Microwave-Assisted Preparation of Polylactide/Organomontmorillonite Nanocomposites via *In Situ* Polymerization

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ABSTRACT: Microwave technology was introduced to assist the synthesis of polylactide (PLA)/organomontmorillonite (OMMT) nanocomposites in bulk by the *in situ* ring-opening polymerization of D,L-lactide. Factors that influenced the polymerizing effects, such as the microwave power, irradiation time, and dosages of the catalyst and OMMT, were studied in terms of tensile strength. The polymerization time was decreased dramatically to 10 min under 90 W of microwave irradiation, and the mechanical and thermal properties of the PLA/OMMT nanocomposites were significantly improved. The composite with the highest mechanical properties was obtained when the dosages of the OMMT and the catalyst were 1.0 and 0.6 wt % of the lactide, respectively. The initial decomposition temperature of the PLA/OMMT(1.0 wt % OMMT) nanocomposite was heightened 11.5°C compared with that of pure PLA. The results of scanning electron microscopy confirmed an improvement in the toughness with the addition of OMMT. The transmission electron microscopy and X-ray diffraction results indicate that an exfoliated and intercalated nanocomposite was successfully prepared. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1468–1473, 2010

Key words: clay; nanocomposites; polyesters

INTRODUCTION

In recent years, because of ecological imperatives, the applications of biodegradable aliphatic polyesters have been extended from the field of medical research into everyday materials.[1] Polylactide (PLA) is a promising biodegradable and biocompatible material. Because PLA can be synthesized from lactic acid, which is the product of fermented starch, and can be degraded into nontoxic end products, it is an environmentally friendly material.[2–4]

Because PLA is of relatively low strength, it is necessary to improve the characteristics of PLA via modification in terms of its mechanical properties.[5–8] The introduction of nanofillers in biodegradable matrices has allowed improvement in the range of properties and possible uses of PLA. Compared with other conventional high-level (>30 wt %) loaded composites, nanocomposites need significantly smaller loadings (0.5–5.0 wt %) to achieve similar results, if not better.[9–12] To improve the dispersability of the nanoparticles in the matrix of polymers, *in situ* polymerization was introduced as an effective technique.[13–15]

In other relevant studies, PLA nanocomposites based on layered aluminosilicates have represented an attractive solution for achieving mechanical improvements; thereby, layered aluminosilicates, which consist of sheets arranged in a layered structure, such as montmorillonite (MMT), have been largely studied.[16–18] These layered aluminosilicates can potentially force gas and water molecules to follow a more tortuous path through the polymer matrix.[19,20] As the intercalation of polymer chains into the interlayer spacing of layered aluminosilicates (MMT) brings noticeable improvements in the mechanical, thermal, and barrier properties in contrast with pure polymers, the complete delamination of the clay platelets by polymer chains has proven to enlarge the extension of its application.[21]

Recently, many scholars have focused on microwave technology because of its high efficiency and homogeneous heating manner. The reaction time with microwave heating can be significantly reduced in chemical synthesis compared with conventional heating on account of the special internal heating of microwave irradiation.[22–28]

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To our best knowledge, there have been few reports on the synthesis of PLA/organomontmorillonite (OMMT) nanocomposites under microwave irradiation. In our previous study, we managed to synthesize PLA in which the viscosity-average molecular weight was over 2.0×10^5 under microwave irradiation in minutes via ring-opening polymerization.[23]

In this study, we aimed to synthesize PLA-based nanocomposites by the *in situ* ring-opening polymerization of D,L-lactide (DLLA) with the introduction of nanoscale OMMTs under continuous microwave irradiation. The behaviors of the PLA nanocomposites were analyzed through their thermomechanical properties and morphologies. The properties of the nanocomposites were characterized by tensile testing, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

OMMT was purchased from Zhejiang Fenghong Clay Chemical Co., Ltd. (Huzhou, Zhejiang, People's Republic of China). The synthesis and purification of DLLA was done according to Zhang et al.[29] Stannous octoate [$Sn(Oct)_2$] without further purification was used as the catalyst. Ethanol, toluene, and tetrahydrofuran were analytically pure.

Modifications to a domestic microwave oven

A microwave oven (Sanyo MCL-2, with a frequency of 2.45 GHz) modified to have adjustable and continuous power, was used as the microwave source. Figure 1 shows a picture of the modified microwave oven. The following states the modifications in detail:

1. The power supply circuit of the magnetron in the microwave oven was reconstructed. A voltage regulator [Fig. 1(a)] was added to regulate the output anode voltage of the magnetron. Also, an ammeter [Fig. 1(b)] was connected in the circuit to indicate the output power based on a power versus current curve.
2. The area of the microwave energy feed was enlarged to ensure the uniformity of the energy distribution.
3. Two holes at the top of the microwave oven were opened according to the needs of our experiments. Cutoff waveguide tubes [Fig. 1(c)] were mounted at the opening holes to shield the microwave.
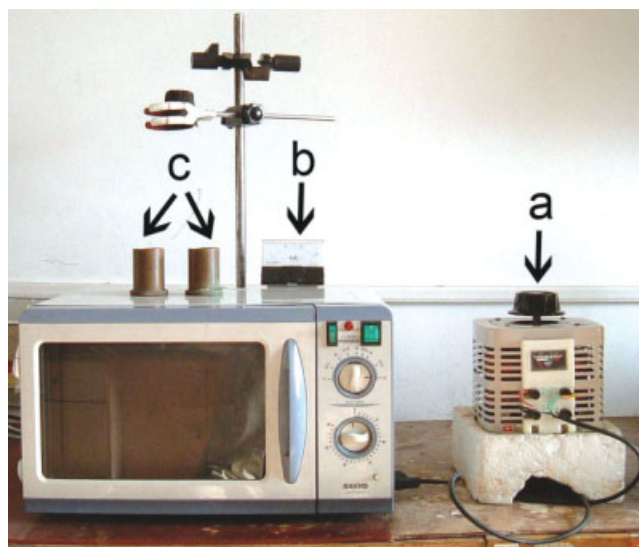

Figure 1 Picture of the modified microwave oven: (a) a voltage regulator, (b) an ammeter, and (c) holes mounted with cutoff waveguide tubes. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Synthesis of PLA/OMMT

The OMMT was first dried overnight at 70°C and then at the same temperature under reduced pressure for 4 h, whereas the DLLA was dried at 40°C under reduced pressure for 24 h before use. During the procedure, the DLLA and OMMT in a certain proportion were mixed in the high-speed mixer for several minutes under a nitrogen atmosphere, and then, 10 g of the as-formed mixture was transferred into a 50-mL open beaker. After the addition of $Sn(Oct)_2$ as the catalyst, the beaker containing the reactant was placed on a heat-resistant evaporating dish that contained assisted heating medium in the microwave oven and was irradiated by continuous microwave irradiation for minutes to obtain the PLA/OMMT nanocomposites.

Measurements

Tensile strength testing of all of the samples was carried out according to the Chinese standard GB1040-92 with the WD-1 at a crosshead rate of 10 mm/min at room temperature. The specimens for tensile testing were prepared by hand injection molding at 230°C.

TGA was performed from room temperature to 600°C with a Pyris-1 TG-DTA thermogravimetric analyzer from PerkinElmer (Watham, MA) at a heating rate of 10 K/min under an air flow (70 cm^3/min).

The fracture surfaces obtained during tensile strength testing were covered by a carbon layer and
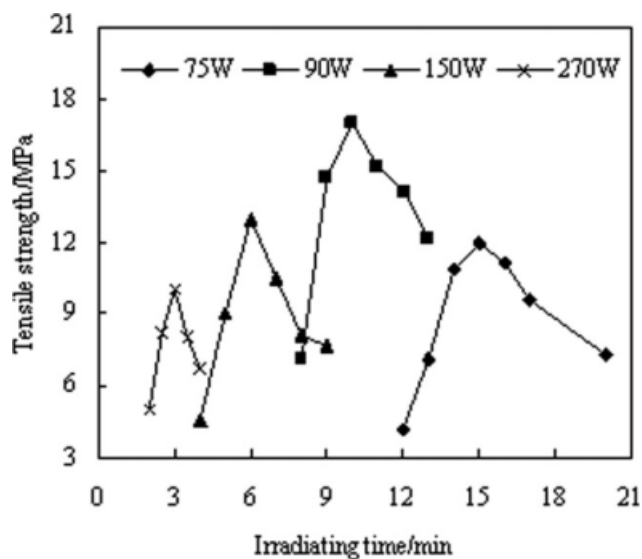
Figure 2 Effects of the microwave power and irradiation time on the tensile strength (0.5 wt % catalyst, 1.0 wt % OMMT).

observed with a JSM-6700F (Tokyo, Japan) scanning electron microscope.

We performed XRD using a Scintag XDS 2000 (Cupertino, CA) diffractometer (operated at 47 kV/ 20 mA with a scanning rate of 0.030°/min) to determine the degree of exfoliation of the PLA/OMMT nanocomposites. Samples were scanned in a continuous mode with counting time of 1.8 s under a diffraction angle (2θ) in the range 1.00–11.98°. The basal spacing of the silicate layer (d) was calculated with Bragg's equation: $\lambda = 2d \sin \theta$ [λ(Cu Kα1) = 0.15406 nm].

For TEM, we first prepared the PLA/OMMT nanocomposite film sample by cutting thin ($\sim$ 200 nm) slices. The film was embedded in TEM-grade epoxy, then precut, and ultramicrotomed at room temperature on a JEOL (Tokyo, Japan) JEM-1200EX.

RESULTS AND DISCUSSION

Effects of the microwave power and irradiation time

The output power, ranging from 20 to 600 W, could be controlled at the exact value we wanted after the modification. In addition, the stability of the microwave irradiation was enhanced. The temperature of the reactants rose rapidly and smoothly at first and then remained relatively steady in the modified microwave oven.[30] The temperature of the reactants system evolved smoothly without step as the temperature control was a crucial factor in the microwave-assisted synthesis.

Because of the smoothness and speed of the increasing temperature, the microwave oven modi-

fied to have continuous and adjustable microwave irradiation was used as the microwave source in further experiments.

Figure 2 shows the effects of the microwave power and irradiation time on the mechanical properties of the PLA/OMMT nanocomposites. All of the tensile strength curves ascended in the beginning and then dropped under different predetermined power values. It was obvious that in the microwave oven, the longer the irradiation time was, the higher the temperature was. At the start of the reaction, the catalyst was active for the propagation of the polymer chains, and the tensile strength of the nanocomposite was enhanced. However, with increasing reaction time, cyclic oligomers tended to appear, and polymer chain propagation was hindered.[31] In addition, the overheated system resulted in the loss of some oligomers of lower mass during the polymerization; thus, a product with a lower tensile strength was obtained. The picture also shows that the optimum reaction time was shortened with increasing microwave power. When the whole process was conducted at 270 W, the reaction needed less than 3 min and was rather difficult to control. Also, the highest tensile strength of the PLA nanocomposites produced under this power was relatively low. On the contrary, the PLA nanocomposite with a tensile strength of 17 MPa was obtained at 90 W and an irradiation time of 10 min. In this way, we concluded that microwave-assisted polymerization is effective and is an extraordinary time-saving method in comparison with reported research on the *in situ* intercalative polymerization of PLA/(organo)clay nanocomposites under conventional heating, generally over 48 h.[32] With regard to the energy consumption, mechanical properties, and maneuverability, a power of 90 W and an irradiation time of 10 min were selected for further reactions.
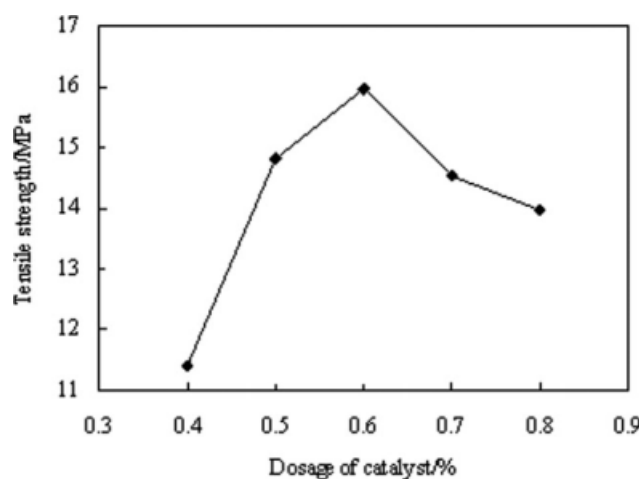

Figure 3 Effects of the dosage of catalyst on the tensile strength (1.0 wt % OMMT).
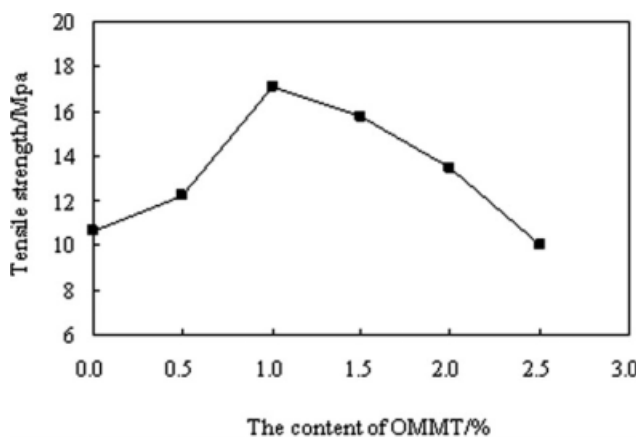
Figure 4 Effects of the content of OMMT on the tensile strength.

Effects of the dosage of the catalyst

The effects of the amount of $Sn(Oct)_2$ as the catalyst are shown in Figure 3. The ring-opening polymerization of the lactide induced by $Sn(Oct)_2$ was coincident with the coordinate-intercalated mechanism. The molecular weight of PLA was affected significantly by the amount of the catalyst, as it accelerated not only the polymerization but also the decomposition.[23] As shown in Figure 2, the tensile strength increased with increasing amount of $Sn(Oct)_2$, and the composite with a tensile strength of 15.96 MPa was prepared when the catalyst amount was 0.60 wt % of the lactide. Nevertheless, when the $Sn(Oct)_2$ dosage was above that point, the surplus active centers resulted in a decomposition that caused a decrease in the tensile strength, and the product turned black with a burnt smell. Thereby, a catalyst dosage of 0.6 wt % of the lactide was selected for further reactions.

Effects of the OMMT content

Figure 4 displays the mechanical strength of the samples with different OMMT contents. Interaction
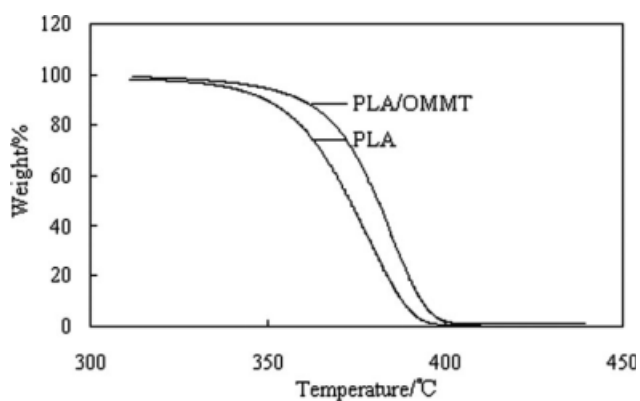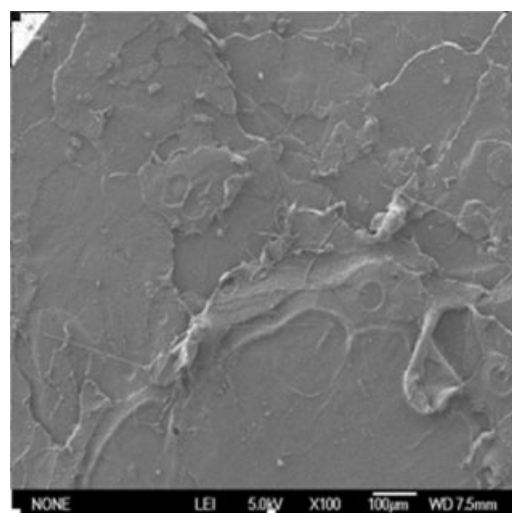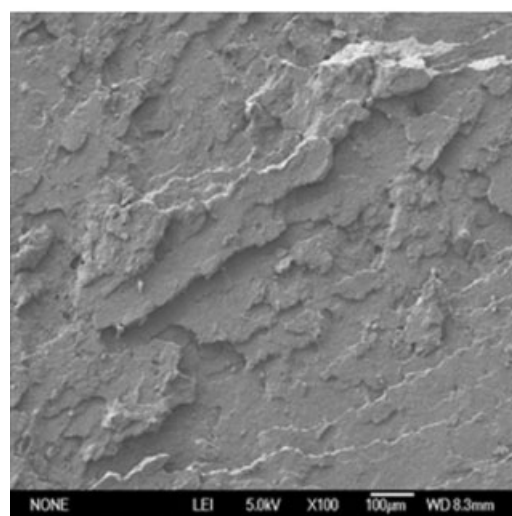

Figure 5 TGA traces of PLA and PLA/OMMT.

Figure 6 SEM images of the tensile fracture of the PLA and PLA/OMMT nanocomposite.

with OMMT greatly improved the mechanical properties of PLA. The composite with only a 1.0 wt % OMMT content exhibited a tensile strength of 17.12 MPa, which was 1.6 times that of the pristine PLA. This great enhancement of the mechanical properties mainly was due to a feature of the nanocomposite where there was strong interaction between PLA and OMMT. However, when the OMMT content was over 1.0 wt %, the tensile strength began to decrease, and this may have been because of the aggregation of nanoscale OMMT particles with higher surface energy when the OMMT content was high enough.[17]

Thermal stabilities

The initial decomposition temperature of the PLA/OMMT nanocomposites increased 11.5°C in contrast
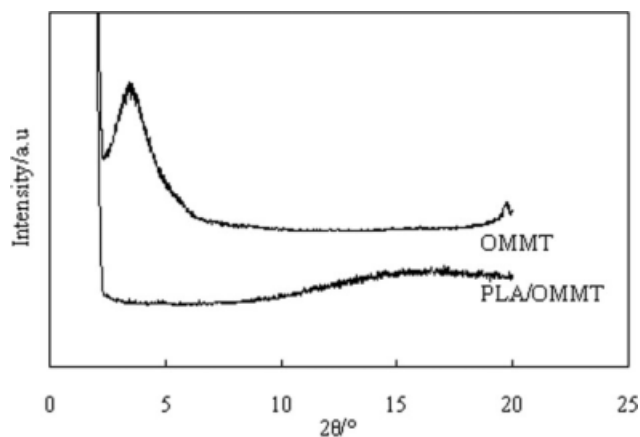
Figure 7 XRD patterns of the OMMT and PLA/OMMT nanocomposite.

with neat PLA according to the TGA results shown in Figure 5. Such behavior was explained by the relative extent of exfoliation and the interaction between the OMMT particles and the polymer matrix.[9] In this way, the barrier properties of the OMMT played the role of not only the thermal barrier, which protects the polymer from fire, but also the mass transport barrier, which makes it difficult for degradation products to leave the polymer.[33] As a result, the PLA nanocomposite containing 1.0 wt % OMMT exhibited a more stable thermal resistance because of the good thermal insulation effect of the nanoscale OMMT. The amount of nonvolatile residue that remained at the end of a TGA run was in accordance with the OMMT content.

Morphology of the PLA/OMMT nanocomposites

The surface morphology of the tensile fracture was observed by SEM in Figure 6. As shown, the tensile fracture of the neat PLA was smooth, and no obvious tensile yield phenomenon was found. This is a typical characteristic of brittle fracture. The tensile fracture of PLA/OMMT was rough, and some microvoids and layered structure were displayed. The fracture direction tended toward decentralization and ductile fracture, which resulted in the improved toughness and deformation of PLA.

Dispersability of the OMMT in PLA

The compatibility with the polymer was improved when the MMT was modified with an organic compound, and the OMMT layers interreacted easily with the polymer. The interlayer spacings of the OMMT were calculated from the XRD measurements (as shown in Fig. 7). The OMMT of decreasing interlayer d-spacings was 2.8 nm in order. Through comparison of the diffractograms of the PLA/OMMT nanocomposites with OMMT particles, we found that the total absence of a diffraction peak at low 2θ angles (complete disappearance of the d-spacing at 2.8 nm) suggested the formation of the exfoliated structure.[9] However, the disappearance of the d (001) diffraction peak in the nanocomposite may also mean that the content of OMMT was too low to be detected.[34] Thus, TEM was carried out to further determine the distribution of OMMT. The TEM picture of this nanocomposite is shown in Figure 8, and the results reveal that the exfoliated OMMT platelets [Fig. 8(a-B)] coexisted with a limited amount of intercalated stacks [Fig. 8(a-A)] and were extremely well dispersed. As shown in Figure 8(b), the ordered lamellar structure of the OMMT was destroyed, and the interlayer d-spacing was enlarged.
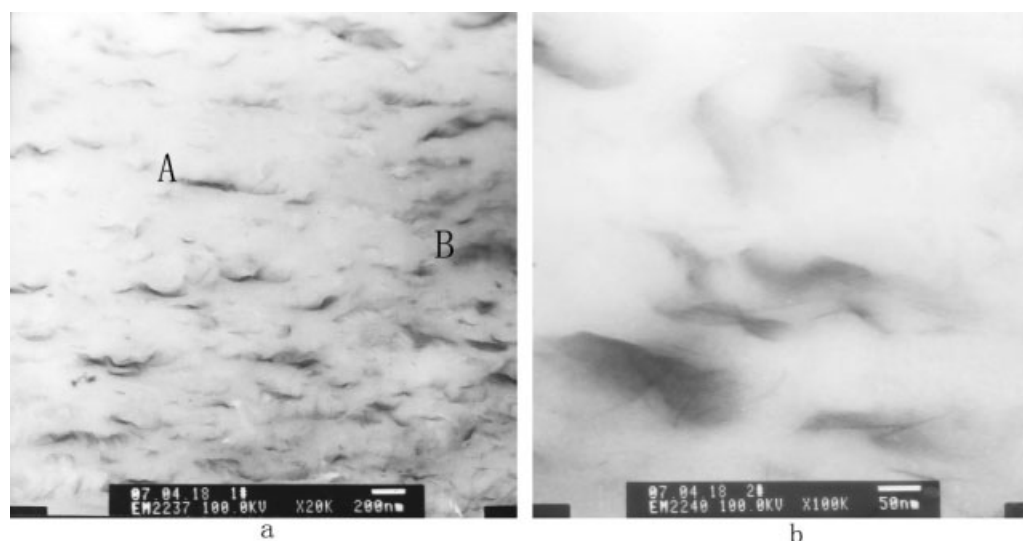

Figure 8 Typical TEM images of the PLA/OMMT nanocomposite showing (a) low magnification and (b) high magnification.

CONCLUSIONS

PLA/OMMT nanocomposites were successfully synthesized by the *in situ* polymerization of DLLA in bulk under continuous microwave irradiation. The introduction of microwave heating considerably cut the whole procedure time down to 10 min at 90 W. These PLA/OMMT composites had better mechanical properties than pure PLA and had a more stable thermal character. Also, it was established that OMMT was finely dispersed in the PLA matrix and formed a nanocomposite in which the exfoliated structure dominated and the intercalated structure also coexisted. Microwave-assisted *in situ* polymerization proved to have low energy consumption, high efficiency, and easy handling. In this aspect, we think that it is a promising method for synthesizing PLA/OMMT nanocomposites.

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