

Mechanical, Barrier, and Thermal Properties of Poly(lactic acid)/Poly(trimethylene carbonate)/Talc Composite Films

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ABSTRACT: Poly(L-lactic acid) (PLA) is now a very attractive polymer for food packaging applications. In this study, PLA/poly(trimethylene carbonate) (PTMC)/talc composite films were prepared by solvent casting. The influence of the talc loading (0, 1, 2, and 3 wt %) on the phase morphology of the PLA/PTMC/talc composites and the improvement in the resulting properties are reported in this article. The scanning electron microscopy images of the composite films demonstrated good compatibility between the PLA and PTMC, whereas talc was not thoroughly distributed in the PLA matrix at talc contents exceeding 3 wt %. The tensile strength and elongation at break of the composite films significantly improved ($p < 0.05$). On the contrary, the water vapor permeability and oxygen properties of the composite films decreased by 24.7 and 39.2%, respectively, at the 2 wt % talc loading. Differential scanning calorimetry showed that the crystallinity of the PLA phase increased with the presence of talc filler in the PLA/PTMC/talc composites. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40016.

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INTRODUCTION

During recent decades, several biodegradable polymers have been investigated as alternatives to the nondegradable polymers currently used in film production.¹ Poly(L-lactic acid) (PLA) is a biodegradable, thermoplastic, aliphatic polyester derived from renewable resources (i.e., corn starch or sugarcane) by bacterial fermentation.^{2,3} Among the biobased polymers emerging on the food packaging market, the semicrystalline polyester PLA is one of the most applied because of its relatively low cost and ease of processing.⁴

However, an important function of packaging is not only to ensure food safety but also to guarantee the sensory qualities of the packed product during storage.⁵ Semicrystalline PLA is brittle and shows a relatively low resistance to oxygen and water vapor permeation compared with conventional nondegradable polymer resins. Therefore, various approaches, including copolymerization, blending, and the incorporation of organic or/and inorganic materials, have been used to improve the flexibility, toughness, and barrier properties of pure PLA films.⁶ Much attention has been paid to the blending of PLA with low-molecular-weight or low glass-transition temperature (T_g) polymers, such as poly(ϵ -caprolactone), poly(ethylene glycol), and

poly(propylene glycol), to achieve high elongation and flexibility.^{7,8} Poly(trimethylene carbonate) (PTMC) is a biodegradable amorphous polymer with a low T_g between -14 and -25°C . High-molecular-weight PTMC holds elastic properties at ambient temperature.^{9,10} The blending of PTMC with PLA reduces the brittleness of PLA and improves its elongation at break (E).¹¹ In our previous study, we tried to prepare PLA/PTMC blends with various blend ratios (PLA/PTMC = 90/10, 80/20, 70/30, 60/40, and 50/50 w/w). PLA and PTMC showed partial miscibility. The PLA/PTMC (70/30) blend film appeared to be softer and more elastic than those with different blend ratios (data not shown in this article). So, PLA/PTMC (70/30) was selected for use in this study.

It was found that the addition of inorganic fillers, such as nano-clay, talc, and calcium carbonate, to binary blends helped to improve the barrier and mechanical properties of polymers.⁷ Talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] is a 2:1 trioctahedral layered silicate having three octahedral Mg positions per four tetrahedral Si positions.^{12–14} It can be a strong reinforcing filler and can be very useful in a large number of industrial applications, including food packaging. To exploit the enhanced barrier properties of polymers, various studies have been performed on the preparation of composite films. For example, Sekelik et al.¹⁵ reported

an improvement in the oxygen barrier properties with the incorporation of impermeable phaselike talc platelets (1–20 wt %). Murthy et al.¹⁶ observed that talc acted as a nucleating agent and increased the crystallinity in polymers, and thereby, the oxygen permeability and the water vapor transmission rates (WVTRs) were similarly reduced by talc. Jain et al.⁷ reported that the oxygen and water vapor barrier properties of composite films were improved by 33 and 25%, respectively, at a 3 wt % talc loading. When talc was only emended in PLA, the tensile strength and modulus increased with the amount of talc, whereas E decreased. So, the content of PTMC and talc in PLA should be optimized to provide a balance between the mechanical and barrier properties.

In this study, PLA/PTMC/talc composites containing 0, 1, 2, and 3 wt % talc were produced, and the effect of the talc content on the mechanical, barrier, and thermal properties were investigated. A structure–property relationship for the PLA/PTMC/talc composites was also determined.

EXPERIMENTAL

Materials and Chemicals

PLA [weight-average molecular weight (M_w) = 280 kDa, M_w /number-average molecular weight (M_n) = 1.98] was obtained from NatureWorks LLC (Nebraska). PTMC (M_w = 120 kDa, M_w/M_n = 1.71) was prepared in the laboratory of the Engineering Research Center of Biopolymer Functional Materials of Yunnan, Yunnan University of Nationalities (Yunnan, China). Talc, with an aspect ratio of 1–20 and a thickness of about 2 μm , was obtained from Sichuan University (Chengdu, China). Chloroform was purchased from Chengdu Kelong Chemical Co., Ltd (Sichuan, China). All other reagents and chemicals used in the study were analytical grade.

Preparation of the Films

Before preparation, the PLA resins and talc were dried in a vacuum oven at 60°C for 24 h. The PLA/PTMC/talc composites were prepared by a solvent casting method. An amount of 2 g of PLA/PTMC (70/30) was dissolved in 50 mL of chloroform with a batch mixer. Then, 0, 1, 2, and 3 wt % talc was added to the PLA/PTMC chloroform solution by vigorous mixing. The solutions were strained and cast onto a polytetrafluoroethylene plate for the preparation of the films. All of the films were dried in a vacuum oven at room temperature and cut into pieces 10 \times 2.54 cm². Talc was emended into PLA/PTMC at 0, 1, 2, and 3 wt % loadings; the samples with these contents were named PLA/PTMC, PLA/PTMC/talc-1, PLA/PTMC/talc-2, and PLA/PTMC/talc-3, respectively.

Film Thickness Measurements

The film thickness was measured with a digital micrometer (Mitotuyo No. 7327, Tokyo, Japan). Ten replications were conducted for each sample. The measurements were taken at 10 different locations in each film sample, and the mean values were calculated.

Mechanical Testing

The tensile modulus, tensile strength (TS), and E values of the samples were measured with a universal tensile machine (CMT 4104, MTS Systems Co., Ltd., China). The initial grip separation

was set at 100 mm, and the crosshead speed was set at 50 mm/min. The mechanical test was replicated five times for each sample, and the average values are reported.

Scanning Electron Microscopy (SEM)

SEM was used to observe the cross-sectional morphology of the PLA/PTMC/talc composite films. The fractured surfaces of the samples were first sputter-coated with a thin conductive gold layer that was 20 nm thick, and then, the morphology was studied with a Hitachi S-4800 (Japan).

Water Vapor Permeability (WVP)

The WVPs of the film samples were determined gravimetrically at 25°C under 50% relative humidity conditions with a water vapor transmission measuring cup in accordance with the ASTM E 96-95 standard method.¹⁷ The covered acrylic cups were placed in a temperature-and relative-humidity-controlled chamber with the same conditions required for film equilibration. The weight loss of the cup was considered to be equal to the weight of the transferred water through the film and adsorbed by the desiccant. The weight loss from each cup was measured as a function of time for 12 h.¹⁸ The WVP of the film was calculated with the following equation.¹⁹

$$\text{WVP} = (\text{WVTR} \times L / \Delta P) \quad (1)$$

where WVTR is the water vapor transmission rate (g/m²·s) through the film, L is the average film thickness (m), and ΔP is the partial water vapor pressure difference (Pa) between the two sides of the film. Tests were done in triplicate, with the mean values being reported.

Oxygen Transmission Rate (OTR)

The OTRs of the film samples were measured at 23°C under 100% dry oxygen with an oxygen permeation analyzer (STG-V2, Labstone Instruments Technology Co., Ltd., China) according to ASTM standard method D 3895-95. The testing film with a 14-cm diameter was conditioned at the testing cell for 10 h. The oxygen permeability (cc/m²·day·0.1 MPa) was calculated by the multiplication of the OTR by the film thickness.^{20,21} This test was replicated three times, and the mean value is reported.

Differential Scanning Calorimetry (DSC)

The thermal behavior of the PLA/PTMC/talc composites was measured by a TA Instruments differential scanning calorimeter (DSC-200PC, Netzsch, Germany). About 10-mg samples were heated as follows. First, the sample was heated from 20 to 210°C at a heating rate of 10°C/min, and then, it was held for 5 min to eliminate the thermal history. Subsequently, the sample was cooled to room temperature at a cooling rate of 10°C/min to record the crystallization temperature.

Thermogravimetric Analysis (TGA)

The thermal stability of the PLA/PTMC/talc composites was studied with the TA Instruments DSC instrument. TGA was carried out from 20 to 500°C at a rate of 10°C/min in a nitrogen environment.

Transparency

The transparency of the film samples was determined by the measurement of the percentage transmittance at 600 nm with

Table I. Mechanical Properties of the PLA, PTMC, PLA/PTMC, and PLA/PTMC/Talc Composites

Sample	Tensile modulus (MPa)	TS (MPa)	E (%)
PLA	1701.85 ± 54.36 ^d	45.76 ± 1.73 ^c	5.39 ± 0.02 ^a
PLA/PTMC	793.22 ± 30.62 ^a	16.02 ± 2.13 ^a	22.02 ± 1.87 ^b
PLA/PTMC/talc-1	825.26 ± 37.30 ^a	17.67 ± 0.85 ^a	33.96 ± 0.88 ^c
PLA/PTMC/talc-2	988.24 ± 15.71 ^b	20.14 ± 1.16 ^b	69.94 ± 1.02 ^e
PLA/PTMC/talc-3	1072.35 ± 76.08 ^{bc}	19.64 ± 0.61 ^b	56.03 ± 0.50 ^d

All values are the mean plus or minus the standard deviation of the three replicates. Values followed by different small letters (a-e) in the same column were significantly different ($p < 0.05$), where a is the lowest value.

an ultraviolet-visible spectrophotometer (T90, Beijing Purkinje General Instrument Co., Ltd., Beijing, China). Each film sample was cut into a rectangle piece and directly placed in a spectrophotometer test cell. An empty test cell was used as the reference.²² The transparency at 600 nm (T_{600}) was obtained with the following equation:²³

$$T_{600} = -\log(\%T/b) \quad (2)$$

where % T is the percentage transmittance and b is the film thickness (mm).

Statistical Analysis

A completely randomized designed was used. The SPSS statistical computer software package (SPSS version 13.0) was used in this study. Three replicate experiments were carried out, and the statistical significance was defined at $p < 0.05$.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties, including the tensile modulus, TS, and E , of different PLA/PTMC/talc composites are summarized in Table I. We observed that the tensile moduli of the PLA/PTMC/talc composites were improved by 4, 25, and 35% upon the incorporation of 1, 2, and 3 wt % talc contents, respectively. The increase in the tensile modulus of the PLA/PTMC films with the addition of talc is a typical effect of inorganic fillers on polymer matrix.¹⁶ This might have occurred because the incorporation of platelet fillers, such as talc, into the PLA polymer matrix leads to better stress transferability and improves the tensile modulus of the composite.²⁴ This also inferred that the talc particles were distributed uniformly but not randomly and did not aggregate, even at the highest incorporation content.²⁵

PLA displayed brittle behavior, and PTMC was a more ductile polymer than PLA. TS and E of the pure PLA film were 45.76 ± 1.73 MPa and 5.39 ± 0.02%, respectively. TS of the PLA/PTMC composites decreased sharply compared to that of the pure PLA film (Table I). The brittleness of PLA was improved apparently by its blending with PTMC. Furthermore, the PLA/PTMC/talc composites with talc showed a slight increase in TS compared to the PLA/PTMC composites without talc filler.

The E values of the pure PLA and PLA/PTMC composites were found to be 5.39 ± 0.02 and 22.02 ± 1.87 MPa, respectively. The E values of the PLA/PTMC/talc composites increased gradually

with increasing talc content. Similar results were reported by Yu et al.²⁶ when they studied the influence of talc addition on the mechanical properties of PLA films. Talc particles induced microcracks in the polymer matrix around them, released the constraints for shear yielding, and resulted in high E . With the addition of 2 wt % talc, the PLA/PTMC/talc composites film had the highest value of E (69.94%). This might have contributed to the fact that the high talc content led to material defects such as voids. The results showed that a suitable content of talc in the composites was about 2 wt %. When used in appropriate amounts, it led to obvious improvements in the mechanical properties of the composites, but additional increases in the amount of talc did not improve the mechanical properties any more.²⁷

Barrier Properties

A main function of food packaging materials is to impede gas and water vapor transfer between food and the surrounding atmosphere, so the WVP and OTR of films should be as low as possible.^{28,29}

The WVP values of the PLA/PTMC and PLA/PTMC/talc composites films are shown in Table II. We observed that the WVP values of the PLA/PTMC/talc composites films were significantly ($p < 0.05$) lower than those of the PLA/PTMC blend films. The WVP values of the PLA/PTMC/talc composites films changed significantly ($p < 0.05$) depending on the talc content. This result was mainly attributed to the fact that the hydrophobicity of the films increased with increasing talc filler content. On the other hand, the density of the PLA/PTMC/talc composites films increased with increasing talc

Table II. WVP and OTR Values of the PLA/PTMC and PLA/PTMC/Talc Composites

Sample	WVP × 10 ⁻¹⁴ (kg·m m ⁻² ·s ⁻¹ ·Pa ⁻¹)	OTR (cc m ⁻² · day ⁻¹ ·0.1 MPa ⁻¹)
PLA/PTMC	5.92 ± 0.05 ^c	879.11 ± 30.7 ^d
PLA/PTMC/talc-1	5.17 ± 0.34 ^b	608.93 ± 10.5 ^c
PLA/PTMC/talc-2	4.46 ± 0.20 ^a	534.17 ± 0.80 ^b
PLA/PTMC/talc-3	5.41 ± 0.40 ^{bc}	442.99 ± 1.28 ^a

All values are the mean plus or minus the standard deviation of the three replicates. Values followed by different small letters (a-d) in the same column were significantly different ($p < 0.05$), where a is the lowest value.

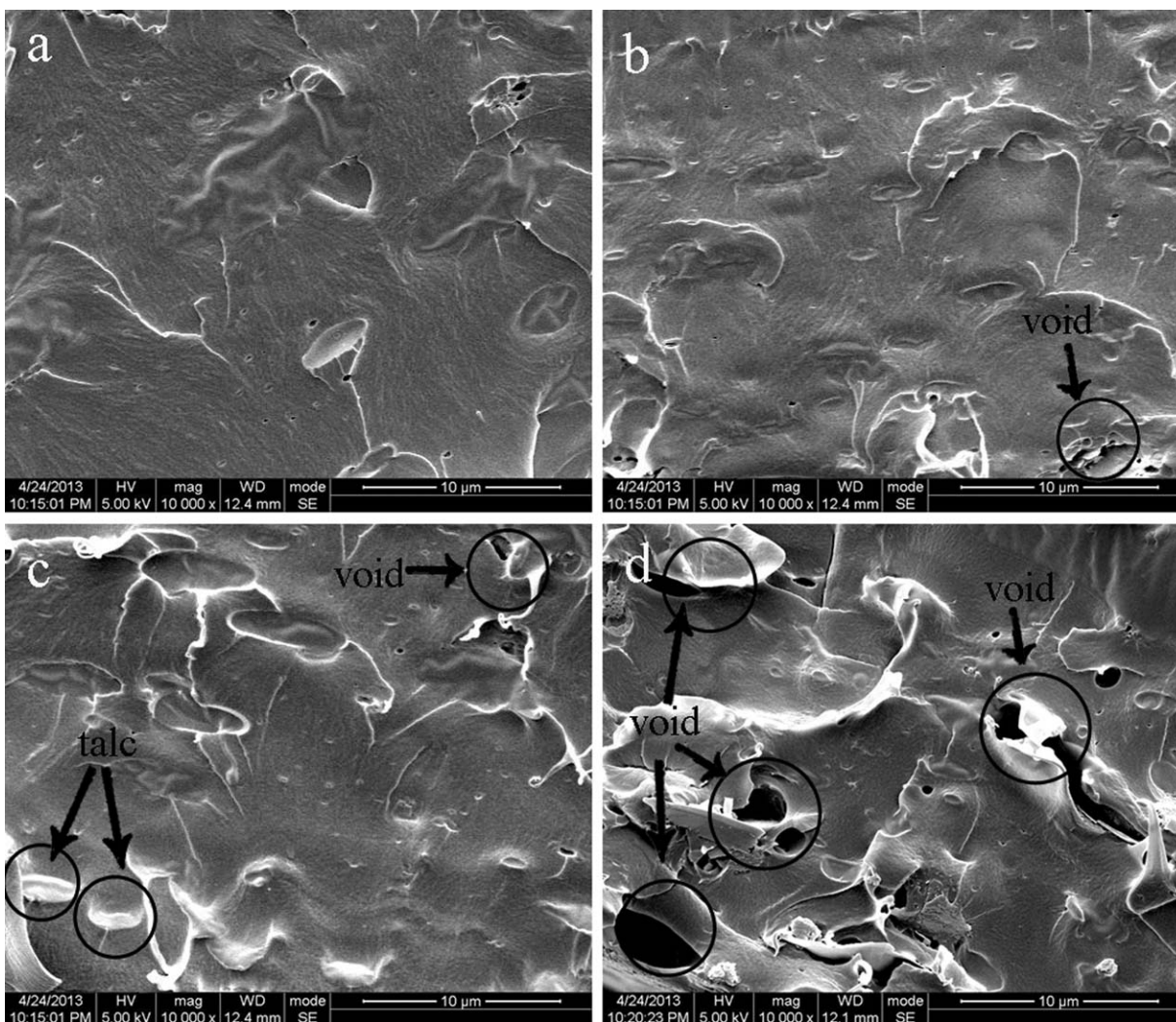


Figure 1. SEM micrographs of the fracture morphology of (a) PLA/PTMC, (b) PLA/PTMC/talc-1, (c) PLA/PTMC/talc-2, and (d) PLA/PTMC/talc-3 (10,000 \times magnification).

filler content. A higher density of the films decreased the interstitial space in the polymer matrix and thus allowed for a decreased diffusion rate of water molecules through the films.³⁰ We observed that the addition of 1 and 2 wt % talc in the PLA/PTMC/talc composites decreased the WVP values by 12.7 and 24.7%, respectively. However, the water vapor barrier properties decreased when 2 wt % talc was loaded. This was verified by SEM [Figure 1(a–d)], which showed that many voids existed in PLA/PTMC/talc-3, and this permitted more water vapor transfer.

The oxygen permeability of the PLA/PTMC and PLA/PTMC/talc composites films are given in Table II. There were 30.8, 39.2, and 49.6% improvements in the oxygen barrier properties at 1, 2, and 3 wt % of talc in the PLA/PTMC/talc composites, respectively. The oxygen barrier properties significantly ($p < 0.05$) increased with increasing amount of Talc.

DSC

Talc is a strong nucleating agent in the process of polymer crystallization, Deshmukh et al.³¹ showed that both talc and mica behaved as nucleating agents and accelerated crystallization. In

this study, DSC measurements were carried out to determine the T_g , peak crystallization temperature (T_c), and melting temperature (T_m) values. T_g was taken at the inflection point of the first endothermic transition.⁸ The DSC thermograms are shown in Figure 2. The characteristic temperatures of the detected transitions are summarized in Table III.

The T_g value shifted from 55.1 $^{\circ}$ C (PLA) to 46.3 $^{\circ}$ C (PLA/PTMC). Such a decrease in the T_g value for plasticized PLA systems is very common and was attributed to the segmental mobility of the PLA chains due to plasticization.⁶ This confirmed that PTMC exerted a plasticizer effect. There was no significant difference in the T_g value with increasing amount of talc filler, as all of the values were close to those obtained for the unfilled PLA/PTMC blends. This suggested that there was no competition between the plasticizer (PTMC) and the PLA chains for interacting with talc filler. So, PTMC could keep its plasticizing effect after the addition of talc filler.¹

The crystallinity percentage (X_c) of the PLA phase in the composite was determined by the following formula:

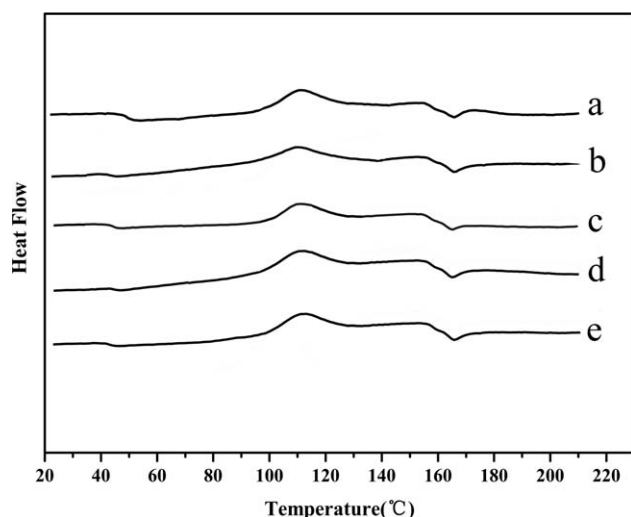


Figure 2. DSC curves of (a) PLA, (b) PLA/PTMC, (c) PLA/PTMC/talc-1, (d) PLA/PTMC/talc-2, and (e) PLA/PTMC/talc-3.

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} w \times 100 \quad (3)$$

where ΔH_m is the melting enthalpy (J/g) of the sample, ΔH_m^0 is the melting enthalpy of the 100% crystalline PLA (93.7 J/g), and w is the mass fraction of PLA in the composite.¹²

From the recorded DSC curves, X_c was calculated, and the values are shown in Table III. We observed that the crystallinity of the PLA phase increased with the presence of talc filler in the PLA/PTMC/talc composites. There were 18.4, 23.6, and 12.8% increases in the crystallinity of the PLA phase in the PLA/PTMC/talc composites with the addition of 1, 2, and 3% talc filler, respectively. Meanwhile, the crystallization peak of the PLA/PTMC/talc composites shifted to a lower temperature compared to those of the corresponding unfilled matrices. The crystallization temperature decreased by 3.2°C in 3 wt % talc filled PLA/PTMC. The noticeable changes in the crystallinity of the PLA phase and the crystallization temperature revealed that the presence of talc improved the crystallization ability of PLA. Furthermore, the increase in crystallinity favored the mechanical properties.⁵² The evolution of the material crystallinity could also improve the barrier properties of the blend films for food packaging applications.³³

TGA

The thermal degradation of the neat PLA, PLA/PTMC, and PLA/PTMC/talc composites are shown in Figure 3. Determining the temperature corresponding to the onset of degrada-

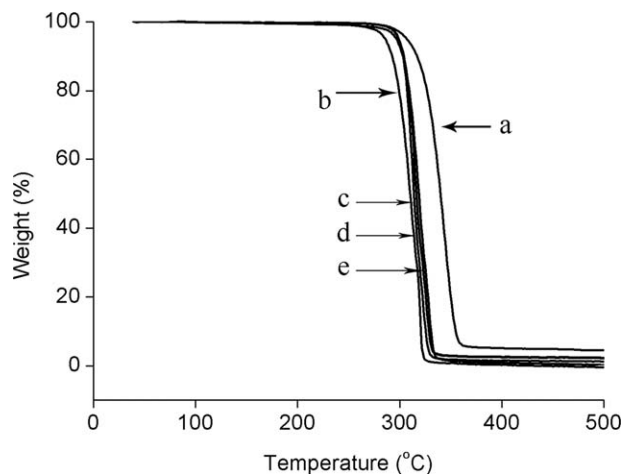


Figure 3. TGA curves of (a) PLA, (b) PLA/PTMC, (c) PLA/PTMC/talc-1, (d) PLA/PTMC/talc-2, and (e) PLA/PTMC/talc-3.

tion (T_{onset}) for a polymer is essential for evaluating its thermal stability. T_{onset} of PLA/PTMC (293.4°C) was lower than that of pure PLA. However, the PLA/PTMC/talc composites showed a slightly higher T_{onset} value when compared to the unfilled PLA/PTMC blends. This indicated that the talc filler improved the thermal stability of the PLA/PTMC/talc composites.

Transparency

The results of the transparency determined by %T indicated that the transparency of the PLA/PTMC composite films decreased significantly ($p < 0.05$) compared to that of the PLA/PTMC film (Table IV). Films in which the talc content was greater were more opaque (lower T_{600} value). The decrease in the film transparency as a consequence of the addition of inorganic filler has also been reported with other base polymers. Such an effect of an inorganic filler on the optical properties was explained as being not only due to the types of polymer matrix but also to the compatibility between the polymer matrix and the filler.³⁴ Hong and Rhim³⁵ reported that a polyethylene film without clay filler was more transparent than those with clay filler.³⁵ Ogata et al.³⁶ reported that addition of clay to the PLA film resulted in a decrease in its transparency.

SEM Analysis

To explore the reinforcing and toughening mechanisms, the morphology of the PLA/PTMC/talc composites was studied by SEM, and the images are shown in Figure 1(a–d). Figure 1 showed that in the PLA/PTMC/talc composites, talc fillers

Table III. Thermal Characteristics of the PLA/PTMC and PLA/PTMC/Talc Composites

Sample	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PLA	55.1	107.3	167.5	41.8	44.6
PLA/PTMC	46.3	102.2	165.9	30.6	46.7
PLA/PTMC/talc-1	45.8	100.4	165.5	35.9	55.3
PLA/PTMC/talc-2	46.0	98.5	166.3	37.1	57.7
PLA/PTMC/talc-3	45.7	99.0	165.8	33.5	52.7

Table IV. Transparency of the PLA/PTMC and PLA/PTMC/Talc Composites

Sample	T_{600}
PLA/PTMC	54.86 ± 1.36^d
PLA/PTMC/talc-1	43.26 ± 2.99^c
PLA/PTMC/talc-2	39.60 ± 0.63^b
PLA/PTMC/talc-3	31.83 ± 1.24^a

All values are the mean plus or minus the standard deviation of the three replicates. Values followed by different small letters (a-d) in the same column were significantly different ($p < 0.05$), where a is the lowest value.

were dispersed uniformly in the PLA–PTMC matrix without obvious aggregation. The interlayer interaction of talc was weak, and the talc platelets were bonded by van der Waal's forces. These talc platelets could slide against each other. This caused a good dispersion of talc in the matrix; therefore, the enhancement in strength increased with increasing talc content.¹² Furthermore, the platy nature of talc led to a large interfacial area between the talc and the polymer matrix. This resulted in an increase in E and showed that talc had a significant toughening effect.

It is worth noting that many voids are shown in Figure 1(d). These voids might have been induced by the debonding of talc particles from the matrix or the shelling of the middle talc layers.²⁶ This indicated that the talc platelets of PLA/PTMC/talc-1 and PLA/PTMC/talc-2 were embedded in the PLA–PTMC matrix better than those of PLA/PTMC/talc-3. A good wetting of talc filler in the polymer matrix could increase the strength of the polymer composites. The reduction in the extent of voiding could also contribute to an improvement in the barrier properties of food packaging materials.

CONCLUSIONS

The effects of talc filler on the structure–properties relationships were analyzed. This study showed that the addition of talc filler improved the TS and E values of the composite films. The WVP and OTR values of the films were improved by the addition of talc. The best compromise between the mechanical, barrier, and thermal properties was achieved by the addition of 2 wt % talc to the PLA/PTMC blends. This approach could be very useful in the preparation of a material with improved barrier performances for food packaging applications.

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