Iranian Polymer Journal
17 (12), 2008, 947-952

Preparation of Poly (lactic acid)/Etherified Starch Composites

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Received 25 September 2008; accepted 2 December 2008

ABSTRACT

Poly (lactic acid) (PLA) is one of the most promising biodegradable materials with excellent mechanical properties, but the disadvantages of stiffness, poor thermal stability, and high costs limit its applications in general use plastics such as industrial packaging and agriculture films. In present work, biodegradable PLA/starch composites are prepared from PLA and etherified starch (EST) by extrusion and uniaxial orientation processing with a pretreated mixing procedure under a programmed temperature. The products are examined using Fourier transform infrared (FTIR) spectroscopy technique. The results revealed that small amount of PLA molecules have strong interaction with EST which may be ascribed to the esterification between the terminal carboxyl groups of PLA and hydroxyl groups in EST. The morphological properties observed by scanning electron microscopy (SEM) technique confirmed that the composites with a pretreatment procedure had much better dispersion and homogeneity of starch in the PLA matrix than the composites without the pretreatment procedure. Consequently, an improvement in mechanical properties has been achieved. Comparing with the samples without the pretreatment procedure, the mechanical performances such as tensile strength, elongation-at-break and modulus of the composites with a pretreatment procedure were significantly improved. This approach is identified as a reasonable method to produce commercial PLA/starch composites with economical feasibility.

Key Words:

biodegradable;
poly(lactic acid);
etherified starch;
composites;
pretreatment.

INTRODUCTION

Poly (lactic acid) (PLA), as a biodegradable material with excellent mechanical properties and biocompatibility has been widely studied and applied in biomedical materials. Recently, with the increased pollution and growing costs of traditional polymeric materials, PLA attracts great attention in replacement of traditional petroleum-based materials. However, disadvantages such as stiffness, poor thermal stability, and high costs limit its applications in general use plastics such as industrial packaging and agricultural films. Therefore, it is necessary to make the modification on PLA in order to improve its properties and reduce its cost. Some novel composites

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combining PLA with renewable natural resources have been highly expected [1-8]. Starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost, otherwise, starch and its derivatives have better reactivity than the other biodegradable natural biopolymers, such as cellulose, chitin, etc. Therefore, corporating PLA with starch have been considered in this work. However, the thermodynamical immiscibility between the two phases of PLA and starch results in composites with poor performance [8-10]. Generally, adding some plasticizers or compatibilizers to the composite would be a promising approach to enhance the interfacial interactions. For example, some small molecular agents, such as citric acid ester[9], poly(propylene glycol), citrates, glycerol, sorbitol, poly(ethylene glycol), triethyl citrate, and acetyl-triethyl citrate (ATC)[10] have been frequently chosen as plasticizers; moreover, some reactive coupling agents, such as MDI, TDI, and HMDI have been applied [5] as well.

In addition, some graft copolymers, such as starch grafted poly(*L*-lactide)[11], maleic anhydride grafted PLA [12], acrylic acid grafted PLA [13], also have been considered as compatibilizers. But all these methods are not easily amenable to practical applications because of the additional production costs and the undesirable full-biodegradation.

In this work, a biodegradable PLA/EST composite has been prepared successfully, and a pretreated mixing procedure was conducted before extrusion in order to improve the compatibility of PLA and EST which was proved by FTIR and SEM analysis. As a result, the mechanical property of the composites produced by this approach was effectively enhanced. To the best of our knowledge, improving compatibility of PLA and starch involving a pretreated mixing procedure has not been reported and this biodegradable PLA/starch composite material can be produced in an environmentally friendly approach, and as all the procedures are solvent-free, it may be good candidate for general use.

EXPERIMENTAL

Materials

PLA (M_η = 45,359 Da and M_w = 79,776 Da) was purchased from JiuDing Bio-Engineerjing Co. Ltd. (Nantong City, China). EST (HP-F Series, hydroxypropyl etherified cassava starch, etherified DS = 3-5%) was purchased from TingFung Starch Development Co. LTD. (Tianjin City, China).

Pretreated Mixing of PLA /EST

PLA pellets were grinded by a high-speed herbal medicine grinder machine (FW135, Tianjin Test Instrument Co. Ltd., China) into powder (average particle size: 75-250 μm and GFW: 1.25/0.56). The PLA and EST powders were dried in a vacuum oven at 60ºC for 48 h before processing.

Dried PLA and EST powders were added to a 1L flask with weight ratios of 90:10, 80:20, 70:30, and 60:40, respectively, and then the flask was connected to a rotary vacuum evaporator (Model Laborota 4000, Heidolph, Germany) with a mechanical stirrer. The temperature of the mixture was maintained at 80ºC for 1 h, and then raised to 135ºC with a heat rate of 5ºC/30 min and kept for a desired time. All processes were conducted under vacuum (1 mm Hg).

For comparison, the PLA/EST was prepared under the same condition but a catalyst ($SnCl_2$•$2H_2O$, 0.05 wt%) for esterification was added during the mixing procedure. Each batch of PLA and EST powders with respective weight ratios of 90:10, 80:20, 70:30, and 60:40, was mixed mechanically in the rotary vacuum evaporator at room temperature (25ºC) with the same stirrer rate and the same mixing time.

Preparation of PLA/EST Composites by Extrusion and Uniaxial Orientation Processing

PLA/EST composites were produced by extrusion using a lab-scale, single-screw extruder (Model CTSE-2, CW Brabender, Inc., S Hackensack, NJ, USA) with a screw diameter of 19.1 mm and a length to diameter ratio of 25:1. The rotation speed was keep at 30 rpm and the processing temperature was set at 100, 160, 165, and 140ºC from feed inlet to the die.

The sheet extrudates were produced by a 3-mm thickness die nozzle and oriented uniaxially at 70ºC by an affiliated tension roller. The final sheets were cut into tensile bars following ASTM Method D 1708 and then cooled to room temperature under ambient conditions. All moulded tensile bars were preconditioned at 25ºC and 30% RH for one week to relax internal stresses prior any mechanical tests.

Measurements

Fourier Transform Infrared (FTIR) Spectroscopy

The Fourier transform infrared (FTIR) Spectroscopy was measured with BRUKER FTIR EQUINOX 55 IR Spectrum Scanner (Bruker, Germany). The extruded blend strips were pressured to slices with the thickness of around 0.2 mm in the Flat Sulphuration Machine (769YP-15A, Keqi High & New Technology Corporation, Tianjin City, China).

Scanning Electron Microscopy

The morphology of tensile fracture surfaces of the composites was observed by SEM at room temperature. A Shimadzu SEM (model SS-550) with field emission gun and accelerating voltage of 20 kV was used to collect SEM images for the composites specimens. A gold coating of a few nanometers in thickness was coated on impact fracture before testing.

Mechanical Testing

A mechanical testing machine, AX Testometric M500-10KN (UK) was used to measure the mechanical properties according to ASTM D 1708 standard and the tensile testing rate was 10 mm/min. All results presented are the average values of five parallel samples.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR) Spectroscopy

Figure1 shows the FTIR spectra of the composites residues which soxhleted by dichloromethane for 10 h to eliminate the non-esterified PLA. Three composites were chosen for this analysis: (a) PLA/EST (70/30 w/w%) composite without pretreatment which was recorded as PLA/EST-30, (b) PLA/EST (70/30 w/w%) composite with pretreatment and addition of catalyst during the pretreatment procedure which was recorded as pre-PLA/EST-CAT-30, and finally (c) PLA/EST (70/30 w/w%) composite with pretreatment but without the presence of catalyst, and recorded as pre-PLA/EST-30.

In Figure 1, as it is shown in spectrum (a) no characteristic peak at 1750 cm^{-1}, formally attributed to the vibration of PLA carbonyl group, has been detected. This showed that there was no strong molecular interaction between PLA and EST in the PLA/EST composite without any pretreatment, and the unreacted PLA has been eliminated from the composite by extracted with dichloromethane. However, a small absorption peaks at about 1750 cm^{-1} was found in both spectra of (b) and (c) which revealed that few PLA molecules have formed strong interactions with EST and could not have been removed by extraction. We may assume that it may be related to the esterification reaction between the terminal carboxyl groups of PLA and hydroxyl groups of EST. Furthermore, the carbonyl absorption peak in spectrum (b) is stronger than the same peak in spectrum (c). This may indicate that the esterification catalyst can improve the esterification efficiency. Unfortunately, as it is evident in Table 1, the existence of catalyst decreases the mechanical properties of the PLA/EST composites, as it has accelerated the acidification degradation in the melt extrusion processing. Thus, we have mainly focused our studies on the composites prepared in the absence of catalyst.

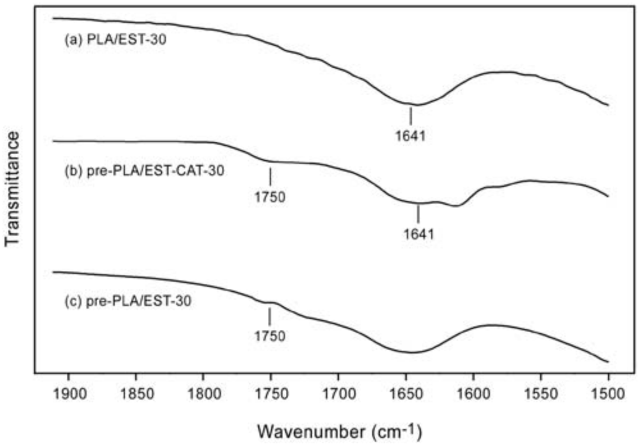


Figure 1. FTIR spectra of the residual solids extracted from composites: (a) PLA/EST, (b) pre-PLA/EST-CAT-30, and (c) pre-PLA/EST-30.

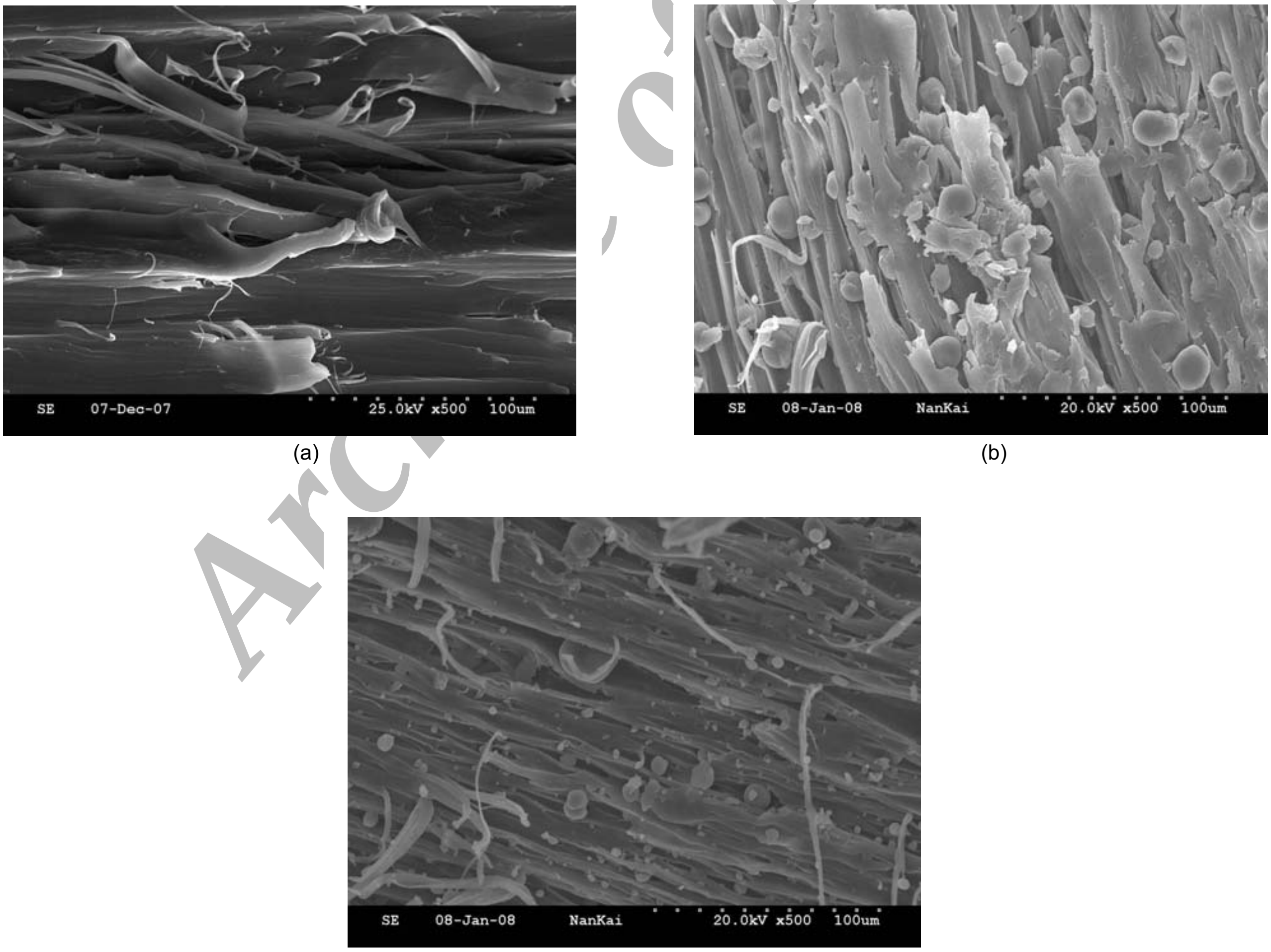
Morphology of PLA/EST Composites

It is well known that the properties of a polymer blends are strongly dependent on the compatibility of two components which is related to the phase morphology of the system. Figure 2 illustrates the SEM images of pure PLA (a), PLA/EST-30 composite (b),

Table 1. Mechanical properties of PLA/EST composites with or without pretreatment.

Samples	EST content (%)	Tensile strength (MPa)	Elongation-at-break (%)	Young's modulus (MPa)
PLA/EST-30	30	38.4(±7.1)	29.1(±8.7)	791.1(±20.6)
Pre-PLA/EST-CAT-30	30	47.5(±3.2)	44.8(±8.2)	744.2(±12.4)
Pre-PLA/EST-30	30	69.0(±0.3)	49.2(±0.6)	852.9(±1.2)
PLA/EST-40	40	36.7(±9.9)	16.1(±12.8)	720.8(±28.1)
Pre-PLA/EST-40	40	53.1(±0.5)	45.2(±0.8)	776.1(±2.5)
Pure PLA	0	74.5(±0.1)	55.7(±0.2)	899.4(±1.2)

and pre-PLA/EST-30 composite (c), respectively. Compared with the smooth fracture structure of pure PLA (a), the PLA/EST-30 composite (b) and pre-PLA/EST-30 composite (c) exhibit the typical two-phase polymer blend structures in which PLA is the continuous phase and starch is the filler. EST particles retained their granular structure in the composites. For PLA/EST-30, the morphology was very coarse, as expected for an uncompatibilized blend. The dispersion of etherified starch in PLA matrix is imperfect. The starch phase presented a non-uniform size distribution with particles ranging form 12 to 18 μm (Figure 2b). In contrast, the EST particles in the composites of pre-PLA/EST-30 exhibited much



(a) (b) (c)

Figure 2. SEM micrographs of fractured tensile bars of: (a) pure PLA, (b) PLA/EST-30, and (c) pre-PLA/EST-30.

finer and more homogeneous dispersion. The particles were nearly spherical with diameters ranging from 2 to 10 µm (Figure 2c). The results indicate that simple blending by extrusion of two immiscible components could not achieve a composite with desired characteristics because of the high interfacial tension existing between the two phases. The PLA is hydrophobic with poor polarity while the EST is hydrophilic with strong polarity [14]. Therefore, the dispersed EST component preferred to coalesce and aggregate into large scale in the PLA matrix during the extrusion. However, the pretreatment before extrusion can improve the compatibility of the blends due to partial esterification between PLA and EST which has been confirmed by FTIR analysis. Then, the blends showed much finer phase structure which is expected to have good mechanical properties.

Mechanical Properties of PLA/EST Composites

The mechanical test has been conducted according to ASTM D1708[14] and the resulting data have been summarized in Table 1. The mechanical performance of pre-PLA/EST composite is much better than that of the composite without pretreatment. For example, the tensile strength, elongation-at-break and Young's modulus of pre-PLA/EST-30 are about 69.0 MPa, 49.2%, and 852.9 MPa, respectively, however, those of PLA/EST-30 without pretreatment are only about 38.4 MPa, 29.1%, and 791.1 MPa, respectively. The results are consistent with what have been observed in FTIR and SEM studies.

Although, the mechanical properties of PLA/EST composites produced by this approach are not as good as those of pure PLA, they are sufficiently suitable for producing biodegradable plastic films. Simultaneously, the total cost of the PLA/EST composites has been cut down efficiently by increasing starch content. Hence, the solid phase esterification approach for strengthening the PLA/EST composites markedly shows an economically feasible perspective to expand the applications of PLA.

CONCLUSION

PLA/EST composites were produced by extrusion and uniaxial orientation processing after pretreated mixing. The FTIR analysis confirmed that there has been a strong interaction between PLA and EST due to partial esterification reaction between the terminal carboxyl groups of PLA and hydroxyl groups in EST. SEM observations showed that the pretreatment can improve the compatibility of the PLA and EST and exhibit fine dispersion morphology. Consequently, an improvement was also observed in mechanical properties. This approach is recognized to be a reasonable method to produce an economical and commercial production of PLA/starch composites.

ACKNOWLEDGEMENTS

We are grateful for the financial support of Tianjin Science and Technology Key grants and the helps of Dr. Xiu-ping Lu and Dr. Su-hua Wu in Tianjin University of Science and Technology on the materials extrusion processing.

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