Physical Characteristics of Sweet Potato Pulp/Polycaprolactone Blends

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ABSTRACT: Sweet potato pulp (SSP) obtained as a by-product from starch extraction was blended with polycaprolactone (PCL) to prepare a biodegradable plastic material. In the blends, PCL was used as a reinforcing agent. The SPP/PCL blends were prepared by compression-molding under high temperature and pressure, at different SPP/PCL ratios, and the mechanical properties of the molded specimens were tested. Matrix structure and thermal properties were measured by using a Fourier transform infrared (FTIR) spectrophotometer, scanning electron microscope (SEM), differential scanning calorimetry (DSC), and thermogravimetric analyzer (TGA). Mechanical properties (tensile and flexural properties) were also measured to find the most suitable ratio in a SSP/PCL blend. During compression molding of the SPP/PCL blends under high pressure and temperature, chemical reaction occurred between SPP and PCL, and thus, thermal stability and mechanical strength of the blends increased and water uptake decreased. Also, by increasing the PCL content in the blend, the matrix in the blend became more homogeneous, and consequently, mechanical strength of the molded specimen increased. At 7/3 or 6/4 weight ratio of SSP/PCL, water uptake of the molded specimen became substantially less than that at 8/2. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 861–866, 2004

Key words: SSP/PCL blend; sweet potato pulp; thermal characteristics; water uptake; mechanical strength

INTRODUCTION

Along with modern industrialization, plastic consumption has been increasing worldwide. The large volume of plastics, used particularly for disposables, such as packaging materials for the fast food industry, picnic tableware, and agricultural film, became a public concern because of huge environmental accumulation and resulting pollution.[1] The lack of degradability of plastics impacts significantly the depletion of landfill sites, and thus, the littering problem. Because of these recent trends in solid waste management, there is great interest in biodegradable plastic products, and efforts in developing and using environmentally friendly materials have increased. Development of biodegradable plastics is considered to be one of the ultimate solutions to the environmental problem caused by the disposal of nondegradable plastic wastes.[2–5]

In this respect, biodegradable materials, including polycaprolactone (PCL) and bacterial polyesters such as polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV), were introduced as replacements for nondegradable synthetic plastics. They are biocompatible thermoplastics which may be used as commodity plastics or as specialty polymers for medical application.[6] Among these biodegradable polymers, PCL has good mechanical properties and compatibility with other polymers.[7] Up to the present, however, these biodegradable polyesters, including PCL, are not widely used because of their substantially high unit prices.[8] In contrast, starch, one of the natural biodegradable polymers obtained from agricultural crops, is produced at a relatively low cost.[9] Unfortunately, starch, by itself, exhibits too poor mechanical properties to apply in commodity plastics, although processing with starch may be possible.[10] To enhance the mechanical properties of starch-based products, blending or grafting with functional synthetic polymers is commonly exercised.[9–18]

Sweet potato pulp (SPP) is obtained as a residual by-product in large quantities during the starch extraction process from sweet potato. A part of the SPP is currently used as an animal feed, but most is disposed of into the deep sea or landfill in most Asian countries.

In the present study, the feasibility of SPP as a biodegradable plastic material was examined by blending with PCL. The effect of the PCL particles as

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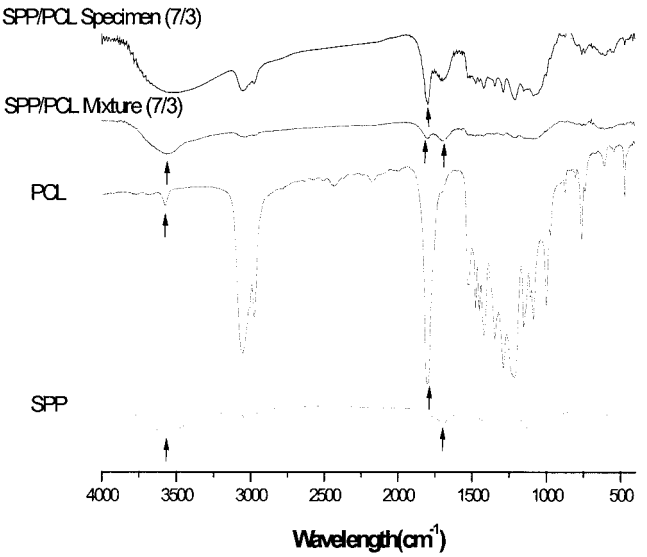

Figure 1 FTIR spectra if SSP, PCL, SSP/PCL mixture, and SSP/PCL blend.

a reinforcing agent, and molding conditions of the SPP/PCL matrix, on the structure, thermal, and mechanical properties of the SPP/PCL blend were investigated.

EXPERIMENTAL

Materials

Dried SPP was obtained from Kwakji Agricultural Ind. Co. (Cheju Island, Cheju, Korea), ground, and screened through a sieve (100 mesh) prior to use. SPP contained mainly cellulose (44.6%) and starch (42.5%) according to an analysis by Megazyme kit (Megazyme International Ireland Ltd., Ireland). Commercial PCL (Tone P-767, M_n 40,000) was supplied by Union Carbide Co. (Danbury, CT).

Preparation of blends

SPP and PCL were mixed at various weight ratios of SSP/PCL (9/1, 8/2, 7/3, and 6/4) by using a Haake Polylab Mixer (Haake Inc., Karlsruhe, Germany) at 100°C and 100 rpm for 20 min. The mixture was cooled, ground, and screened through a 50-mesh sieve. Six grams of the mixture powder was put in a rectangular mold (60 × 25 × 3 mm) and then compressed under a pressure of 75 or 90 KN, at 130 or 150°C for 30 min.

Structural characterization

Fourier transform infrared (FTIR) spectra were obtained from KBr pellets with SSP, PCL, and SSP/PCL blends by using a FTIR spectrometer (Perkin–Elmer Spectrum GX, Beaconsfield, UK).

The morphology of SSP, PCL, and SSP/PCL blends was investigated by using a scanning electron microscope (SEM, JSEM5410LV System, Osaka, Japan). The samples were coated with gold/palladium on an ion sputter coater and observed by using 7 kV secondary electrons.

Thermal analysis

Thermal characteristics of SSP, PCL, and SSP/PCL blends were measured by using a differential scanning calorimeter (DSC6100, Seiko, Chiba, Japan) in a temperature range from −100 to 150°C at a heating rate of 10°C/min, and a thermal gravimetric analyzer (TGA, Mettler TG 50, Greifense, Switzerland) in a temperature range from 20 to 600°C at a heating rate of 10°C/min.

Water uptake

The SPP/PCL blends were vacuum-dried overnight at 40°C and immersed in distilled water (50 mL), for 3 days: the samples were occasionally taken out and weighed after surface water was removed with a paper towel. The percentage weight gain based on initial dry weight was calculated as water uptake.

Tensile strength test

Tensile strength of the SSP/PCL blends was measured by using an Instron Universal Tester (Model 4465, Instron Corp., Canton, MA, USA). The sample size, crosshead speed, and grip distance were 65 × 25 × 3 mm, 2 mm/min, and 13 mm, respectively. The measurements were repeated more than three times, and the average value was obtained.

Flexural test

Flexural test was performed according to ASTM D790 method with an Instron Universal Tester (Model 4465, Instron Corp., Canton, MA, USA).[11] Each specimen was supported on two rollers near the ends, loaded downward by a roller in the middle. The span diameter and length was 5 and 90 mm, respectively. The crosshead speed was 5 mm/min. The measurements were repeated more than three times, and an average value determined.

Statistical analysis

The data were analyzed with a statistical analysis system (SAS 1990). Significant difference was calculated by using Duncan's multiple test.

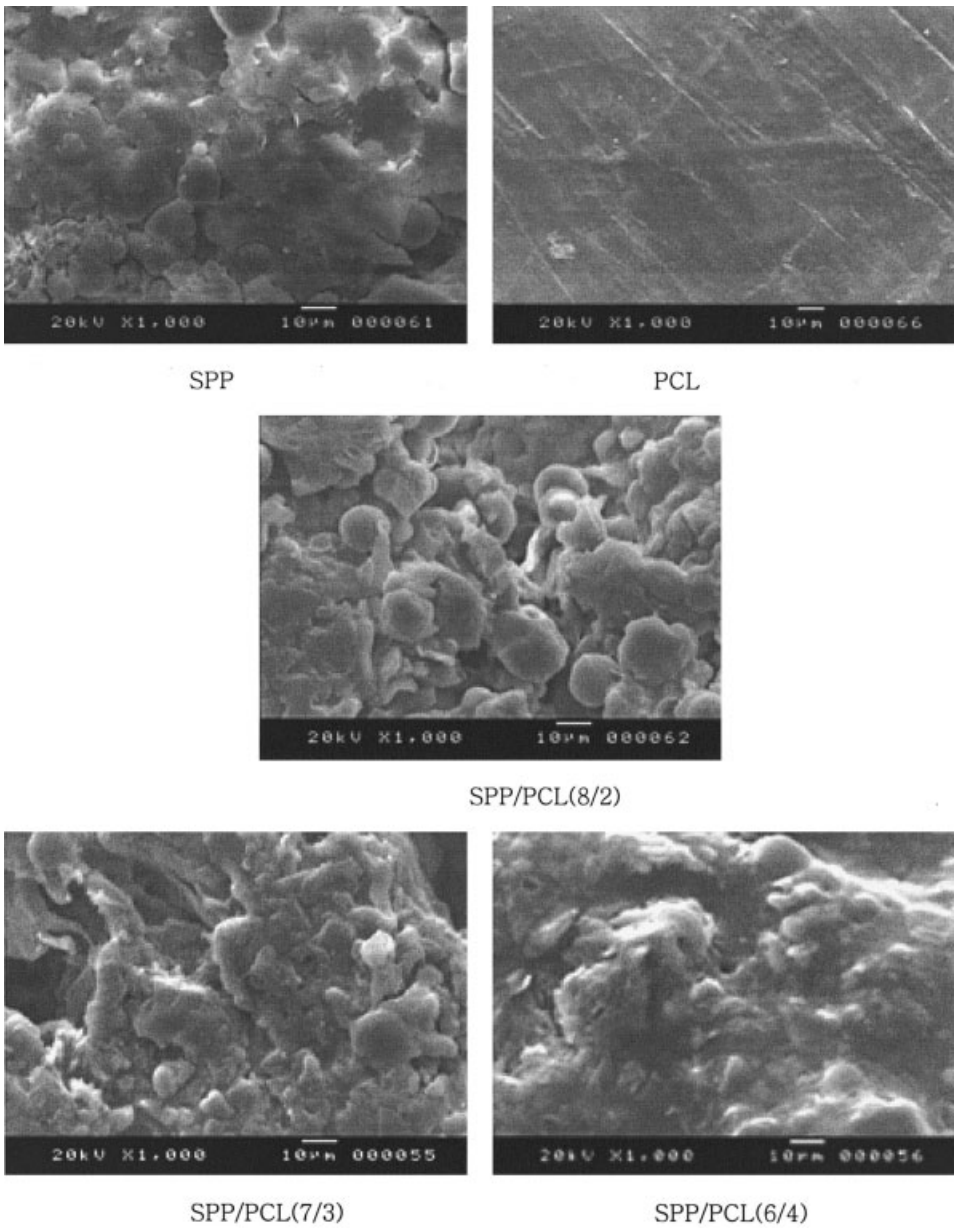

Figure 2 SEM of SSP, PCL, and SSP/PCL blends.

RESULTS AND DISCUSSION

Structural characterization of SSP/PCL blends

When SSP/PCL blend specimens were prepared by compression-molding the blends with pressure and heat, chemical linkages were supposed to occur between SSP and PCL. To confirm the chemical reactions between SPP and PCL, FTIR spectra were measured (Fig. 1). The pure SSP and PCL showed a broad peak in the FTIR spectra, at approximately 3600 cm^{-1} for typical hydroxyl groups, 1650 cm^{-1} for —C—O—C— in SSP, and also 1760 cm^{-1} for internal ester groups of PCL (marked by arrows in Fig. 1). The SSP/PCL mixture with a ratio of 7/3, prior to compression-molding, showed all those characteristic peaks for SSP/PCL (3600, 1650, and 1760 cm^{-1}). Other mixtures with different ratios of SPP and PCL showed similar spectra (data not shown). However, by compression-molding for 30 min at 130°C and 75 KN, the molded specimen of SPP/PCL blend showed an increase of peak intensity at 1760 cm^{-1} (marked by an arrow), which was presumably attributed to carbonyl groups formed by esterification reactions between SSP and PCL. Other SSP/PCL specimens with different ratios showed similar results (data not shown). Among the specimens tested having different ratios, the 7/3 blend showed the greatest increase of the peak intensity at 1760 cm^{-1}. This might suggest that the esterification between SSP and PCL was most effective at the 7/3 ratio of SSP/PCL.

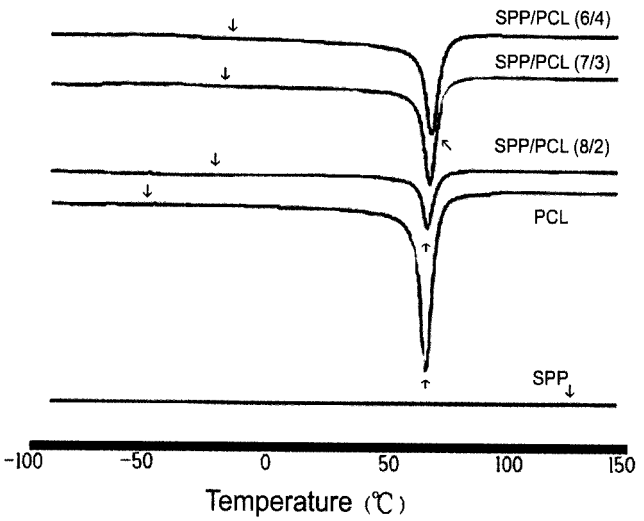

Figure 3 DSC thermograms of SSP, PCL, SSP/PCL, and SSP/PCL blends.

Morphologic characterization

To investigate morphological changes in the molded SSP/PCL blends, the fractured surface of samples was observed by SEM (Fig. 2). The surface of the pure SSP specimen, which was fragile, was not smooth, and starch granules were evident embedded in the pulp matrix. The surface of pure PCL was smooth and uniform. In the case of the SSP/PCL blend at a ratio of 8/2, the starch granules were not completely mixed with PCL. However, for the SSP/PCL at the ratio of 7/3, the starch granules were embedded better, showing few starch granules in the matrix. By increasing the PCL content at a 6/4 ratio, the starch granules were fully embedded in the PCL matrix, and thereby, the surface became smoother and the structure was more uniform.

TABLE I
Glass Transition and Melting Characteristics of the SSP/PCL Blends

	Temperature (°C)				
	T_g	T_o	T_p	T_c	ΔH (J/g)
SPP/PCL(8/2)	−24.3	61.6	65.7	70.2	55.3
SPP/PCL(7/3)	−18.2	61.7	66.7	71.7	49.1
SPP/PCL(6/4)	−17.1	62.3	67.4	72.6	48.6
PCL	−54.1	60.1	65.3	69.9	57.2

Thermal characteristics

Thermal characteristics of the SPP/PCL blends were measured by DSC and TGA (Figs. 3 and 4). As shown in Figure 3, the pure SSP did not show any transition peak, because sufficient water is needed to show the transition peak for starch. The water content of SPP used in our study was about 13%. In a differential DSC curve for SSP (data not shown), a characteristic peak was found at around 131°C as a second-order transition (glass transition) (marked by an arrow in Fig. 3). The PCL showed a sharp endothermic peak for melting at 60°C, and a second-order transition (glass transition) was shown at −54°C (marked by arrows). The SPP/PCL blends displayed an endothermic peak for PCL melting, and glass transitions at slightly higher temperatures than those of PCL (marked by arrows). The increased T_g was attributed to interactions between PCL and SSP during the molding process. The peak temperatures and enthalpy for melting, measured by DSC, are shown in Table I. With an increase in the PCL content from 20 to 40%, the melting enthalpy value decreased from 55.8 to 48.8 J/g. In the case of SSP/PCL 7/3 ratio especially, the enthalpy value decrease was more prominent than those for other specimens. This result may indicate that, at a

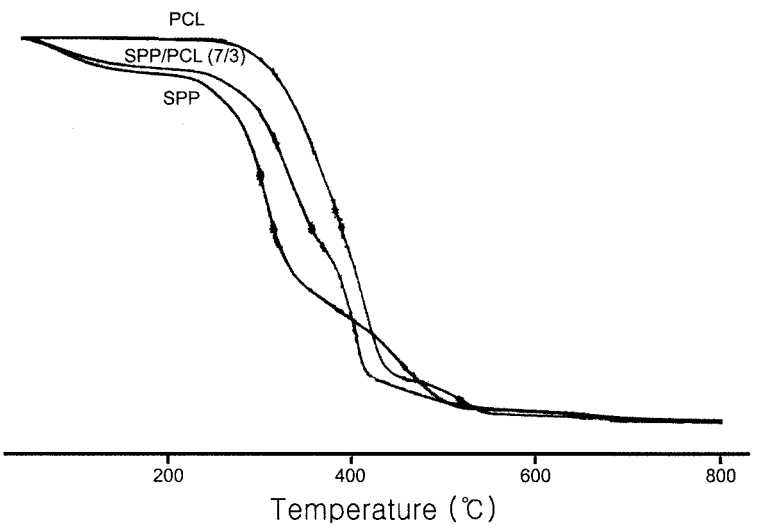

Figure 4 TGA thermograms of SSP, PCL, and SSP/PCL blend (7/3).

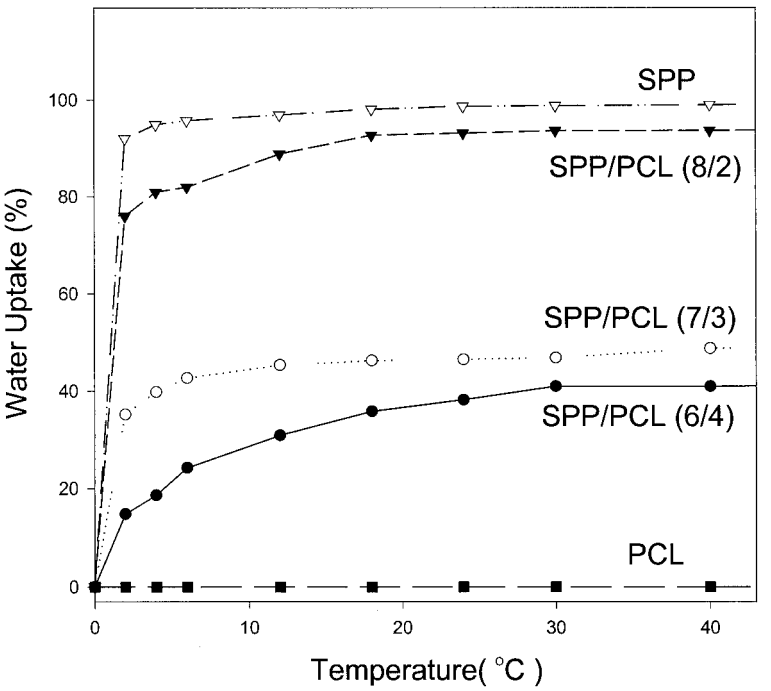

Figure 5 Water uptake of SSP, PCL, and SSP/PCL blends.

ratio of 7/3, the SSP/PCL blend had a significant crystalline change by SPP addition, possibly due to the high miscibility between SSP and PCL.

As shown in Figure 4, the initial degradation temperatures for SSP and PCL was around 250 and 350°C, respectively, and the degradation progressed as the temperature was increased by more than 100°C. By blending SSP, the initial degradation temperature for PCL was shifted to a higher temperature by 20°C, which might indicate that the thermal stability was raised by blending the SSP due to intermolecular interactions.

Water uptake

The water absorbed by SSP/PCL blends was measured as a function of immersion time (Fig. 5). The pure SSP absorbed water rapidly and then easily disintegrated within 1 h. With the presence of PCL, however, the water uptake was progressively reduced be-

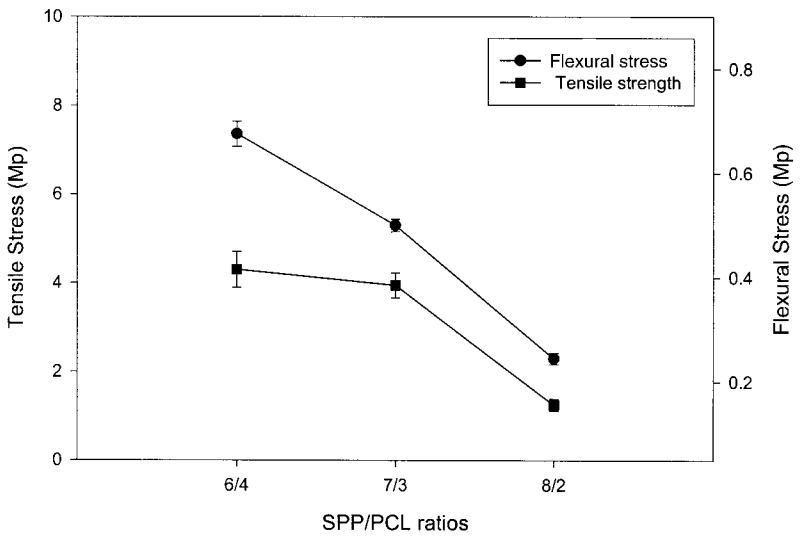

Figure 6 Tensile strength and fracture strength of SSP/PCL blend at different PCL ratios.

cause the pure PCL did not absorb water. By increasing PCL content from 20 to 40%, the water uptake after 24 h immersion decreased from 85 to 40%. Among the SSP/PCL blends with different ratios of SSP/PCL, the specimen at 7/3 ratio showed a prominently reduced water uptake, in comparison to that at 8/2. As discussed for previous data, this result suggests that the 7/3 blend for the SPP/PCL mixture was appropriate for good miscibility, which thereby made a matrix having good water resistance.

Mechanical strength

To investigate the change of mechanical strength for SSP/PCL blends with different ratios, tensile and fracture strengths were measured (Fig. 6). It was impossible to measure the mechanical strength for pure SSP because the molded specimen was too fragile. As shown in Figure 6, there was no significant difference in tensile strength among the specimens of different SPP/PCL ratios but, by increasing the PCL content from 20 to 40%, the fracture stress increased from 2.29 to 7.36 mPa.

CONCLUSION

SSP can be used as a biodegradable material in a blend with PCL. Both polymers can be blended by mixing at high temperature, and the blends can be molded by compression. By increasing the PCL content in the blend, the mechanical strength and water resistance were increased. Among the various SSP/PCL blends of different ratios tested, the blend at a weight ratio of 7/3 exhibited the most effective result, using PCL, on physical and mechanical properties of the molded specimen of SSP/PCL blend.

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