

Properties and Structures of Polylactide Filled with Poly(ϵ -caprolactone)-Coated Calcium Carbonate

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ABSTRACT: The poly(ϵ -caprolactone) (PCL)-coated microsized calcium carbonate (CaCO_3) was prepared by high-speed hybrid mechanical coating. Polylactide (PLA) was melt-blended with neat and modified CaCO_3 particles. Phase morphology, microstructure, and thermal dynamic rheological and mechanical properties of the composites were investigated. Differential scanning calorimetry reveals that the addition of coated CaCO_3 remarkably makes the cold crystallization temperature decrease but has little influence on the final degree of crystallinity of PLA. Dynamic rheological tests indicate that complex viscosity and loss modulus of modified CaCO_3 system are lower than those of neat CaCO_3 system. Scanning electron microscopic results show that the coated CaCO_3 micropar-

ticles disperse more uniformly in the PLA matrix compared with neat particles. The smooth and round coated particles promote the dispersion of CaCO_3 particles in the PLA matrix, and PCL enhances the interfacial adhesion between CaCO_3 particles and the PLA matrix. From mechanical tests, it is found that toughness of the composites is greatly improved by the incorporation of PCL-coated CaCO_3 microparticles. It is glad to see that the elongation at break of the composite with 15 phr coated CaCO_3 is as high as 310%. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 952–958, 2012

Key words: composites; modification; mechanical properties; microstructure; differential scanning calorimetry

INTRODUCTION

With increasing environmental awareness around the world, biodegradable polymers have attracted more and more attention.^{1–3} Polylactide (PLA) has been viewed as the most popular commercial biodegradable material, because it is biodegradable, compostable, and nontoxic to both human body and environment.^{4–6} However, some of its poor physical properties, such as poor toughness, dimensional instability, low melt viscosity, and crystallization rate, restrict its processing and applications.^{7–9} However, some properties can be improved to a large extent by adding nucleating agents,^{10–12} blending with fiber or particles,^{13,14} chain extending,^{15,16} and crosslinking.^{17,18}

Some approaches such as copolymerization and adding plasticizers have been reported to improve the toughness of PLA. A relatively new concept is using rigid filler particles as toughening agent to mimic the rubber toughening.¹⁹ Inorganic particles are well-known materials for the improvement in physical properties of PLA as well as for cost reduction. Luo et al.²⁰ discovered that the elongation of PLA composites was increased to 25.3% at 0.5 wt %

TiO_2 and reached a maximum (ca. 37.6%) at 1 wt % TiO_2 . Meng et al.²¹ discovered that PLA can be toughened by poly(ϵ -caprolactone) (PCL)-coated nanotitania; and they found that the composites exhibited a much higher elongation at break; the elongation reached the maximum (64.7%) at a loading of about 26.4 wt % C- TiO_2 .

Recently, calcium carbonate (CaCO_3) has received a lot of attention because of its wide range of potential applications and its low cost. Researchers have reported many polymer materials containing CaCO_3 , and their results have revealed that CaCO_3 is safe to use in clinical setting.^{22–25} Only a few literatures reported that the introduction of CaCO_3 in PLA matrix not only improved the elasticity modulus and ductile of the composite²⁶ but also changed the hydrolysis rate.²⁷ Branka et al.²⁸ found that CaCO_3 had no influence on glass transition or melting point of PLA but lowered its cold crystallization temperature. Hideki et al.²⁹ reinforced PLA with CaCO_3 and other particle-type inorganic fillers. They found that the composites with CaCO_3 exhibited higher tensile strengths and Young's modulus; further, CaCO_3 whiskers were more effective than the other particle-type fillers.

In this work, PLA composites containing PCL-coated CaCO_3 were prepared. Homogeneous dispersion of CaCO_3 particles was obtained in the composites. When compared with former works, the method largely improves the toughness, lowers cost,

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and maintains the biodegradability of PLA at the same time.

EXPERIMENTAL SECTION

Materials

A commercially available PLA (Nature-Works, PLA 2002D) with a melt flow index of 3.4 g/10 min (190°C, 2.16 kg), a weight-average molecular weight of 208,000 g/mol, and a density of 1.26 g/cm³ was purchased from Nature Works. CaCO₃ (2200 mesh) was obtained from Sichuan Shude High-Tech (China); and the particles did not undergo any surface treatment. PCL was supplied by Shenzhen Bright Industrial (China).

Preparation of the composites

PLA and PCL were both dried in a vacuum oven (negative 0.04 MPa) at 40°C for at least 24 h before processing by melt-blending. CaCO₃ was dried at 100°C for 24 h under negative 0.04 MPa in a vacuum oven prior to use. Then CaCO₃ and PCL were put into a high speed micronizer to mix for 20 min at 20,000 r/min. PCL was coated onto the surface of CaCO₃ particles by strong friction heat, which made the PCL melt, stemmed from high-speed rotation of mill machine.

PLA composites containing different concentrations of neat CaCO₃ and coated CaCO₃ were prepared by a Haake mixer (Haake Rheometer XSS-300). The components were mixed at a speed of 50 rpm for 7 min at 175°C. In addition, the neat PLA was subjected to the mixing condition to create the same thermal history as that of the blends.

Then, all of the samples were compression-molded into sheets with thicknesses of 1.0 and 2.0 mm at 175°C for various tests.

Characterization and measurements

The mechanical properties of the samples were measured in accordance with ISO527 using an Instron universal testing machine (Instron-4302, Canton, MA). The samples were cut from the previously compression-molded sheet into a dumbbell shape. The tests were conducted at a crosshead speed of 20 mm/min at room temperature (about 25°C). At least five runs for each sample were measured, and the results were averaged.

Differential scanning calorimetry (DSC; DSC-204 F1, Netzsch, Germany) was used to characterize the thermal properties of neat PLA and its composites under a nitrogen flow. Because it is the crystalline state of PLA samples that could influence mechanical properties of the blends, only the DSC data from the first heat scan are presented. The melting point

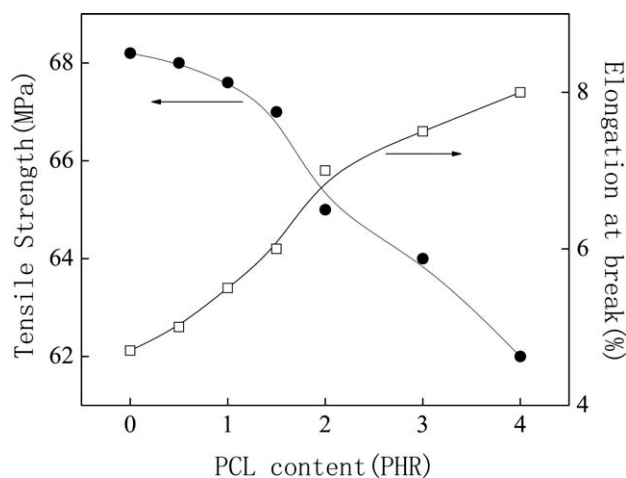


Figure 1 Tensile properties versus PCL content of PCL/PLA composites.

(T_m), glass-transition temperature (T_g), enthalpy of cold crystallization (ΔH_c), and enthalpy of melting (ΔH_m) of each sample were measured from 10 to 200°C under nitrogen at a heating rate of 10°C/min.

Dynamic rheological tests were conducted by a Rheometer (AR 2000EX, TA Instruments, USA) in parallel plate configuration at a temperature of 175°C. Plates with a thickness of 1.5 mm were chosen for these tests. The strain and frequency range used during testing were 5% and 80 ~ 0.01 Hz, respectively.

The morphology of the fractured surfaces of the specimens was examined with a scanning electron microscope (SEM; JSM-5900LV, JEOL, Japan). To obtain a random brittle-fractured surface, the samples were frozen well in liquid nitrogen and quickly broken off. A layer of gold was sputter-coated uniformly over all of the brittle-fractured and tensile-fractured surfaces before SEM observations. The SEM images were collected at an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Mechanical properties

To clarify the effect of coating agent on the mechanical properties of composites, the binary blends with various contents of PCL were studied, and the result is shown in Figure 1. It is seen that with the increasing content of PCL, tensile strength of the material becomes lower while elongation at break increases. But PLA/PCL composites are still brittle. For example, elongation at break of material with 4 phr PCL reaches only 8%. It is to say that small dose of PCL is not the key factor to toughen the PLA/coated-CaCO₃ composites.

The results of mechanical tests were presented in Figure 2, where mass ratio of CaCO₃ and PCL is

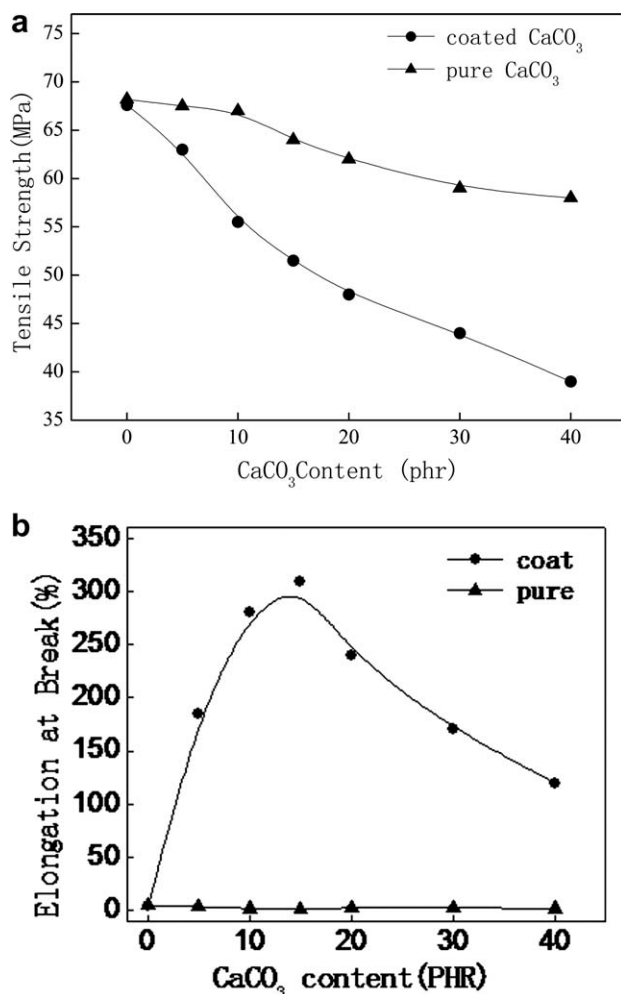


Figure 2 (a) Comparison of tensile strength versus CaCO₃ contents in coated and uncoated system. (b) Comparison of elongation at break versus CaCO₃ contents in coated and uncoated system.

100/10 in coated CaCO₃. From Figure 2(a), it can be seen that the tensile strength decreases with the increase of CaCO₃ content, but the strength of the PLA/coated CaCO₃ system decreases faster than that of PLA/neat CaCO₃ composites. For example, the tensile strength of the composite filled with 20 phr coated and uncoated CaCO₃ is 48 and 62 MPa, respectively, which decrease 9.4 and 8.8% compared with that of pure PLA, respectively. This phenomenon is due to plasticizing effect of the softened PCL in the PLA matrix.²¹

The elongation at break of PLA/coated CaCO₃ composites improves evidently compared with that of PLA/neat CaCO₃, as shown in Figure 2(b). At the same time, it is also noticed that the elongation of the PLA/coated CaCO₃ samples first increases and then decreases with the increase of CaCO₃ content, similar to the results reported by Meng et al.²¹ The elongation of composite containing 15 phr coated CaCO₃ reaches a maximum of 310%, while PLA/40

phr coated CaCO₃ still shows a elongation of 120%. Meanwhile, coated CaCO₃ with a CaCO₃/PCL ratio of 100/10 can significantly improve the toughness. However, the change of elongation with content variation of neat CaCO₃ is not significant in PLA/neat CaCO₃. It remains about 5%, approximately the same as neat PLA.

CaCO₃ is a hydrophilic material, it has a poor compatibility with PLA; Further, the sharp edges of uncoated particles are not conducive to toughening PLA.³⁰ So, it is difficult for neat CaCO₃ particles to disperse during processing, they tend to aggregate, which brings many defects such as gaps and fractures. Consequently, the composites show low tensile strength and elongation at break. However, for the particles coated with PCL, the surface free energy of CaCO₃ is weaker than that of neat particles,³¹ which could lead to a better dispersion of the particles in the matrix. Further, volume strain in the matrix is released by the debonding of coated particles.³⁰ As a result, shear yielding can take place, and the material is able to absorb large quantities of energy on fracture.³¹ When CaCO₃ content is low, toughening effect of low content filler is not that obvious because PLA matrix still act as the main load bearer.³² However, with continuous addition of CaCO₃ content, when filler content is higher than 15 phr, the decline in elongation at break may be partly due to poorer debonding of the particles or poorer dispersions of the particles.³¹ The dispersion of the particles is critical in these composites and at high filler loads it is difficult to avoid aggregates. Aggregates lead to less ductile behavior.³³ That is to say, 15 phr is the optimum load in this study.

Thermal properties

The crystallization of PLA matrix plays a significant role in toughening³⁴; the toughness is not sensitive to the variation of crystallinity within a relatively low level range (0–8%).³⁵ In order to clarify whether PLA crystallization had any influence on toughening in the blend system, the crystallization and melting behaviors of the PLA component in the blends were examined.

Thermal properties of the composites were studied by DSC, and the glass transition temperatures (T_g), cold crystallization temperatures (T_c), melting point (T_m), enthalpies of melting (ΔH_m), crystallinity (χ_c) of composites are listed in Table I. Based on these DSC data, the crystallinity (χ_c) of each specimen was estimated from the following equation

$$\chi_c = 100 \cdot (\Delta H_m + \Delta H_c) / (\Delta H_0 \times \phi),$$

where ΔH_m and ΔH_c are the enthalpies of melting and cold crystallization, respectively; ϕ is the weight

TABLE I
Thermal Properties and the Crystallinity of Neat PLA and the Blends with Fillers

Samples	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_c (J/g)	χ (%)
PLA	54.7	124.9	147.3	3.467	-2.763	0.75
5 phr neat CaCO ₃	56.4	124.9	149.1	11.5	-6.121	6.33
15 phr neat CaCO ₃	56.6	122.4	148.3	8.292	-5.753	3.12
5 phr coated CaCO ₃	54.2	116.3	147.7	17.95	-17.08	0.97
15 phr coated CaCO ₃	54.7	109.9	144.3	20.7	-20.69	0.0

fraction of PLA matrix. Here, the value of ΔH_0 , the melting enthalpy of 100% crystalline poly(lactic acid), was taken to be 93.7 J/g from the literature.³⁶

In Table I, it is shown that the accession of coated CaCO₃ makes no significant increase in crystallinity. The heating scan of neat PLA sample showed a glass transition temperature centered at 54.7°C, an exothermic crystallization peak at 124.9°C and an endothermic melting peak at 147.3°C, as well as a crystallinity of 0.75%. PLA/5 phr neat CaCO₃ presents a crystallinity of 6.33%, higher than that of neat PLA. But in composites with 15 phr uncoated CaCO₃, a lower crystallinity is observed, but higher than that of neat PLA. In composites with 5 phr coated CaCO₃ crystallinity of the blend is 0.97%, a little higher than neat PLA. When 15 phr coated CaCO₃ is added, crystallinity of the blend drops to 0. At the same time, DSC results indicate that coated systems show lower cold crystallization temperatures and more conspicuous peaks than uncoated composites. Composite with 15 phr coated CaCO₃ has the lowest cold crystallization temperature of 109.9°C, reduced by 15°C compared with neat PLA. The rigid CaCO₃ particles act as a nucleating agent for crystallization and contribute to a higher crystallinity and crystallization rate. On the other hand, filler particles restrict the chain mobility in matrix polymer.³⁷ In condition of 5 phr neat CaCO₃, nucleation effect plays the leading role and a relatively high crystallinity is obtained. In higher filler content condition, the restriction on chain mobility enhanced and the composite shows a lower crystallinity. In the composites with 5 phr coated filler, coating treatment increases the chain mobility of matrix chains, as the dynamic rheological results will show later. So, the composite shows a slightly higher crystallinity than neat PLA, but lower than that of neat CaCO₃-filled system. This is attributed to great reduction in nucleation of the PCL-coated CaCO₃. When 15 phr coated CaCO₃ is added, the latter factor plays the dominant role, that is, PLA chains are further restricted in mobility, presenting the characterization of a noncrystalline material. On the basis of the above results, the crystallization of PLA matrix does not appear to be a contributing factor in resulting in improving the toughness of the composites.

Morphology

Figure 3 illustrates the SEM images of coated and pure CaCO₃. In Figure 3(a), for uncoated CaCO₃, it can be characterized by the presence of a rough surface with many sharp edges and corners and a wide range of particle size. However, CaCO₃ particles become smooth and round after coated, as shown in Figure 3(b). The sharp edges and corners bring a poor interfacial interaction and stress concentration happens easily, resulting in a decrease in mechanical properties. Consequently, it is expected that the coated CaCO₃ could improve the interfacial interaction and, therefore, enhance mechanical properties.

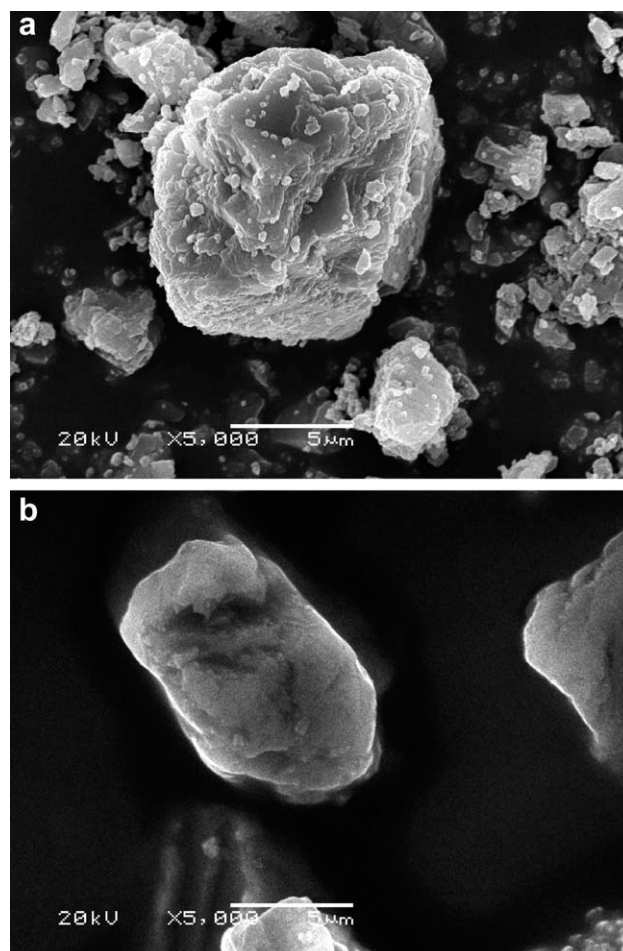


Figure 3 (a) SEM image of neat CaCO₃. (b) SEM image of coated CaCO₃.

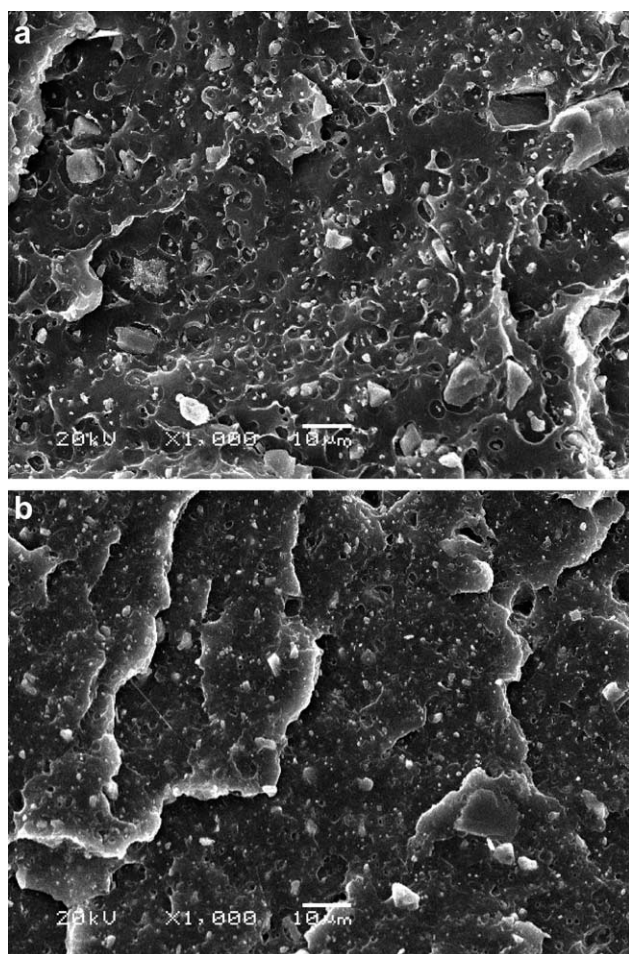


Figure 4 (a) Representative SEM micrograph of the cryofracture surface of PLA/15 phr neat CaCO_3 composite. (b) Representative SEM micrograph of the cryofracture surface of PLA/15 phr coated CaCO_3 composite.

Figure 4 shows the SEM images of the brittle fractured surfaces of PLA/15 phr neat CaCO_3 and PLA/15 phr coated CaCO_3 system. Clear differences in the dispersion and surface texture between the two composites are displayed. For PLA/15 phr neat CaCO_3 composites shown in Figure 4(a), many CaCO_3 particles protrude out and many oval cavities scatter on the surface. Besides, gaps between CaCO_3 particles and the PLA matrix and the aggregations of CaCO_3 particles could also be seen, which indicates a poor interfacial interaction between filler and the matrix. From Figure 4(b), however, a much smoother surface without obvious pit and aggregation can be seen compared with the previous micrograph. The interface between CaCO_3 particles and PLA became fuzzy and joint well. Consequently, CaCO_3 particles can disperse homogeneously and bond tightly with the PLA matrix after coated with PCL.

The SEM micrographs of tensile fractured surfaces of the composites with neat CaCO_3 and coated

CaCO_3 are shown in Figure 5. PLA composite filled with 15 phr neat CaCO_3 [Fig. 5(a)] presents a relatively smooth fractured surface without plastic deformation, and CaCO_3 particles distribute the matrix and scatter throughout the surface. It can be inferred that brittle fracture occurs in PLA composites filled with 15 phr neat CaCO_3 during uniaxial tension. However, after the addition 15 phr coated particles, the tensile fracture surface presents a completely different micrograph [Fig. 5(b)]. Plastic deformation occurs on the whole fracture surface and as a result, many filaments can be observed on the surface. Therefore, the interface and adhesion between CaCO_3 particles and PLA matrix can be improved by coating CaCO_3 particles with PCL.

Dynamic rheological behavior

The effect of the filler on the isothermal (175°C) frequency dependence of the loss modulus (G'') of the prepared composites is reported in Figure 6. The curves of CaCO_3 filled samples have the same shape

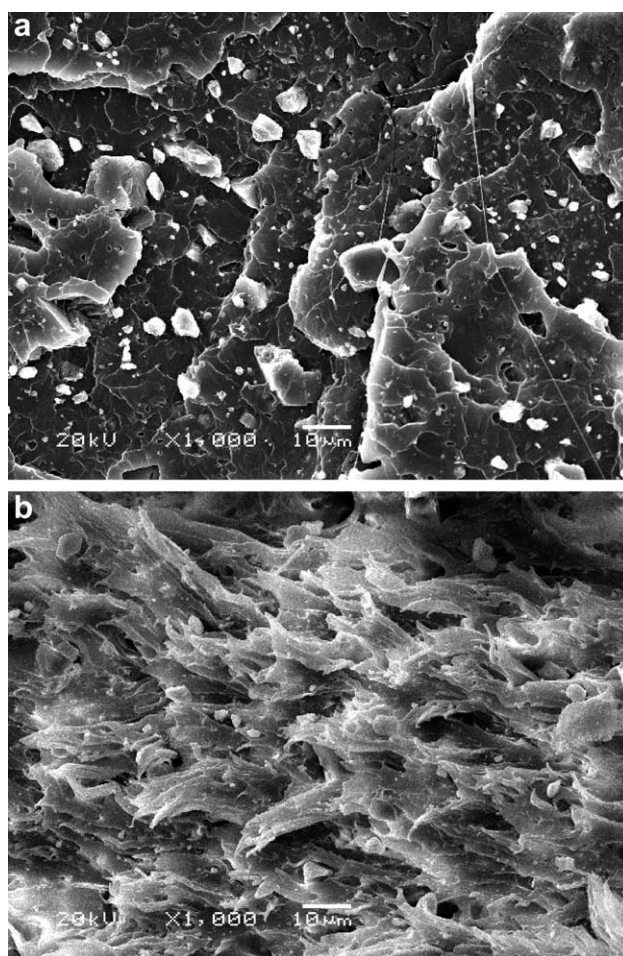


Figure 5 (a) Representative SEM image of the tensile fracture surface of PLA/15 phr neat CaCO_3 . (b) Representative SEM image of the tensile fracture surface of PLA/15 phr coated CaCO_3 .

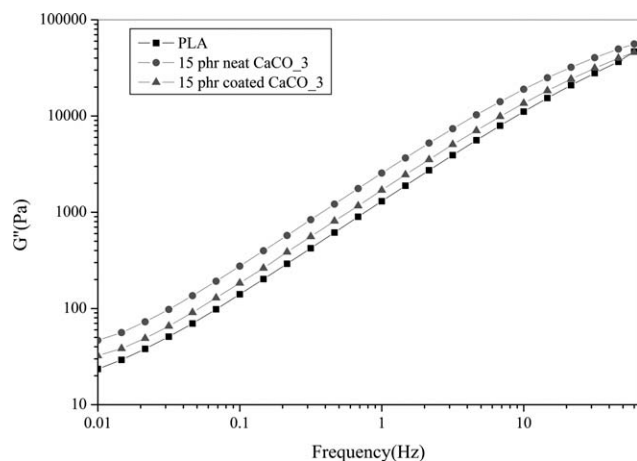


Figure 6 Loss modulus, G'' , of PLA-PCL- CaCO_3 composites.

as PLA and each system shows a higher loss modulus than that of neat PLA. According to literatures,^{38–40} complex viscosity and loss modulus usually increase several orders of magnitude in a filled system (especially in low frequency region). Interestingly, for composites added 15 phr coated CaCO_3 , the value of G'' is lower than that of composites filled neat CaCO_3 but higher than that of neat PLA.

Figure 7 shows the complex viscosity (η^*) of PLA and filled PLA samples as a function of frequency. PLA, PLA/ CaCO_3 , and PLA/coated CaCO_3 composites show a trend of non-Newtonian flow and the curves of the three different systems show similar shape with each other because of the major role of the interaction between PLA molecular chain segments.⁴¹ PLA/15 phr coated CaCO_3 sample exhibits a value of η^* higher than neat PLA but lower than that of the other composites. This may mean that the increase of η^* is brought by the phase boundary in filled composites.³¹ However, the complex interaction between PCL and CaCO_3 particles lead to a

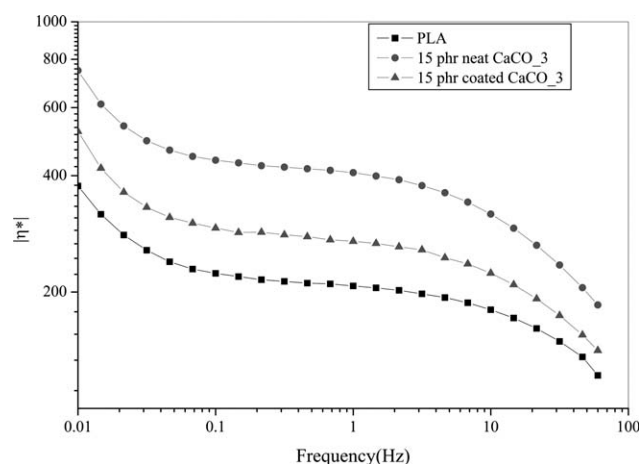


Figure 7 Complex viscosity, $|\eta^*|$, of PLA-PCL- CaCO_3 composites.

better phase interface and weakened the effect in the increase of complex viscosity.

Thus, the coated particles can improve the movement of the PLA chains compared with neat particles, which is of great importance to processing. This is also in agreement with the DSC results.

CONCLUSIONS

PLA/coated or neat CaCO_3 blends were prepared by melt blending using a Haake mixer. It is the effects of neat CaCO_3 and PCL-coated CaCO_3 on mechanical, thermal, morphological properties, and dynamic rheological behavior of the blends that were investigated. Mechanical testing shows that small dose of PCL hardly affect the ductile of PLA and addition of CaCO_3 coated with PCL brings a tremendous growth in toughness. With the increase of coated CaCO_3 content, elongation at break of PLA/coated CaCO_3 composites increases to a maximum value, 310%, and then drops. Tensile strength of composites drops with increasing coated filler content but it is still appreciable. For example, when 40 phr filler is added, the composite still shows good strength of about 40 MPa. DSC analysis indicates that coated CaCO_3 shows no significant influence on crystallinity of PLA matrix, thus crystallinity of the composites is not a key effect factor of toughness. From SEM images, particles coated with PCL are rounder than neat CaCO_3 , and the coated fillers disperse more uniformly with less aggregation in the matrix. Therefore, coating with PCL could improve the interfacial interaction between filler and the matrix. Furthermore, fracture surfaces were observed in composites after tension. For PLA/coated CaCO_3 composites, many filaments stick out as a result of plastic deformation; but for PLA/neat CaCO_3 , it is very smooth. Therefore, round shape and good dispersion of particles contribute to the excellent toughness of the composite. The dynamic rheological results show that PLA/coated CaCO_3 system exhibits a data higher than neat PLA but lower than PLA- CaCO_3 in both loss modulus and complex viscosity due to the complex interaction among PCL, CaCO_3 particles, and the PLA matrix.

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