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Fabrication and Characterization of PLA/SiO₂/Al₂O₃ Composites Prepared by Sol-Gel Process

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In this study, polylactic acid (PLA)/SiO₂/Al₂O₃ composites were prepared using a sol-gel process. The influences of SiO₂, Al₂O₃ and SiO₂/Al₂O₃ content on the physical properties of the PLA composites were investigated. The experimental results showed that SiO₂ and Al₂O₃ were uniformly distributed in the PLA matrix, and increased the storage modulus of the PLA. A thermochemical analysis (TMA) indicates that the coefficient of thermal expansion (CTE) values of PLA/SiO₂ 4%/Al₂O₃ 1% were 225 times higher than that of PLA. A thermogravimetric analysis (TGA) indicated that the thermal degradation (T_d) of PLA decreased following the addition of Al₂O₃; however, adding SiO₂ does not significantly prevent the T_d of PLA.

Keywords Composites; PLA; Sol-gel process

INTRODUCTION

Poly(lactic acid) (PLA) has received a great deal of attention, because it can be produced using renewable resources. It has applications in the packaging^[1,2], engineering^[3,4], textiles^[5], automotive^[6], biomedical^[7–10] and tissue engineering fields^[11–13]; however, the relatively low thermal dimensional stability and mechanical properties of PLA limits its potential applications^[14–19]. Many scholars have attempted to modify the physical and mechanical properties of PLA by using relevant fillers^[20–26] or fiber^[27,28]. The sol-gel method is a potential technique for preparing PLA composites. It is easy to process at low temperatures and yields a strong chemical homogeneity^[29].

Wu et al.^[30] and Yeh et al.^[31] showed that SiO₂ and SiO₂-TiO₂ could be well-dispersed in acrylic acid grafted poly(lactides) (PLA-g-AA). The study also demonstrated that a

10 wt.% of SiO₂ and SiO₂-TiO₂ was optimal for enhancing the thermal and mechanical properties of PLA nanocomposites. Huang et al.^[32,33] revealed that silica particles were well-dispersed in PLA, and that fillers increased the mechanical properties, thermal stability, and crystallinity of the structures. Bang and Kim^[34] reported that silica particles increased the resistance to gas permeation, retaining a high level of transparency. Yuzay et al.^[35] reported that aluminum oxide (Al₂O₃) particles increased the ultraviolet (UV) barrier of PLA composites.

This study examines PLA composites with various compositions, such as SiO₂, Al₂O₃, and SiO₂/Al₂O₃, which were prepared using a sol-gel process. The influences of the morphological, thermal, mechanical, and optical properties of PLA/SiO₂/Al₂O₃ composites are discussed.

EXPERIMENTAL

Materials

The PLA (NPC0005) was purchased from Wei-Mon Industry, Taiwan. Acetylacetone (acac), Tetraethoxy silane (TEOS) and tris(2, 4 -pentanedionato) aluminum (III) was produced by TCI, Japan. Ethanol, tetrahydrofuran (THF) and acetone were purchased from ECHO Chemical Co. Ltd, Taiwan.

PLA/SiO₂ Composite Preparation

An appropriate amount of tetraethyl orthosilicate (TEOS), water, and ethanol was weighed to perform a hydrolysis and condensation reaction. A silica (SiO₂) inorganic sol was formed in an acidic environment (pH 2–4). Next, appropriate amounts of PLA and tetrahydrofuran (THF) solvent were weighed and added to a 150-mL three-necked bottle. After mixing until the solvent was completely dissolved, the silica (SiO₂) and inorganic sol were added and stirred for 30 min. The PLA/SiO₂ solution was then dried at 70°C in a vacuum oven for 24 h to remove residual solvent.

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PLA/ Al_2O_3 Composite Preparation

An appropriate amount of PLA and THF solution was weighed and added to a 150-mL three-necked bottle, and stirred until completely dissolved. Next, appropriate amounts of $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ and THF were stirred and dissolved. This mixture was added to the dissolved PLA solution. Subsequently, appropriate amounts of water and ethanol were added to perform hydrolysis and condensation reactions. The mixture was stirred to induce a reaction in an acidic environment (pH 2–4) for 30 min. The PLA/ Al_2O_3 solution was dried at 70°C in a vacuum oven for 24 h to remove residual solvent.

PLA/ Al_2O_3 / SiO_2 Composite Preparation

Appropriate amounts of PLA and THF solution were weighed and added to a 150-mL three-necked bottle and stirred until completely dissolved. Next, TEOS, $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$, water, and ethanol were added to perform hydrolysis and condensation reactions. The mixture was stirred to induce a reaction in an acidic environment (pH 2–4) for 30 min. The PLA/ Al_2O_3 / SiO_2 solution was dried at 70°C in a vacuum oven for 24 h to remove residual solvent.

Characterization

Fourier Transform Infrared Spectrometer (FTIR) spectra were recorded on a Nicolet 320 FTIR spectrometer (USA), using the KBr pellet technique. Morphology was evaluated using a scanning electron microscopy (SEM, TOPCON ABT-150S, Japan) with an energy-dispersive X-ray spectroscopy (EDS, LINK exL II). XPS measurements were carried out on a ULVAC-PHI (PHI 5000 Versa Probe, Japan) instrument equipped with an analysis chamber ($< 3 \times 10^{-8}$ Torr). The samples were irradiated with monochromatic Al K α ($h\nu = 280$ eV) and a takeoff angle of 45° with respect to the sample surface. Dynamic mechanical analyzer (DMA) was performed on a TA instrument (model No. Q800, USA), sample were heated from 30 to 120°C at a heating rate of 3°C min⁻¹ under a frequency of 1 Hz.

Thermomechanical analysis (TMA) was performed on a TA instrument (model No. Q400, USA), sample were heated from 30 to 150°C at a heating rate of 5°C min⁻¹. Thermogravimetric analysis (TGA) was performed on a TA instrument (model No. Q500, USA), sample were heated from 30 to 700°C at a heating rate of 10°C min⁻¹ in a nitrogen atmosphere. Tensile tests were measured by a Universal Tensile Tester using a cross-head speed of 5 mm min⁻¹ in compliance with the specifications of ASTM D638. Haze value (H) and the total light permeation coefficient (T) were measured by a Haze/Turbidimeter (Nippon Denshoku Industries, Japan, model No. NDH 2000) according to the ASTM-D1003 methods. The transmission of visible and UV light was measured on a UV-Vis spectrometer (UV/Vis, Jasco CARY 100CONC, Japan).

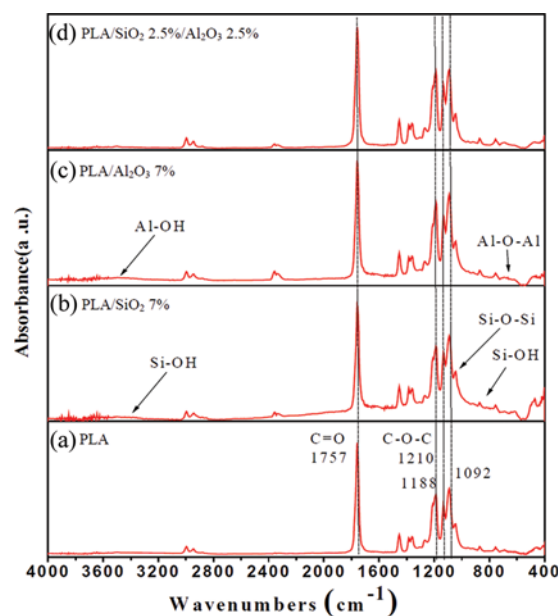


FIG. 1. The FTIR curves of PLA/ Al_2O_3 / SiO_2 composites. (Color figure available online.)

The spectra were recorded at a scanning rate of 480 nm/min, from 200 to 900 nm.

RESULT AND DISCUSSION

FTIR Spectral Analysis

Figure 1 shows that the PLA absorption peak was C = O at 1757 cm⁻¹ and C-O-C at 1210 cm⁻¹, 1188 cm⁻¹, and

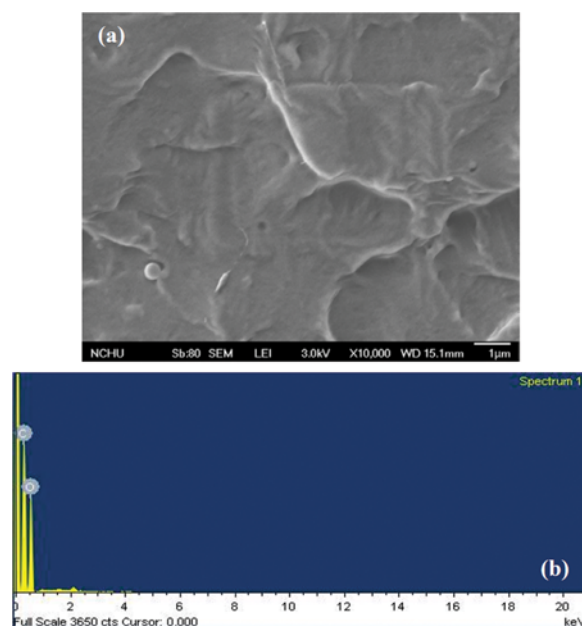


FIG. 2. (a) SEM micrographs ($\times 10,000$) and (b) EDS analyses of pure PLA. (Color figure available online.)

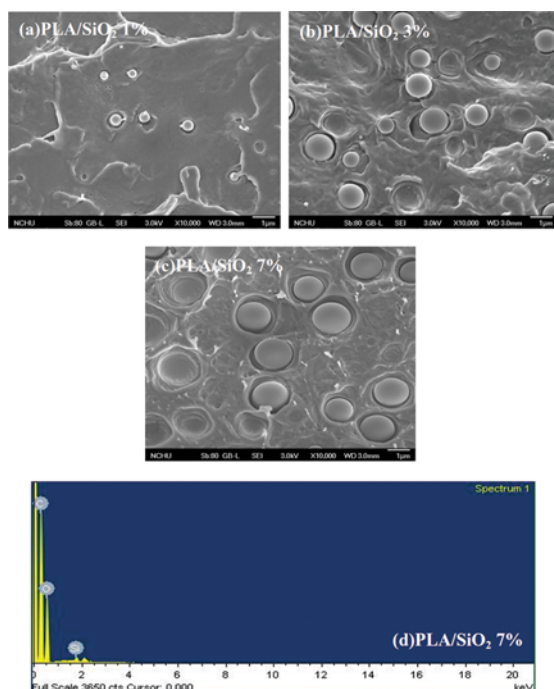


FIG. 3. SEM micrographs ($\times 10,000$) on (a) PLA/SiO₂ 1%, (b) PLA/SiO₂ 3% and (c) PLA/SiO₂ 7% in the PLA matrices. (c) EDS analyses of PLA/SiO₂ 7%. (Color figure available online.)

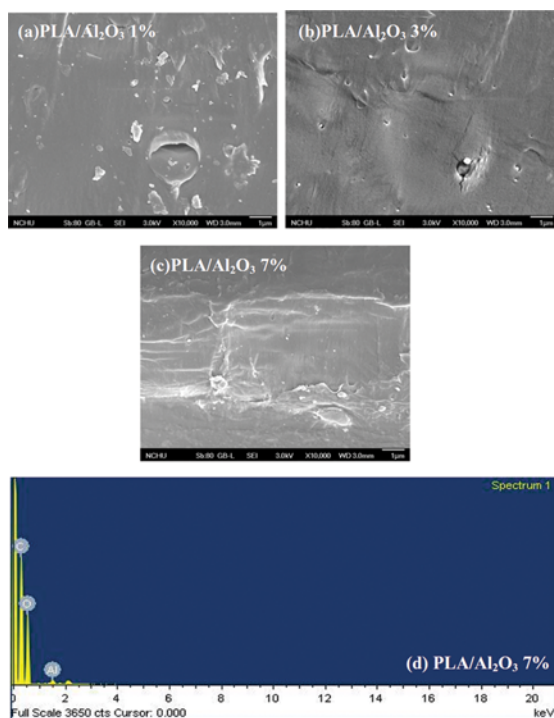


FIG. 4. SEM micrographs ($\times 10,000$) on (a) PLA/SiO₂ 4%/Al₂O₃ 1%, (b) PLA/SiO₂ 1%/Al₂O₃ 4% and (c) PLA/SiO₂ 2.5%/Al₂O₃ 2.5% in the PLA matrices. (c) EDS analyses of PLA/SiO₂ 2.5%/Al₂O₃ 2.5%. (Color figure available online.)

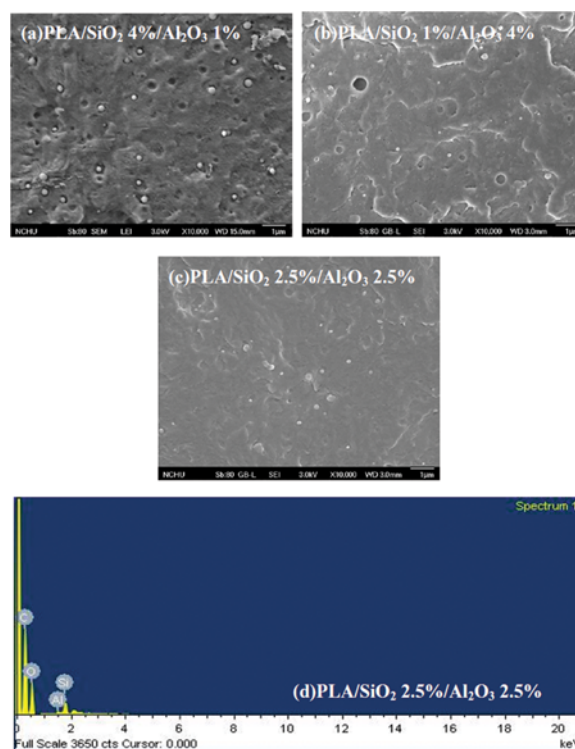


FIG. 5. SEM micrographs ($\times 10,000$) on (a) PLA/SiO₂ 4%/Al₂O₃ 1%, (b) PLA/SiO₂ 1%/Al₂O₃ 4% and (c) PLA/SiO₂ 2.5%/Al₂O₃ 2.5% in the PLA matrices. (c) EDS analyses of PLA/SiO₂ 2.5%/Al₂O₃ 2.5%. (Color figure available online.)

1092 cm⁻¹. The PLA/SiO₂ and PLA/Al₂O₃ had ambiguous -OH absorption peaks between 3400 and 3500 cm⁻¹ and the absorptions peaks were Si-O-Si at 1087 cm⁻¹ and Al-O-Al at 697 cm⁻¹. These results show that using the sol-gel method to prepare PLA/SiO₂/Al₂O₃ composites produces an interpenetrating polymer network of Si-O-Si and Al-O-Al. This enhances the heat resistance and mechanical properties of the PLA.

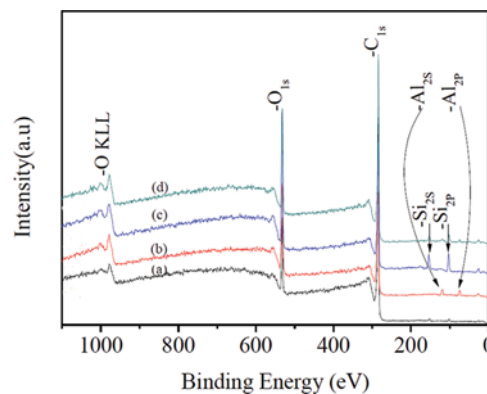


FIG. 6. The XPS curves of (a) PLA, (b) PLA/Al₂O₃ 7%, (c) PLA/SiO₂ 7%, (d) PLA/SiO₂ 2.5%/Al₂O₃ 2.5%. (Color figure available online.)

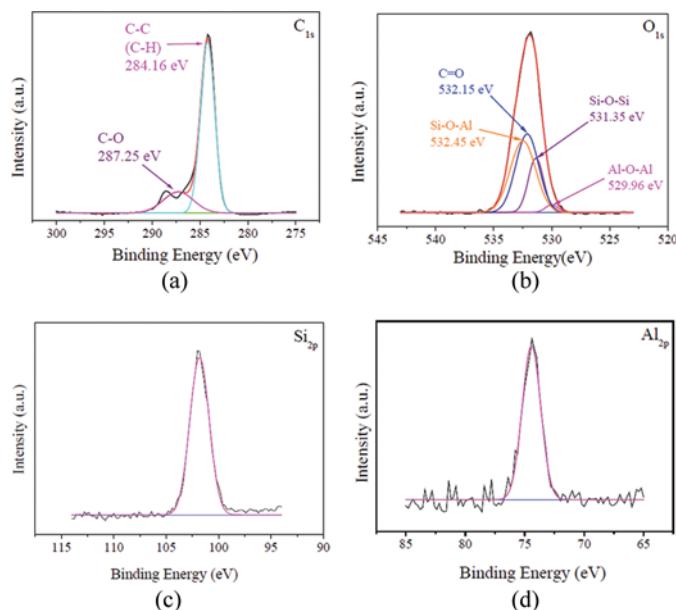


FIG. 7. The (a) C_{1s} , (b) O_{1s} , (c) Si_{2p} , and (d) Al_{2p} Gaussian peak of PLA/SiO₂ 2.5%/Al₂O₃ 2.5% composite. (Color figure available online.)

Morphology

Figures 2–5 show SEM images of pure PLA, PLA/SiO₂, PLA/Al₂O₃, and PLA/SiO₂/Al₂O₃. Figure 2 shows the creased morphology of pure PLA. The EDS spectrum further proves the existence of only C and O. Figure 3(a)–(c) shows the dispersion of varying SiO₂ particles among PLA. This indicates that SiO₂ particles tend to grow as their contents increase. The EDS spectrum shown in Figure 3(d) verifies that the PLA contains Si elements. Figures 4(a)–(c) show the dispersion of varying Al₂O₃ particles in the PLA. The results show the incomplete formation of Al₂O₃ particles.

TABLE 1
XPS analysis of PLA/Al₂O₃, PLA/SiO₂, and PLA/
Al₂O₃/SiO₂ composition

Code	Element	Binding energy	Peaks and assignments
PLA	C_{1s}	284.00	C-H, C-C
		287.25	C-O
PLA/SiO ₂ 2.5%/ Al ₂ O ₃ 2.5%	O_{1s}	532.42	C=O
	C_{1s}	284.16	C-H, C-C
		287.25	C-O
	O_{1s}	532.15	C=O
		529.96	Al-O-Al
		531.33	Si-O-Si
		532.45	Si-O-Al
	Si_{2p}	101.86	Si-O
	Al_{2p}	74.45	Al-O

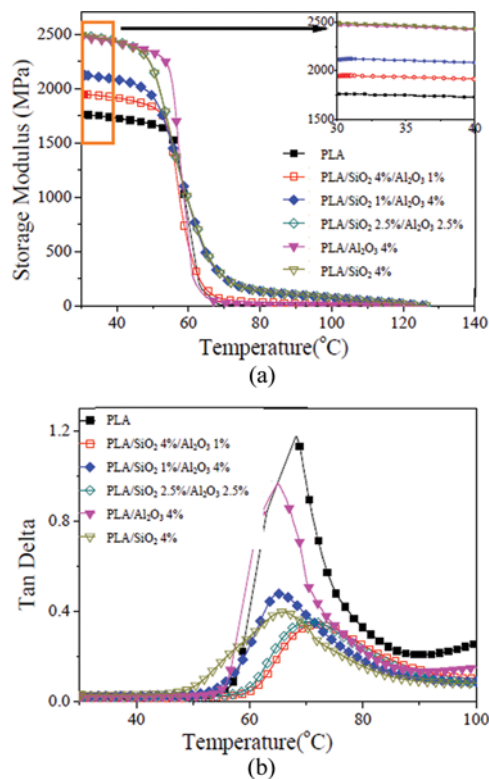


FIG. 8. (a) Storage modulus and (b) tan delta of PLA/SiO₂/Al₂O₃ of composites. (Color figure available online.)

The EDS spectrum shown in Figure 4(d) verifies the presence of Al. Figure 5 (a)–(c) shows the dispersion of varying Al₂O₃/SiO₂ particles in the PLA. The results indicate that size of the particles is less than 1 μ m. The EDS spectrum shown in

TABLE 2
Thermal properties of PLA/Al₂O₃, PLA/SiO₂, and PLA/
Al₂O₃/SiO₂

Sample	TMA 40–70°C CTE (ppm/°C) ^a	DMA T _g (°C) ^b	TGA T _{d5} (°C) ^c
PLA	4062	68	315.55
PLA/Al ₂ O ₃ 1%	1485	65	229.52
PLA/Al ₂ O ₃ 4%	961	64	212.71
PLA/Al ₂ O ₃ 7%	253	66	199.51
PLA/SiO ₂ 1%	942	64	328.34
PLA/SiO ₂ 4%	348	65	327.78
PLA/SiO ₂ 7%	55	66	320.16
PLA/SiO ₂ 4%/Al ₂ O ₃ 1%	18	72	324.81
PLA/SiO ₂ 1%/Al ₂ O ₃ 4%	96	65	236.86
PLA/SiO ₂ 2.5%/Al ₂ O ₃ 2.5%	46	70	303.79

^aCoefficient of thermal expansion (CTE) at 40–70°C.

^bGlass transition temperature (T_g).

^cDecomposition temperature in 5% weight loss (T_{d5}).

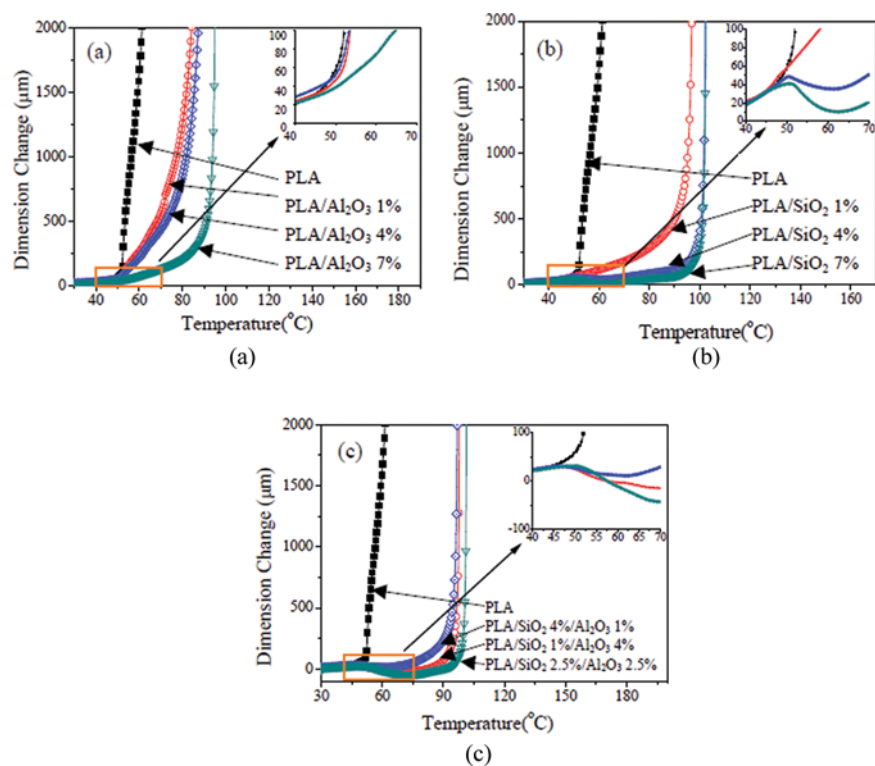


FIG. 9. Dimension change versus temperature plots for (a) PLA/ Al_2O_3 , (b) PLA/ SiO_2 , and (c) PLA/ $\text{SiO}_2/\text{Al}_2\text{O}_3$. (Color figure available online.)

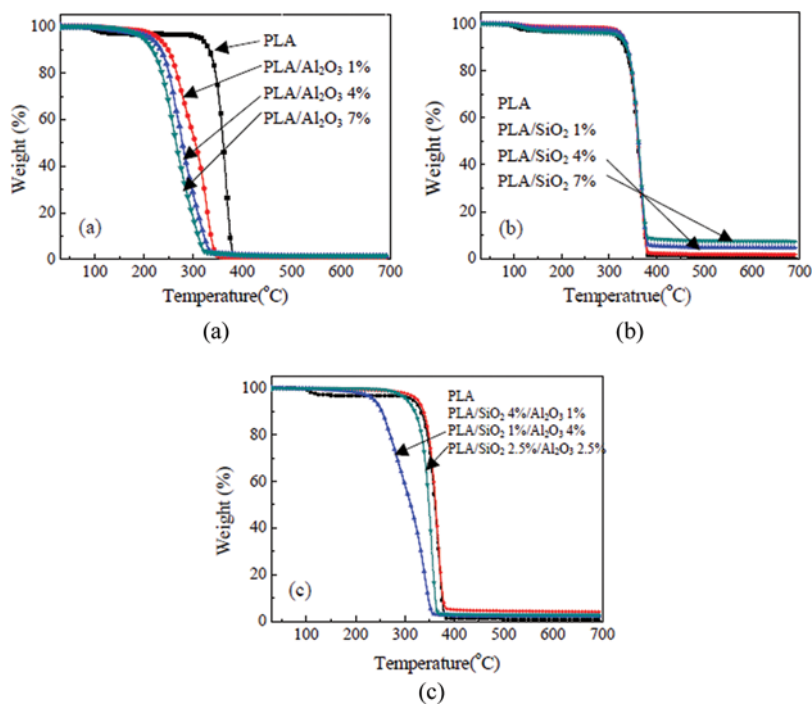


FIG. 10. TGA traces of the (a) PLA/ Al_2O_3 , (b) PLA/ SiO_2 , and (c) PLA/ $\text{SiO}_2/\text{Al}_2\text{O}_3$. (Color figure available online.)

TABLE 3

Mechanical properties of PLA/ Al_2O_3 / SiO_2 composites

Sample	Tensile strength (MPa)
PLA	45.5
PLA/ Al_2O_3 1%	52.2
PLA/ Al_2O_3 4%	49.6
PLA/ Al_2O_3 7%	48.9
PLA/ SiO_2 1%	53.6
PLA/ SiO_2 4%	52.4
PLA/ SiO_2 7%	47.9
PLA/ SiO_2 4%/ Al_2O_3 1%	59.9
PLA/ SiO_2 1%/ Al_2O_3 4%	59.2
PLA/ SiO_2 2.5%/ Al_2O_3 2.5%	56.6

Figure 5(d) verifies that PLA/ SiO_2 2.5%/ Al_2O_3 2.5% contains the elements Si and Al.

XPS Spectroscopy Analysis

Figure 6(a)–(d) shows that the XPS for PLA, PLA/ Al_2O_3 7%, PLA/ SiO_2 7%, and PLA/ SiO_2 2.5%/ Al_2O_3 2.5%. Figure 6(b) shows the bond energy between Al_{2s} and Al_{2p} . Figure 6(c) shows the bond energy between Si_{2s} and Si_{2p} . Figure 6(d) shows the bond energy among Al_{2s} , Al_{2p} , Si_{2s} , and Si_{2p} . Figures 7 (a)–(d) shows the O_{1s} , Si_{2p} , and Al_{2p} Gaussian wave peak of PLA/ SiO_2 2.5%/ Al_2O_3 , which may be separated into peaks for the C=O, Si-O-Si, Al-O-Al, and Si-O-Al bonds (Table 1).

DMA Analysis

Figure 8 (a)–(b) shows that the storage modulus increases after SiO_2 and Al_2O_3 are added to PLA. Thus, the glass transition temperature (T_g) does not significantly change. In addition, the PLA damping value declines as the SiO_2 and Al_2O_3 content increases. The PLA/ SiO_2 4%/ Al_2O_3 1% damping value declined 3 times more than that of the PLA.

TMA Analysis

Figure 9 shows that adding SiO_2 and Al_2O_3 to PLA contributes to reducing the coefficient of thermal expansion (CTE) of PLA, because SiO_2 and Al_2O_3 have lower CTEs than PLA. Table 2 shows that the CTE values of PLA/ Al_2O_3 7% and PLA/ SiO_2 7% are 16 and 74 times greater than that of PLA, respectively. The CTE of PLA/ SiO_2 4%/ Al_2O_3 1% is 225 times greater than that of PLA.

TGA Analysis

Figure 10(a)–(c) show the TGA results for the PLA/ SiO_2 / Al_2O_3 composite (Table 2). These values indicate that after adding Al_2O_3 to PLA, the T_d decreased. Adding SiO_2 did not significantly change T_d . Figure 10(c) shows that when PLA composites contain Al_2O_3 , their pyrolysis temperatures decline as the amount of Al_2O_3 increases.

Mechanical Properties

Table 3 shows that adding SiO_2 and Al_2O_3 to PLA increases the tensile strength of the PLA. When 1% SiO_2

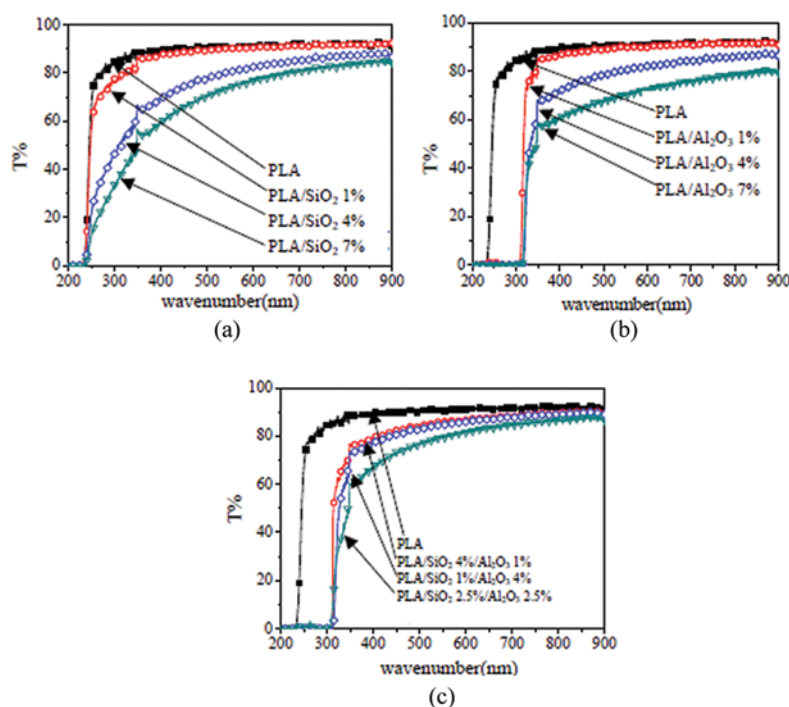


FIG. 11. Transmittance traces of the (a) PLA/ SiO_2 , (b) PLA/ Al_2O_3 , and (c) PLA/ SiO_2 / Al_2O_3 . (Color figure available online.)

and Al_2O_3 is added, the peak tensile strength is achieved because the sol-gel method ensures uniform distribution in the PLA. When the SiO_2 and Al_2O_3 content is greater than 1%, the tensile strength of the PLA gradually declines because of agglomeration.

Optical Properties

Figure 11 shows that optical transmissions decline following the addition of SiO_2 and Al_2O_3 to the PLA. In other words, optimal transmissions decline as the amount of SiO_2 and Al_2O_3 increases, which is particularly evident when the Al_2O_3 content reaches 7% and the optical transmission of the PLA declines approximately 1.29 times.

CONCLUSION

Poly(lactic acid) composites with compositions of SiO_2 , Al_2O_3 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ were prepared using a sol-gel method. Referencing the FTIR and XPS analysis spectra, we determined that the PLA/ $\text{SiO}_2/\text{Al}_2\text{O}_3$ composite contained the functional groups and bond energy of Si-O-Si, Al-O-Al, Si-OH, and Al-OH. The SEM images indicated that SiO_2 and Al_2O_3 were uniformly distributed in the PLA matrix. The EDS analysis showed that the particles contained Si and Al. The DMA analysis indicated that the storage modulus of PLA increased following the addition of SiO_2 and Al_2O_3 . The TMA analysis indicated that the CTE values of PLA/ Al_2O_3 7% and PLA/ SiO_2 7% were 16 and 74 times those of the PLA, respectively. The CTE of the PLA/ SiO_2 4%/ Al_2O_3 1% was 225 times higher than that of the PLA. The TGA analysis indicated that the T_d of the PLA decreased following the addition of Al_2O_3 . Adding SiO_2 did not significantly alter the T_d .

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