

Soy Protein–Lignosulphonate Plastics Strengthened with Cellulose

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ABSTRACT: A series of biodegradable plastics from soy protein and lignosulphonate (SL) were strengthened with cellulose powder (CP) by melt blending and compression molding. The effects on the morphology and properties of the blends of introducing CP were investigated by wide-angle X-ray diffraction, differential scanning calorimetry, dynamic mechanical thermal analysis, scanning electron microscopy, and tests of tensile and water absorption. It is worth noting that introducing CP obviously improved the mechanical properties and water resistivity of composite

plastics. With an increase in CP content, the tensile strength and Young's modulus of the blend materials increased. The experimental results indicate that a certain degree of miscibility between SL and CP and a strong interaction among various molecules of the components, resulting in strengthened materials. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1685–1689, 2003

Key words: lignin; soy protein; cellulose; biodegradable plastics; mechanical properties

INTRODUCTION

Plastics made from abundant and low-cost soy protein were evaluated as potential substitutes for petroleum-based plastics because of their renewable, biodegradable, and environmentally friendly features. Thus, more and more attention has been directed toward developing soy protein plastics by compression molding, injection molding, and screw extrusion.^{1–4} However, soy protein plastics are brittle and water sensitive. Therefore, chemical and physical modifications have been used to explore improvement in the processibility, mechanical properties, and water resistance of soy protein materials. These modifications include acetylation,⁵ esterification,⁶ and denaturation⁷ of soy protein; guanidine hydrochloride⁸ and sodium dodecyl sulfate modification⁹; incorporation of filler^{10,11}; and blending with other biodegradable polymers.^{12–16}

In a previous work lignosulphonate (LS) was introduced into soy protein plastics by blend and by hot press and hence interacted with the soy protein molecules to form networks with physical crosslinks, resulting in improvement of mechanical properties and a decrease in water sensitivity of soy protein materials, especially simultaneous enhancement of strength and

elongation.¹⁷ In addition, alkaline lignin (AL) as filler was blended with soy protein isolated (SPI) and then compression-molded to form the sheets. The addition of AL enhanced water resistivity of the materials because of the hydrophobic nature of AL and increased the strength of the blends.¹⁸

Cellulose, the most abundant natural polymer, is a hard and inelastic polysaccharide and is recommended as a suitable function material because of its excellent biocompatibility, biodegradability, nontoxicity, reactivity, and so forth.¹⁹ Therefore, long-fiber, short-fiber, and microcrystalline cellulose have been incorporated as filler into soy protein plastics at various levels.¹¹ Typically, cellulose molecules with stiffness strengthened the materials and slightly improved water absorption. Thus, we attempted to enhance the strength of soy protein–lignin plastics by introducing cellulose. In this work the composite sheets from cellulose powder (CP) and an SPI–LS blend were prepared by melt blending in an intensive mixer and then compression molding. The effects of CP on the morphology and properties of the blends were investigated by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), scanning electron microscopy (SEM), and tensile and water absorption tests.

EXPERIMENTAL

Materials

Soy protein isolate (SPI) with a moisture content of 6.8% was purchased from Dupont Yunmeng Protein,

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Ltd. (Hubei, China), and was used without further treatment. Lignosulphonate calcium (LS) was supplied by the Guangzhou Chemistry Institute of Chinese Academy of Sciences (China). Cellulose powder (CP) was obtained from the EMK Co. (Germany), and its viscosity-average molecular weight (M_v) was determined to be 9.74×10^4 by viscometry. Analytical-grade glycerol (GL) was purchased from Shanghai Chemical Co. (China).

Preparation of samples

Mixtures (75 wt %) of SPI-LS (7:3 weight ratio) and 0, 5, 10, 15, 20, 25 parts of CP (100 parts for total mixture) with the addition of 25 wt % GL as plasticizer were mechanically mixed at room temperature, followed by melt blending with an intensive mixer (Brabender Instruments Co., Germany) at 120°C and 50 rpm for 8 min. Subsequently, the resulting blend was placed in a mold covered with two polished stainless-steel plates and then compression-molded using a hot press. The sheet was molded at 160°C and 20 MPa for 5 min and then wind-cooled to about 50°C for 30 min under a constant pressure before removal from the mold to obtain the blend sheets. All the sheets were coded as SL-C0–SL-C5 according to the CP content from 0 to 25 parts.

Characterization

Wide-angle X-ray diffraction (WAXD) patterns of the sheets were recorded on a D/max-1200 X-ray diffractometer (Rigaku Denki, Japan) with Cu K α radiation ($\lambda = 1.5405 \times 10^{-10}$ m), and the samples were examined with 2θ ranging from 6° to 40° at a scanning rate of 10°/min.

Scanning electron microscope (SEM) images were taken on a Hitachi S-570 microscope (Japan). The cross sections of the snapped sheets were coated with gold for SEM observation.

The tensile strength (σ_b), breaking elongation (ϵ_b), and Young's modulus (E) of the sheets were measured on a CMT6503 universal testing machine (Shenzhen Sans Test Machine Co., Ltd., China) with a tensile rate of 10 mm/min, according to ISO6239-1986 (E).

Differential scanning calorimetry (DSC) was performed on a DSC-204 apparatus (Netzsch Co., Germany) under a nitrogen atmosphere at a heating rate of 10°C/min from -150°C to 100°C. Prior to the test the samples were heated from room temperature to 100°C and then cooled to -150°C at a rate of 20°C/min.

Dynamic mechanical thermal analysis (DMTA) was carried out using a DMTA-V dynamic mechanical analyzer (Rheometric Scientific Co., USA) at a frequency of 1 Hz. The temperature ranged from -100°C to 120°C, with a heating rate of 5°C/min.

TABLE I
Results of DSC and WAXD for SL-C Sheets

Sample	$T_g/^\circ\text{C}$	$\Delta C_p/\text{J g}^{-1} \text{K}^{-1}$	χ_c
SPI	—	—	0.31
LS	—	—	amorphous
CP	—	—	0.60
SL-C0	-73.1	0.20	0.28
SL-C1	-71.4	0.15	0.31
SL-C2	-73.1	0.17	0.32
SL-C3	-84.4	0.23	0.35
SL-C4	-79.4	0.24	0.35
SL-C5	-75.5	0.19	0.35

Water absorption

Water absorption was measured according to ASTM standard D 570-81 with minor modifications. The blend sheets were vacuum-dried for 72 h and then dried at 50°C for 24 h in an oven. Subsequently, they were cooled in a desiccator for a few minutes, weighed, and submerged in distilled water at room temperature for 26 h. The extra water on the surface of the sheet after water soaking was removed with a paper towel, and the sheet was then weighed again. The container with water after removing the soaking sheet was placed in an air oven at 50°C for 72 h to evaporate the water, and the water-soluble content was equal to the increase in the container weight. Water absorption (Ab) was calculated by the following:

$$Ab = (W_1 - W_0 + W_{\text{sol}})/W_0$$

where W_1 , W_0 , and W_{sol} are the weights of the sheet containing water, of the dried sheet, and of the water-soluble residuals, respectively.

RESULTS AND DISCUSSION

Crystalline and morphology

The degree of crystalline (χ_c) and WAXD patterns for SL-C sheets with different CP contents are shown in Table I and Figure 1, respectively. Usually, a very miscible blend would result in a decrease in χ_c . However, the SL-C sheets containing CP exhibited higher χ_c than the sheet SL-C0 without CP, but significantly lower than CP, suggesting a certain phase separation between CP and the soy protein–lignin in the composite plastics. Moreover, the relative intensities of crystalline peak at $2\theta = 22^\circ$ assigned to CP increased with an increase in CP content, indicating that CP is immiscible with blends of soy protein and lignin at the molecular level.

The SEM images of the fracture surfaces for the SL-C sheets are shown in Figure 2. It is obvious that the SL-C sheets exhibited more coarse cross sections

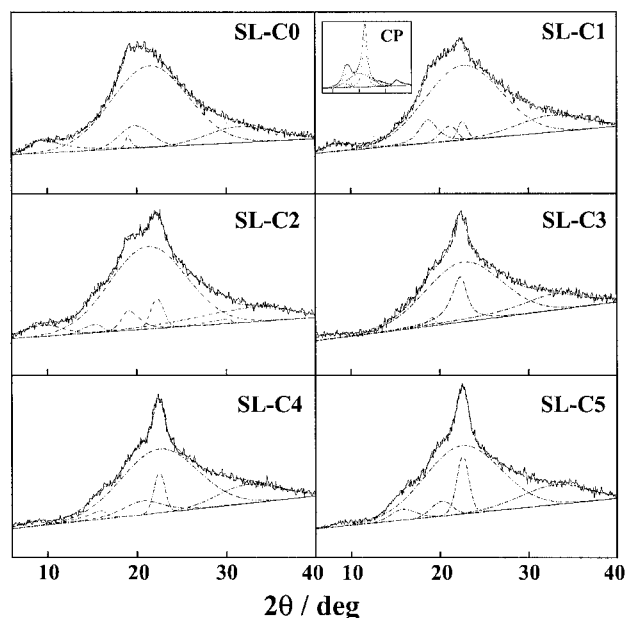


Figure 1 WAXD patterns of the SL-C sheets with various CP contents.

than SL-C0 without CP, suggesting the existence of a certain phase separation because of the addition of CP. At the same time, with an increase in CP content, the cross sections became more and more coarse, indicat-

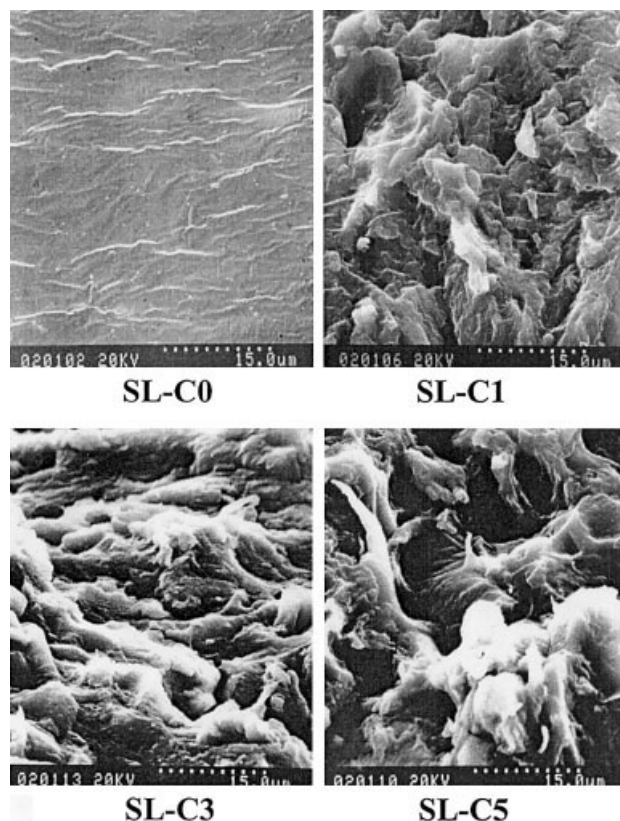


Figure 2 SEM images of the cross sections for the sheets SL-C0, SL-C1, SL-C3, and SL-C5.

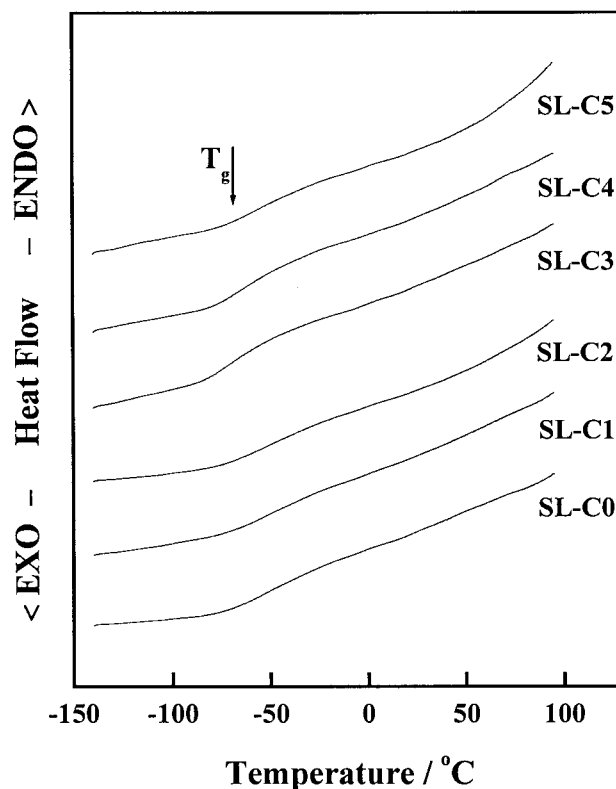


Figure 3 DSC thermograms of the SL-C sheets with various CP contents.

ing that the extent of phase separation expanded. However, it was not observed that the obvious phase separation between CP particles and SL occurred in the structure of the SP-L plastics. Although the fracture surface was very coarse, the whole structure was continuous from the adhesive among components, suggesting the existence of a certain degree of miscibility between CP and SL.

Thermal properties

DSC thermograms of the SL-C sheets are shown in Figure 3, and the glass-transition temperatures (T_g) and change of heat capacities (ΔC_p) are listed in Table I. Compared with the sheet SL-C0 without CP, the T_g of SL-C2–SL-C5 shifted to a low temperature, suggesting the existence of microphase separation in the blends. However, SL-C1 exhibited a slightly higher T_g than SL-C0 without CP, suggesting a certain interaction between SL and CP. At the same time, with an increase in CP content, the T_g decreased until 15 parts of CP and then slightly increased, indicating that the CP content affected the interaction of components and even the motion of molecules or segments.

DMTA curves of the SL-C sheets are shown in Figure 4, and the related information is summarized in Table II. The storage modulus ($\log E'$) for all the tested sheets first increased slightly with an increase of tem-

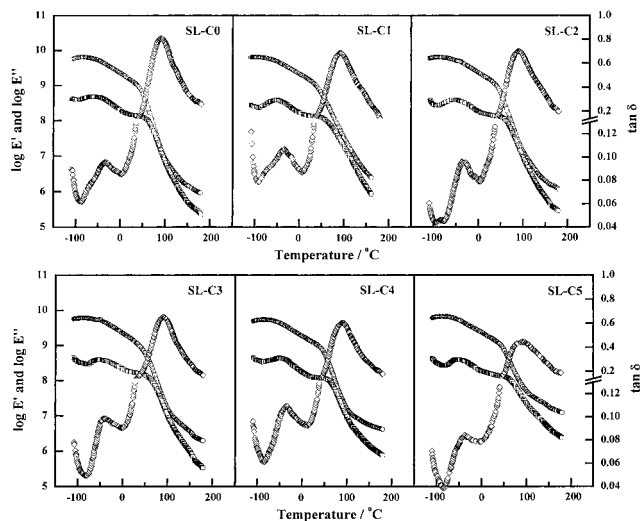


Figure 4 Storage modulus ($\log E'$), loss modulus ($\log E''$), and $\tan \delta$ as functions of temperature for the SL-C sheets.

perature, and then gradually decreased, indicating a complex composite for the SL-C sheets. The increase of $\log E'$ at low temperature for all the sheets mainly resulted from the antiplasticization of GL to SPI, which stiffened SPI molecules.

The $\tan \delta$ - T curves from DMTA can usually be utilized to discern information about molecular and/or segmental motions in polymers. Except for SL-C1, the T_α of the SL-C sheets containing CP was lower than SL-C0, suggesting that the addition of CP resulted in freer motion for the chain or segment of SPI molecules because of a certain phase separation in the materials. The SL plastics exhibited strong interaction with the physical crosslink, and thus little CP dispersed into the SL plastics to form a relatively weak adhesion. However, the higher T_α of SL-C1 may result from relatively strong interaction between LS and SPI molecules. In addition, the loss peak at high temperature resulted from the thermodynamic relaxation of the materials, namely, the slow vaporization of GL and other volatile components. With an increase in CP content, the height of the loss peak decreased, whereas T_{\max} shifted to a low temperature.

TABLE II
DMTA Results for SL-C Sheets

Sample	α Transition		Loss peak	
	T_α (°C)	$\tan \delta$	T_{\max} (°C)	$\tan \delta$
SL-C0	-35.02	0.096	92.11	0.81
SL-C1	-32.78	0.107	92.54	0.68
SL-C2	-36.01	0.096	91.30	0.70
SL-C3	-42.03	0.099	91.16	0.65
SL-C4	-35.77	0.109	90.83	0.60
SL-C5	-36.92	0.084	90.57	0.44

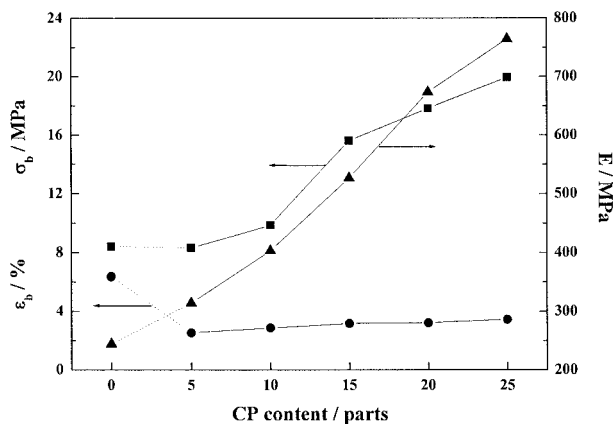


Figure 5 (■) Tensile strength, σ_b ; (●) breaking elongation, ϵ_b ; and (▲) Young's modulus, E ; of the SL-C sheets with various CP contents.

Mechanical properties

The effects of CP content on tensile strength (σ_b), breaking elongation (ϵ_b), and Young's modulus (E) for the SL-C sheets are shown in Figure 5. The σ_b and E of the materials simultaneously increased with an increase in CP content, suggesting that a relatively strong interaction exists between SL and CP. If the extent of phase separation has been very severe, the strength of the materials should decrease. Introducing CP hardly affected the ϵ_b . The results for the mechanical properties supported the existence of a certain degree of miscibility in the composite plastics. Therefore, cellulose plays an important role in the enhancement of strength and rigidity of the materials.

Water absorption

As shown in Figure 6, the introduction of CP can effectively restrict the water absorption of soy protein-

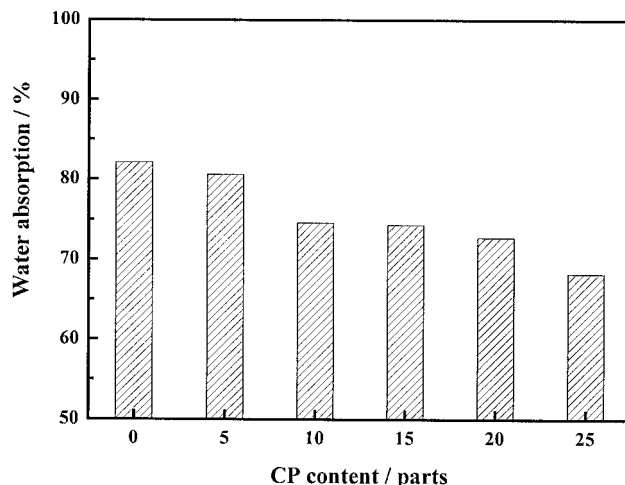


Figure 6 Effects of CP content on water absorption of SL-C sheets immersed in water for 26 h.

lignin plastics, and the water absorption decreased with an increase in CP content. Rigid CP molecules may have formed the framework for the materials and have further effectively weakened the swelling of soy protein in the soy protein-lignin plastics in water.

CONCLUSIONS

A composite plastics based on soy protein and lignosulphonate (SL) was strengthened with cellulose powder (CP) by the process of blending and compression molding. The introduction of CP obviously improved the mechanical properties and hence effectively restricted the water absorption of the blends. With an increase in CP content, tensile strength and Young's modulus of the materials increased, whereas breaking elongation was almost unchanged. A certain degree of miscibility and a strong interaction among soy protein, lignosulphonate, and cellulose in the SL-C sheets resulted in the improvement of the mechanical properties and water resistivity.

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