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THERMAL PROPERTIES OF POLY(LACTIC ACID)/ORGANO-MONTMORILLONITE NANOCOMPOSITES

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Poly(lactic acid)/organo-montmorillonite nanocomposites were prepared by melt intercalation technique. Maleic anhydride-grafted ethylene propylene rubber (EPMgMA) was added into the PLA/OMMT in order to improve the compatibility and toughness of the nanocomposites. The samples were prepared by single screw extrusion followed by compression molding. The effect of OMMT and EPMgMA on the thermal properties of PLA was studied. The thermal properties of the PLA/OMMT nanocomposites have been investigated by using differential scanning calorimeter (DSC) and thermo-gravimetry analyzer (TG). The melting temperature (T_m), glass transition temperature (T_g), crystallization temperature (T_c), degree of crystallinity (χ_c), and thermal stability of the PLA/OMMT nanocomposites have been studied. It was found that the thermal properties of PLA were greatly influenced by the addition of OMMT and EPMgMA.

Keywords: *EPMgMA, nanocomposites, organo-montmorillonite, poly(lactic acid), thermal properties*

Introduction

Polymer/layered silicate nanocomposites have attracted significant attentions from both academic and industrial area because they exhibit remarkable enhancement in certain physical and chemical properties compared to the pure material or conventional composites [1–4]. Intercalation of polymer in layered hosts, such as hectorite and montmorillonite type silicates has been proven to be a successful approach to synthesis polymer/layered silicate nanocomposites [5, 6]. The properties of the polymer/layered silicate nanocomposites depend on the distribution and dispersion of the layered silicate in the polymer matrix.

There are several possible structures of the polymer-layered silicate composite; these include exfoliated, intercalated, flocculated or disordered intercalated form. The balance between intercalation and exfoliation strongly depends on the nature of the matrix, the layered silicate and the method of synthesis and preparation of the composites [2]. There are three main preparations of polymer/layered silicate nanocomposites, which are in-situ polymerization, solution intercalation and melt intercalation method. However, it is difficult to disperse the clay filler in the polymer matrix because of the tendency for face-to-face stacking in agglomerated tactoids and their inherent hydrophilic properties [3, 7].

Melt intercalation is a method where blending polymer and silicate layers, followed by molding to form a polymer-layered silicate nanocomposites. In general, for intercalation, polymers and layered hosts are annealed above the softening point of the polymer. The melt intercalation method has great advantages over either polymerization intercalation or solvent intercalation. First, this method is environmentally benign due to the absence of organic solvents. Secondly, it is compatible with current industrial compounding and molding techniques [8].

It is often needed to render the naturally hydrophilic clay filler in order to increase its compatibility with organic polymeric material [2]. Organo-montmorillonite (OMMT) is the commonly used layered silicates in the category of smectite group especially in the research of polymer nanocomposites technology attributed to the highly abundant of the clay. OMMT enable expansion of the clay galleries and exfoliation of the silicate layers into single layer [9]. A large aspect ratio of the silicate layers results in a high interfacial area minimizes the chain mobility, and creating a reinforcement effect. In addition, this interface facilitates stress transfer to the reinforcement phase, thus leads to improvement of the properties for polymers [10]. Polymer/layered silicate nanocomposites demonstrate nanoscale distribution of high aspect ratio fillers which could improve the properties of polymer matrix in term of mechanical, fire retardancy, rheological, gas barrier and optical properties at low clay content compared with conventional microcomposites [2, 10].

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Table 1 Materials designation and composition

Designation	PLA/mass%	OMMT/mass%	EPMgMA/phr
Neat PLA	100	–	–
PLA/OMMT1	99	1	–
PLA/OMMT1/EPMgMA5	99	1	5

Poly(lactic acid) (PLA) has received attention due to its renewable resources, biocompatibility, biodegradation, fabric ability, excellent thermal and mechanical properties, and superior transparency. Furthermore, with the increasing of crude oil's price and global warming, the most attractive behavior of PLA that is biodegradability and biocompatibility are being emphasized [11]. PLA nanocomposites have been studied in recent years. The potential application of PLA based nanocomposites are food packaging, medical application and tissue culture [1, 10]. The combination of PLA and montmorillonite layered silicate may result a nanocomposite with good barrier properties that are suitable for a film packaging material [10]. The modulus of PLA was increased by the addition of montmorillonite. However, the incorporation of the montmorillonite clay into PLA could decrease the toughness of the PLA composites [12]. There are some technical approach to achieve a balance of good strength and toughness of PLA nanocomposites. The addition of the poly(ethylene gycol) could act as a good plasticizer in PLA/clay systems [11].

In our previous research on PLA/OMMT nanocomposites, it was found that a balance of mechanical properties of PLA could be achieved by the addition of 1 mass% OMMT. This paper examines the effects of OMMT and EPMgMA on the thermal and morphological properties of PLA. The thermal properties of PLA and its nanocomposites were characterized using DSC and TG.

Experimental

Materials

Sample preparation

The PLA used in this study was kindly supplied by Mitsui Chemicals Inc. Japan. The density of the PLA is 1.23 g cm^{-3}. The OMMT (Nanomer® I.28E Nanoclay) was supplied by Nanocor Inc., USA. Maleic anhydride grafted ethylene propylene rubber (EPMgMA) was supplied by Exxon Mobil. The EPMgMA was grafted with 1% of maleic anhydride. The composition and designation of materials are shown in Table 1.

Extrusion and compression molding

PLA pellets and OMMT were dried over night in an oven at 90°C. PLA pellets and OMMT powders were premixed manually. The mixture was then melt-compounded by using a single-screw extruder (Betol Machinery Ltd., England). The extrusion temperature was ranged from 165–175°C. The screw speed of the extruder was set at a rate of 15 rpm. The extrudates were pelletized using a pelletizer. The compounded pellets were predried at 90°C for 8 h prior to compression molding. 1 mm thickness sample plates were prepared by compression molding (Gotech, Taiwan) at 180°C.

Methods

X-ray diffraction (XRD)

X-ray diffraction analysis was performed for the OMMT powder, PLA and PLA/OMMT nanocomposites on Siemens Diffractometry 5000, Germany. The samples were scanned in fixed step size, 0.050 with a step-time of 0.1 s in the range of 1–10°. An XRD diffractorgram (intensity·2θ) was obtained from the analysis. The *d*-spacing (*d*) of the interlayer gallery of OMMT and the PLA based nanocomposites was calculated using Bragg's law equation (as shown in Eq. (1)).

$$n\lambda = 2d\sin\theta \tag{1}$$

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c). DSC analyses were carried out in a Perkin Elmer DSC 6 thermal analyzer under nitrogen atmosphere, using 10–12 mg sample sealed into aluminum pans. In order to avoid any effect of moisture, all the test specimens were predried using vacuum oven at 90°C prior to the measurements. The samples were initially heated from 30–180°C at a rate of 10°C min^{-1}, held at 180°C for 1 min, and then cooled down to 30°C with a rate of 10°C min^{-1}. Second heating similar to the first heating was then performed in order to erase the thermal history. The DSC traces are registered during second heating. The degree of crystallinity (χ_c) of the samples can be calculated by comparing the heat of fusion obtained for the tested sample with that of a reference sample with 100% crystallinity. For composites reinforced with fillers or fibers, the degree of crystallinity can be determined by using Eq. (2):

$$\chi_c(\%)=\frac{\Delta H_m}{\Delta H_f(1-W_f)}\cdot 100\% \qquad (2)$$

where ΔH_m is the heat of fusion of sample; ΔH_f corresponds to the heat of fusion for 100% crystalline material, and W_f is the mass fraction of the fillers [13]. The crystallinity of PLA in the composites was calculated, where the heat of fusion of 100% crystalline PLA ($\Delta H_{f,PLA}$) was set equal to 93.6 J g^{-1} [14].

Thermogravimetry analysis (TG)

Thermogravimetry analysis (TG) was carried out on a Perkin Elmer Pyris 6 thermogravimetry analyzer (USA). The PLA and its nanocomposites were heated from room temperature to 500°C at a heating rate of 20°C min^{-1} under nitrogen atmosphere. The resulting mass change *vs*. temperature curve provides information of thermal stability for the samples.

Results and discussion

X-ray diffraction (XRD)

XRD allows a direct evidence of the intercalation of the polymer chain into the silicates galleries. Figure 1 shows the XRD diffractorgrams of OMMT, PLA and PLA/OMMT nanocomposites prepared by melt intercalation method. From Fig. 1, it can be seen that the OMMT shows the characteristic peak at 2θ=3.4° (*d*-spacing=2.535 nm). The PLA/OMMT nanocomposite shows an increment of the interlayer spacing, where the *d*-spacing is 3.447 nm. This indicates that melt intercalation method enable the intercalation of PLA polymer chain into the gallery of OMMT. The increment of *d*-spacing showed that the PLA polymer chain was successfully intercalated in between the silicate layer of OMMT. For the PLA/OMMT1/EPMgMA5, one can observe that there is a board peak appeared at 2θ=2.45°, which the *d*-spacing=3.517 nm. There is an increment of *d*-spacing when the EPMgMA was introduced into PLA/OMMT. This indicates that the EPMgMA was able to intercalate into the gallery of the OMMT silicate layer and further increase the interlayer *d*-spacing.

According to Feijoo *et al.* [6], the shiftment of the 2θ (lower angle, higher *d*-spacing) in the PLA/OMMT material was dominated by the steric effect of the long alkyl chains of the ammonium salt present in the OMMT. Besides, Sinha Ray *et al.* [5] reported that a well ordered intercalated polymer layered silicate nanocomposites were formed and coherence order of the silicate layers increase with increasing of organo-modified silicate layer. According to Thellen *et al.* [10], the process condition (screw speed and feed rate) can affect the increment of the *d*-spacing of the nanocomposites.

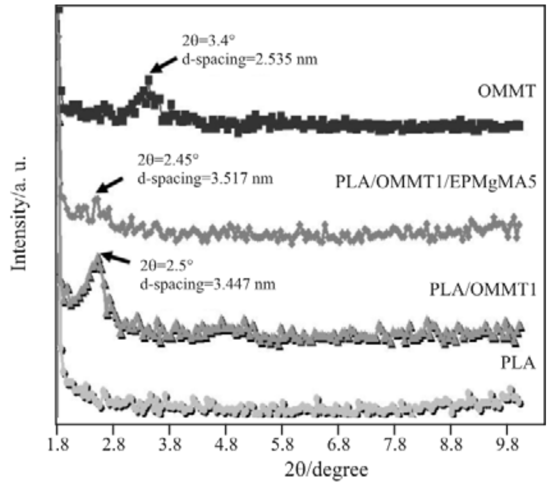

Fig. 1 XRD diffractograms of OMMT, PLA, PLA/OMMT1 and PLA/OMMT/EPMgMA5 nanocomposites prepared by melt intercalation method

Differential scanning calorimetry (DSC)

Figure 2 shows the DSC curves of neat PLA and its nanocomposites prepared by melt intercalation. Table 2 shows the DSC characteristics of PLA and its nanocomposites. The glass transition temperature (T_g) and melting temperature of pristine PLA is 61.1 and 168.8°C, respectively. The first melting temperature of PLA and PLA/OMMT nanocomposites ranged from 166–168°C. According to Wang *et al.* [14], raw PLA has a melting temperature of approximately 170°C and a broad crystallization peak ranging from 100–150°C. It can be seen that the addition of OMMT and EPMgMA did not influence much on the T_m of PLA.

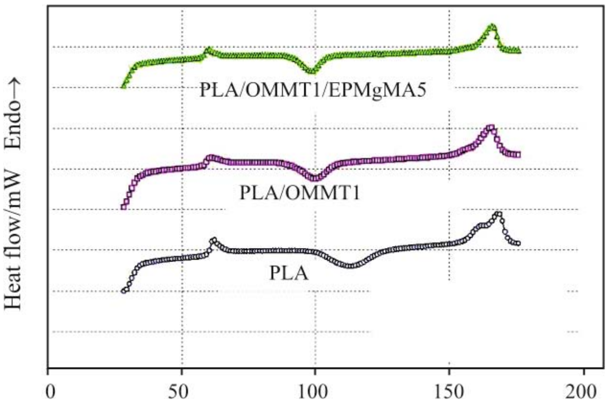

Fig. 2 DSC curves of PLA and PLA/OMMT nanocomposites

Table 2 DSC data of neat PLA and PLA/OMMT nanocomposites prepared by melt intercalation

Sample	Temperature/°C				
	T_g	T_c	T_{m_1}	T_{m_2}	χ_c/%
Neat PLA	61.1	113.2	161.2	168.8	22.0
PLA/OMMT1	60.4	100.1	–	166.8	24.6
PLA/OMMT1/EPMgMA5	60.8	99.1	–	167.0	15.2

A small shoulder endothermic peak at approximately 161°C was observed for unfilled PLA, however, no similar peak was revealed for either PLA/OMMT or PLA/OMMT/EPMgMA composites. According to Martin and Avérous [15] a very small melting endotherm at 152°C was recorded for the pure PLA, and this is corresponding to the residual crystallinity. Di Lorenzo [16] have reported that poly(*L*-lactic acid) (PLLA) is a polymorph material that presents several crystal modification. PLLA crystals can grow in several structural modifications, characterized by different helix conformations and cell symmetries that developed upon different thermal and/or mechanical treatments. Martin and Avérous [15] reported that most melting endotherms for plasticized PLA show two distinct peaks, owing to the lamellar re-arrangement during crystallization of PLA. A shoulder or low temperature peak is formed on the melting endotherm of the original crystallites [17]. Scheirs [18] reported that multiple melting peaks can be observed in a number of semicrystalline polymers during a DSC scan. These occur when imperfect crystals that have melted at a lower temperature, recrystallize to give crystals at a higher temperature.

There is no any significant changing of T_g of PLA by the addition of OMMT. The glass transition temperature depends primarily on chain flexibility, molecular mass, branching/crosslinking, intermolecular attraction and steric effects [19]. According to Paul *et al.* [2], the clay filler did not influence the T_g and the T_m of the PLA matrix. The recrystallization temperature (T_c) of PLA is 113°C. The T_c of PLA/OMMT1 and PLA/OMMT1/EPMgMA5 is 100 and 99°C, respectively. The T_c of PLA matrix was greatly reduced by addition of OMMT. Note that the recrystallization of PLA/OMMT has been occurred at lower temperature. Similar observation was reported by Day *et al.* [20]. The T_c of neat PLA and PLA/nanoclay nanocomposites was recorded at 104.59 and 100.28°C, respectively. According to Day *et al.* [20], the presence of the clay nanoparticle appears to be influencing the nucleation and crystal growth rate of the PLA. The crystallization rate of PLA is enhanced by a factor of about 15 to 20 by the addition of nanoclay. Lee *et al.* [19] studied the thermal properties of PLA nanocomposites system and found that the T_c decreased by the addition of clay when compared to neat PLA. The large surface areas of nanoclay facilitate the PLA crystallization process and subsequently decrease the T_c of PLA. The nanosized OMMT plates provide large surface area due to their small size and thus it is reasonable to consider that the clay particles could act as effective nucleating sites of PLA crystallization [19]. Lewitus *et al.* [21] reported that when Cloisite 25A clay was incorporated into the PLLA, the crystallization temperature is about 10°C lower than that of neat PLLA, indicating the nucleation effects of the clay.

The degree of crystallinity of PLA and its composites was calculated and shown in Table 2. The degree of crystallinity for PLA, PLA/OMMT1 and PLA/OMMT1/EPMgMA are 22.0, 24.6 and 15.2%, respectively. From Table 2, it can be seen that the degree of crystallinity of PLA increased slightly in the presence of OMMT. It is believed that OMMT could act as a nucleating agent to increase the crystallinity of PLA. Interesting to note that, the addition of EPMgMAH maybe restricts the crystallization process and crystallite formation of PLA, which subsequently reduce the degree of crystallinity of PLA/OMMT nanocomposites. One may believe that the nucleating efficiency maybe disappeared attributed to the compatibilizer which encapsulates the heterogeneous particles. The crystallinity of polypropylene (PP) was reduced with the addition of natural rubber (NR) indicated the kinetic restriction on the crystallization process [22].

Thermogravimetric analysis (TG)

Generally, the incorporation of clay into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition [23]. Figure 3 shows TG curve of neat PLA and PLA/OMMT nanocomposites prepared by melt intercalation methods. Table 3 shows T_5, T_{50} and T_{95} of neat PLA and PLA/OMMT nanocomposite. T_5 refers to the temperature at which the remained mass of the materials is 5%. On the other hand, T_{95} refers to the temperature at which the remained mass of the materials is 95%.

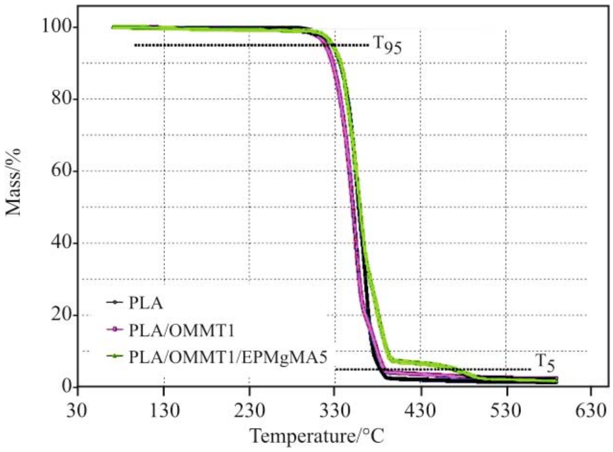

Fig. 3 TG traces of PLA and PLA/OMMT nanocomposites

Table 3 TG data of PLA and its nanocomposites

Sample	Temperature/°C		
	T_5	T_{50}	T_{95}
Neat PLA	383.4	326.9	358.1
PLA/OMMT1	387.1	319.4	356.1
PLA/OMMT1/EPMgMA5	469.7	327.5	359.0

The T_{95} of PLA and PLA/OMMT1 is 327 and 319°C, respectively. It can be revealed that the addition of OMMT decreased the T_{95} of PLA. This may be associated to the decomposition of the organic intercalant component of the OMMT and subsequently accelerates the decomposition of PLA. The T_{95} values of PLA/OMMT1 and PLA/OMMT1/EPMgMA5 is comparable, which recorded at approximately 327°C. At the temperature of T_5, the OMMT slightly increased the decomposition of PLA. This may be attributed to the MMT layered silicate which could acted as heat barrier at that temperature. Recall that the MMT could be a good heat barrier and assist the char formation during thermal decomposition. However, it is also reported in the opened literature that some of the organic-modified MMT are susceptible to the thermal degradation. Interesting to note that the T_5 of PLA/OMMT1/EPMgMA5 is recorded at 469.7°C, which is higher than that of both PLA and PLA/OMMT1. This is attributed to the thermal stability of EPMgMA. Another possible reason is that the EPMgMA facilitate the intercalation of OMMT silicate layer which could subsequently increase a larger physical protective barrier of OMMT on the surface for the PLA matrix.

In polymer layered silicate nanocomposites, the increment in the thermal stability can be attributed to an ablative reassembling of the silicate layers. This may occur on the surface of the nanocomposites creating a physical protective barrier on the surface of the material. On the other hand, volatilization might also be delayed by the labyrinth effect of the silicate layers dispersed in the nanocomposites [24]. There had been reported that clays seemed to hinder the degradation of the crystalline structures of PLA hybrids at low temperatures. However, some researchers observed that the clays could act as deformation accelerators at higher temperatures [11, 24].

The clay acts as a heat barrier, which enhances the overall thermal stability of the polymer layered silicate nanocomposites, as well as assists in the formation of char after thermal decomposition. In the early stages of thermal decomposition, the clay would shift the decomposition to higher temperature. After that, this heat barrier effect would result in a reverse thermal stability. In other words, the stacked silicate layers could hold accumulated heat that could be used as a heat source to accelerate the decomposition process, in conjunction with the heat flow supplied by the outside heat source [23].

Conclusions

An intercalated PLA nanocomposites was formed by the addition of OMMT. Further intercalation was facilitated by the addition of EPMgMA. The degree of crystallinity of PLA was increased by the incorporation of OMMT. However, the incorporation of EPMgMA reduced the degree of crystallinity of PLA/OMMT nanocomposites. The crystallization temperature of PLA was decreased by the addition of OMMT and EPMgMA. It is believed that the OMMT could act as nucleating agent for PLA. The thermal stability of PLA and its nanocomposites could be assessed using T_5, T_{50} and T_{95} recorded from TG. Interesting to note that, the thermal stability of PLA/OMMT was greatly enhanced by the addition of EPMgMA.

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