Synthesis and characterization of starch-graft-polycaprolactone as compatibilizer for starch/polycaprolactone blends

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SUMMARY: Polycaprolactone (PCL) was grafted onto starch through introduction of urethane linkages. The grafting reaction was carried out in two steps. The first step was the reaction of hydroxyl-terminated PCL with 2,4-tolylene diisocyanate. The isocyanate terminated PCL was then reacted with starch to obtain starch-graft-polycaprolactone (starch-g-PCL). The grafting reaction was confirmed by FT-IR spectroscopy. The compatibility of the starch/PCL blend was enhanced with a compatibilizer, starch-g-PCL, whose amount was 3 wt.-% of the blend. The tensile strength and morphology of the compatibilized blend were determined. It was found that the compatibilized starch/PCL blend has finer phase domains and an improved interfacial adhesion. Mechanical properties of the compatibilized blend were found to be significantly higher than those of the corresponding uncompatibilized starch/PCL blend.

Introduction

Polymer blends form a vital part of the modern plastic industry. Developing a blend with satisfactory overall physicomechanical behavior depends on a proper interfacial tension to generate a small phase size and strong interfacial adhesion to transmit an applied force effectively between the component phases. Methods to improve phase adhesion and to reduce interfacial energy between two immiscible phases have been a subject of considerable research activity, often of a proprietary nature. This process of stabilizing polymer blends is commonly called compatibilization. A compatibilization strategy that is frequently proposed is the addition of a premade block/graft copolymer composed of blocks that are each miscible with one of the homopolymers. These compatibilizers have turned several otherwise incompatible blends into compatible and useful materials. The choice of a block or graft copolymer is based on the miscibility of its segments with the blend components and such a copolymer tends to concentrate at the interface as an emulsifier. However, it appears that all commercial blends made from highly immiscible polymers are compatibilized reactively. That is, a block or graft copolymer is formed by the coupling of reactive groups on each of the immiscible polymers.

Research conducted in our laboratories indicates that blends of anhydride functional polymers and starch could lead to products with useful end-group properties. Bagley et al. studied the properties of various starch-graft-polystyrene blends. Patil and Fanta evaluated the properties of starch-graft-poly(methyl acrylate) films. The reactions of isocyanates with alcohols and carboxylic acids have been well studied and reviewed earlier. Tsubokawa et al. reacted isocyanate-capped polymers with carboxyl and phenolic hydroxyl groups on the surface of carbon black. Polymers such as isocyanate terminated poly(amide-imide) and tolylene diisocyanate-terminated poly(propylene glycol) were readily grafted onto carbon and glass fiber surfaces.

In this paper we report the synthesis of starch-graft-polycaprolactone as a compatibilizer for starch/PCL blends. The starch-g-PCL was synthesized in two steps. First, the isocyanate-terminated PCL was prepared by reacting terminal hydroxyl groups of PCL with diisocyanate. Then the isocyanate-terminated PCL was grafted onto starch through the introduction of urethane links. The compatibilizing effect of this starch-g-PCL was studied in starch/PCL blend by means of tensile strength and blend morphology.

Experimental part

Materials

Polycaprolactone diol (TONE POLYOL 1270) was obtained from Union Carbide Chemicals and Plastics Company, Inc.; the number-average molecular weight of the PCL diol is 4000, the polydispersity index is approximately 2, and the hydroxyl number is 27.8 mg KOH/g. The PCL diol was dried in a vacuum oven at 50°C for 24 h prior to use. Industrial corn starch (SMP 1100) was obtained from Cargill Inc. 2,4-Tolylene diisocyanate (TDI) was obtained from Aldrich Chemical Company. Other solvents used in this study were analytical grade and also obtained from Aldrich Chemical Company.

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Preparation of isocyanate terminated polycaprolactone

Isocyanate-terminated PCL was prepared by reacting TDI with hydroxyl-terminated PCL in bulk. 50 g dried hydroxyl-terminated PCL was added to the reaction flask containing an excess of TDI (7.5 ml) based on the concentration of hydroxyl groups of PCL. The reaction was allowed to take place at 100°C for 3 h under nitrogen atmosphere.

Synthesis of starch-graft-polycaprolactone

Starch (10 g) was first dried in a vacuum oven and then dissolved in dry dimethyl sulfoxide (DMSO) and further dried by azeotropic distillation with toluene. This dried solution of starch was slowly added to isocyanate-terminated PCL in the reaction flask equipped with a stirrer and N₂ inlet. The reaction was carried out at 100°C for 3 h under N₂ atmosphere. The graft copolymer was precipitated in methanol and Soxhlet-extracted with toluene for 20 h to remove any unreacted PCL homopolymer. The yield of the graft copolymer was 89%.

Blend preparation

A starch/PCL blend containing 3 wt.-% of starch-g-PCL was prepared at 120°C in both batch mixer and extruder. The batch mixer was equipped with roller blades (C. W. Brabender Instruments Inc., South Hackensack, NJ, USA) and connected to a variable speed motor through a torque meter.

The extruder used in the blending was a corotating twin-screw laboratory scale extruder (Haake Instruments, Paramus, NJ). The barrel length to diameter ratio was 20:1 and the extruder was maintained at 120°C. The materials were extruded through a capillary die held constant at 110°C. The amount of starch in the blend was 70 wt.-%. Starch/PCL blends without compatibilizer (starch-g-PCL) were made at the same processing conditions for comparison purpose.

Tensile strength

Samples for testing were made by both compression and injection molding to get ASTM-specified (Test method D-638) tensile bars. Compression molding was accomplished using Power-Twin Compression molding equipment (Owatonna Tool Company, MN, USA). Samples were obtained using a force of 12 t at a mold temperature of 120°C. A Boy 50 M injection molding machine with reciprocating screw was used to mold dog-bone samples at an injection pressure of 140 bar and at temperatures of 120 and 130°C.

Characterization

FT-IR spectra were recorded with a Nicolet 7000 series instrument. The spectra were recorded on polymer samples in KBr pellets at 2 cm⁻¹ resolution.

Tensile strength and elongation at break were determined at room temperature using a MTS tensile testing machine (Type T5002) with a cross-head speed of 3 mm/min. Each value reported is an average of four specimens.

The starch/PCL blend morphology were examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For SEM, samples were fractured in liquid nitrogen and stuck to aluminum stubs. The samples were then coated with a gold/palladium alloy by vapor deposition and observed with a JEOL 840II electron microscope. For TEM, samples were microtomed to a thickness of about 100 nm at -70°C using a Reichert-Jung FC4E cryo-ultramicrotome. A JEOL JEM-1210 electron microscope was employed at 120 kV to image the samples.

Results and discussion

Starch-graft-polycaprolactone was synthesized in two steps. The polycaprolactone terminated with the isocyanate group at both ends was prepared by reacting the hydroxyl-terminated PCL with an excess amount of diisocyanate. The isocyanate-terminated PCL was then grafted onto starch through the formation of urethane linkages.

In the IR spectrum of isocyanate-terminated PCL (Fig. 1), the absorption at 2260 cm⁻¹ assigned to the isocyanate groups and the absorptions due to the urethane groups at 3350 cm⁻¹ and near 1520 cm⁻¹ (NH), along with the aromatic ring absorptions at 1600 cm⁻¹, can be observed. These results strongly suggest that the PCL chain ends are terminated with isocyanate groups. The IR spectrum of starch-g-PCL (Fig. 2a) after Soxhlet extraction with toluene for 20 h shows absorption at around 1734 cm⁻¹ assigned to the ester carbonyl, as well as the aromatic ring absorption at 1600 cm⁻¹. However, the absorptions due to the urethane groups at 3300 cm⁻¹ are overlapped with the absorbance of starch hydroxyl groups. The reaction between PCL and starch without diisocyanate was also carried out at the same condition as a
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Fig. 2. FT-IR spectra of starch-g-PCL; (a) starch-g-PCL after Soxhlet extraction, (b) starch/PCL blend without diisocyanate, (c) pure starch

control experiment. The IR spectrum (Fig. 2b) of the control reaction product after extraction resembles that of pure starch (Fig. 2c) which indicates that no reaction occurs between starch and PCL in the absence of diisocyanate.

**Tensile strength**

Tab. 1 shows the tensile strength and percent elongation of uncompatibilized and compatibilized starch/PCL blends. The blend containing compatibilizer shows a 3-fold increase in tensile strength. This results indicate that starch-g-PCL improves the interfacial adhesion between starch and PCL in the blend.

Tab. 1. Tensile strength of uncompatibilized and compatibilized starch/PCL blends

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile Strength</th>
<th>Elongation</th>
</tr>
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<tbody>
<tr>
<td>Starch/PCL</td>
<td>4.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Starch/PCL/Starch-g-PCL(a)</td>
<td>15</td>
<td>8.1</td>
</tr>
<tr>
<td>Starch/PCL/Starch-g-PCL(b)</td>
<td>19</td>
<td>6.5</td>
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\(a\) Contain no compatibilizer.
\(b\) Compression molded.
\(c\) Injection molded.

**Blend morphology**

Generally, the properties of the blends depend on their morphology (phase structure) and the interfacial adhesion between starch and synthetic polymers. Fig. 3 shows the scanning electron micrograph of uncompatibilized (Fig. 3a) and compatibilized (Fig. 3b) starch/PCL blends. It can be seen that in the uncompatibilized blend the starch granules are not homogeneously dispersed in the polymer matrix. However, in the blend containing 3 wt.-\% compatibilizer (Fig. 3b), the starch granules are well dispersed within the polymer matrix. Also, these blends show an improved tensile strength which indicates that the compatibilizer reduces the interfacial energy and thereby produces a finer and more uniform morphology. The dimensions of the dispersed starch phase as revealed by SEM are in reasonable agreement with our earlier study\(^{9}\).

The interfacial adhesion between starch and PCL was observed by transmission electron microscopy. Fig. 4a and 4b shows the TEM photograph of uncompatibilized and compatibilized starch/PCL blends, respectively. In the uncompatibilized blend (Fig. 4a), poor adhesion between the starch and PCL can be observed, as demonstrated by the sharp interface between starch granules and the continuous phase, whereas in the case of compatibi-
lower, indicating that the starch may be partially diffused with the synthetic polymer phase.

**Conclusions**

Polycaprolactone was grafted onto starch through the introduction of urethane linkages by reacting the isocyanate-terminated PCL with starch. Blends of starch and PCL are immiscible and incompatible with poor interfacial adhesion and large phase domains and difficult to process. Starch-g-PCL was found to be quite effective in enhancing the compatibility between starch and PCL. The tensile strength and morphology of the compatibilized starch/PCL blend indicates that the compatibilizer influences significantly the properties of the blend. The toughness of the compatibilized blend increases with the expected improvement of interfacial adhesion and the observed finer phase domains.

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Fig. 4. Transmission electron micrograph of starch/PCL blend; (a) without compatibilizer, (b) with compatibilizer

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