

Morphology, Mechanical Properties, and Thermal Stability of Poly(L-lactic acid)/Poly(butylene succinate-co-adipate)/Silicon Dioxide Composites

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ABSTRACT: Poly(butylene succinate-co-adipate) (PBSA) and two types of SiO₂ (hydrophilic or hydrophobic) were used to modify poly(L-lactic acid) (PLLA). The mechanical properties, rheological and thermal behavior, phase morphology, and thermal stability of PLLA/PBSA/SiO₂ composites were investigated. The impact strength, flexural strength, and modulus of PLLA/PBSA blends increased after the addition of hydrophobic SiO₂ without decreasing the elongation at break, and the elongation at break monotonically decreased with increasing hydrophilic SiO₂ content. The melt elasticity and viscosity of the PLLA/PBSA blend increased with the addition of SiO₂. The hydrophilic SiO₂ was encapsulated by the dispersed PBSA phase in the com-

posites, which led to the formation of a core-shell structure, whereas the hydrophobic SiO₂ was more uniformly dispersed and mainly located in the PLLA matrix, which was desirable for the optimum reinforcement of the PLLA/PBSA blend. The thermogravimetric analysis results show that the addition of the two types of SiO₂ increased the initial decomposition temperature and activation energy and consequently retarded the thermal degradation of PLLA/PBSA. The retardation of degradation was prominent with the addition of hydrophobic SiO₂. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3630–3637, 2009

Key words: biodegradable; composites; silicas

INTRODUCTION

Poly(L-lactic acid) (PLLA), as a biodegradable polyester from renewable resources, has attracted much research attention in past decades.^{1–5} PLLA possesses high tensile strength and modulus and excellent transparency; this makes it attractive for the production of environmentally friendly plastics. However, the inherent brittleness of PLLA is one of the disadvantages that restrict its applications. To improve the mechanical properties, copolymerization and blending have been used to modify PLLA.^{6–9} Blending PLLA with other polymers can substantially modify its mechanical and thermal properties, degradation rate, and melt rheology.² To retain the advantage of biodegradability, the blending of PLLA with flexible and biodegradable polymers, such as poly(ϵ -caprolactone),^{10–16} poly(butylene succinate),^{17–21} and poly(butylene adipate-co-terephthalate),²² has been investigated. The incorporation of flexible materials could improve the ductility but sacrifice the high strength and modulus of PLLA.

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Inorganic fillers are often introduced into polymer blends as reinforcing agents to increase their stiffness and improve their processability and heat resistance.^{23–29} Filler dispersion and phase morphology are two keys for the best combination of properties of the composites, which are significantly affected by the composition, processing conditions, and adhesion between the filler and polymers.^{30–35} Three types of microstructure may form in the ternary composites according to the location of filler: a separated dispersion structure, in which the filler mainly locates in the continuous matrix; a core-shell structure, in which the filler is preferentially encapsulated by the dispersed phase; and a mixture of the former two structures.^{30–32} In addition to its advantage of improving the properties of polymers, inorganic fillers are benign to the environment. So the inorganic fillers in biodegradable polymer blends could serve as reinforcing agents without polluting the environment.

In this study, PLLA was blended with poly(butylene succinate-co-adipate) (PBSA) at a fixed weight ratio of 70/30, as the ductility of PLLA was greatly improved at this blending ratio. Two different types of SiO₂ (hydrophilic and hydrophobic) were separately added to the PLLA/PBSA blends. The effects

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of the type and content of SiO₂ on the mechanical properties and rheological behavior of the PLLA/PBSA/SiO₂ composites were investigated. The phase morphology, thermal behavior, and thermal stability of the composites were characterized by field emission scanning electron microscopy (FESEM), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

PLLA, 3051D, was produced by Natureworks LLC (USA) and had a number-average molecular weight of 1.42×10^4 g/mol, a melt flow index (190°C, 2.16 kg) of 10–20 g/10 min, and a specific gravity of 1.25 g/cm³. PBSA, EnPol G4460, was produced by Ire Chemical Co. (South Korea) and had a number-average molecular weight of 1.1×10^5 g/mol, a melt flow index of 1.8 g/10 min, and a specific gravity of 1.22 g/cm³. Hydrophilic fumed SiO₂ [Aerosil 200 (A200)] had an average diameter of 12 nm and a specific surface area of 200 ± 25 m²/g, and hydrophobic fumed silica [Aerosil RA200HS (RA200)] was treated with hexamethyl disilazane and aminosilane based on A200; both were supplied by Degussa AG (Shanghai, China).

Sample preparation

PLLA and PBSA were dried in a vacuum oven at 70°C for 12 h before use, and SiO₂ was dried at 120°C for 3 h to remove water. The samples were prepared in the mixing chamber of a Haake Rheometer RC90 (Haake Mess-Technic GmbH, Germany) at 180°C and 50 rpm for 5 min. The compositions were preheated at 180°C for 5 min and then compression-molded for 2 min into sheets with thicknesses of 1 and 3 mm. The compositions were as follows: 70/30 PLLA/PBSA, 70/30/2 PLLA/PBSA/SiO₂, 70/30/5 PLLA/PBSA/SiO₂, and 70/30/10 PLLA/PBSA/SiO₂ (where the numbers indicate the weight ratios).

Measurements^{27,28,32}

The tensile properties were measured with an Instron 4465 machine (Instron Co., USA) at a crosshead speed of 20 mm/min. The dimensions of the dumbbell-shaped samples for tensile testing were $75 \times 4 \times 1$ mm³. The notched Izod impact strength was tested with a Ray-Ran Universal pendulum impact tester according to ASTM D 256. The flexural properties were measured with the Instron 4465 machine at a speed of 2 mm/min according to ASTM D 790. The dimensions of the samples for impact and flexural testing were $63.5 \times 12.7 \times 3$ mm³.

The rheological behavior was measured on a parallel-plate rheometer (Gemini 200 rheometer, Bohlin Co., United Kingdom) equipped with a parallel-plate geometry with a 25-mm diameter and a gap of 1 mm at 180°C with dynamic oscillation frequency sweeps from 0.01 to 100 rad/s in the linear viscoelastic range (strain = 5%).

DMA was carried out on an IDMA2980 instrument (TA Instruments, USA) in the tensile mode. Specimens ($4 \times 1 \times 20$ mm³) were measured from –60 to 100°C at a frequency of 1 Hz and a heating rate of 2°C/min, and the storage modulus (*E'*) and $\tan \delta$ were recorded as functions of temperature.

The morphology of the composites was observed by FESEM (JSM-7401F, Jeol Co., Japan). All specimens were cryofractured after immersion in liquid nitrogen, and the surfaces were coated with thin layers of gold of about 10 nm.

TGA was performed with a TGA 7 analyzer (PerkinElmer, Inc., USA) from room temperature to 600°C at a heating rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Mechanical properties

As shown in Table I, PLLA was rigid and brittle with a high tensile strength, low impact strength, and low elongation at break. The ductility of PLLA

TABLE I
Mechanical Properties of PLLA and the PLLA/PBSA/SiO₂ Composites

Sample	Notched Izod impact strength (J/m)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)
PLLA	28 ± 2	69.3 ± 0.9	4 ± 1	105.2 ± 1.7	3672 ± 14
PLLA/PBSA	56 ± 5	43.3 ± 0.6	343 ± 14	68.6 ± 0.1	2305 ± 5
A200-2	73 ± 2	44.3 ± 0.6	302 ± 13	69.2 ± 0.2	2316 ± 13
A200-5	70 ± 2	42.1 ± 0.6	108 ± 14	72.0 ± 0.4	2321 ± 13
A200-10	105 ± 5	43.8 ± 0.6	33 ± 10	78.7 ± 0.8	2625 ± 59
RA200-2	72 ± 4	42.0 ± 1.6	370 ± 9	69.3 ± 0.7	2379 ± 24
RA200-5	92 ± 4	42.3 ± 0.7	322 ± 12	70.9 ± 1.1	2396 ± 70
RA200-10	116 ± 3	42.7 ± 0.6	261 ± 18	74.1 ± 0.9	2674 ± 57

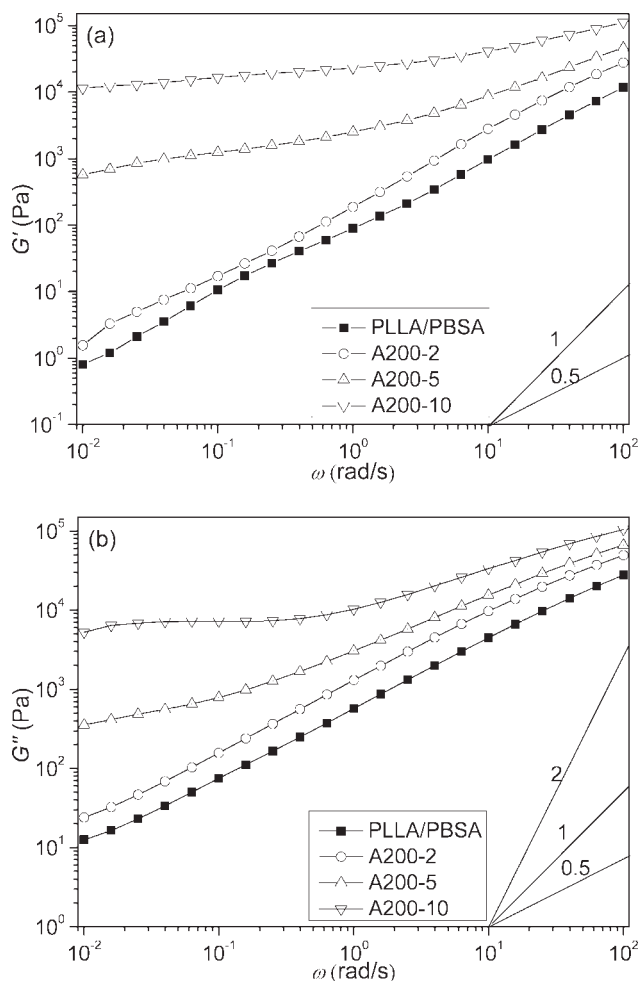


Figure 1 (a) G' and (b) G'' of PLLA/PBSA/hydrophilic SiO_2 (A200) composites.

significantly increased with the incorporation of 30 wt % PBSA, as evidenced by the increase in the elongation at break and impact strength. Moreover, the tensile strength and modulus substantially dropped, which was because of the lower tensile strength and modulus of flexible PBSA than those of PLLA.

The mechanical properties of the PLLA/PBSA blend were significantly affected by the type and content of SiO_2 . The notched impact strength of the PLLA/PBSA blend increased upon addition of SiO_2 , which was prominent with the addition of hydrophobic SiO_2 (RA200). The PLLA/PBSA/hydrophobic SiO_2 (70/30/10) composite had the highest notched impact strength of 116 J/m. The elongation at break of the composites remained high with the addition of hydrophobic SiO_2 but monotonically decreased with increasing hydrophilic SiO_2 content (A200). The flexural strength and modulus of the composites filled with both types of SiO_2 were higher than those of the PLLA/PBSA blend, which both increased with increasing SiO_2 content; this indicated the rein-

forcing effect of SiO_2 on the blend, and the differences between the reinforcement of hydrophilic and hydrophobic SiO_2 were marginal. These results indicate that the composites with hydrophobic SiO_2 had better mechanical properties than those with hydrophilic SiO_2 .

Rheological behavior

The storage modulus (G') and loss modulus (G'') versus the frequency for the composites with different types and contents of SiO_2 are shown in Figures 1 and 2, respectively. Both G' and G'' monotonically increased with increasing SiO_2 content in the covered frequency range. The increase in modulus was prominent in the low-frequency range. This was attributed to the fact that, at low frequencies, there was enough time to unravel the entanglements so that a large amount of relaxation occurred, which resulted in a lower modulus. At high frequencies, the entanglements did not have the time to relax, and therefore, the modulus increased. The terminal-region slopes of the curves for G' and G'' are

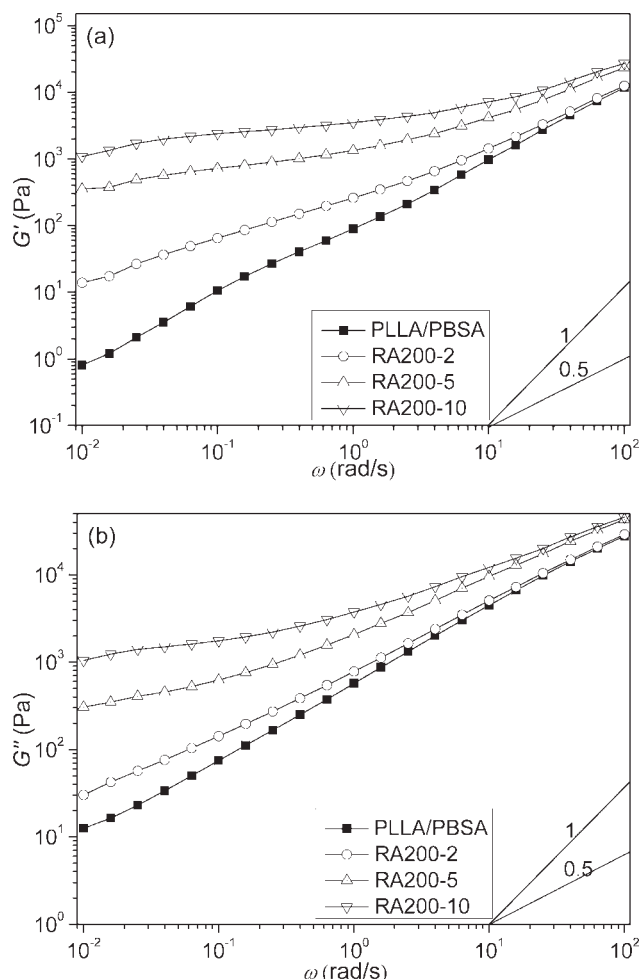


Figure 2 (a) G' and (b) G'' of PLLA/PBSA/hydrophobic SiO_2 (RA200) composites.

TABLE II
Terminal Region Slopes of G' and G'' Versus ω (<5 rad/s) for the PLLA/PBSA/SiO₂ Composites

A200 content (phr)	Slope of G' versus ω	Slope of G'' versus ω	RA200 content (phr)	Slope of G' versus ω	Slope of G'' versus ω
0	1.01	0.86	0	1.01	0.86
2	1.03	0.89	2	0.63	0.72
5	0.32	0.54	5	0.30	0.47
10	0.16	0.17	10	0.20	0.26

presented in Table II. With increasing hydrophobic SiO₂ content, the frequency dependence of G' and G'' at low frequencies monotonically decreased from $\omega^{1.01}$ to $\omega^{0.20}$ and from $\omega^{0.86}$ to $\omega^{0.26}$, respectively (where ω is the angular frequency). The effect of hydrophilic SiO₂ content on the frequency dependency of G' and G'' was similar to that of hydrophobic SiO₂ except for the loading of 2 phr, in which the slopes remained unchanged compared with those of the PLLA/PBSA blend. The change in the behavior

was correlated with the structure of the composites, which is discussed further later. In fact, G' and G'' of the composites with high SiO₂ contents were nearly independent of the frequency at low frequencies; this indicated that the composite melt exhibited pseudo-solidlike behavior. The independence of frequency for G' and G'' at low frequencies was attributed to the formation of a physical network of SiO₂ particles, which has been confirmed by other researchers.^{28,32,36}

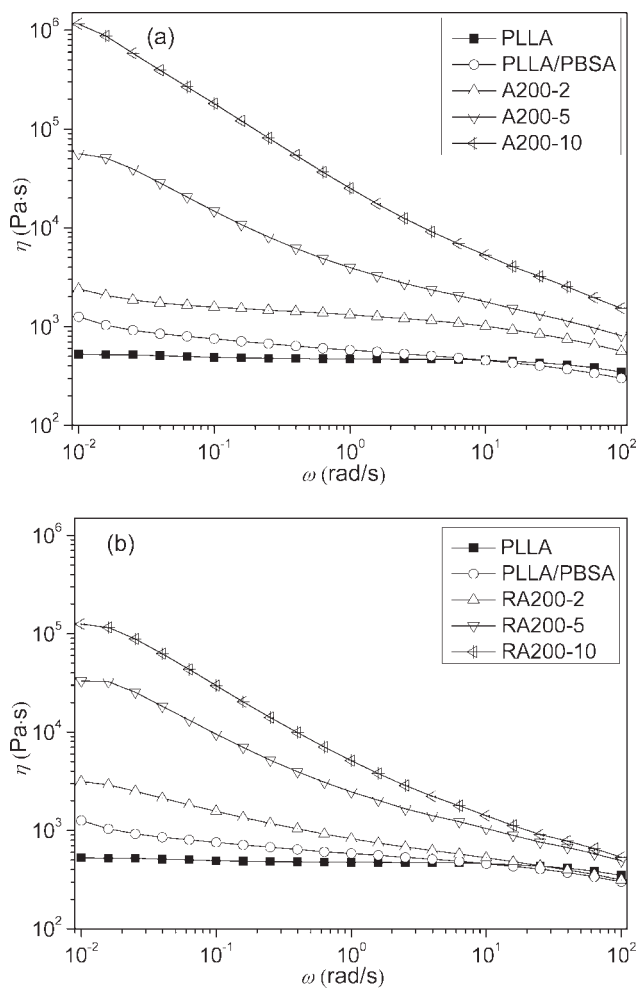


Figure 3 ω dependence of the complex viscosity (η) for PLLA and PLLA/PBSA/SiO₂ composites: (a) hydrophilic SiO₂ and (b) hydrophobic SiO₂.

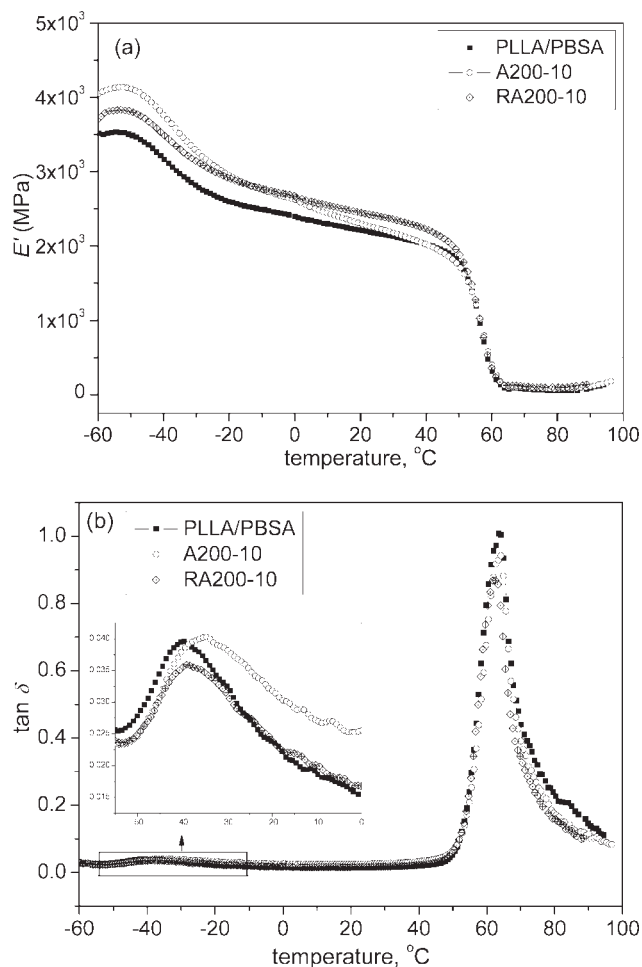


Figure 4 Temperature dependence of (a) E' and (b) $\tan \delta$ of PLLA/PBSA/SiO₂ composites.

TABLE III
Dynamic Mechanical Properties of the
PLLA/PBSA/SiO₂ Composites

Sample	T_g (°C)		E' (MPa)		
	PBSA	PLLA	-50°C	25°C	80°C
PLLA/PBSA	-40.0	63.7	3494	2166	54
A200-10	-36.0	63.9	4119	2239	78
RA200-10	-38.5	62.2	3811	2403	98

The dynamic complex viscosity versus frequency curves for PLLA and the PLLA/PBSA/SiO₂ composites are shown in Figure 3. The melt viscosity monotonically increased with increasing SiO₂ content, which may have been related to the flow restriction of the polymer chains in the molten state by the SiO₂ particles.²⁸ At low frequencies (<10 rad/s), PLLA exhibited Newtonian behavior, for the viscosity was almost unchanged, whereas the other samples showed shear-thinning tendencies, and the shear thinning became more apparent with increasing SiO₂ content. At a given SiO₂ content, the PLLA/PBSA/hydrophobic SiO₂ composites had lower complex viscosity values than the correspond-

ing PLLA/PBSA/hydrophilic SiO₂ composites; this was apparently because of the surface treatment of the SiO₂ particles. The surface treatment of the filler could have caused a reduction in the viscosity of the composites, as it acted to wet and disperse the particles or to lubricate the filler surface so that slippage between the polymer and filler occurred.³⁰

Thermal analysis

DMA results of the PLLA/PBSA blend and PLLA/PBSA/SiO₂ (70/30/10) composites are shown in Figure 4, and the corresponding parameters are summarized in Table III. The samples had two tan δ peaks [Fig. 4(b)], which corresponded to the glass transition of the PLLA and PBSA components; this indicated the incompatibility of PLLA and PBSA. The presence of SiO₂ particles did not lead to a significant broadening of the tan δ peaks but rather a slight change in the peak temperatures. After the addition of 10-phr hydrophilic SiO₂, the glass-transition temperature (T_g) of PBSA increased from -40 to -36°C, which was ascribed to the restriction of SiO₂ particles on the mobility of polymer chains at the

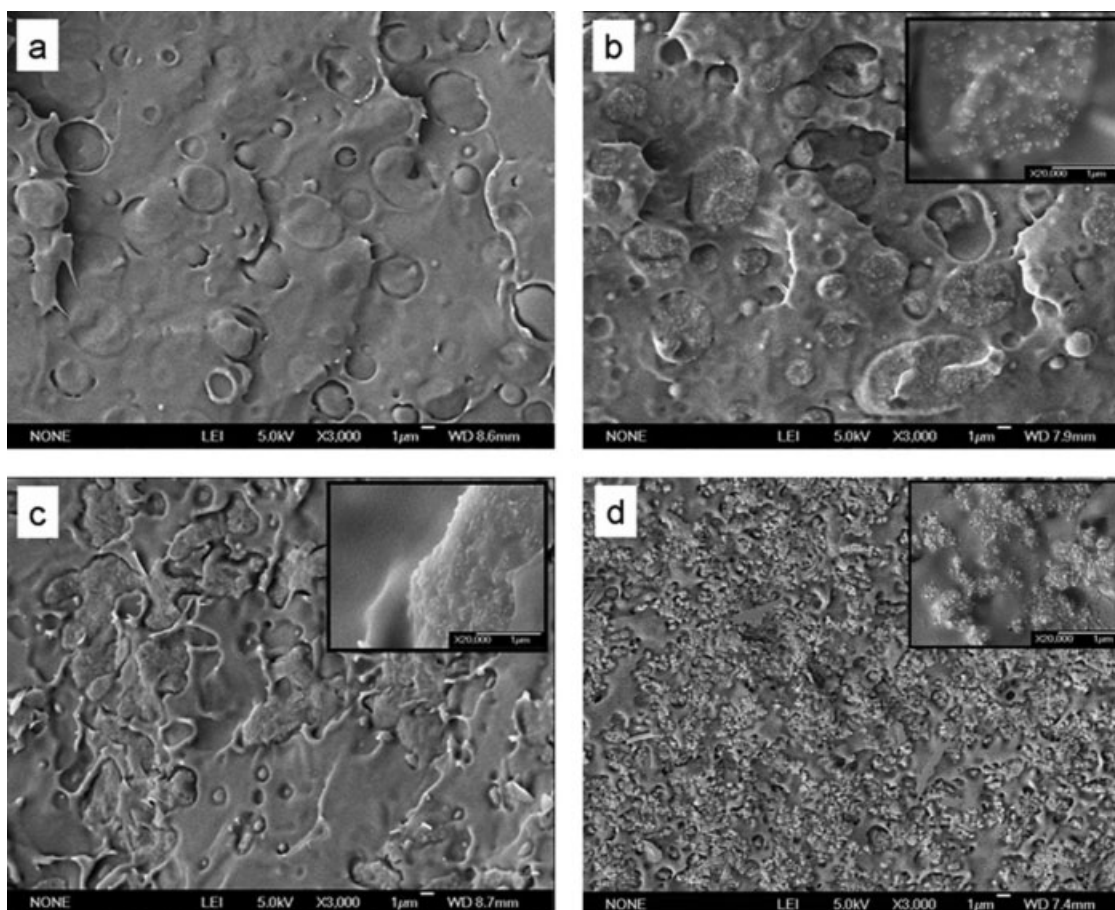


Figure 5 FESEM images of PLLA/PBSA/hydrophilic SiO₂ composites with various amounts of SiO₂: (a) 0, (b) 2, (c) 5, and (d) 10 phr.

organic–inorganic interface of the composites.^{32,34} The PLLA/PBSA/SiO₂ composites showed a higher elastic modulus (E') than the PLLA/PBSA blend in the whole temperature range; this indicated that the addition of SiO₂ improved the elasticity of the PLLA/PBSA blend. E' of the PLLA/PBSA/hydrophilic SiO₂ composite was higher than that of the PLLA/PBSA/hydrophobic SiO₂ composite at low temperatures but shifted to a lower value when the temperature was above the glass-transition region of the PBSA component ($>-30^{\circ}\text{C}$). This might have been correlated with the location of SiO₂, which is discussed later.

Morphology analysis

FESEM micrographs of the PLLA/PBSA blend and PLLA/PBSA/SiO₂ composites are shown in Figures 5 and 6. Phase separation occurred in the PLLA/PBSA blend [Fig. 5(a)], for oval cavities and enclosed round PBSA particles were clearly visible. The interface between PLLA and PBSA was clear, which indicated weak interactions between PLLA and PBSA. For the PLLA/PBSA/SiO₂ composites, the large view images show the distribution of the SiO₂ particles within the polymer matrix, and the higher magnification images permit the observation of discrete SiO₂ particles. The results show that the structure of the composites strongly depended on the type and content of SiO₂. As seen in Figure 5(b,c), at low SiO₂ contents (2 and 5 phr), the hydrophilic SiO₂ particles were preferentially encapsulated by the dispersed PBSA phase; thus, the core–shell microstructure was formed, and the boundary between PLLA and PBSA was clearly shown. Compared with hydrophilic SiO₂, hydrophobic SiO₂ was much more uniformly dispersed. The hydrophobic SiO₂ particles mainly located in the continuous PLLA phase, and some particles located at the interface of PLLA and PBSA, which resulted in an unclear boundary between PLLA and PBSA, as shown in Figure 6(a,b). At a 10-phr SiO₂ content, the SiO₂ particles agglomerated together and pervaded over the polymer matrix, and it was difficult to distinguish the PBSA phase from the PLLA phase [Figs. 5(d) and 6(c)]. The agglomeration of hydrophilic SiO₂ was much more severe than that of the hydrophobic SiO₂, which was attributed to the stronger hydrogen bonding among the hydrophilic SiO₂ particles. The interactions between the PLLA/PBSA chains and SiO₂ should have been some physical interactions, such as hydrogen bonding and van der Waals forces.

As discussed before, filler dispersion and phase morphology are two keys to the best combination of mechanical properties of composites. According to the mechanical properties of the PLLA/PBSA/SiO₂

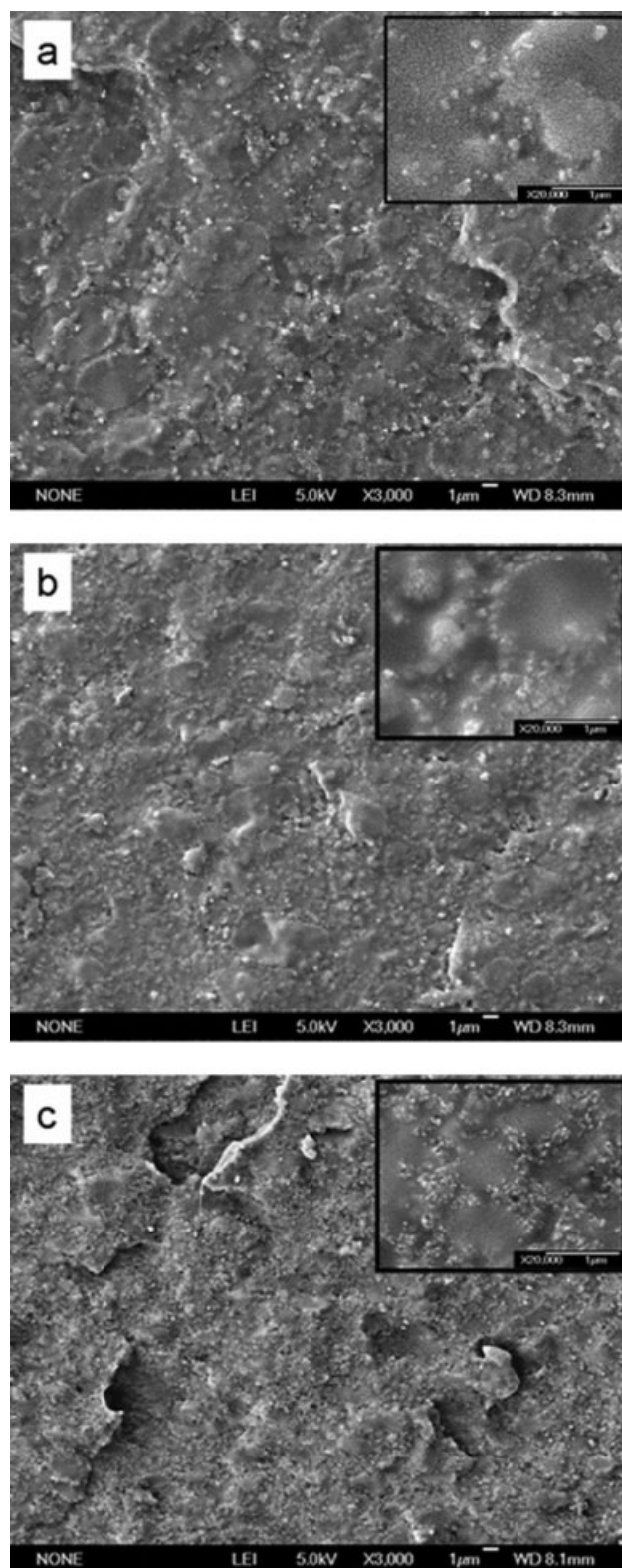


Figure 6 FESEM images of PLLA/PBSA/hydrophobic SiO₂ composites with various amounts of SiO₂: (a) 2, (b) 5, and (c) 10 phr.

composites, we concluded that the better dispersion structure formed after the addition of hydrophobic SiO₂, in which the SiO₂ particles mainly located in

the PLLA matrix, without affecting the PBSA phase, was desirable for optimum reinforcement of the PLLA/PBSA blend. The location of SiO₂ might have also induced the difference between the E' values of the composites. Hydrophilic SiO₂ was preferentially encapsulated by the dispersed PBSA phase, and the reinforcement to the PLLA matrix became weak when the temperature was above T_g of PBSA. Thus, the E' value of the PLLA/PBSA/hydrophilic SiO₂ composite was lower at high temperatures in comparison with that of the PLLA/PBSA/hydrophobic SiO₂ composite.

Thermal stability

Figure 7 shows the TGA curves of the PLLA/PBSA blend and PLLA/PBSA/SiO₂ composites. All of the samples displayed single-step degradation process, and the onset temperature of thermal degradation of the composites significantly increased after compounding with SiO₂. The char yield of the composites increased with increasing SiO₂ content. W_{120} is

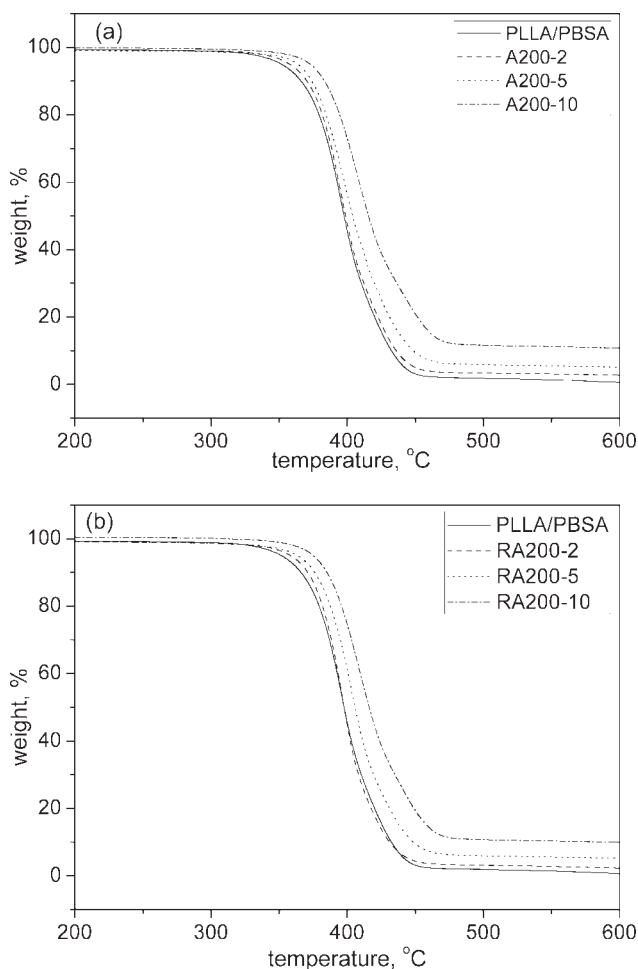


Figure 7 TGA curves of PLLA/PBSA/SiO₂ composites: (a) hydrophilic SiO₂ and (b) hydrophobic SiO₂.

TABLE IV
Thermal Stability Parameters of the PLLA/PBSA/SiO₂ Composites

Sample	W_{120} (%)	$T_{5\%}$ (°C)	E_t (kJ/mol)
PLLA/PBSA	0.43	353	206
A200-2	0.48	359	234
A200-5	0.58	364	239
A200-10	0.36	374	250
RA200-2	0.48	359	238
RA200-5	0.52	365	242
RA200-10	0.42	375	264

the weight-loss percentage of samples at 120°C, and $T_{5\%}$ is the temperature corresponding to the 5% weight loss of the composites. Their values are summarized in Table IV. The activation energy for thermal decomposition was calculated from the TGA curves by the integral method proposed by Horowitz and Metzger with eq. (1)³⁷:

$$\ln[\ln(1/1 - \alpha)] = E_t \theta / RT_{\max}^2 \quad (1)$$

where α is the decomposed fraction of the sample, E_t is the activation energy for decomposition, T_{\max} is the temperature at the maximum rate of weight loss, θ is $T - T_{\max}$ (where T is the temperature), and R is the gas constant. E_t was calculated from the slope of the straight line of $\ln[\ln(1/1 - \alpha)]$ versus θ and is summarized in Table IV.

As shown in Table IV, the composites filled with SiO₂ exhibited higher $T_{5\%}$ and E_t values, which increased with increasing SiO₂ content. This revealed that the thermal stability of the PLLA/PBSA blend significantly improved after the addition of SiO₂. The improvement of the thermal stability of the composites should have been a consequence of the existence of SiO₂ in the polymer matrix, which resulted in the reduction of the gas and heat permeability in the matrix during the heating scan.³⁴ The PLLA/PBSA/hydrophobic SiO₂ composites showed higher E_t values than the PLLA/PBSA/hydrophilic SiO₂ composites at a given SiO₂ content, which might have been related to the better dispersion of hydrophobic SiO₂ than that of hydrophilic SiO₂.

CONCLUSIONS

PLLA/PBSA/SiO₂ composites were prepared by the compounding of PLLA/PBSA (70/30) with hydrophilic and hydrophobic SiO₂, respectively. The impact strength, flexural strength, and modulus of the composites were simultaneously enhanced after the addition of SiO₂. The PLLA/PBSA/hydrophobic SiO₂ (70/30/10) composite had the highest impact strength of 116 J/m, which was four times superior to that of PLLA. The elongation at break of PLLA

was greatly increased with the incorporation of flexible PBSA and remained high after the addition of hydrophobic SiO₂ but monotonically decreased with increasing hydrophilic SiO₂ content. The melt elasticity and viscosity of the composites also increased after the addition of SiO₂. The type and content of SiO₂ greatly affected the morphology of the composites. The addition of hydrophilic SiO₂ induced the formation of a core-shell structure, whereas hydrophobic SiO₂ was more uniformly dispersed in the PLLA matrix, which was beneficial for the improvement of the mechanical properties of the composites. The thermal stability of the PLLA/PBSA blend was improved after the addition of SiO₂, for the composites began to degrade at higher temperatures in comparison with the PLLA/PBSA blend, and the activation energy for thermal decomposition increased with increasing SiO₂ content, which was much more apparent in the PLLA/PBSA/hydrophobic SiO₂ composites.

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