins in PLA were investigated. As shown in Fig. 6, the phenol resins with medium amounts of hydroxyl group (OH), namely, PN resin, TPM resin, and PX resin, showed high dispersibilities in PLA. In contrast, PB resin with a small amount of OH or C resin with a large amount of OH showed low dispersibilities in PLA, resulting in larger dispersion particle sizes than those of the others. From these results, it is cleared that the differences in the polarities of the phenol resins affect their dispersibilities in PLA.

Table 3
Flame retardancy of PLA composites.[a]

Tested phenol resin	Dispersion phase in PLA	Amount of char (%)	Flame retardancy	
			UL94V 1.6 mmt	Total after the flaming time (s)
C resin	Hetero-geneous	28	V-l	85
TPM resin	Homo-geneous	36	V-l	37
PN resin	Homo-geneous	38	V-l	44
PX resin	Homo-geneous	24	NOT	–
PB resin	Hetero-geneous	53	V-l	115

[a] PLA: 50 wt%; AH: 44.5 wt%; Phenol resin: 5 wt%.

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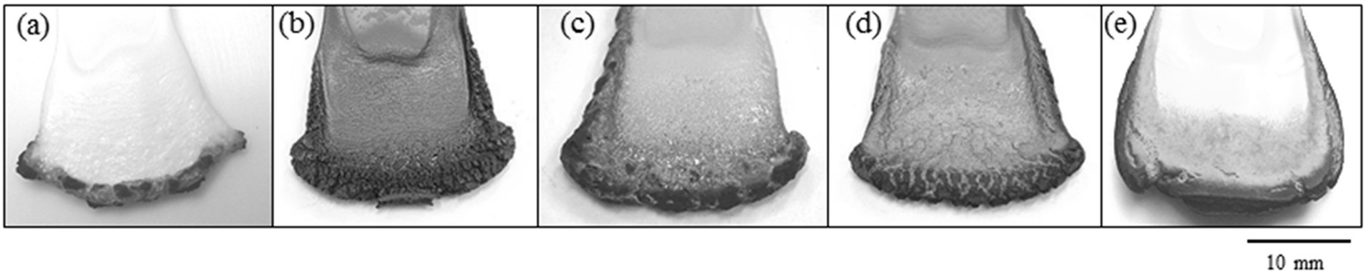

Fig. 3. Self-extinguished PLA composites: (a) AH 49.5 wt%, (b) C resin 5 wt% + AH 44.5 wt%, (c) TPM resin 5 wt% + AH 44.5 wt%, (d) PN resin 5 wt% + AH 44.5 wt% and (e) PB resin 5 wt% + AH 44.5 wt%.

Consequently, the PLA composites including phenol resins with low dispersibilities in PLA showed low flame retardancy regardless of the large amounts of formed chars.

According to the above-described results, dual use of AH with PN resin or TPM resin produced about the same level of high flame-retarding PLA composites, which were results of the formation of larger amounts of chars as well as the higher dispersibilities of those resins in PLA than those of the other phenol resins. When the PLA composites containing PN resin or TPM resin were ignited, larger amounts of chars uniformly covered their ignited surfaces of the PLA composites; consequently, they showed high flame retardancy. As shown in Fig. 7, the uniformly covered char suppressed the diffusion of decomposed gasses from the resin parts, and, finally, a foamed layer was formed by both these decomposed gasses and the volatile water from AH. This foamed layer was able to play the role of a heat insulator [15,16], therefore, the PLA composites showed high flame retardancy.

Finally, we selected the dual use of AH with PN resin and estimated the other properties of the composites.

3.3. Other properties of PLA composites by dual use of aluminum hydroxide and phenol resins

Other properties of the PLA composites with the low-alkali-content AH and PN resin are listed in Table 2. By using 5 wt% of PN resin, the flame retardancy, flexural strength, and fluidity of PLA composites were improved. The high flexural strength is mainly originated from the rigidity and resistance to deformation of aromatic rings in PN resin. The good fluidity is obtained from the high dispersibility and low melt viscosity of PN resin in the PLA composites. Furthermore, by decreasing the content of AH from 49.5 to 44.5 wt% by dual use of AH and PN resin, the fluidity, i.e., spiral flow, of the PLA composite was increased by 8%. Accordingly, by dual use of AH and PN resin and by decreasing the content of AH, this PLA composite maintained the same level of flame retardancy and achieved 25% higher spiral flow than that of a PLA composite with AH alone.

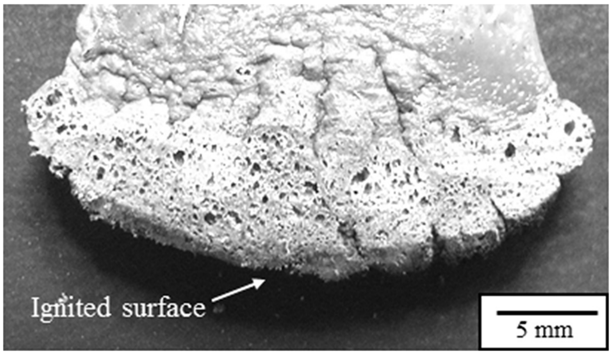

Fig. 4. Cross-section image of self-extinguished PLA composite (PN resin: 5 wt%; AH: 44.5 wt%).

3.4. Improvement of crystallization speed of PLA composites with phenol novolac resins

Although the PN resins adversely affected the action of an organic crystalline nucleus agent for PLA, a phenol novolac resin with high molecular weight (HMw PN resin) improved the problem because its concentration in the PLA composite was able to be reduced due to its highly flame-retarding effect.

Inorganic crystalline nucleus agents such as talc are widely used [17] in PLA composites because PLA has low crystallization speed. However the agents must be added over 5 wt% to PLA due to its relatively insufficient effect, causing to decrease the mechanical properties of PLA. In contrast, the use of organic crystalline nucleus agents brings PLA's high crystallization speed, while generally maintaining its mechanical properties. Accordingly, we tested an organic crystalline nucleus agent, called N,N′-ethylenebis 12-hydroxystearylamide [18] originated from castor oil, which especially enhances crystallization speed of PLA in terms of high efficiency with a small quantity. The crystallization of a PLA composite including 1 wt% of the organic agent and 49.5-wt% AH was almost finished (the degree of relative crystallinity was over 90%) under

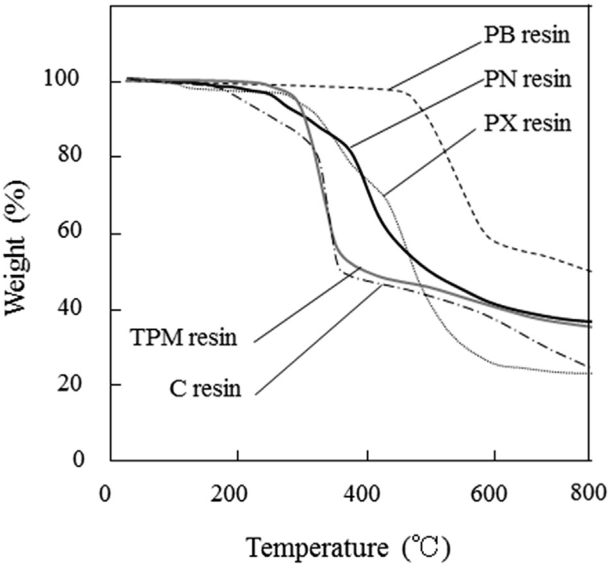

Fig. 5. Thermo-gravimetric analysis of phenol resins (under N_2 gas).

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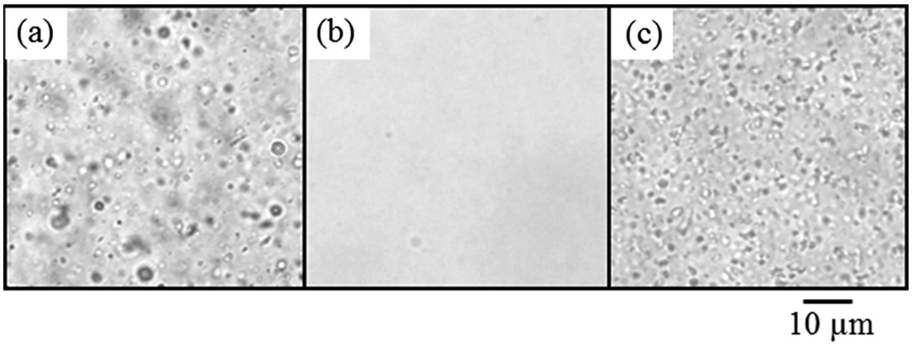

Fig. 6. Dispersion of phenol resins in PLA (concentration: 10 wt%) (a) C resin, (b) PN resin (TPM resin, PX resin, and High Mw PN resin showed almost the same fine dispersions), and (c) PB resin.

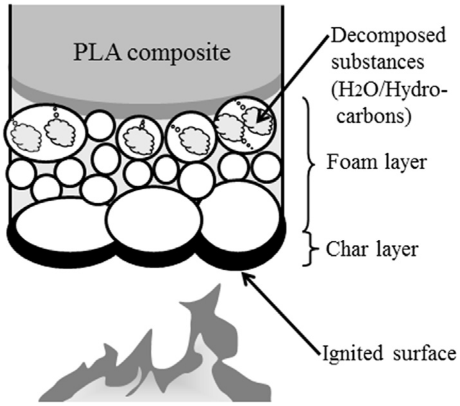

Fig. 7. Self-extinguishing mechanism in PLA composite.

the condition of holding for 60 s in the mold at 105 ± 5 °C (Table 4). However, in the case of a PLA composite including 5-wt% PN resin, 1 wt% of the organic agent and 49.5-wt% AH, the crystallization of PLA was retarded, namely the degree of relative crystallinity of the PLA was about 54% under the same condition (Table 4).

This problem, namely, retarding the nucleation of the organic crystalline nucleus agent by PN resin is able to be solved by decreasing the amount of PN resin. However, the flame retardancy of the PLA composite would be understandably deteriorated. Accordingly, we applied a phenol novolac resin with high molecular weight (HMw PN resin) with highly flame-retarding effect. Adding HMw PN resin greatly increased the flame retardancy of the PLA composite compared with the usual low-molecular-weight phenol resin (PN resin as above mentioned); only 1 wt% of HMw PN resin brought the high flame retardancy of the PLA composite with 49.5-wt% AH (Table 4). The high flame retardancy determined as UL 94 V-0 rating was produced because HMw PN resin uniformly disperses in PLA and makes a larger amount of char than that of the usual PN resin (Fig. 8). The increase in the amount of the char after pyrolysis of HMw PN resin is due to the following reason. In the process by which phenol novolac resins form chars, volatilization of low-molecular-weight materials and reaction of condensed materials (due to the dehydrogenation of two hydroxyl groups) occur simultaneously. In particular, HMw PN resin shows high melt viscosity at high temperatures and forms a small amount of volatile materials with low molecular weight. Consequently, the amount of the char by using HMw PN resin was larger than that of the usual PN resin with the low molecular weight.

As a result, the crystallization of the PLA composite with 1-wt% HMw PN resin (1 wt% of the organic agent and 49.5-wt% AH) was almost completed (namely, degree of relative crystallinity of over 90%) at the usual molding condition as above mentioned.

Other characteristics except the flame retardancy and fluidity of the PLA composite with HMw PN resin were decreased by the reduction of its amount. However, the most of characteristics* of the PLA composite with 1-wt% HMw PN resin and 44.5-wt% AH were superior to those of the PLA composite with only 44.5-wt% AH as shown in Table 2 (*flexural strength: 75 MPa; flexural modulus: 8.5 GPa; melt flow rate: 100). The other characteristics (flexural strain, impact strength and HDT) were almost the same as those of the PLA composite with AH alone.

Table 4
Characteristics of PLA composites with AH and phenol resins.

Properties	Composition					
	PLA	49	44	48	44	48
	Aluminum hydroxide (AH)	49.5	49.5	49.5	49.5	49.5
	PN resin		5	1		
	HMw PN resin				5	1
	Polytetra- fluorethylene	0.5	0.5	0.5	0.5	0.5
	Organic crystalline nucleus agent	1	1	1	1	1
Flame retardancy	UL94V 1.6 mmt	NOT	V-l	V-l	V-0	V-0
	Total after-flame time (s)		52	106	7	39
Degree of crystallization[a]	%	95	54	97	30	91
HDT at l.8 MPa	°C	91	D[b]	89	D[b]	90

[a] Mold at 105 ± 5 °C for 60 s.

[b] Hardly deformed when removed from the mold. It was impossible to measure HDT.

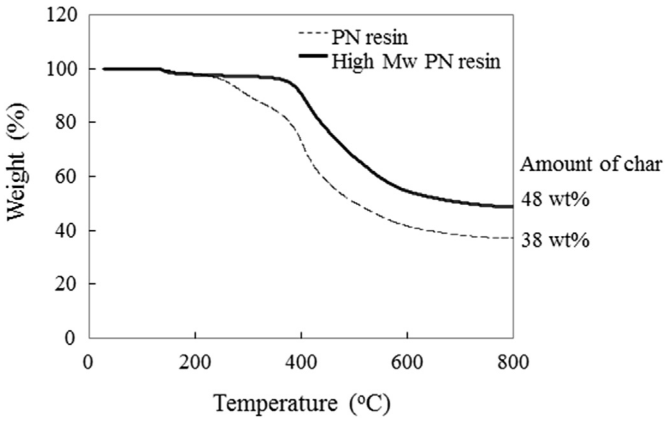

Fig. 8. Thermo-gravimetric analysis of phenol resins (under N_2 gas).

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4. Conclusion

We improved flame retardancy of polylactic acid (PLA) by dual use of aluminum hydroxide (AH) and phenol resin as safe flame retardants to allow PLA to be widely applied in durable products including electronic devices. The flame retardancy of PLA was sufficiently improved by adding more than 50 weight-percent of a specific AH which contains a low concentration of alkali elements, whereas other important characteristics of PLA, such as flexural strength and fluidity were reduced due to the large amount of AH. Simultaneous addition of the specific AH and phenol resins including phenol novolac resin improved the flame retardancy of the PLA composites, which permitted the AH's concentration to be reduced, resulting in the improvement of these characteristics of the PLA composites. Particularly, a high-molecular-weight phenol novolac resin (HMw PN resin) produced high flame retardancy of the PLA composites with a small quantity. Although the use of phenol resins adversely affected the action of an organic crystalline nucleus agent for PLA, the defect was improved by the use of HMw PN resin because its concentration in the PLA composites was reduced owning to its enhanced flame-retarding effect.

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