

Crystallization, Mechanical and Flame-retardant Properties of Poly(lactic acid) Composites with DOPO and DOPO-POSS

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Abstract Poly(lactic acid) (PLA) composites with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and DOPO-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) were prepared *via* melting extrusion and injection molding. The crystallization, mechanical, and flame-retardant properties of PLA/DOPO and PLA/DOPO-POSS were investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD), tensile testing, thermogravimetric analysis (TGA), limiting oxygen index (LOI), and cone calorimeter test. The DSC results showed that the DOPO added could act as a plasticizer as reflected by lower glass transition temperature and inhibited crystallization of part of the PLA; the DOPO-POSS acted like a filler in the PLA matrix and slightly improved the crystallinity of the PLA matrix. The XRD and DSC analyses indicated that the PLA composites by cold molding injection were amorphous, and the PLA composites following a heat treatment in an oven at 120 °C for 30 min achieved crystallinity. All the PLA and its composites after heat treatment had improved mechanical properties. The thermogravimetric analysis (TGA) tests showed that the PLA, DOPO and DOPO-POSS decomposed separately in the PLA/DOPO and PLA/DOPO-POSS, respectively. The cone calorimeter tests offered clear evidence that addition of the DOPO-POSS resulted in an evident reduction of 25% for the peak of heat release rate (p-HRR). It was also confirmed that the crystalline flame-retardant PLA composites after heat treatment had better flame retardant properties than the amorphous PLA composites prepared by the cold molding.

Keywords Poly(lactic acid); DOPO-POSS; Crystallization; Mechanical property; Flame retardancy

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INTRODUCTION

With pollution and resource shortage problems arising from the application of the traditional fossil-based polymeric materials, more and more attention has been paid to the research and development of the environmental friendly polymeric materials^[1–3]. As a semi-crystalline linear aliphatic polyester, poly(lactic acid) (PLA) is one of the most promising biodegradable polymeric materials due to its biocompatibility and reasonable mechanical properties. It has potential applications such as in automotive components, electrical industry, due to ecological and economic advantages^[4].

PLA items produced by injection molding usually exhibit poor mechanical strength and stiffness owing to incomplete crystallinity resulting from the slow crystallization. Furthermore, flammability is their main limitation for their wide practical applications^[5]. Therefore, increasing the crystallinity and flame retardance of the PLA materials is critical to their applications. The fabrication of composites with a small amount of nanofillers added to the PLA melts

offers a convenient route to improve the mechanical properties and flame retardancy of PLA^[6].

Annealing is a kind of heat treatment process altering the physical properties of a material by influencing its microstructures. Annealing of PLA is beneficial to its higher crystallinity. Srithep *et al.*^[7] found out that the annealing for PLA at 80 °C for 30 min and at 65 °C for 31 h resulted in the increase of over 17% and 26% in the tensile strength, respectively, because of the improved degree of crystallinity. Lv *et al.*^[8] reported that annealing was beneficial to the samples to reach a higher crystallinity of the PLA/starch blends as shown by the XRD patterns. However, the TGA results indicated that the annealed samples did not show any higher thermal stability than the virgin samples. Pérez-Fonseca *et al.*^[9] prepared poly(lactic acid) biocomposites by a combination of extrusion and injection molding with the cellulosic (agave, coir, and pine) reinforcements. The results revealed that annealing increased the impact strength and flexural modulus of PLA and PLA biocomposites, while decreasing their flexural strength. The main conclusion is that the fiber addition combined with thermal annealing could substantially increase the thermal stability of the PLA materials.

For fire retardance of PLA, many researchers have reported that 9,10-dihydro-9-oxa-10-phosphaphenanthrene-

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10-oxide (DOPO) and DOPO-containing halogen-free flame retardants presented unique flame retardancy for PLA systems. However, introduction of DOPO into PLA decreased the initial degradation temperature, leading to poor thermal stability, and declined the mechanical properties (e.g. flexural strength)^[10–12].

Different kinds of polyhedral oligomeric silsesquioxanes (POSS) have been introduced into PLA, resulting in faster crystallization, higher thermal stability, and better mechanical properties, indicating the role of POSS as a reinforcing filler and flame retardant in the PLA matrix. Sirin *et al.*^[13] studied the effects of the POSSs of three different functional groups (octa(3-chloroammoniumpropyl)-silsesquioxane (OCAPS), octa(3-chloropropyl)silsesquioxane (OCPS), octavinylsilsesquioxane (OVPS)) and their loading level on the morphological, mechanical and thermal properties of PLA composites. POSS particles dispersed homogeneously in polymer matrix improved significantly the Izod impact strength and increased thermal decomposition temperature of PLA composites. Tang and Qiu^[14] found that the PEG-POSS increased the ductility of PLLA as an efficient plasticizer and still maintained high Young's modulus. Turan *et al.*^[15] also demonstrated that 1%–3% of amine functionalized POSS particles added to the PLA enhanced both the modulus and elongation at break, however, mechanical properties of these composites decreased with further addition of POSS. Xuan *et al.*^[16] investigated the improvement of fire retardancy by addition of trisilanolisobutyl POSS (TIB-POSS) to PLA with intumescent flame retardant (IFR) formulation (ammonium polyphosphate/melamine, 22.5 wt%). PLA composites with TIB-POSS (7.5 wt%) added achieved the V-0 rating in UL-94 test and LOI value of 40%.

The chemistry of the side groups on POSS is a crucial importance because it influences the compatibility, solubility, and reactivity between POSS and polymers. Besides, the inorganic structure may provide polymers with molecular reinforcement, high thermal stability and better flame resistance^[17–19].

The DOPO containing POSS (DOPO-POSS) (Scheme 1), a kind of novel inorganic-organic hybrid, was synthesized successfully in our laboratory^[20]. DOPO-POSS has been used in flame-retarding polycarbonate (PC), as a result, the composites exhibited the enhanced mechanical properties resulting from its nanoscale dispersion in PC matrix. When the DOPO-POSS content was 4 wt%, the LOI value of PC increased from 24.1% to 30.5% and the UL-94 rating reached V-0 grade^[21].

The main objective of this work is to introduce the novel DOPO-POSS to the PLA matrix, and focuses on assessing its effects on the crystallization, mechanical properties and the flame retardancy of the PLA composite with a comparison to its analog, the DOPO compound. The enhanced mechanical and flame-retardant properties by DOPO-POSS could promote the application of PLA, which is of great interest and importance from both polymer processing and end use point of view.

EXPERIMENTAL

Materials

PLA (4032D) was purchased from NatureWorks with a melt flow index of 7.6 g/10min (210 °C/2.16kg). 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was provided by Jiangsu Huihong Jingpu Chemical Co., Ltd, China. DOPO-POSS was synthesized in our laboratory^[20]. DOPO-POSS was a mixture of perfect T₈ cage and imperfect T₉ cage with one Si—OH group on it.

Preparation of Flame-retardant PLA Composites

Two kinds of phosphorus-containing flame-retardant PLA composites were prepared, and the formulations of the composites are given in Table 1. PLA, DOPO and DOPO-POSS were all dried in a circulating air oven at 80 °C for 6 h. Poly(lactic acid) was blended with flame retardant using a SJ-20 (Nanjing Giant Machinery Co., Ltd.) twin-screw extruder. The blending was performed at 160–180 °C. The extrudate was quenched in a water bath, the composite was then cut into pellets, and finally dried in a vacuum oven at 80 °C for 6 h. It should be noted that the neat PLA was subjected to the same processing step as a blank test.

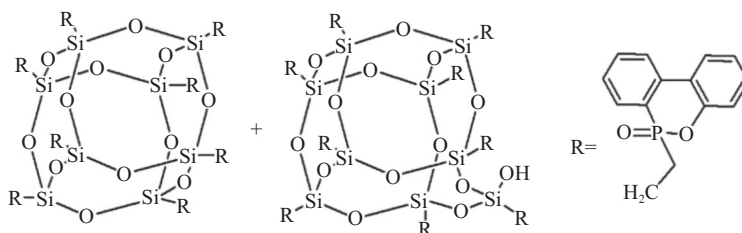
Samples for testing were molded by means of an injection-molding machine (HTF90X1, Haitian Plastics Machinery Ltd.). The temperature distribution in the injection screw was 170–190 °C.

Keeping the mold temperature at room temperature, we obtained the testing specimens in the shape of sheet called as the cold molding specimens. In the cold molding specimens of the PLA and its composites, there might be incomplete crystallization of the PLA. Further, part of the cold molding specimens were brought to bear a heat treatment at 120 °C in an oven for 30 min, which were denoted as the heat treated specimens, to make the PLA crystallize completely.

Characterization

Scanning electron microscopy (SEM)

The samples of the PLA, PLA/DOPO, and PLA/DOPO-POSS were cooled in liquid nitrogen and then fractured. The



Scheme 1 Typical chemical structures of DOPO-POSS molecules

Table 1 Formulations of PLA, PLA/DOPO and PLA/DOPO-POSS composites

Sample	PLA (wt%)	DOPO (wt%)	DOPO-POSS (wt%)
PLA	100	0	0
PLA/DOPO	95	5	0
PLA/DOPO-POSS	95	0	5

distribution and morphology of the brittle fractured sections coated with gold before examination were observed by field-emission scanning electron microscopy (FEI Quanta650).

Differential scanning calorimetry (DSC)

Crystallization and melting behavior were analyzed on a NETZSCH DSC 214 instrument (NETZSCH, Germany) equipped with an IC70 intra-cooler under the protection of nitrogen gas flow (60 mL/min). Samples of about 8–10 mg were placed in aluminum cells, and heated initially from 30 °C to 200 °C at a rate of 20 °C/min and held for 5 min to erase the thermal history in the samples; then the DSC traces showing the crystallization process of the PLA were recorded during cooling at a rate of 2 °C/min; once cooling to 30 °C, the samples were held for 3 min, and then heated to 200 °C at a rate of 10 °C/min in order to measure the melting behavior of the PLA. The degree of crystallinity was calculated using the following equation:

$$X_c = \frac{\Delta H_m + \Delta H_{cc}}{\Delta H_m^0 (1 - W_f/100)} \times 100\%$$

where X_c is the degree of crystallinity; ΔH_m is the melting enthalpy of the sample in the second heating; ΔH_m^0 is the melting enthalpy of 100% crystalline PLA, which is 93 J/g^[22]; ΔH_{cc} is the enthalpy of cold crystallization and W_f is the mass fraction of the flame retardants in the composites (in this paper, it is 5).

X-ray diffraction

The X-ray diffraction patterns were measured on a Rigaku Miniflex desktop X-ray diffractometer with a Ni-filtered Cu K α radiation. The instrument was operated at 40 kV and 200 mA. The scanning range for all samples was 2°–40° (2 θ) at a scanning rate of 2 (°)/min. The repeatability was checked measuring two specimens.

Mechanical testing of composites

The mechanical properties were measured according to GB/T 1040.2-2006 with an electronic tensile testing machine (DXLL-5000, Shanghai D & G Measure Instrument Co. Ltd.) at a tensile rate of 10 mm/min. The dimensions of the dumbbell specimens were the same as those specified in GB/T 1040.2-2006. At least five specimens were tested for each sample to obtain the average values.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was employed to investigate the thermal decomposition behavior of the PLA composites. TGA was performed with a Netzsch 209 F1 thermal analyzer. The measurements were performed under a N₂ atmosphere at a heating rate of 10 °C/min from 40 °C to 700 °C. The sample weight was 2–3 mg.

Limiting oxygen index (LOI)

The LOI test was conducted with sample dimensions 118 mm $\times$ 6.5 mm $\times$ 3 mm according to ASTM D 2863 with a FTAL oxygen index meter (Rheometric Scientific Ltd., U.K.). The samples were pre-conditioned at 23 °C and 50%

relative humidity (RH) for 24 h.

Cone calorimeter test

Combustion experiments were performed using a Fire Testing Technology apparatus (FTT0007) with a truncated cone-shaped radiator according to the ISO 5660 protocol. Specimens (100 mm $\times$ 100 mm $\times$ 3 mm) were exposed to a constant heat flux of 50 kW/m² and ignited. Heat release values and mass reduction were continuously recorded during burning. The samples were pre-conditioned at 23 °C and 50% relative humidity (RH) for 24 h.

RESULTS AND DISCUSSION

Distribution and Morphology of PLA and PLA Composites

The SEM images of PLA, PLA/DOPO and PLA/DOPO-POSS composites are shown in Fig. 1. It could be seen in Fig. 1 that the neat PLA, PLA/DOPO and PLA/DOPO-POSS all showed quite homogeneous and smooth fracture morphologies, and no large DOPO or DOPO-POSS particles were observed. DOPO has a melting point of 120 °C, and DOPO-POSS has a glass transition temperature of 115 °C. Therefore, under processing temperature of 160–180 °C, DOPO and DOPO-POSS could have a good dispersion in the PLA. However, in Fig. 1(c) the small particles of DOPO-POSS embedded in the PLA matrix were observed in the dimensions ranging from 1 μ m to 5 μ m. This demonstrates that DOPO had better compatibility in PLA than DOPO-POSS.

DSC Study on Crystallization of PLA and Its Composites

In the DSC analysis for PLA composites, the initial heating scan was performed to erase the previous thermal history of the samples. Then the cooling process with cooling rate of 2 °C/min could uncover the crystallization process, and determine the crystallization temperature (T_c), enthalpy of crystallization (ΔH_c). The DSC curves in the secondly heating step could uncover the crystalline melting process, and determine the glass transition temperature (T_g), which was taken at the midpoint of the temperature range over which the glass transition takes place between the onset and end of the inflectional tangent, the melting point (T_m), cold crystallization temperature (T_{cc}), enthalpy of cold

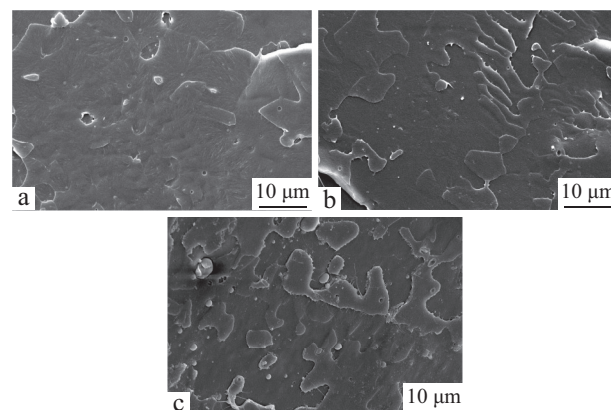


Fig. 1 SEM micrographs of fractured surface of PLA and PLA composites: (a) PLA, (b) PLA/DOPO, (c) PLA/DOPO-POSS

crystallization (ΔH_{cc}), heat of fusion (ΔH_m) and the crystallinity (X_c). This experimental program for the DSC analysis can demonstrate the non-isothermal crystallization behavior of the neat PLA and PLA composites, while the non-isothermal crystallization process may happen in the practical polymer material processing, such as extrusion, molding, and blow molding.

As can be seen from Fig. 2(a) and Table 2, the crystallization temperature of the neat PLA was located at 102.1 °C during the cooling process. PLA/DOPO revealed a reduction about 10 °C of the crystallization temperature (92.5 °C) and a weak crystalline peak during the cooling process compared with the neat PLA. PLA/DOPO had the enthalpy of crystallization 18.4 J/g lower than PLA (29.6 J/g). Furthermore, in Fig. 2(b) PLA/DOPO displayed cold crystallization peak at 102.0 °C and a lower melting point at 165.9 °C than the neat PLA. In addition, PLA/DOPO had a lower glass transition 54.1 °C than that of PLA (63.9 °C). These results indicated that DOPO reduced the crystallization ability of the PLA and plasticized the amorphous phase of PLA^[23, 24]. This may correlate with the melting point of DOPO at 120 °C, while the 120 °C is very close to the crystallization temperature of PLA. Above 120 °C in the cooling program, DOPO is in liquid state, so that it is easy to have interactions with the PLA chains. Even when the temperature is lower than the melting point of PLA, such interactions still exist to certain extent, thus resulting in low glass transition. Accordingly, it suggested the plasticizing effect. It should be especially noted that from Table 2, the X_c of PLA/DOPO experiencing the cold crystallization was the same as that of the neat PLA, which was due to the enthalpy of cold crystallization (ΔH_{cc}) of PLA/DOPO. According to the value of $-\Delta H_{cc}/\Delta H_m \times 100\% = 15\%$, it is indicated that during cooling process, DOPO inhibited 15% of PLA that

should be capable to crystallize due to the plasticization of DOPO. During the second heating process, this part of the PLA could cold crystallize at 102.0 °C in PLA/DOPO, because the temperature was lower than the melting point of the DOPO.

As can be seen from Fig. 2(a) and Table 2, PLA and PLA/DOPO-POSS crystallized completely during the cooling process; PLA/DOPO-POSS exhibited similar crystalline behavior to that of the neat PLA. In Fig. 2(b), the glass transition temperature of PLA was not affected by the inclusion of DOPO-POSS. No exothermic peak (cold crystallization) could be detected from the DSC second heating trace, and the addition of DOPO-POSS had little influence on the position of the melting peak T_m . These are rather similar to the melt behaviors of the neat PLA. The enhanced crystallinity of PLA/DOPO-POSS compared with PLA could be attributed to the heterogeneous nucleating effect of DOPO-POSS for PLA under the same crystallization condition. DOPO-POSS as solid powder could not melt below 200 °C. DOPO-POSS acted as a filler was confirmed by the SEM observation as well.

In summary, DOPO is like a plasticizer in the PLA, while DOPO-POSS acts like a filler in the PLA matrix. Therefore, they have different effects on the crystallization and melting behaviors of the PLA matrix.

X-ray Scattering Spectra Analysis

In the DSC study on crystallization of PLA and its composites, the cooling rate was 2 °C/min. It is a rather slow crystallization process compared to the cooling rate in practical injection molding. Therefore, there may be incomplete crystallization of the PLA under the practical processing conditions, which may affect the mechanical properties of the PLA and its composites.

In this part, X-ray diffraction (XRD) test running at room

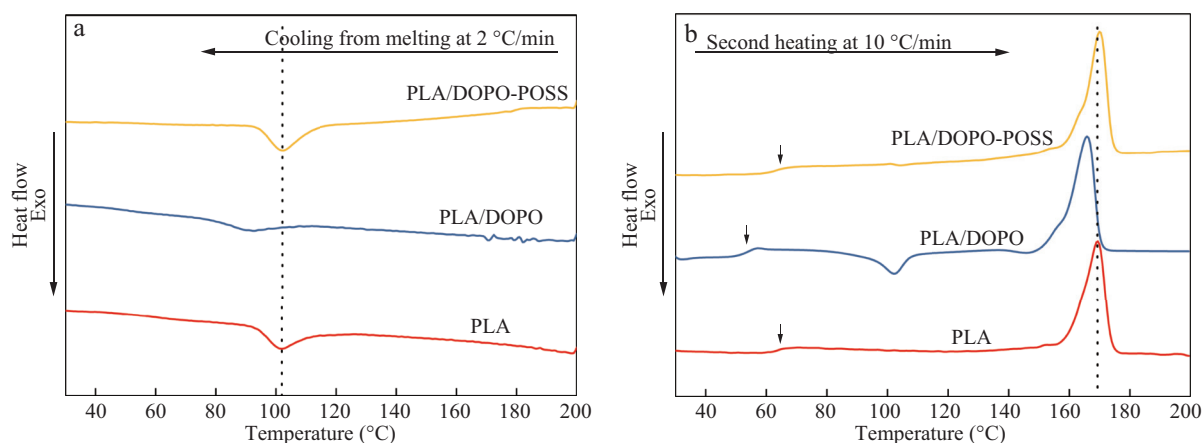


Fig. 2 DSC traces of PLA, PLA/DOPO and PLA/DOPO-POSS composites: (a) cooling from 200 °C at 2 °C/min; (b) second heating at 10 °C/min

Table 2 DSC data of the PLA and PLA composites

Sample	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_{cc} (°C)	ΔH_{cc} (J/g)
PLA	102.1	-29.6	63.9	169.4	31.6	34.0	—	—
PLA/DOPO	92.5	-18.4	54.1	165.9	35.4	34.0	102.0	-5.4
PLA/DOPO-POSS	102.1	-33.8	62.7	170.1	33.2	37.6	—	—

temperature was used to confirm the differences in crystallinity of PLA and its composites between the cold molding specimens from the direct injection molding and the specimens heat treated at 120 °C in an oven for 30 min. Figs. 3(a) and 3(b) show the XRD patterns of the neat PLA, PLA/DOPO and PLA/DOPO-POSS prepared by cold molding and heat treated samples. For comparison, the patterns of DOPO and DOPO-POSS are also presented.

In Fig. 3(a) for the cold molding specimens, XRD pattern of DOPO exhibited the main specific diffractive peaks at $2\theta = 8.8^\circ$, 12.8° , 13.8° , 21.0° , 23.0° , 26.0° . For DOPO-POSS, the diffraction showed an amorphous state with low intensity. All the cold molding samples of the neat PLA, PLA/DOPO and PLA/DOPO-POSS exhibited the broad halos with a maximum at about $2\theta = 16.8^\circ$ and no presence of crystallinity peaks, meaning that they were amorphous. In PLA/DOPO, the amount of DOPO was only 5 wt%, so the characteristic diffraction peaks of DOPO could not be observed. The results mentioned above indicated that in the cold molding specimens from fast injection, PLA could not crystallize. In Fig. 3(b) for the heat treated specimens, the PLA, PLA/DOPO and PLA/DOPO-POSS showed relatively high crystalline peaks of the PLA at $2\theta = 16.7^\circ$, 19.0° and 22.4° corresponding to 200/110, 203 and 210 crystal plane diffractions, respectively, which were the characteristic of the α form of PLA^[25]. This indicated that DOPO and DOPO-POSS did not change the type (α form) of the crystalline structure of the PLA.

For the 200/110 and 203 crystal planes, the full width measured at half maximum (FWHM) of the peak intensities and the crystal size based on the Scherrer's equation were computed as collected in Table 3. It can be obtained that for the 200/110 diffractive peak ($2\theta = 16.7^\circ$), PLA/DOPO-POSS had a smaller crystal size (17.0 nm) than the neat PLA (29.1 nm) and PLA/DOPO (28.3 nm), and the same rule was obtained from the 203 diffractive peak ($2\theta = 19.0^\circ$).

Mechanical Properties of PLA and Its Composites

To set up the relationship between crystallization characteristics and mechanical properties, tensile tests were performed for the cold molding and heat treated PLA specimens. The representative stress-strain curves of all samples are depicted in Figs. 4(a) and 4(b), the tensile strength and strain at break of PLA, PLA/DOPO and PLA/DOPO-POSS composites were measured as shown in Figs. 5(a) and 5(b), and the elastic modulus in tension of the neat PLA and its composites are given in Table 4.

According to the Figs. 4 and 5, for the neat PLA, the tensile strength, strain at break and elastic modulus in tension of the cold molding sample were 68.1 MPa, 6.3% and 396 MPa, respectively, while those of the heat treated sample were 70.3 MPa, 7.1% and 418 MPa, respectively.

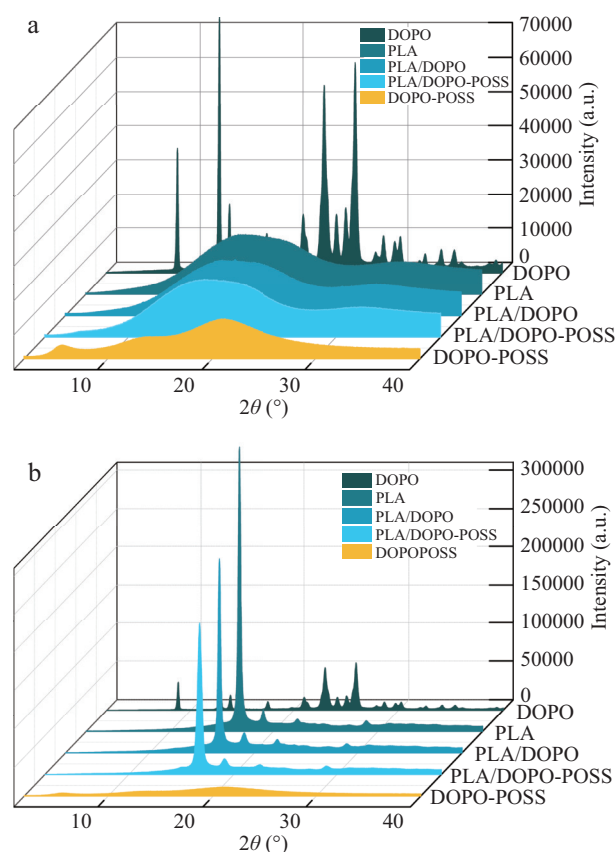


Fig. 3 XRD patterns of the PLA, PLA/DOPO and PLA/DOPO-POSS: (a) cold molding, (b) after heat treatment at 120 °C for 30 min

The PLA, PLA/DOPO and PLA/DOPO-POSS composites prepared through the cold molding also had lower tensile strength and strain at break, especially the strain at break, than the heat treated samples. It was known that the cold molding PLA samples were amorphous. The improved mechanical properties of the heat-treated PLA and composites should be attributed to their higher degree of crystallinity.

Fig. 6 shows the DSC traces of the cold molding and heat treated PLA in first heating. The cold molding PLA showed an evident cold crystallization from 100 °C to 120 °C, but the heat treated PLA did not. Referred to the results in Fig. 4, these confirmed the influence of crystallization characteristics on the mechanical properties of PLA. In Table 4, basically PLA/DOPO had the minimum modulus values, while PLA/DOPO-POSS had the maximum modulus values. However, the experimental measurement results of the elastic modulus in tension of PLA and its composites were out of the range of standard deviation required by the GB/T 1040.1-2006. As PLA is a brittle material with low

Table 3 XRD data of the PLA, PLA/DOPO and PLA/DOPO-POSS after the heat treatment at 200/110 and 203 diffractions

Sample	$2\theta = 16.7^\circ$		$2\theta = 19.0^\circ$	
	FWHM ($^\circ$)	Crystal size (nm)	FWHM ($^\circ$)	Crystal size (nm)
PLA	0.29	29.1	0.40	20.7
PLA/DOPO	0.30	28.3	0.44	19.0
PLA/DOPO-POSS	0.44	18.5	0.49	16.7

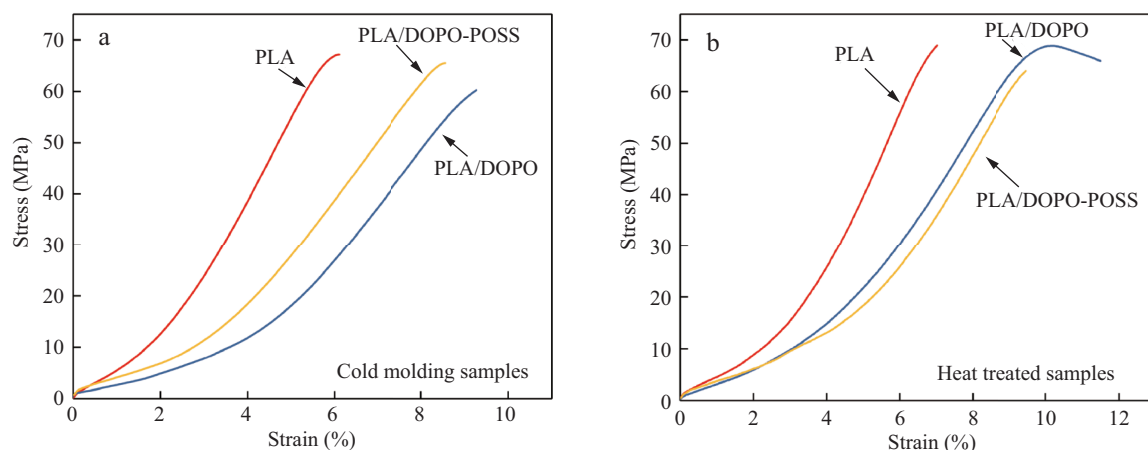


Fig. 4 The representative stress-strain curves of PLA, PLA/DOPO, and PLA/DOPO-POSS: (a) cold molding samples; (b) heat treated samples

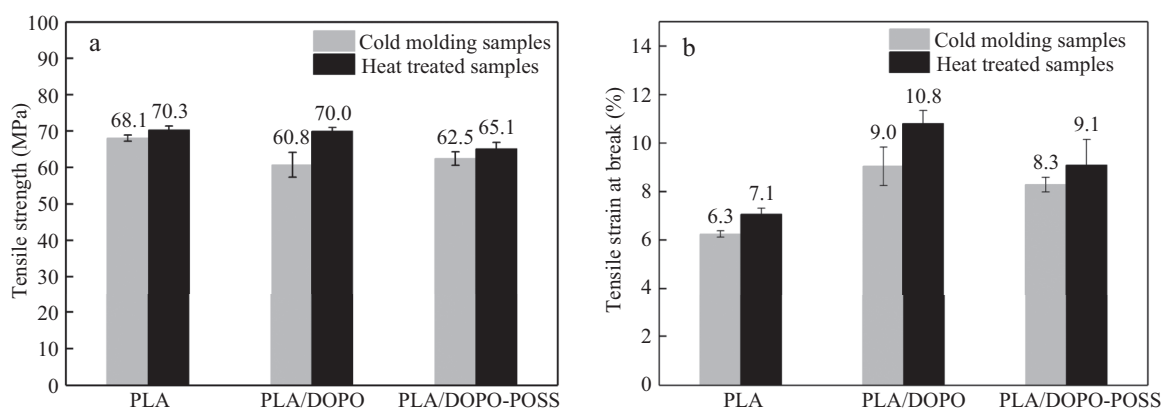


Fig. 5 (a) Tensile strength and (b) strain at break of PLA, PLA/DOPO, and PLA/DOPO-POSS

Table 4 Elastic modulus in tension of the PLA and its composites

Sample	Elastic modulus in tension (MPa)	
	Cold molding	Heat treated
PLA	396 ± 106	418 ± 86.9
PLA/DOPO	394 ± 107	380 ± 6.95
PLA/DOPO-POSS	514 ± 120	453 ± 84.0

strain at break ($< 10\%$), the measurement results of the elastic modulus in tension were unstable, which made the standard deviation in the elastic modulus large. Nevertheless, after heat treatment, the standard deviation of the elastic modulus was reduced.

For PLA/DOPO, we could find that DOPO reduced evidently the tensile strength, but increased the strain at break for the cold molding samples. This is due to the fact that DOPO inhibited the crystallization of PLA to certain extent, and behaved like a plasticizer. For the heat treated PLA/DOPO sample, its tensile strength in tension was increased to 70.0 MPa, nearly the same to that of the heat treated neat PLA, and its strain at break further increased to 11% (higher than 7.1% of the heat treated neat PLA).

For PLA/DOPO-POSS, it was noted that DOPO-POSS reduced the tensile strength. However, whatever for the cold molding or the heat treated samples, DOPO-POSS showed a little increase in the strain at break and the modulus

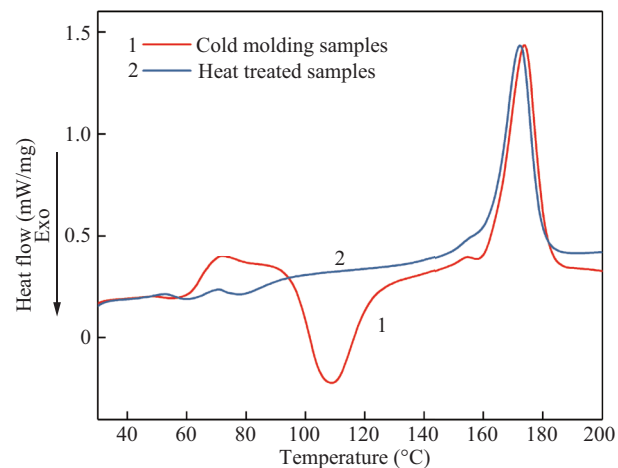


Fig. 6 DSC traces of cold molding and heat treated PLA in the first run

compared with those of the neat PLA, meaning a little toughening effect of DOPO-POSS particles on PLA.

In summary, DOPO acted as a plasticizer, and the PLA/DOPO composite had better strain at break, while DOPO-POSS acted as a filler to reinforce PLA. Heat treatment method could improve the tensile strength and the

strain at break of all the composites, and reduce the standard deviation of elastic modulus in tension of the PLA material in the tensile test.

Thermogravimetric Analysis

Typical TGA and DTGA curves of the DOPO, DOPO-POSS, PLA, PLA/DOPO and PLA/DOPO-POSS composites under nitrogen at a heating rate of 10 °C/min are illustrated in Fig. 7, and the related data are listed in Table 5. Here, the $T_{5\%}$ represents the initial decomposition temperature at 5% weight loss, while $T_{\max}$ is regarded as the temperature at maximum decomposition rate.

In Fig. 7, DOPO had the $T_{5\%}$ at 203.4 °C and the $T_{\max}$ at 275.5 °C. DOPO-POSS had the $T_{5\%}$ of 319.1 °C, the $T_{\max}$ of 480.6 °C, and remained 52.56% residue at 700 °C. Obviously, DOPO-POSS has superior thermal stability compared to DOPO.

The thermal degradation of PLA started at around 332 °C, and ended at about 380 °C, while the $T_{5\%}$ of PLA/DOPO was 276.5 °C. PLA has only a one-stage thermal decomposition, and the $T_{\max}$ was 365.6 °C. However, PLA/DOPO possessed a two-stage decomposition due to the decomposition of DOPO in the range of 200–280 °C. The $T'_{\max}$ of the first decomposition was 241.6 °C which was caused by DOPO, indicating that DOPO and PLA in PLA/DOPO decomposed individually.

PLA/DOPO-POSS also possessed a two-stage decomposition and had a little higher $T_{5\%}$ than the neat PLA (334.8 and 332.1 °C, respectively). The $T_{\max}$ of PLA/DOPO-POSS was 366.2 °C, close to 365.6 °C of PLA, and the $T'_{\max}$ during the second decomposition stage was at about 480 °C, corresponding to the $T_{\max}$ of DOPO-POSS. These results indicated PLA and DOPO-POSS decomposed separately in the PLA/DOPO-POSS. DOPO-POSS increased the residue (5.23%) of PLA at 700 °C to some extent.

Flame Retardancy Properties of PLA and Its Composites

Limiting oxygen index (LOI)

The LOI tests were performed to examine the flame-retardant properties of the neat PLA, PLA/DOPO and PLA/DOPO-POSS composites, and the results are listed in Table 6. PLA is a flammable material with a LOI value of 20.0%.

The LOI values of PLA/DOPO and PLA/DOPO-POSS composites were 26.5% and 21.7%, respectively. It indicated that a small amount of DOPO at 5 wt% could effectively improve the LOI value of PLA, but DOPO-POSS was less effective for increasing LOI of PLA. In addition, compared with the cold molding samples, the LOI values of the heat treated samples showed no apparent changes, meaning that the crystallinity of PLA in the samples seems to be not important for the LOI values. It is suggested that the earlier decomposition of DOPO can delay the speed of fire

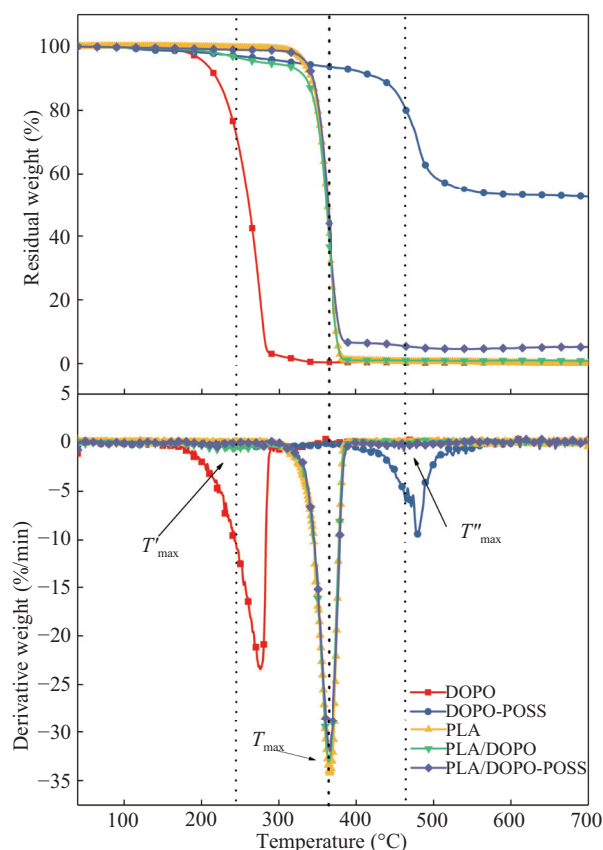


Fig. 7 TGA curves and DTGA curves of DOPO, DOPO-POSS, PLA, PLA/DOPO and PLA/DOPO-POSS composites

Table 6 LOI results of PLA, PLA/DOPO, and PLA/DOPO-POSS composites

Sample	LOI values (%)	
	Cold molding	Heat treated
PLA	20.0	20.2
PLA/DOPO	26.5	26.4
PLA/DOPO-POSS	21.7	21.0

spreading through the gas phase due to its high thermal stability, but lower content of DOPO in the DOPO-POSS has limited effect to improve the LOI value of the PLA.

Cone calorimeter testing

Cone calorimetry is one of the most comprehensive laboratory scale methods to investigate the combustion properties of polymer materials, which is based on the principle of oxygen consumption to measure the rate and amount of heat during combustion in a manner generally relevant to real fires^[26]. It can supply the combustion parameters of the material, such as the heat release rate (HRR), the peak of HRR (p-HRR), the time for ignition (TTI), the time to p-HRR, the total heat release (THR), total

Table 5 TGA data of DOPO, DOPO-POSS, PLA, PLA/DOPO and PLA/DOPO-POSS composites under N₂

Sample	$T_{5\%}$ (°C)	$T'_{\max}$ (°C)	$T_{\max}$ (°C)	$T''_{\max}$ (°C)	Residue (%, 700 °C)
DOPO	203.4		275.5		0.71
DOPO-POSS	319.1		480.6		52.56
PLA	332.1		365.6		0
PLA/DOPO	276.5	241.6	364.2		0.84
PLA/DOPO-POSS	334.8		366.2	462.5	5.23

smoke released (TSR) and the total mass loss (TML). Fig. 8 shows the heat release rate curves of PLA, PLA/DOPO, PLA/DOPO-POSS and the parameters measured by the cone calorimeter are listed in Table 7.

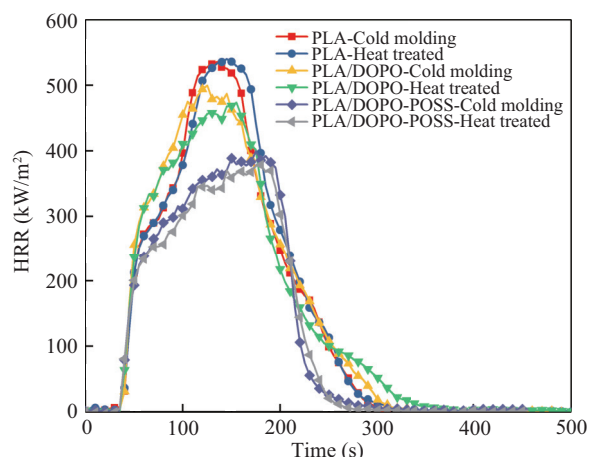


Fig. 8 Heat release rate (HRR) as a function of time of PLA, PLA/DOPO and PLA/DOPO-POSS cold molding and heat treated samples

Fig. 8 and Table 7 show that for the neat PLA sample the p-HRR was 536 kW/m², and THR was 74 MJ/m². For PLA/DOPO, its p-HRR and THR were 500 kW/m² and

72 MJ/m², respectively. For PLA/DOPO-POSS, its p-HRR and THR were 400 kW/m² and 59 MJ/m², respectively. These implied that both DOPO and DOPO-POSS could reduce the heat release of the PLA, while DOPO-POSS was more effective.

As listed in the Table 7, the addition of both DOPO and DOPO-POSS had a negligible influence on the TTI of the PLA. The neat PLA combusted completely and its TSR value was only 2.5 m²/m², whereas TSR values of the PLA/DOPO and PLA/DOPO-POSS were 624 and 434 m²/m², respectively. Apparently, DOPO-POSS could decrease the smoke production compared to DOPO.

Furthermore, according to the Fig. 8 and Table 7, the THR values of every pair of the cold molding and heat treated samples were almost the same, and between the two p-HRR and two TTI values, there were no apparent differences, indicating that the crystallinity of the PLA had no obvious effect on these three parameters.

As for the time to the p-HRR listed in Table 7, the samples after the heat treatment, especially PLA/DOPO, had a longer time than the cold molding samples. It is possible that the melting process of the PLA crystalline could delay the time to reach the peak of HRR of the PLA and its composites.

In summary, DOPO-POSS had better flame retardancy on PLA than DOPO, and the crystallinity of PLA may influence the combustion performance of PLA and its composites to some extent.

Table 7 The data from cone calorimeter test of PLA, PLA/DOPO, and PLA/DOPO-POSS at a heat flux of 50 kW/m²

Sample	TTI (s)	p-HRR (kW/m ²)	THR (MJ/m ²)	Time to p-HRR (s)	TSR (m ² /m ²)	TML (%)
Cold molding specimens						
PLA	35	536	74	135	2.5	100
PLA/DOPO	34	500	72	125	624	99.6
PLA/DOPO-POSS	30	400	59	175	434	98.1
Heat treated specimens at 120 °C for 30 min						
PLA	34	540	74	145	2.5	100
PLA/DOPO	31	474	73	155	659	99.7
PLA/DOPO-POSS	33	379	57	180	326	98.1

CONCLUSIONS

DOPO and DOPO-POSS could achieve good dispersion in the PLA/DOPO and PLA/DOPO-POSS composites prepared *via* melting extrusion and injection molding. The PLA composites from the cold molding were amorphous, and the PLA composites experiencing the heat treatment at 120 °C became crystalline. DOPO in PLA acted as a plasticizer, which could decrease the glass transition temperature and make part of the PLA incapable to crystallize during the cooling process from 200 °C. DOPO-POSS acted like a filler in PLA and slightly increased the degree of crystallinity of PLA. For the mechanical properties, the crystallizing (heat treated) PLA and its composites behaved much better than the amorphous ones (cold molding). It was proven that in the PLA composites, DOPO and DOPO-POSS did not affect thermal decomposition of PLA; PLA, DOPO and DOPO-POSS decomposed individually. For flame retardancy, 5 wt% DOPO increased the limited oxygen index of PLA,

whereas 5 wt% DOPO-POSS only slightly raised it. However, cone calorimetry tests provided clear evidence that DOPO-POSS was more effective than DOPO. DOPO-POSS could reduce the heat and smoke releases of the PLA composites, but DOPO evidently increased the smoke release of the PLA/DOPO compound. The crystallized (heat treated) PLA and its composites showed better flame retardancy than the amorphous (cold molding) according to the time to the peak heat release. The enhanced crystallization, mechanical and flame retardancy properties of PLA and its composites could promote the application of the PLA-based materials.

REFERENCES

- La Mantia, F. P.; Morreale, M. Green composites: a brief review. *Composites Part A* 2011, 42(6), 579–588.
- Mohanty, A. K.; Misra, M.; Drzal, L. T. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. *J. Polym. Environ.* 2002, 10(1), 19–26.

- 3 de Azeredo, H. M. C. Nanocomposites for food packaging applications. *Food. Res. Int.* 2009, 42(9), 1240–1253.
- 4 Carrasco, F.; Pagès, P.; Gámez-Pérez, J.; Santana, O. O.; MasPOCH, M. L. Processing of poly(lactic acid): characterization of chemical structure, thermal stability and mechanical properties. *Polym. Degrad. Stab.* 2010, 95(2), 116–125.
- 5 Ye, L.; Ren, J.; Cai, S. Y.; Wang, Z. G.; Li, J. B. Poly(lactic acid) nanocomposites with improved flame retardancy and impact strength by combining of phosphinates and organoclay. *Chinese J. Polym. Sci.* 2016, 34(6), 785–796.
- 6 Ye, H.; Hou, K.; Zhou, Q. Improve the thermal and mechanical properties of poly(L-lactide) by forming nanocomposites with pristine vermiculite. *Chinese J. Polym. Sci.* 2016, 34(1), 1–12.
- 7 Srithep, Y.; Nealey, P.; Turng, L. S. Effects of annealing time and temperature on the crystallinity and heat resistance behavior of injection-molded poly(lactic acid). *Polym. Eng. Sci.* 2013, 53(3), 580–588.
- 8 Lv, S.; Gu, J.; Cao, J.; Tan, H.; Zhang, Y. Effect of annealing on the thermal properties of poly(lactic acid)/starch blends. *Int. J. Biol. Macromol.* 2015, 74, 297–303.
- 9 Pérez-Fonseca, A. A.; Robledo-Ortiz, J. R.; González-Núñez, R.; Rodrigue, D. Effect of thermal annealing on the mechanical and thermal properties of polylactic acid–cellulosic fiber biocomposites. *J. Appl. Polym. Sci.* 2016, DOI: 10.1002/app.43750.
- 10 Gu, L.; Qiu, J.; Sakai, E. Effect of DOPO-containing flame retardants on poly(lactic acid): non-flammability, mechanical properties and thermal behaviors. *Chem. Res. Chin. Univ.* 2017, 33(1), 143–149.
- 11 Jiang, P.; Gu, X.; Zhang, S.; Wu, S.; Zhao, Q.; Hu, Z. Synthesis, characterization, and utilization of a novel phosphorus/nitrogen-containing flame retardant. *Ind. Eng. Chem. Res.* 2015, 54(11), 2974–2982.
- 12 Yu, T.; Tuerhongjiang, T.; Sheng, C.; Li, Y. Phosphorus-containing diacid and its application in jute/poly(lactic acid) composites: Mechanical, thermal and flammability properties. *Composites Part A* 2017, 97, 60–66.
- 13 Sirin, H.; Kodal, M.; Ozkoc, G. The influence of POSS type on the properties of PLA. *Polym. Compos.* 2016, 37(5), 1497–1506.
- 14 Tang, L.; Qiu, Z. Effect of poly(ethylene glycol)-polyhedral oligomeric silsesquioxanes on the thermal and mechanical properties of biodegradable poly(L-lactide). *Compos. Commun.* 2017, 3, 11–13.
- 15 Turan, D.; Sirin, H.; Ozkoc, G. Effects of POSS particles on the mechanical, thermal, and morphological properties of PLA and Plasticised PLA. *J. Appl. Polym. Sci.* 2011, 121(2), 1067–1075.
- 16 Xuan, S.; Hu, Y.; Song, L.; Wang, X.; Yang, H.; Lu, H. Synergistic effect of polyhedral oligomeric silsesquioxane on the flame retardancy and thermal degradation of intumescent flame retardant polylactide. *Combust. Sci. Technol.* 2012, 184(4), 456–468.
- 17 Qiu, Z.; Pan, H. Preparation, crystallization and hydrolytic degradation of biodegradable poly(L-lactide)/polyhedral oligomeric silsesquioxanes nanocomposite. *Compos. Sci. Technol.* 2010, 70(7), 1089–1094.
- 18 Baldi, F.; Bignotti, F.; Fina, A.; Tabuani, D.; Riccò, T. Mechanical characterization of polyhedral oligomeric silsesquioxane/polypropylene blends. *J. Appl. Polym. Sci.* 2007, 105(2), 935–943.
- 19 Wang, X.; Xuan, S.; Song, L.; Yang, H.; Lu, H.; Hu, Y. Synergistic effect of POSS on mechanical properties, flammability, and thermal degradation of intumescent flame retardant polylactide composites. *J. Macromol. Sci. Part B Phys.* 2012, 51(2), 255–268.
- 20 Zhang, W.; Yang, R. Synthesis of phosphorus-containing polyhedral oligomeric silsesquioxanes via hydrolytic condensation of a modified silane. *J. Appl. Polym. Sci.* 2011, 122(5), 3383–3389.
- 21 Zhang, W.; Li, X.; Guo, X.; Yang, R. Mechanical and thermal properties and flame retardancy of phosphorus-containing polyhedral oligomeric silsesquioxane (DOPO-POSS)/polycarbonate composites. *Polym. Degrad. Stab.* 2010, 95(12), 2541–2546.
- 22 Tsuji, H.; Ikada, Y. Crystallization from the melt of poly(lactide)s with different optical purities and their blends. *Macromol. Chem. Phys.* 1996, 197(10), 3483–3499.
- 23 Yang, G. Z.; Chen, X.; Wang, W.; Wang, M.; Liu, T.; Li, C. Z. Nonisothermal crystallization and melting behavior of a luminescent conjugated polymer, poly(9,9-dihexylfluorene-alt-co-2,5-didecyloxy-1,4-phenylene). *J. Polym. Sci., Part B: Polym. Phys.* 2007, 45(8), 976–987.
- 24 Gumus, S.; Ozkoc, G.; Aytac, A. Plasticized and unplasticized PLA/organoclay nanocomposites: short- and long-term thermal properties, morphology, and nonisothermal crystallization behavior. *J. Appl. Polym. Sci.* 2012, 123(5), 2837–2848.
- 25 Zhang, J.; Tashiro, K.; Tsuji, H.; Domb, A. J. Disorder-to-order phase transition and multiple melting behavior of poly(L-lactide) investigated by simultaneous measurements of WAXD and DSC. *Macromolecules* 2008, 41(4), 1352–1357.
- 26 Scharrel, B.; Hull, T. R. Development of fire-retarded materials—Interpretation of cone calorimeter data. *Fire Mater.* 2007, 31(5), 327–354.