Preparation and Properties of Water-Resistant Soy Dreg/Benzyl Konjac Glucomannan Composite Plastics

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ABTSRACT: Biodegradable plastics based on soy dreg (SD) were prepared with glycerol as a plasticizer via compression molding at 110–160°C. The effects of the glycerol content and molding temperature on the processability and mechanical properties were investigated. For enhanced water resistivity of the SD plastics, thermoplastic benzyl konjac glucomannan (B-KGM) films were covered on SD sheets in a lamination compression process, and SD/B-KGM (SB) composite sheets were obtained. The structure and properties of the SB sheets were studied with Fourier transform infrared spectroscopy, dynamic mechanical thermal analysis (DMTA), scanning electron microscopy, and tensile testing. The results indicated that the tensile strength of the SB sheets was enhanced to 13.2 MPa in the dry state and to 11.4 MPa in the wet state. The water resistivity of the SB sheets with B-KGM covers increased from 0.03 to 0.86 with an increase in the B-KGM thickness from 0 to 35 μm. The multipeaks of a tan δ relaxation that appeared in the DMTA spectra for SB series sheets were due to multicomponents such as soy protein, cellulose, polysaccharide, and B-KGM. The tan δ transition temperature and the decomposition temperature of cellulose in SB sheets were higher than those in SD sheets without B-KGM covers. This work provided a simple way of improving the compression-molding processability and water resistivity of SD plastics for practical applications. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3790–3796, 2003

Key words: biodegradable; plastics; mechanical properties

INTRODUCTION

With an increase in worldwide environmental pollution caused by nonbiodegradable polymers, research into biodegradable polymers is both necessary and valuable, supporting global sustainability and helping to solve the petroleum crisis and environmental problems.[1] Commercially available soy products, such as soy oil, soy protein isolate (SPI), soy whole flour (SWF), and soy protein concentrate have attracted much attention because of their abundant resources, low cost, and good biodegradability.[2] Recently, these soy products have been considered environmentally friendly materials for adhesives,[3] food,[4] health care,[5] plastics,[6,7] textile fibers,[8,9] and various binders.[10] Soy-based adhesives were first developed in 1923, when a patent was granted for a soy-meal-based glue,[11] and the use of soy proteins as plastics can be traced back to the 1930s and 1940s.[12] Soy plastics made from soy products by compression molding and screw extrusion with glycerol (GL) or water as a plasticizer exhibit moderate strength and good biodegradable performance[13,14] as well as brittleness and water sensitivity.[15] To improve their mechanical properties and water resistivity (R_σ), researchers have blended SPI and SWF with natural or synthetic biodegradable polymers such as starch, sodium alginate,[16] water-blown polyurethane foams,[17] poly(vinyl alcohol),[9] methylene diphenyl diisocyanate modified polycaprolactone,[15] and anhydride-grafted polyesters,[18] modified them by organic or inorganic agents such as acetic anhydride,[19] succinic anhydride,[20] guanidine hydrochloride,[21] epichlorohydrin,[7] urea,[22] and ZnSO$_4$,[7] or crosslinked them with glutaraldehyde[23] and dialdehyde starch[24] to prepare biodegradable plastics with various properties and functions.

Soy dreg (SD) is an abundant byproduct from the isolation process of soy protein and mainly contains cellulose, dietary fiber, and soy protein.[25] Much attention has been paid in recent years to research on making plastics with SPI and SWF, but there has been little effort with SD. The difficult processability is due to there being no effective ways of dissolving or melting SD and the poor R_σ values of SD caused by hydrophilic groups in the protein and cellulose. A way of improving the processability of SD has been studied in

our laboratory,[25] in which SD plastics are prepared with GL as a plasticizer and glutaraldehyde as a crosslinker by compression molding. The tensile strength (σ_b) and R_σ values of sheets coated with a castor-oil-based polyurethane/nitrochitosan IPN coating are enhanced to 24.6 MPa and 0.4, respectively. Recently, benzyl konjac glucomannan (B-KGM) films have been prepared by solution casting, and they exhibit good biodegradability and R_σ.[26] B-KGM is a type of thermoplastic material that can be compression-molded at 130–140°C. To enhance the R_σ values of plastics made from SD, we attempted to use B-KGM to cover SD sheets to prepare composites. Their mechanical properties and R_σ values were investigated, and they are discussed in this article.

EXPERIMENTAL

Materials

All the chemical reagents used were obtained from commercial sources in China. SD, with a moisture content of about 10%, was purchased from Hubei Yunmeng Protein Technologies Co. (China). It was milled with an 80-mesh sieve, scrap iron was removed with a magnet, and the SD was treated with acetone and vacuum-dried for 24 h at 60°C. The main components and their contents in SD were determined: about 77% cellulose, 12% protein, and 11% polysaccharide.[25] Purified konjac glucomannan was supplied by the Zhuxi Konjac Institute of China. GL was analytical-grade. N,N-Dimethylformamide (DMF) was analytical-grade and was dried with molecular sieves before use.

Preparation of the SD sheets

The hot-press device used in this study was made in our laboratory.[27] SD was mixed with GL, pestled in a mortar for 15 min, and finally sealed in plastic to equilibrate for 24 h. Each sheet was compression-molded according to the following procedure: 4.8 g of a premix was placed in a mold and covered with a polished stainless steel plate on either side. The molding temperature was controlled within the range of 110–160°C, and then the pressure was quickly increased from 0.5 to 20 MPa for 1 min and kept there for 6 min. Immediately, the mold was cooled below 50°C with a fan at a rate of 10°C/min. A brown sheet was released from the mold and stored in a desiccator. With different compression temperatures (110, 120, 130, 140, 150, or 160°C), a series of SD plastic sheets with the same 30 wt % GL content were prepared (SD1-3, SD2-3, SD3-3, SD4-3, SD5-3, and SD6-3, respectively). The mixture of SD and GL (70/30 w/w) was coded SD-0. By alterations in the GL content (w/w; e.g., 25.0, 30.0, 35.0, and 40.0%), a series of SD

plastic sheets at the same molding temperature of 130°C were prepared (SD3-2, SD3-3, SD3-4, and SD3-5, respectively).

Preparation of B-KGM

The preparation of the B-KGM films was carried out according to a previous method.[26] Konjac glucomannan (5 g) and 0.1 g of tetramethylammonium iodide were dissolved in 200 mL of water and then were put into a three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a condenser. The flask was placed in an oil bath at 40°C and stirred vigorously, and 50 g of a 40 wt % aqueous sodium hydroxide solution was added dropwise. The resulting alkali–KGM slurry was stirred at 40°C for 1 h before the dropwise addition of 15 g of benzyl chloride. The reaction was performed at 100°C for 2 h, a slightly yellow product was obtained as a precipitate. The precipitate was extracted with ethanol and then washed with ethanol and water; this was followed by vacuum drying at room temperature, and a white powder of B-KGM was obtained. A DMF solution with 20 wt % B-KGM was poured into a mold, and the casting solutions were heated at 60°C for 4 h; dried films were formed that were 10–50 μm thick.

Preparation of the SD/B-KGM (SB) composite

The SB composite sheets were prepared with a lamination technique. The SD3-3 sheets were covered with B-KGM films on both sides and then were compressed in a mold at 130°C and 20 MPa for 6 min. The other process was the same as the preparation of the SD sheets. B-KGM films of different thicknesses (10, 17.5, 25, 27.5, and 35 μm) led to a series of SB composite sheets covered with B-KGM films (SB-1, SB-2, SB-3, SB-4, and SB-5, respectively).

Characterization

Infrared (IR) spectra were recorded with a Fourier transform infrared (FTIR) spectrometer (FTIR-8201, Shimadzu, Japan). The samples were mixed with KBr to laminate. Scanning electron microscopy (SEM) micrographs were taken on a scanning electron microscope (S-570, Hitachi, Japan). The samples were frozen in liquid nitrogen and fractured immediately and then were vacuum-dried and coated with gold for SEM observations of the free surfaces and cross sections. Dynamic mechanical testing was carried out on a dynamic mechanical analyzer (DMTA-V, Rheometric Scientific Co., United States) at a frequency of 1 Hz. The temperature ranged from −100 to 300°C, and the heating rate was 5°C/min.

The mechanical properties of the samples were measured on a universal testing machine (CMT6503, Shen-

zhen SANS Test Machine Co., Ltd., China) according to ISO6239-1986 (E) at a tensile rate of 5 mm/min. The mean values of σ_b and the elongation at break (ϵ_b) were obtained from more than three samples. For the study of R_σ, SB sheets were immersed in water at 25°C for 1 h, and then the σ_b values of the sheets in the wet state were measured. The R_σ values of the sheets were evaluated from σ_b in the dry state ($\sigma_{b(\mathrm{dry})}$) and in the wet state ($\sigma_{b(\mathrm{wet})}$) with the following equation:[27]

$$R_\sigma = \sigma_{b(\mathrm{wet})}/\sigma_{b(\mathrm{dry})}$$

RESULTS AND DISCUSSION

Structure and morphology

FTIR spectra of powders SD and SD-0, sheets SD3-3 and SB-4, and B-KGM are shown in Figure 1. The IR spectrum of B-KGM exhibited characteristic absorptions at 3031 (C—H aromatic stretching), 2873 (—CH$_2$ stretching), 1498 and 1456 (C—H aromatic in-plane deformation), and 739 and 698 cm^{-1} (C—H aromatic out-of-plane deformation, which implied monosubstituted benzene). Meanwhile, the SD powder showed a strong band at 3420 cm^{-1} that was attributed to the stretching vibrations of —OH and —NH. In comparison with the absorption at 3420 cm^{-1} for SD, the peaks for SD-0, SD3-3, and SB-4 broadened and shifted to 3373, 3371, and 3386 cm^{-1}, respectively. This implied that the hydrogen bonds between SD and GL or B-KGM strengthened. The relative intensity of the peaks at 1738 cm^{-1} gradually decreased from SD-0 to SD3-3 and SB-4, suggesting that the free —COOH groups in the soy protein decreased and new bonds occurred in the hot-press process. The absorption of C=O of amide (amide I)[7] at 1646 cm^{-1} for SD moderately shifted to 1652 cm^{-1} for SD-0 and SD3-3 because of the changes in the hydrogen bonds formed by —CONH$_2$ after the introduction of GL and during the process of compression molding. These IR results indicated that there was a certain degree of interaction between SD and B-KGM molecules in the interface, and new bonds occurred during the compression-molding process.

SEM images of the free surfaces and cross sections of SD3-3 and SB-4 are shown in Figure 2. The free surfaces of SD3-3 and SB-4 were smooth, and this indicated a compact microstructure; the cross sections of SD3-3 and SB-4 were rough because of the multicomponents in SD. In the hot-press process, both B-KGM and SD were softened and motioned, and some of the B-KGM and SD molecular chains entangled with one another; this resulted in the interactions between the covers and the substrate materials. Cross-section graphs for SB-4 containing B-KGM covers and SD substrates are shown in Figure 2(E,F). B-KGM covered SD tightly like a layer of skin. As the arrows
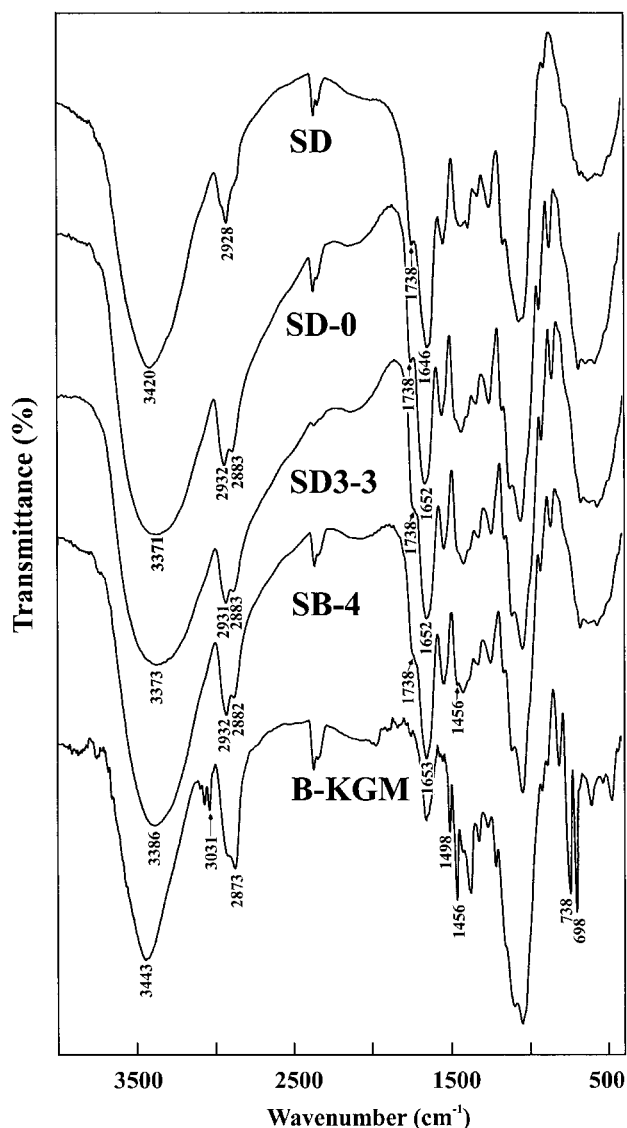

Figure 1 FTIR spectra of SD, SD-0, B-KGM, SD3-3, and SB-4 composite sheets.

show, there was no gap between the skin layer and SD, and this suggested that the interaction between B-KGM and SD was strong. The thickness of the B-KGM covers was measured to be about 27 μm from the SEM image in Figure 2(E).

Dynamic mechanical thermal analysis (DMTA) spectra of SD3-3 and SB series sheets and B-KGM are shown in Figures 3 and 4. The glass-transition temperature (T_g) of B-KGM occurred at 146°C in the DMTA spectrum of a B-KGM film.[26] Multipeaks of tan δ relaxation occurred in SD3-3 and SB sheets because of complex components, such as soy protein, cellulose, polysaccharide, and B-KGM, in the sheets. It has been reported that the tan δ transition temperature range of SPI plastics depends on the moisture and GL content.[7,28] The tan δ relaxation peak at −62°C for the sheets was attributed to the T_g value of thermoplastic
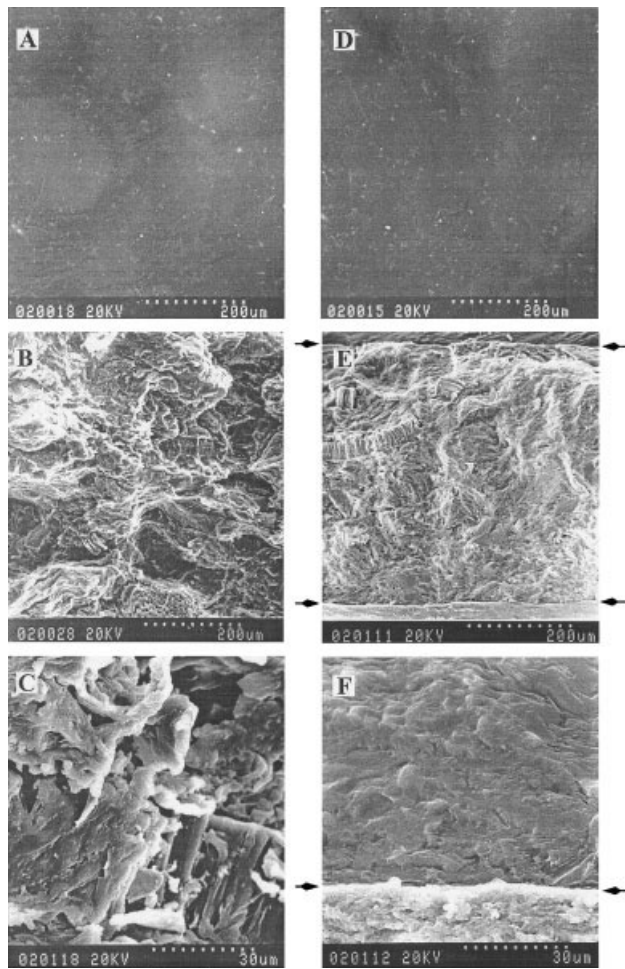
Figure 2 SEM photographs of (A) a free surface of SD3-3, (B,C) cross sections of SD3-3, (D) a free surface of SB-4, and (E,F) cross sections of SB-4.

SPI plasticized with GL; this was proven with DMTA and differential scanning calorimetry (DSC) by Zhang et al.[29] The compression-molding process and the covers of B-KGM hardly changed T_g of the SPI component. However, the peak at 79°C for SD moved to about 110°C for SB-2, SB-4, and SB-5, and this indicated that the covers of B-KGM restricted the mobility of molecular chains coexisting in SD near the interfaces and led to an increase in the tan δ transition temperature. Furthermore, for the same reasons, the thermal decomposition peak of the cellulose appeared at 230°C for SD3-3, whereas that for the SB composite sheets shifted to a higher temperature, from 250 to 270°C. At room temperature, the modulus of the SB sheets was higher than that of SD3-3 because of the interaction between the B-KGM cover and SD.

Properties of the plastic sheets

Figures 5 and 6 show the effects of the compression temperature and GL content on σ_b and ε_b of the SD sheets. The compression temperature is one of the important factors in the hot-press process.[13] In this work, SD with 30 wt % GL was molded into specimens at six different temperatures. σ_b and ε_b of the molded specimens increased with an increase in temperature from 110 to 130°C and then decreased with a further increase in the compression temperature. Therefore, the suitable molding temperature was 130°C. When the GL content was less than 25 wt %, the compression-molding process was very difficult, and the resulting sheets became very brittle. With an increase in the GL content, σ_b decreased, whereas ε_b
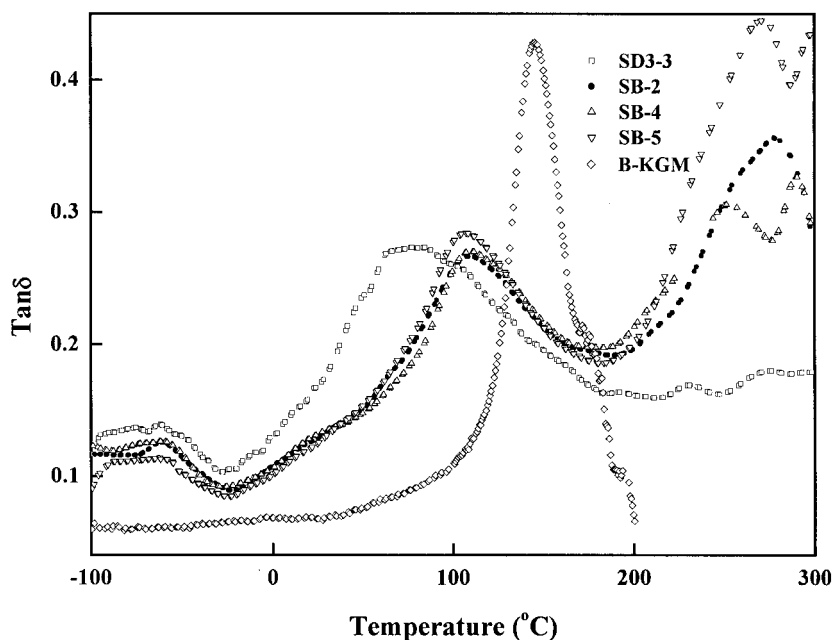

Figure 3 Temperature dependence of tan δ for SD, B-KGM, and SB composite sheets.
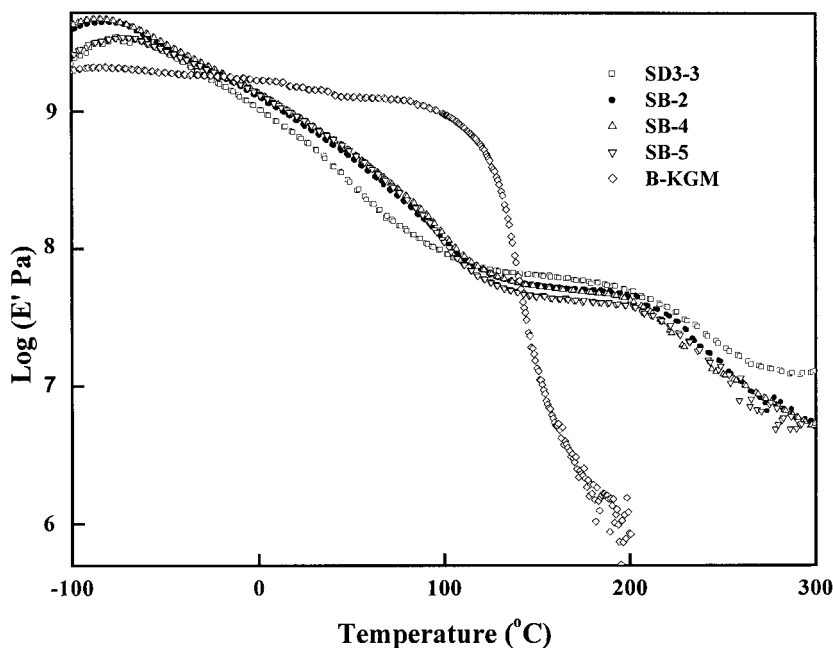
Figure 4 Temperature dependence of the storage modulus (log E') for SD, B-KGM, and SB composite sheets.

increased. Thus, the suitable GL content was in the range of 30–35%; both the processability of SD and the mechanical properties of the resulting sheets were better than those of the others. When the GL content was 30%, an SD sheet at a compression temperature of 130°C had a σ_b value of 8.5 MPa and an ε_b value of 3.8%. The soy protein in SD consists of polar and nonpolar groups with strong intramolecular and intermolecular interactions, such as hydrogen-bonding, dipole–dipole, charge–charge, and hydrophobic inter-

actions.[7] Those interactions between the protein molecules might be reduced, and the flexibility, extensibility, and processability of the SD sheets increased because of the plasticization of GL. Cellulose, as a main component of SD, is hard to compression-mold. However, when the cellulose powder size was about 20 μm, a transparent cellulose plate was prepared with water as a plasticizer during a hot-press treatment.[30] SD is the residual material in the process of extracting SPI from SWF. However, the σ_b value of the
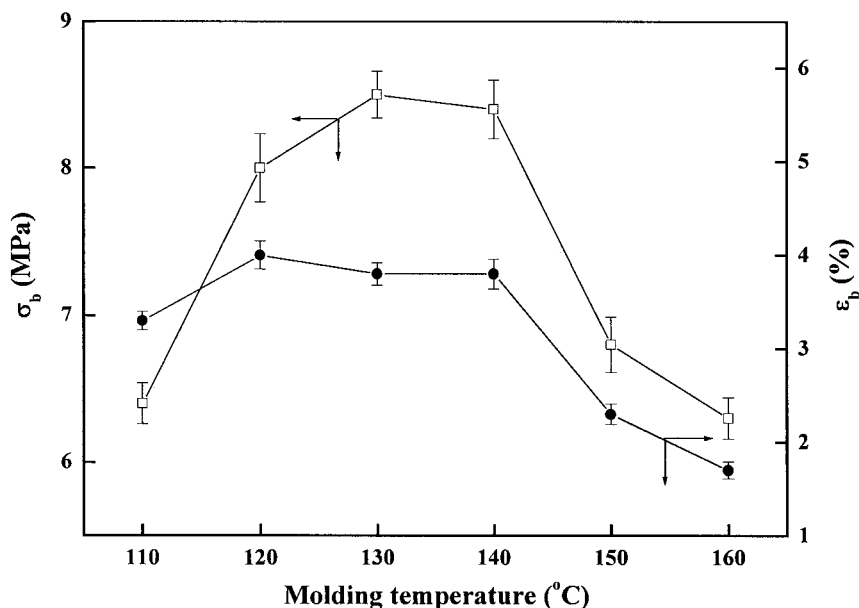

Figure 5 Effect of the compression temperature on σ_b and ϵ_b of SD series sheets.
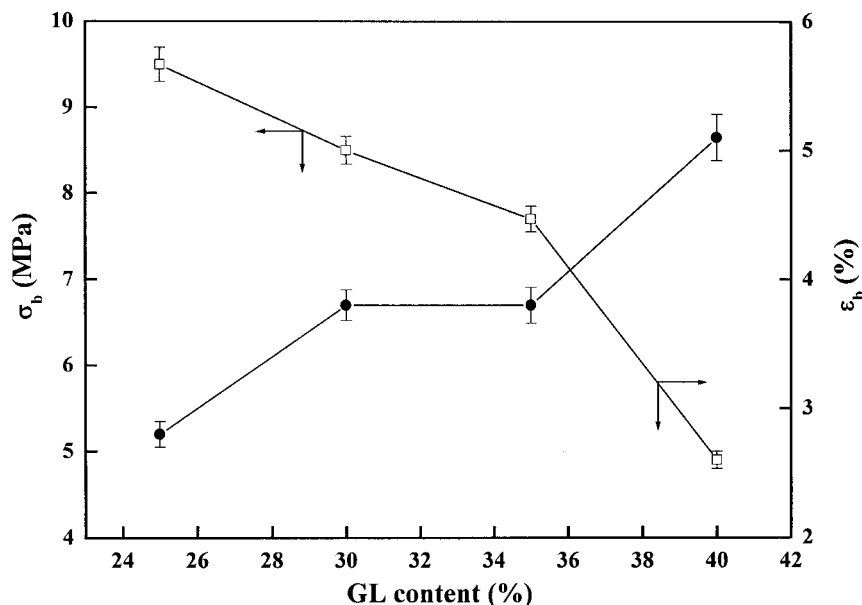
Figure 6 Effect of the GL content on σ_b and ε_b of SD series sheets compression-molded at 130°C.

SD3-3 sheet was higher than that of the SPI sheet compression-molded with the same GL content,[27] and this implied a strengthening function of the cellulose components in SD.

The σ_b and R_σ values of SD3-3, B-KGM, and SB sheets and the thicknesses of B-KGM films covering SD3-3 are listed in Table I. The σ_b and R_σ values of the SB sheets were significantly higher than those of the SD3-3 sheet. When the thickness of a B-KGM film covering SD3-3 increased beyond 17 μm, σ_b of SB sheets in a dry state increased beyond 13 MPa. R_σ of the SB sheets with B-KGM covers increased from 0.03 to 0.86 with an increase in the B-KGM thickness from 0 to 35 μm. When the SD3-3 sheet without B-KGM covers was soaked in water, the water directly attacked the surface, penetrated the interior, and led to rapidly decreasing strength. However, after being covered by hydrophobic B-KGM films, the composite sheets behaved as if they were wearing water-resistant clothes; this resulted in an enhancement of R_σ. Therefore, the composite could be used as a water-resistant and environmentally friendly material in one-off bottles, boxes, and other packages.

CONCLUSIONS

A soy-product-based plastic sheet (SD3-3), which had relatively good mechanical properties, was prepared from SD with 30 wt % GL as a plasticizer under a pressure of 20 MPa at 130°C. σ_b of the plastic SD sheet was higher than that of an SPI sheet prepared with the same GL content because of the strengthening effect of the cellulose components in SD. Moreover, water-resistant and biodegradable composite plastic sheets of SB were obtained by SD3-3 sheets being covered by thermoplastic B-KGM films via compression molding at 130°C. The occurrence of multipeaks of the tan δ transition in the DMTA spectra for SD and SB sheets resulted from the multicomponents of the materials. Meanwhile, the B-KGM covers restricted the mobility of some molecules in SD, and this resulted in an increase in the tan δ transition temperature of the protein component and the decomposition temperature of the cellulose component for the SB sheets. In comparison with those of the SD3-3 sheet, σ_b and R_σ of the SB sheets with B-KGM thicknesses of 18–35 μm in the dry and wet states were obviously improved.

TABLE I
σ_b and R_σ for SD, B-KGM, and SB Composite Sheets

Sample code	SD3-3	SB-1	SB-2	SB-3	SB-4	SB-5	B-KGM
$d_{\text{B-KGM}}$ (μm)	0	10	17.5	25	27.5	35	25[a]
$\sigma_{b(\text{dry})}$ (MPa)	8.5	10.4	13.8	13.2	13.8	13.2	57.7
$\sigma_{b(\text{wet})}$ (MPa)	0.26	3.3	6.0	8.5	10.3	11.4	54.7
R_σ	0.03	0.32	0.43	0.64	0.75	0.86	0.95

$d_{\text{B-KGM}}$ = the mean value of single-side thickness for B-KGM films covered on the SD3-3 sheet.
[a] The thickness of the pure B-KGM film chosen to be tested.

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