

## Physical properties and crystallization behavior of poly(lactide)/poly(methyl methacrylate)/silica composites

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**ABSTRACT:** Poly(lactide)/poly(methyl methacrylate)/silica (PLA/PMMA/SiO<sub>2</sub>) composites were fabricated using a twin-screw extruder. Nanosilica particles were incorporated to improve the toughness of the brittle PLA, and a chain extender reagent (Joncryl ADR 4368S) was used to reduce the hydrolysis of the PLA during fabrication. Highly transparent PLA and PMMA were designated to blend to obtain the miscible and transparent blends. To estimate the performance of the PLA/PMMA/SiO<sub>2</sub> composites, a series of measurements was conducted, including tensile and Izod impact tests, light transmission and haze measurements, thermomechanical analysis, and isothermal crystallization behavior determination. A chain extender increases the ultimate tensile strength of the PLA/PMMA/SiO<sub>2</sub> composites by ~43%, and both a chain extender and nanosilica particles increase Young's modulus and Izod impact strength of the composites. Including 0.5 wt % nanosilica particles increase the elongation at break and Izod impact strength by ~287 and 163%, respectively, compared with those of the neat PLA. On account of the mechanical performances, the optimal blending ratio may be between PLA/PMMA/SiO<sub>2</sub> (90/10) and PLA/PMMA/SiO<sub>2</sub> (80/20). The total light transmittance of the PLA/PMMA/SiO<sub>2</sub> composites reaches as high as 91%, indicating a high miscible PLA/PMMA blend. The haze value of the PLA/PMMA/SiO<sub>2</sub> composites is less than 35%. Incorporating nanosilica particles can increase the crystallization sites and crystallinities of the PLA/PMMA/SiO<sub>2</sub> composites with a simultaneous decrease of the spherulite dimension. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42378.

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### INTRODUCTION

Poly(lactic acid) (PLA) is an aliphatic and thermoplastic polyester that has attracted considerable attention because of its biodegradability, biocompatibility, compostable characteristic, and nontoxicity to the human body and environment.<sup>1–5</sup> The inherent brittleness and low elongation at break (~4.5%), and high expense restrict its range of application. In our previous study, we have fabricated PLA/SiO<sub>2</sub> composites by using an extrusion technique. The nanosilica particles content in less than 1.5 wt % increased the Young's modulus ( $E$ ), elongation at break ( $\epsilon_b$ ), Izod impact strength (IS), and heat deflection temperature (HDT) of the PLA/SiO<sub>2</sub> composites by ~21.7%, 267%, 227%, and 25°C, respectively, compared with those of the neat PLA. Incorporating nanosilica particles also increased the crystallinities of the PLA/SiO<sub>2</sub> composites with a simultaneous decrease in spherulite dimensions.<sup>6</sup>

Poly(methyl methacrylate) (PMMA) is a glassy and transparent polymer that demonstrates excellent properties for the packaging industry and optical or biomedical applications<sup>7</sup> because of

its high strength, optical clarity, desirable dimensional stability, and weatherability. PMMA exhibits a high brittleness because of its high stiffness and this limits its potential application areas.<sup>8</sup> Eguibururu *et al.* proposed that blending PMMA with poly(L-lactide) (PLLA) yields a single glass transition temperature based on differential scanning calorimetry (DSC) scans when the PLLA content is lower than 20% or higher than 90%, indicating that PLLA/PMMA blends exhibit complete miscibility when the PLLA content is lower than 20%. Blending amorphous poly(D-lactide) (PDLA) with PMMA shows a high degree of miscibility.<sup>9</sup> Both PLA and PMMA are transparent polymers, but PMMA is a nonbiodegradable polymer. Considering environmental friendliness, blending PMMA with biodegradable PLA can decrease the consumption of PMMA.

Light-emitting diode (LED) lighting has recently received considerable attention. However, LED lighting exhibits the characteristic of a point-light-source. The basic requirements of LED lamp-masks are light transmittance higher than 90%, high light uniformity, and working temperature higher than 60°C.<sup>10</sup> It was

proposed that the LED light could be evenly spread out from the LED lamp-masks by incorporating inorganic particles into the polymer lamp-masks. To date, the LED light-masks are mainly composed of polycarbonate (PC). PLA exhibits biodegradable, biocompatible, and high light transmission characteristics, and it can be miscible with PMMA. Based on the strategy of environmental friendliness, the PLA/PMMA blends might potentially replace PC polymers in the application of LED light masks. Practically, the working temperatures of LED lighting generally range from  $-20$  to  $40^{\circ}\text{C}$ . As stated above, the PLA/SiO<sub>2</sub> composites increased the HDT from  $55.2^{\circ}\text{C}$  for neat PLA to  $80.2^{\circ}\text{C}$  for the 1.5 wt % PLA/SiO<sub>2</sub> composite, much higher than the working temperature of LED lighting. PMMA is a high brittleness polymer,<sup>8</sup> PLA/PMMA blends should also exhibit high brittleness. Except for the increase of the HDT of PLA/SiO<sub>2</sub> composites, the inclusion of SiO<sub>2</sub> into PLA can significantly improve the toughness of the PLA by  $\sim 227\%$ .<sup>6</sup> The inclusion of SiO<sub>2</sub> into PLA/PMMA blends could also greatly improve the toughness of the blends.

Based on our previous study on the PLA/SiO<sub>2</sub> composites, our objective in this study is to extend the applications of PLA to the PLA/PMMA/SiO<sub>2</sub> composites. However, another difficulty in fabricating the PLA is the thermal hydrolysis. Oever *et al.* reported that PLA is sensitive to hydrolytic degradation under melt processing conditions in the presence of small amounts of water, and they proposed that kneading the predried neat PLA for 13 min at  $190^{\circ}\text{C}$  resulted in a considerable reduction in intrinsic viscosity.<sup>11</sup> He *et al.* proposed that incorporating multi-walled carbon nanotubes can accelerate the hydrolytic degradation of PLLA.<sup>12</sup> Furthermore, it was reported that using a chain extender could improve the thermal hydrolysis, compatibility, and processability of PLA.<sup>13,14</sup>

In this study, a chain extender reagent (Joncryl ADR 4368CS, BASF), which is a styrene-acrylic multi-functional-epoxide oligomeric agent, was used to improve the thermal hydrolysis and processability of PLA. This reagent can react with the end groups (carboxylic and hydroxyl groups) of the PLA polymer through its functional epoxide to improve the extent of thermal hydrolysis of PLA.<sup>15</sup> The nanosilica particles were pretreated with stearic acid to improve the dispersion of the nanoparticles in the nonpolar polymer matrix. A chain extender and nanosilica particles were incorporated into the PLA/PMMA blends to fabricate the PLA/PMMA/SiO<sub>2</sub> composites. These PLA composites were fabricated to improve the toughness of the brittle PLA matrix, reducing the hydrolytic degradation of PLA, and retaining the high transparency to light while adequately increasing the haze value of the resulting PLA/PMMA/SiO<sub>2</sub> composites. Finally, the PLA/PMMA/SiO<sub>2</sub> composites may extend their application range to LED lighting.

## EXPERIMENTAL

### Materials

PLA (NatureWorks 4032D) was purchased from NatureWorks, and it contains 92% L-lactide and 8% meso-lactide. The molecular weight ( $M_w$ ) and density of PLA are  $1.8 \times 10^5 \sim 2.0 \times 10^5$  g/mol and  $1.25$  g/cm<sup>3</sup>, respectively. PMMA (Acryrex CM-205) was purchased from Chi-Mei Corporation, Taiwan. The molecu-

**Table I.** Recipes for the Preparation of PLA/PMMA/SiO<sub>2</sub> Composites

Sample	PLA	PMMA	ADR	SiO <sub>2</sub>
Neat PLA	100	-	-	-
PLA/ADR	99.5	-	0.5	-
PLA/SiO <sub>2</sub>	99.0	-	-	0.5
PLA/PMMA/SiO <sub>2</sub> (90/10)	89.05	10	0.45	0.5
PLA/PMMA/SiO <sub>2</sub> (80/20)	79.1	20	0.4	0.5
PLA/PMMA/SiO <sub>2</sub> (60/40)	59.2	40	0.3	0.5
PLA/PMMA/SiO <sub>2</sub> (40/60)	39.3	60	0.2	0.5
Neat PMMA	-	100	-	-

The chain extender from BASF (Joncryl ADR 4368S) is denoted as ADR. All of the contents are in terms of wt %.

lar weight ( $M_w$ ), density and melt index ( $MI$ ) of PMMA are  $3.0 \times 10^5 \sim 3.5 \times 10^5$  g/mol,  $1.19$  g/cm<sup>3</sup>, and  $1.8$  g/10 min (at  $230^{\circ}\text{C}$  and  $3.8$  kg), respectively. Chain extender (Joncryl ADR 4368S), which is a styrene-acrylic multi-functional-epoxide oligomeric agent, was purchased from BASF, and its molecular weight and density are  $6.8 \times 10^3$  g/mol and  $1.08$  g/cm<sup>3</sup>, respectively. The SiO<sub>2</sub> nanoparticles with diameter  $\sim 24$  nm and purity  $\sim 99.9\%$  were purchased from the Plasmachem GmbH, Germany/Russian. The density of SiO<sub>2</sub> is  $2.65$  g/cm<sup>3</sup>.

### Surface Modification of Nanosilica

The as-received nanosilica particles were subjected to surface modification by using stearic acid to impart the hydrophobic characteristic onto the surface of the silica particles. The stearic acid ( $M_w = 284.48$  g/mol, mp =  $68\text{--}71^{\circ}\text{C}$ , bp =  $361^{\circ}\text{C}$ )<sup>16</sup> was first added to isopropyl alcohol, and the mixture was stirred for  $\sim 1$  h at room temperature. Then, the silica nanoparticles were added to the mixture so that the carboxylic group of stearic acid was expected to physically attract with the silica particles to impart a hydrophobic characteristic on the surface of the silica particles.<sup>14</sup> In this study, stearic acid with a concentration of 2% (of the weight of silica) was applied to estimate the effect of the surface modification. After the surface modification, the stearic-acid-modified nanosilica was dried at  $60^{\circ}\text{C}$  for 48 h and then stored in a desiccator before use.

### Fabrication of PLA/PMMA/SiO<sub>2</sub> Composites

The PLA/PMMA/SiO<sub>2</sub> composites were fabricated by mixing PLA and PMMA with stearic-acid-modified nanosilica by using a twin-screw extruder (Nanking Jia-Ya SHJ-20, China). Table I lists the compositions of the PLA/PMMA/SiO<sub>2</sub> composites, indicating that the nanosilica content in the composites was 0.5 wt %. The chain extender content was 0.5% of the weight of PLA. The PLA and PMMA pellets were dried at  $80^{\circ}\text{C}$  for 24 h before being kneaded to remove the moisture. The PLA, PMMA, chain extender, and silica nanoparticles were introduced into the extruder at  $200^{\circ}\text{C}$  to allow the components to mix efficiently. After extrusion, the resulting composites were cut into pellet forms, measuring 2–3 mm in size. A vacuum compression molding operating at  $200^{\circ}\text{C}$  was used to prepare the specimens for tensile, notch impact, and dynamic mechanical properties measurements.

### Tensile and Impact Tests

Room temperature tensile test was conducted in accordance with the ASTM standard D638. A Instron 3369 to obtain the ultimate tensile strength (UTS),  $E$ , and  $\epsilon_b$ . The dog-bone shaped specimens have the dimension of  $120 \times 10.32 \times 4.24 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness). The cross-head speed was set to be 10 mm/min. The test result is typically the average of 10 specimens. Room temperature Izod impact test was conducted in accordance with the ASTM standard D256-06a. The notched specimens with notched depth of 10.03 mm were fabricated. A Yang-Yi QC-639E (made in Taiwan) universal digital impact tester was applied to conduct the impact test. The Izod impact test result is typically the average of 10 specimens, and the IS is expressed as  $\text{kJ/m}^2$ .

### Light Transmission and Haze Measurements

The haze and luminous transmittance were determined according to the ASTM D 1003-11. A specimen less than 0.25 mm in thickness was used to measure by a haze meter (HM-150). Total transmittance ( $T_t$ ) and diffuse transmittance ( $T_d$ ) were estimated, and the percent haze was calculated as follows:

$$\text{haze} = T_d / T_t \times 100\% \quad (1)$$

### Dynamic Mechanical Analysis

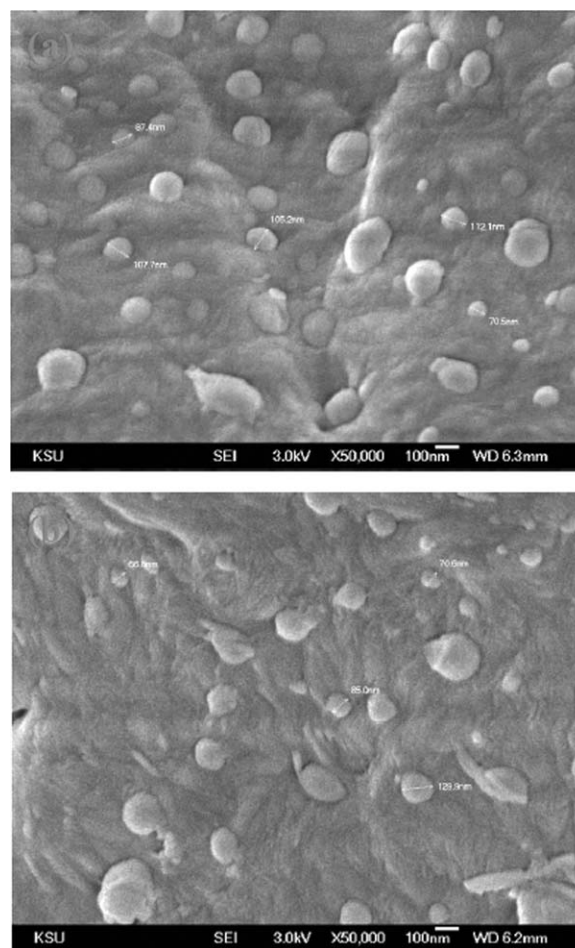
Glass transition temperature, storage modulus, and damping factor of the resulting PLA composites were measured using a dynamic mechanical analyzer (DMA, TA Q800). The specimens with dimension of  $40.33 \times 7.52 \times 1.72 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness) were fabricated for the test of dynamic mechanical analysis. A tension mode testing was applied during the DMA scans, and the scanning range was from  $-40$  to  $140^\circ\text{C}$  at a heating rate of  $2^\circ\text{C}/\text{min}$  and at a frequency of 1 Hz under nitrogen atmosphere.

### Isothermal Crystallization Behavior Determination

A TA differential scanning calorimeter (TA Q2000) was applied to investigate the isothermal crystallization behavior of the neat PLA and PLA/PMMA/SiO<sub>2</sub> composites. The sample was heated up to  $200^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere. At  $200^\circ\text{C}$ , this sample was held for 5 min to remove the previous thermal history, and then it was quenched to a predetermined temperature of  $135^\circ\text{C}$  to undergo the isothermal crystallization process. After the isothermal crystallization process, the sample was subsequently heated to  $185^\circ\text{C}$  to conduct the second-heating run and to estimate the melting temperature ( $T_m$ ).

### Microstructure and Fractural Surface Observations

A Zeiss Axioskop 40A polarized optical microscope (POM) was used to evaluate the spherulite dimensions of neat PLA and PLA/PMMA/SiO<sub>2</sub> composites under isothermal crystallization. A thin piece of sample was sandwiched between two glass coverslips and placed on a digital hot-stage under nitrogen atmosphere. The hot-stage was rapidly heated to  $200^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  and held for 5 min to erase the thermal history of specimens. Then, the neat PLA or PLA/PMMA/SiO<sub>2</sub> melt was quenched to a predetermined temperature of  $135^\circ\text{C}$  and kept at this temperature to observe spherulite morphologies of the neat PLA and PLA/PMMA/SiO<sub>2</sub> composites. A Jeol 6700F field emission scanning



**Figure 1.** The SEM micrograph showing distribution of nanosilica particles in (a) PLA/PMMA/SiO<sub>2</sub> (90/10) and (b) PLA/PMMA/SiO<sub>2</sub> (60/40) composites.

electron microscope (SEM) was used to estimate the nanosilica dispersion of the broken specimens after tensile test.

## RESULTS AND DISCUSSION

### Dispersion of Nanosilica in the PLA Matrix

Figure 1 shows the distribution of nanosilica (0.5 wt %) in the PLA/PMMA/SiO<sub>2</sub> (90/10) and PLA/PMMA/SiO<sub>2</sub> (60/40) composites. The nanosilica particles in the PLA/PMMA blend were dispersed homogeneously, and the domains of the silica particles in the PLA ranged from 66 to 130 nm, corresponding to three to six particle clustering. It is observed that the distribution of nanosilica particles in the PLA/PMMA blends has the similarity when the composition of the blend is changed.

### Room Temperature Tensile and Impact Properties of the PLA/PMMA/SiO<sub>2</sub> Composites

Table II shows the mechanical properties, including UTS,  $E$ ,  $\epsilon_b$ , and IS, of the neat PLA, PMMA,<sup>8</sup> and PLA/PMMA/SiO<sub>2</sub> composites. In this study, the values of the UTS,  $E$ , and  $\epsilon_b$  for the neat PLA are 64.9 MPa, 2050 MPa, and 4.5%, respectively. Blending PLA with PMMA increases the tensile strength of the PLA/PMMA/SiO<sub>2</sub> composites, and the UTS values of the resulting composites increases with the amount of PMMA. The UTS

**Table II.** The Ultimate Tensile Strength (UTS), Young's Modulus ( $E$ ), Elongation at Break ( $\epsilon_b$ ), and Izod Impact Strength (IS) of the Neat PLA, PMMA, and PLA/PMMA/SiO<sub>2</sub> Composites

Sample	UTS (MPa)	$E$ (MPa)	$\epsilon_b$ (%)	IS (kJ/m <sup>2</sup> )
Neat PLA	64.9 ± 2.7	2050 ± 137	4.5 ± 0.4	2.6 ± 0.3
PLA/ADR	61.0 ± 1.8	2186 ± 107	10.0 ± 1.8	5.2 ± 0.4
PLA/SiO <sub>2</sub>	58.0 ± 2.1	2293 ± 139	17.6 ± 2.1	6.7 ± 0.2
PLA/PMMA/SiO <sub>2</sub> (90/10)	61.5 ± 0.9	2466 ± 117	17.0 ± 3.0	6.8 ± 0.2
PLA/PMMA/SiO <sub>2</sub> (80/20)	62.7 ± 2.5	2581 ± 135	9.6 ± 1.6	5.4 ± 0.4
PLA/PMMA/SiO <sub>2</sub> (60/40)	63.9 ± 2.0	28099 ± 183	7.4 ± 2.6	4.3 ± 0.3
PLA/PMMA/SiO <sub>2</sub> (40/60)	65.5 ± 2.5	3032 ± 140	5.7 ± 1.6	4.0 ± 0.3
Neat PMMA <sup>a</sup>	73.5	3300	10.0	2.0

<sup>a</sup>The tensile properties and Izod impact strength (IS) of PMMA were cited from the specification of PMMA (Acryrex CM-205), Chi-Mei Corporation, Taiwan.

value of the PLA/SiO<sub>2</sub> composite is lower than that of the neat PLA by ~6.9 MPa, corresponding to a 10.6% decrease. This decrease in UTS might be attributed to the hydrolytic degradation of PLA and to the stress concentrator effect induced by the inclusion of nanosilica. The nanosilica might play a role of stress concentrator and make the UTS of the resulting PLA composites lower. Oever *et al.* reported that PLA is sensitive to hydrolytic degradation under melt processing conditions.<sup>10</sup> He *et al.* proposed that incorporating multi-walled carbon nanotubes can accelerate the hydrolytic degradation of PLLA.<sup>11</sup> However, the chain extender in the PLA (PLA/ADR)—which had no added silica—decreased the UTS value from 64.9 MPa for the neat PLA to 61.0 MPa for the PLA/ADR, corresponding to a 6.0% decrease. Compared with the 10.6% decrease for the PLA/SiO<sub>2</sub> composite, we observed that adding a chain extender (Joncryl ADR 4368S) during PLA melt compounding can lower the decrement of UTS by ~43% (decrement from 10.6 to 6.0%). This indicates that adding a chain extender can considerably decrease the occurrence of hydrolytic degradation.

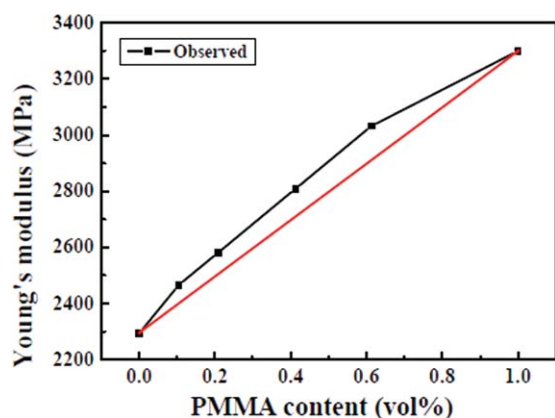
Regarding the effect of incorporating nanosilica particles on the  $E$  of the neat PLA, including 0.5 wt % nanosilica particles

increases the  $E$  value of the resulting composite from 2050 to 2293 MPa. Adding a chain extender can also increase the  $E$  value from 2050 to 2186 MPa. Furthermore, blending PLA with PMMA greatly increases the  $E$  values of the resulting composites because of the high  $E$  value (3300 MPa) of PMMA. According to the rule of mixtures (ROM), the calculated  $E$  of a composite can be determined as following:<sup>17</sup>

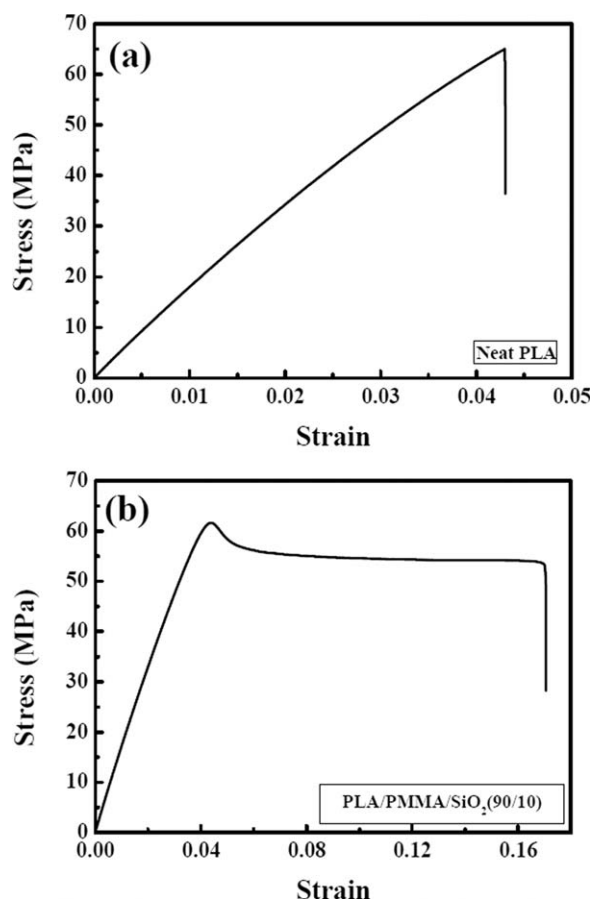
$$E = V_f E_f + (1 - V_f) E_m, \quad (2)$$

where  $E_f$  and  $E_m$  are the moduli for the filler and matrix, respectively, and  $V_f$  is the volume fraction of filler. The densities of PLA, PMMA, and nanosilica are 1.25, 1.19, and 2.65 g/cm<sup>3</sup>,<sup>17</sup> respectively. Figure 2 illustrates the calculated and observed  $E$  of the PLA/PMMA/SiO<sub>2</sub> composites; the  $E$  value for the zero PMMA content of the composite is 2293 MPa because of the incorporation of nanosilica particles. Obviously, the observed moduli of the PLA/PMMA/SiO<sub>2</sub> composites are significantly coherent with the calculated moduli (red line in Figure 2).

In our previous study on the PLA/SiO<sub>2</sub> composites, incorporating nanosilica particles into the PLA polymer greatly increased the  $\epsilon_b$  of the resulting composites. A silica content of 0.8 wt % in the PLA matrix can increase the elongation from 4.5% for neat PLA to 16.6% for PLA/SiO<sub>2</sub> composites.<sup>6</sup> In this study, the amount of nanosilica in the PLA/PMMA blends is 0.5 wt %. Adding nanosilica particles can also increase the  $\epsilon_b$  of the neat PLA from 4.5% to as high as 17.6%. As reported, the nanosilica particles can reduce the melt viscosities of PEN and PET and act as a lubricant in the polymers because they exhibit spherical shape and smooth non-porous surface, which would lower the friction coefficient.<sup>18,19</sup> As mentioned in our previous study on the PLA/SiO<sub>2</sub> composites, the SiO<sub>2</sub> particles are basically spherical in shape.<sup>6</sup> Accordingly, the major sliding that appeared in the PLA/SiO<sub>2</sub> composites may follow the lubricant hypothesis. Moreover, adding the chain extender at 0.5 wt % (of the weight of PLA) can markedly increase the  $\epsilon_b$  value from 4.5 to 10.1%, as shown in Table II. Blending PLA with PMMA can lower the  $\epsilon_b$  value of the PLA/PMMA/SiO<sub>2</sub> composites because of the low  $\epsilon_b$  value (4.5%) for the neat PLA. The  $\epsilon_b$  value starts to decrease from 17.0% for PLA/PMMA/SiO<sub>2</sub> (90/10) to 5.7% for PLA/PMMA/SiO<sub>2</sub> (40/60).



**Figure 2.** The calculated (red line) and observed (black line) Young's moduli of the PLA/PMMA/SiO<sub>2</sub> composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** The sliding behavior induced by the inclusion of nanosilica particles in the PLA/PMMA/SiO<sub>2</sub> composite during tensile testing. (a) Neat PLA and (b) PLA/PMMA/SiO<sub>2</sub> (90/10) composite.

Obviously, the optimal blending ratio may be between PLA/PMMA/SiO<sub>2</sub> (90/10) and PLA/PMMA/SiO<sub>2</sub> (80/20).

Previous discussions have proven that incorporating nanosilica particles can improve the  $\epsilon_b$  of both PLA/SiO<sub>2</sub> and PLA/PMMA/SiO<sub>2</sub> composites. The major sliding and lubricant hypothesis in the PEN and PET composites may also work in the PLA/SiO<sub>2</sub> and PLA/PMMA/SiO<sub>2</sub> composites. Figure 3 shows this sliding behavior exhibited in the PLA/PMMA/SiO<sub>2</sub> composites during tensile testing. The neat PLA [Figure 3(a)] exhibits brittle characteristic, and the PLA/PMMA/SiO<sub>2</sub> (90/10) composite [Figure 3(b)] exhibits plastic flow and ductile characteristic. Including spherical nanosilica particles may be responsible for the sliding characteristic. Based on the lubrication sliding and the ductile behavior, incorporating nanosilica particles into PLA/PMMA blends can undoubtedly improve the toughness of the PLA/PMMA/SiO<sub>2</sub> composites.

As shown in Table II, both a chain extender and nanosilica particles can increase the  $\epsilon_b$  of the resulting composites. Consequently, they can also improve the IS of the PLA/PMMA/SiO<sub>2</sub> composites. The IS value for the PLA/PMMA/SiO<sub>2</sub> (90/10) composite reached 6.8 kJ/m<sup>2</sup>, an increment of 163% compared with that of the neat PLA. Increasing the amount of PMMA in the PLA/PMMA/SiO<sub>2</sub> composites could lower the IS value of

the composites because of the brittleness of the PMMA polymer. The IS value (4.0 kJ/m<sup>2</sup>) for a mixing ratio of 40/60 (PLA/PMMA) is still higher than that of the neat PLA, indicating that incorporating a chain extender and nanosilica particles can positively contribute to improving the toughness of the brittle PLA/PMMA blends. Physically, adding PMMA can increase the UTS and  $E$  values of the PLA/PMMA/SiO<sub>2</sub> composites but decrease the  $\epsilon_b$  and IS of the resulting composites. However, adding a chain extender and nanosilica particles compensates the lowering in  $\epsilon_b$  and IS values of the PLA/PMMA/SiO<sub>2</sub> composites. Adding a chain extender can reduce the occurrence of hydrolytic degradation, and adding nano-silica particles can impart the lubrication sliding and ductile behavior to the PLA/PMMA/SiO<sub>2</sub> composites.

### Light Transmission Properties of the PLA/PMMA/SiO<sub>2</sub> Composites

Table III shows the total light transmittance ( $T_t$ ) and haze values of the neat PLA, PMMA, and PLA/PMMA/SiO<sub>2</sub> composite films. The total light transmittances for neat PLA and PMMA films are extremely close, indicating the transparency of the PLA polymer. Accordingly, the blending ratio of the PLA/PMMA produces little effect on the total light transmittance of the resulting PLA/PMMA/SiO<sub>2</sub> composite films. The  $T_t$  value increases slightly with an increase in the PMMA ratio. Moreover, adding a chain extender and nanosilica particles into the PLA or PLA/PMMA blends exert little effect on the total light transmittance of the neat PLA or PLA/PMMA blends. Furthermore, including nanosilica particles significantly increases the diffuse transmittance and the haze value of the PLA/PMMA/SiO<sub>2</sub> composites. The haze value of the PLA composites increases with increasing blending ratio of PLA in the PLA/PMMA blends, increasing from 25.92 for PLA/SiO<sub>2</sub> to 34.00 for PLA/PMMA/SiO<sub>2</sub> (60/40) and then decreasing to 29.96 for PLA/PMMA/SiO<sub>2</sub> (40/60). The increase in haze value for the PLA/PMMA/SiO<sub>2</sub> composites may be attributed to the micro-phase separation in the PLA/PMMA blends. Eguiburu *et al.* proposed that the segregated crystalline micro-domains might occur in the PLLA/PMMA blends.<sup>9</sup>

Presumably, the boundaries among the crystallites of PLLA may diffuse the paths of visible light. Because of the addition of nanosilica particles and the microdomains of crystalline PLA, the haze value of the PLA/PMMA/SiO<sub>2</sub> composite was considerably increased compared with that of the neat PLA and PMMA. Notably, adequately increasing the haze value while keeping the total light transmittance constant may enhance the performance of the PLA/PMMA/SiO<sub>2</sub> composites in the LED lighting applications.

### Thermo-Mechanical Properties of the PLA/PMMA/SiO<sub>2</sub> Composites

Regarding the thermomechanical properties of the PLA/PMMA/SiO<sub>2</sub> composites, adding a chain extender and nanosilica particles can increase the storage modulus of the resulting PLA/PMMA/SiO<sub>2</sub> composites [Figure 4(a)]. As stated, a chain extender can lower the decrement of UTS by ~43% compared with that of the PLA/SiO<sub>2</sub> counterpart. It can also increase the  $E$  value from 2050 to 2186 MPa for the neat PLA and PLA/

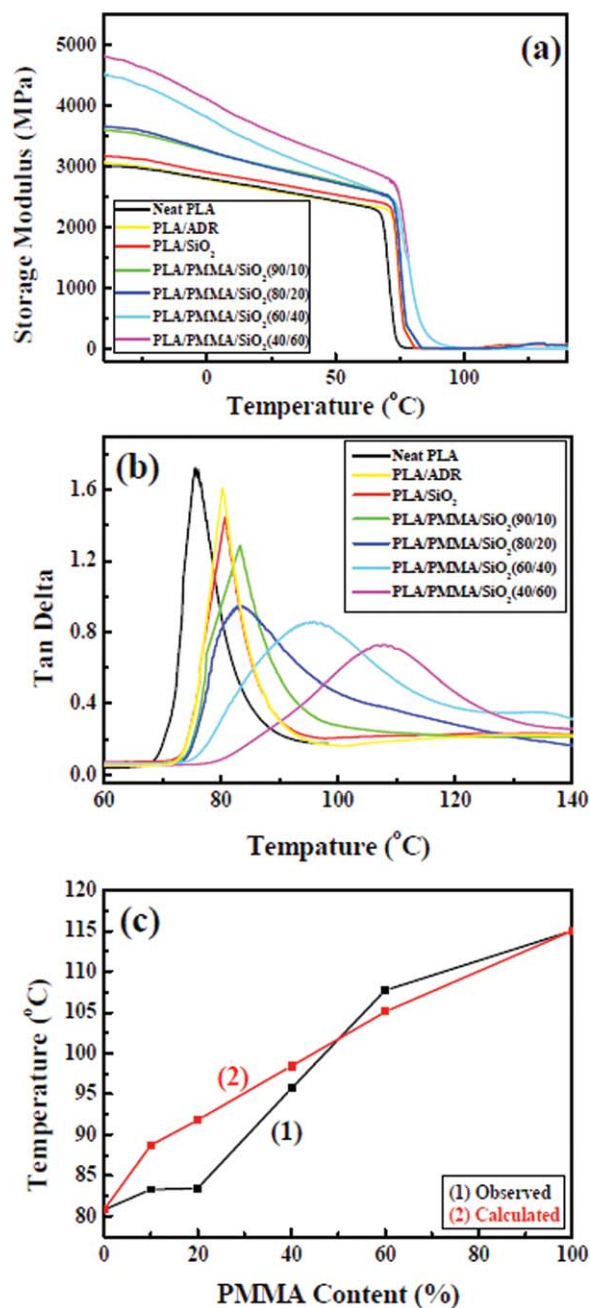
**Table III.** The Total Light Transmittance ( $T_t$ ), Diffuse Transmittance ( $T_d$ ), and Haze Values of the Neat PLA, PMMA, and PLA/PMMA/SiO<sub>2</sub> Composite Films

Sample	$T_t$	$T_d$	Haze
Neat PLA	91.84	15.83	17.23
PLA/ADR	91.65	18.16	19.81
PLA/SiO <sub>2</sub>	91.50	23.72	25.92
PLA/PMMA/SiO <sub>2</sub> (90/10)	91.65	25.40	27.71
PLA/PMMA/SiO <sub>2</sub> (80/20)	91.80	28.15	30.66
PLA/PMMA/SiO <sub>2</sub> (60/40)	91.29	31.04	34.00
PLA/PMMA/SiO <sub>2</sub> (40/60)	92.30	27.65	29.96
Neat PMMA	92.35	14.76	15.98

ADR, respectively. Furthermore, incorporating nanosilica particles can increase the  $E$  value from 2050 MPa for the neat PLA to 2293 MPa for the PLA/SiO<sub>2</sub> composite. Blending PLA with stiff PMMA can increase the  $E$  values of the resulting PLA/PMMA/SiO<sub>2</sub> composites (Table II). The storage spectra of the neat PLA, PLA/ADR, and PLA/PMMA/SiO<sub>2</sub> composites are consistent with the bulk modulus ( $E$ ) of those specimens.

In Figure 4(b), the  $\tan \delta$  (Tan delta) spectrum of each PLA/PMMA/SiO<sub>2</sub> composite exhibits a single peak, indicating that there is no macrophase separation in the PLA/PMMA blend. The peak values of the  $\tan \delta$  spectra of the PLA/ADR, PLA/SiO<sub>2</sub>, and PLA/PMMA/SiO<sub>2</sub> composites are less than that of the neat PLA. The peak value decreases with increasing PMMA content, indicating that including a chain extender, nanosilica, or brittle PMMA substantially decrease the damping property of the neat PLA. This seems to contradict the increases in the  $\epsilon_b$  and IS when the chain extender or nanosilica was incorporated (Table II). As mentioned, the major sliding in the PLA/PMMA/SiO<sub>2</sub> composites would occur in the plastic region but not in the elastic region (Figure 3). However, during the DMA measurement, the magnitude of the applied sinusoidal deformation is linear and is too low to cause an apparent sliding in the PLA matrix, unlike the massive fractural forces in the tensile and impact tests. Therefore, the decrease in the damping factor of the PLA/PMMA/SiO<sub>2</sub> composites should be associated with the increase of their  $E$  values instead of the decreases in their  $\epsilon_b$  and IS. Tsagaropoulos and Eisenberg envisaged three regions around a nanoparticle; an inner tightly bound layer in which polymer motion is severely restricted by interactions with the surface, an intermediate but more loosely bound layer, and finally the unrestricted bulk polymer.<sup>20,21</sup> According to the proposed model, polymer reinforced with inorganic fillers would become more rigid close to the interface of the fillers. Accordingly, the resulting polymer nanocomposites would possess higher modulus when the fillers are incorporated. They also proposed that nanofillers increased the bulk modulus with a simultaneous decrease in the damping factor ( $\tan \delta$ ) of the resulting polymer nanocomposites.<sup>20–22</sup> The event observed in this study is similar to what Tsagaropoulos and Eisenberg described.

The glass transition temperature ( $T_g$ ) of the PLA/PMMA/SiO<sub>2</sub> composite can be estimated from the  $\tan \delta$  peak of the com-

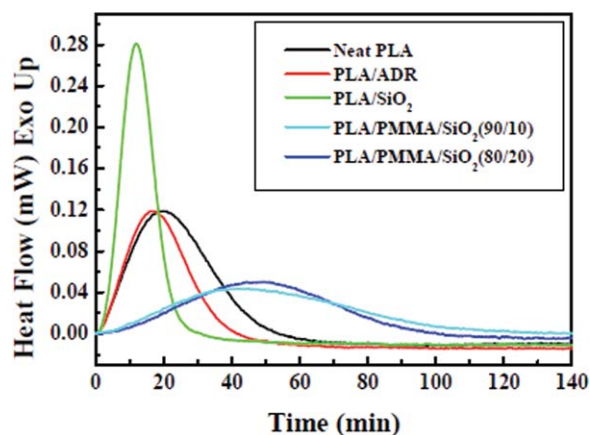


**Figure 4.** The spectra of (a) storage modulus and (b)  $\tan \delta$  of the neat PLA, PLA/SiO<sub>2</sub>, and PLA/PMMA/SiO<sub>2</sub> composites. Plot (c) is the observed and calculated glass transition temperatures of the composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

posite. Moreover, the calculated  $T_g$  value can also be estimated according to the following equation:<sup>23</sup>

$$\frac{1}{T_g} = \frac{w_1}{T_g^1} + \frac{w_2}{T_g^2} \quad (3)$$

$T_g^1$ ,  $T_g^2$ , and  $T_g$  are the glass transition temperatures (in terms of K) of PLA/SiO<sub>2</sub>, neat PMMA, and the resulting PLA/PMMA/SiO<sub>2</sub> composites, respectively, and the values of  $T_g^1$  and  $T_g^2$  are 253.95 K (80.8°C) and 388.15 K (115°C), respectively.<sup>24</sup>  $w_1$  and



**Figure 5.** The DSC crystallization traces for the neat PLA, PLA/SiO<sub>2</sub>, and PLA/PMMA/SiO<sub>2</sub> composites isothermally crystallized at 135°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$w_2$  are the weight fractions of PLA and PMMA, respectively. Figure 4(c) presents the observed and calculated glass transition temperatures of the PLA/SiO<sub>2</sub>, neat PMMA, and the resulting PLA/PMMA/SiO<sub>2</sub> composites. The  $T_g$  value of the PLA/PMMA/SiO<sub>2</sub> composite increases with an increasing PMMA weight fraction because of the high  $T_g$  value (115°C) of the neat PMMA. Apparently, blending PLA with a high PMMA- $T_g$  value can significantly increase the glass transition temperature of the resulting PLA/PMMA/SiO<sub>2</sub> composites.

#### Isothermal Crystallization Behavior of PLA/PMMA/SiO<sub>2</sub> Composites

The isothermal crystallization of the neat PLA, PLA/ADR, PLA/SiO<sub>2</sub>, and PLA/PMMA/SiO<sub>2</sub> composites were performed using DSC at a predetermined temperature of 135°C for 160 min. Figure 5 shows the melt-crystallization DSC traces. As shown in Figure 5, the crystallization enthalpies ( $\Delta H_c$ ) and peak crystallization times ( $\tau_p$ ) of the neat PLA and its composites were determined. In addition, the absolute crystallinities ( $X_c$ ) of the neat PLA and its composites can be estimated by using the heat of fusion of an infinitely thick PLA crystal,  $\Delta H_f^0$ .<sup>6,22</sup>

$$X_c = \frac{\Delta H_c}{\Delta H_f^0 W_{\text{polymer}}} \times 100,$$

where  $\Delta H_f^0$  is  $\sim 93.7$  J/g,<sup>25</sup> and  $W_{\text{polymer}}$  is the weight fraction of the polymer matrix. These crystallization parameters are shown in Table IV.

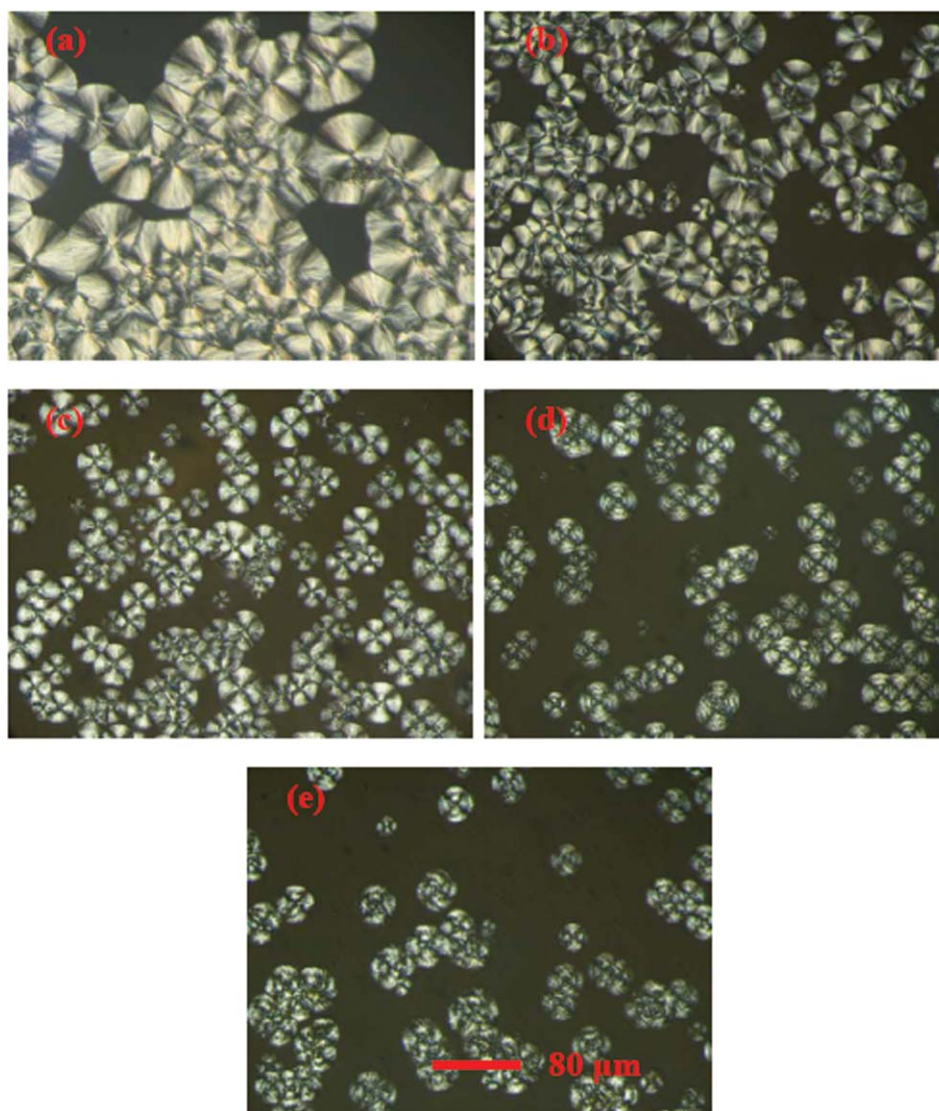
**Table IV.** The Melting Temperatures ( $T_m$ ), Absolute Crystallinities ( $X_c$ ), and Peak Crystallization Times ( $\tau_p$ ) of the Neat PLA, PLA/ADR, PLA/SiO<sub>2</sub>, and PLA/PMMA/SiO<sub>2</sub> Composites Isothermally Crystallized at 135°C

Sample	$T_m$ (°C)	$X_c$ (%)	$\tau_p$ (min)
Neat PLA	169.3	47.4 ± 1.8	20.0
PLA/ADR	168.4	41.2 ± 1.8	16.6
PLA/SiO <sub>2</sub>	167.9	50.3 ± 1.8	12.0
PLA/PMMA/SiO <sub>2</sub> (90/10)	167.5	40.3 ± 1.8	40.9
PLA/PMMA/SiO <sub>2</sub> (80/20)	167.1	38.7 ± 1.8	47.7

As shown in Table IV, the crystallinity of the neat PLA isothermally crystallized at 135°C is 47.4%. Incorporating a chain extender decreases the  $X_c$  value to 41.2%, but including nanosilica particles increases this value to as high as 50.3%. The increase of crystallinity of the PLA/SiO<sub>2</sub> composite may be attributed to the heterogeneous nucleation. Incorporating a chain extender could improve the hydrolysis through the reactions between the epoxy group of the chain extender (Joncryl ADR 4368S) and the carboxy and hydroxyl end groups of the PLA polymer. Furthermore, this chain extender might induce long-chain branching structures.<sup>26</sup> Because of the branching structure, the crystallinity of PLA/ADR decreased as compared with that of the neat PLA. Moreover, blending PLA with amorphous PMMA hindered the diffusion of the crystalline PLA molecules and greatly decreased the crystallinity of the resulting PLA/PMMA/SiO<sub>2</sub> composite. PLA/PMMA/SiO<sub>2</sub> (90/10) decreases the  $X_c$  value from 50.3% for PLA/SiO<sub>2</sub> to 40.3%, and PLA/PMMA/SiO<sub>2</sub> (80/20) decreases the  $X_c$  value to as low as 38.7%. Furthermore, no exothermic or melting peak can be observed when the PLA content in the PLA/PMMA/SiO<sub>2</sub> composites is less than 20%. Eguiburu *et al.* proposed that it is possible to observe the crystallization and melting of the PLLA crystals during the second run when the PLLA content in the PLLA/PMMA blend is higher than 80%.<sup>9</sup> Our observation in the crystallization behavior of the PLA/PMMA/SiO<sub>2</sub> composites is consistent with what Eguiburu *et al.* described.

In this study, peak crystallization time ( $\tau_p$ ) was used to define the time from the onset to a point where the exothermic peak appeared under isothermal crystallization. The peak crystallization time was equal to the crystallization half-life when the DSC crystallization trace was symmetric.<sup>27,28</sup> As shown in Figure 5 and Table IV, incorporating nanosilica particles can significantly decrease the  $\tau_p$  value from 20.0 min for the neat PLA to 12.0 min for the 0.5 wt % PLA/SiO<sub>2</sub> composites. Including nanosilica increases the crystallinity of the PLA/SiO<sub>2</sub> composites but decreases the peak crystallization time which is attributed to the lowering of molecular mobility because of the inclusion of nanosilica. Consequently, the nanosilica particles may exhibit induced heterogeneous nucleation. Incorporating a chain extender can also reduce the peak crystallization time as compared with that of the neat PLA. However, blending PLA with amorphous PMMA considerably hinders the diffusion of the crystalline PLA molecules and increases the  $\tau_p$  value of the resulting PLA/PMMA/SiO<sub>2</sub> composites.

Furthermore, as shown in Figure 6, the dimensions of the PLA spherulites decrease continuously from  $\sim 46$   $\mu\text{m}$  for the neat PLA to 18  $\mu\text{m}$  for the PLA/PMMA/SiO<sub>2</sub> (80/20) composite. Including a chain extender and nanosilica particles increases the crystallization sites but reduces the spherulite dimensions of the resulting composites during crystallization. However, blending crystalline PLA with amorphous PMMA would, thus, dilute the crystallization sites and reduce the spherulite dimensions of the PLA/PMMA/SiO<sub>2</sub> composites. Regarding the melting temperatures of the neat PLA and PLA/SiO<sub>2</sub> composites, incorporating a chain extender slightly decreases the  $T_m$  value (Table IV), compared with the neat PLA. The nanosilica particles increase both crystallization sites and crystallinities; however, they simultaneously



**Figure 6.** The spherulite dimensions of neat PLA, PLA/ADR, PLA/SiO<sub>2</sub>, and PLA/PMMA/SiO<sub>2</sub> composites at 135°C for 8 min. The spherulite dimensions for (a) neat PLA, (b) PLA/ADR, (c) PLA/SiO<sub>2</sub>, (d) PLA/PMMA/SiO<sub>2</sub> (90/10), and (e) PLA/PMMA/SiO<sub>2</sub> (80/20) composites are ~46, 27, 22, 20, and 18 μm, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

decrease the spherulite dimensions of the PLA/SiO<sub>2</sub> composites. Including nanosilica would create smaller spherulites that may exhibit more defects and further decrease the melting temperature of the PLA/SiO<sub>2</sub> composite. Furthermore, as this process occurs in the PLA/SiO<sub>2</sub> composite,<sup>6</sup> blending amorphous PMMA into PLA would introduce more defects into the crystalline PLA matrix and reduce the melting temperature, compared with that of the PLA/SiO<sub>2</sub> composite (Table IV).

The crystallization behavior of the PLA/PMMA/SiO<sub>2</sub> composites may reflect the mechanical properties of the PLA composites. In this study, both nanosilica particles and PMMA increase the  $E$  of the resulting PLA/PMMA/SiO<sub>2</sub> composites. Moreover, incorporating a chain extender and nanosilica particles can improve the  $\varepsilon_b$  and notched IS of the PLA/PMMA/SiO<sub>2</sub> composites, compared with the neat PLA. The decrease in the spherulite dimensions (Figure 6) may account for the improvements in

the  $\varepsilon_b$  and notched IS of the PLA/PMMA/SiO<sub>2</sub> composites. The smaller crystallites in the PLA/PMMA/SiO<sub>2</sub> composites may easily induce a grain boundary sliding, increasing the  $\varepsilon_b$  and improving the IS of the PLA/PMMA/SiO<sub>2</sub> composites. Furthermore, the formation of smaller spherulites may induce an increase of the boundary grain region (spherulites) with higher limit of elasticity/plasticity and an increase of the amorphous phase in front of the crystalline zone. Consequently, incorporating a chain extender and nanosilica into the PLA/PMMA blends increase the crystallization sites and impart smaller crystallites compared with the neat PLA, thus improving the  $E$ ,  $\varepsilon_b$  and IS of the resulting PLA composites.

Regarding the effect of crystallization behavior on the light transmission properties of the PLA/PMMA/SiO<sub>2</sub> composites. Lin et. al, used atomic force microscope (AFM) to characterize the roughness of the surfaces of biaxially-oriented polypropylene



(BOPP) films, and they proposed that the large-scale roughness surface caused primarily by the spherulites, which may be as large as 200  $\mu\text{m}$  in polypropylene films, and the spherulite boundaries. Surface roughness on the submicron size scale, which may be resulted from the lamellar or fibril structure, did not affect the transparency.<sup>29</sup> In this study, the spherulite dimensions for the PLA/PMMA/SiO<sub>2</sub> composites are ~18–46  $\mu\text{m}$ . The inclusion of nanosilica increased the crystallinity from 47.4% for the neat PLA to 50.3% for PLA/SiO<sub>2</sub> composite. As stated previously, this inclusion had little effect on the total light transmittance of the composite. The decrease in spherulite dimension in the PLA composites might compensate the opposite effects of the increase in spherulite boundaries on the total light transmittance of the composite. However, the addition of nanosilica particles and the microdomains of crystalline PLA may diffuse the paths of visible light and increase the haze value of the PLA/PMMA/SiO<sub>2</sub> composites compared with that of the neat PLA and PMMA.

## CONCLUSION

In this study, a chain extender reagent, nanosilica particles, and PMMA were incorporated into the brittle and transparent PLA polymer. Including 0.5 wt % nanosilica particles can increase the  $\epsilon_b$  and IS by ~287 and 163%, respectively, compared with those of the neat PLA. Blending PLA with PMMA could increase the UTS and  $E$  values of the resulting PLA/PMMA/SiO<sub>2</sub> composites, while sacrificing the  $\epsilon_b$  and IS of the composites. Accordingly, PLA/PMMA/SiO<sub>2</sub> (90/10) composite may be the optimal blending ratio of the PLA/PMMA/SiO<sub>2</sub> composites. Furthermore, PLA/PMMA blends can still maintain a high degree of transparency. Including silica nanoparticles into the PLA/PMMA blends increases the haze value of the resulting PLA/PMMA/SiO<sub>2</sub> composites but maintains the high total light transmittance ( $T_t$ ). All of the haze values of the PLA/PMMA/SiO<sub>2</sub> composites are lower than 35%. As stated previously, PLA/PMMA/SiO<sub>2</sub> composites exhibit high HDT (near 80°C), relevant IS, and high total light transmittance with haze value less than 35%. This adequate haze value could lower the LED characteristic of point-light-source and evenly spread out the LED light source from the polymer lamp-masks. Accordingly, PLA/PMMA/SiO<sub>2</sub> composites might have the high possibility in the application of LED lamp-masks.

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## REFERENCES

- Lai, W. H.; Liao, J. P. *Mater. Chem. Phys.* **2013**, *139*, 161.
- Hu, Y.; Rogunova, M.; Topolkarayev, V.; Hiltner, A.; Baer, E. *Polymer* **2003**, *44*, 5701.
- Bitinis, N.; Verdejo, R.; Cassagnau, P.; Lopez-Manchado, M. A. *Mater. Chem. Phys.* **2011**, *129*, 823.
- Anderson, K. S.; Hillmyer, M. A. *Polymer* **2004**, *45*, 8809.
- Jonoobi, M.; Harun, J.; Mathew, A. P.; Oksman, K. *Comp. Sci. Technol.* **2010**, *70*, 1742.
- Wu, J. H.; Yen, M. S.; Kuo, M. C.; Chen, B. H. *Mater. Chem. Phys.* **2013**, *142*, 726.
- Vega-González, A.; Subra-Paternault, P.; López-Periago, A. M.; García-González, C. A.; Domingo, C. *Eur. Polym. J.* **2008**, *44*, 1081.
- Fischer, B.; Ziadeh, M.; Pfaff, A.; Breu, J.; Altstädt, V. *Polymer* **2012**, *53*, 3230.
- Eguiburu, J. L.; Iruin, J. J.; Fernandez-Berridi, M. J.; San Román, J. *Polymer* **1998**, *39*, 6891.
- Li, S. B.; Wu, D.; Liu, Y.; Zhang, Y.; Zhuang, J.; Zhang, Q. *Adv. Mater. Res.* **2013**, *739*, 394.
- van den Oever, M. J. A.; Beck, B.; Mussig, J. *Composites A* **2010**, *41*, 1628.
- He, L.; Sun, J.; Wang, X.; Fan, X.; Zhao, Q.; Cai, L.; Song, R.; Ma, Z.; Huang, W. *Mater. Chem. Phys.* **2012**, *134*, 1056.
- Lee, J. K.; McCarthy, S. J. *J. Polym. Environ.* **2009**, *17*, 240.
- Michell, R. M.; Müller, A. J.; Boschetti-de-Fierro, A.; Fierro, D.; Lison, V.; Raquez, J. M.; Dubois, P. *Polymer* **2012**, *53*, 5657.
- Cailloux1, J.; Santana1, O. O.; Franco-Urquiza1, E.; Bou, J. J.; Carrasco, F.; Gámez-Pérez, J.; Maspocho, M. L. *Express Polym. Lett.* **2013**, *7*, 304.
- Ahn, S. H.; Kim, S. H.; Lee, S. G. *J. Appl. Polym. Sci.* **2004**, *94*, 812.
- Hull, D. *An Introduction to Composite Materials*; Cambridge University Press: Cambridge, UK, **1981**, p 81.
- Kim, S. H.; Ahn, S. H.; Hirai, T. *Polymer* **2003**, *44*, 5625.
- Chung, S. C.; Hahm, W. G.; Im, S. S.; Oh, S. G. *Macromol. Res.* **2002**, *10*, 221.
- Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, *28*, 396.
- Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6067.
- Arrighi, V.; McEwen, I. J.; Qian, H.; Serrano Prieto, M. B. *Polymer* **2003**, *44*, 6259.
- Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
- Ray, S. S.; Yamada, K.; Okamoto, M.; Ueda, K. *Polymer* **2003**, *44*, 857.
- Hilker, B.; Fields, K. B.; Stern, A.; Space, B.; Zhang, X. P.; Harmon, J. P. *Polymer* **2010**, *51*, 4790.
- Antoine, L. D.; Peter, D.; Christophe, B. *Compos. Sci. Technol.* **2010**, *70*, 231.
- Najafi, N.; Heuzey, M. C.; Carreau, P. J.; Wood-Adams, P. M. *Polym. Degrad. Stabil.* **2012**, *97*, 554.
- Munehisa, Y.; Shinsuke, T.; Koji, I.; Yoshinori, O.; Yusuke, D.; Kazuhisa, T. *Polymer* **2006**, *47*, 7554.
- Lin, Y. J.; Dias, P.; Chum, S.; Hiltner, A.; Baer, E. *Soc. Plast. Eng.* **2007**, *47*, 1658.