

Ways of Strengthening Biodegradable Soy-Dreg Plastics

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ABSTRACT: Biodegradable plastics (GSD) based on soy dreg (SD) were prepared by compression-molding, with glycerol as the plasticizer and glutaraldehyde (GA) as the cross-linker. The structure and properties of the GSD sheets were investigated by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), scanning electron microscope (SEM), and tensile test methods. The results indicate that when GA content was 6.8%, the tensile strength (σ_b) of the sheet reached the maximum value of 14.5 MPa. Moreover, the strength and water resistance of the sheets coated with castor-oil-based polyure-

thane/nitrochitosan interpenetrating network (IPN) coating were significantly enhanced to 24.6 MPa in the dry state and 9.8 MPa in the wet state. Simultaneously, the test of biodegradability of the GSD sheet in a mineral salts medium containing microorganisms and agar proved that GSD could be fully biodegradable. This work has provided a novel way to utilize low-cost SD to prepare biodegradable plastics. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 422–427, 2003

Key words: biodegradable; plastics; mechanical properties; IPNs

INTRODUCTION

Petroleum-based plastics dominate today's society because of their high strength, light weight, low cost, easy processibility, and good water barrier properties. However, most of these materials result in an increase in environmental pollution because of their non-biodegradability.¹ Many renewable polymers, such as cellulose, starch, polysaccharides, and protein, may be decomposed into CO₂, water, and organic molecules by microorganisms in the soil, corresponding to the definition of the biodegradable material.² Therefore, the development of new plastics from the renewable resource has drawn much attention, and many applications are focused on soy protein.³ Recently, soy protein has been considered as an alternative to petroleum polymer in the field of adhesives, plastics, and various binders.

Use of soy protein as plastics can be traced back to the 1930s,^{4, 5} and the usual ways to process soy protein plastics are compression-molding and screw-extrusion.^{6, 7} Soy protein plastics exhibit moderate strength

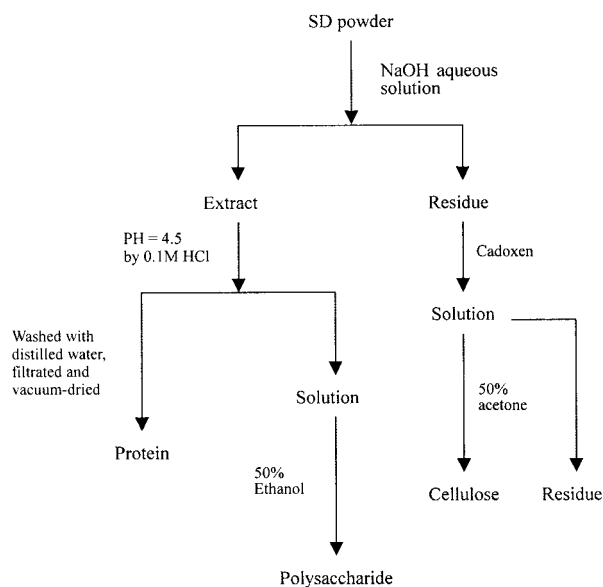
and good biodegradable performance, but they are also brittle and water sensitive.⁸ To improve their mechanical properties and water resistances, soy protein plastics were developed by blending, chemical modification, or cross-linking. Soy protein isolate (SPI) was blended with polycaprolactone (PCL) compatibilized by methylene diphenyl diisocyanate (MDI), and then compression-molded to obtain sheets with relatively higher strength and water resistance.⁸ Acetylated soy protein that was compression-molded at higher temperatures exhibited higher tensile strength (1.95–2.46 MPa in dry state; 0.443–0.789 MPa in wet state created by soaking in distilled water at 23°C for 5 min) and lower water permeability than those at compression-molded at 93.3°C.⁹ It is worth noting that cross-linking with glutaraldehyde (GA) can significantly enhance the tensile strength and breaking elongation of SPI films in the casting process.¹⁰ In addition, soy whole flour (SWF) has been prepared as a biodegradable plastic by compression-molding, but the materials are brittle and exhibit tensile strength of <8 MPa.^{11, 12}

Soy dreg (SD) is an abundant by-product from the isolation process of soy protein that contains mainly soy protein and cellulose. The cost of SD is much lower than that of SPI, and it is consequently usually used as animal feeds. Thus, utilizing SD for biodegradable plastics will be beneficial to alleviate the environmental problems and improve the value of agricultural by-products. As is well known, cellulose is also biodegradable and can act as a reinforcing component in composite material.^{13, 14} Although SD contains these available components, it has been far

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Scheme 1 The isolation process of SD.

from use in a material field until now. In this work, SD was expected to prepare biodegradable plastics with good tensile strength and water resistance. Furthermore, the effect of GA as a cross-linker, as well as the mechanical properties and water resistance of the protein plastic coated with polyurethane/nitrochitosan interpenetrating polymer network (IPN) coating were investigated. The structure and properties were characterized by spectroscopy methods, scanning electron microscope (SEM), and thermal analysis. At the same time, the biodegradability of the materials was evaluated from the conversion of polymeric C into CO₂.

EXPERIMENTAL

Materials

Soy dreg (SD) with ~80% moisture and soy protein isolate (SPI) were purchased from Hubei Yunmeng Protein Technologies Company of China. SD was treated with acetone and then vacuum-dried for 24 h at room temperature before use. The components of SD were isolated by the chemical method shown in Scheme 1, and the main components were estimated to be ~75% cellulose, 12% soy protein, 11% polysaccharide, and 2% residue. Glycerol (Shanghai Chemical Company, China) was of analytical grade. Glutaraldehyde (Guangdong Shantou Xilong Chemical Plant, China) was of analytical grade and contained 25% aqueous solution without further treatment.

Preparation of plastics sheets

A hot-press device was made in our laboratory.¹⁵ SD was mixed with glycerol and glutaraldehyde (GA). When each reagent was added, the premix was

ground by hand with a mortar and pestle for 15 min at room temperature. The ground premix was then stored in a refrigerator at 5°C for 2 days and then compression-molded. The temperature of mold was controlled at 120°C, and the pressure was quickly increased from 0.5 to 20 MPa for 1 min. The sample was kept at 120°C for 10 min, and then wind-cooled to 50°C in 0.5 h to obtain a brown and translucent sheet, which was stored in a desiccator. By adding 25.0, 33.3, 40.0, 45.5, and 50.0% glycerol to the SD, a series of PSD plastic sheets was prepared and coded as PSD, PSD-1, PSD-2, PSD-3, and PSD-4, respectively. By changing GA content to 2.8, 5.0, 6.8, 8.3, and 9.6%, a series of cross-linked GSD sheets with the 25% glycerol content (3 g of SD/1 g of glycerol) was obtained and coded as GSD-1, GSD-2, GSD-3, GSD-4, and GSD-5, respectively. SPI sheets with the same contents of glycerol and GA were compression-molded at the same condition, and coded as GSPI-1, GSPI-2, GSPI-3, GSPI-4 and GSPI-5, respectively, and the sheet from SPI without GA was coded as PSPI.

Preparation of sheets coated with polyurethane/nitrochitosan

According to our previous method,¹⁶ polyurethane/nitrochitosan (PUNC) coating was prepared by mixing 4 g of castor oil-based polyurethane (PU) prepolymer, 0.09 g of 1,4-butanediol (BDO), and 0.46 g of nitrochitosan in 11 g of ethyl acetate. The PUNC coating was diluted with ethyl acetate to 3.9% solid content and then used to coat both sides of the GSD-3 sheet. The coated sheet was cured at 80°C for 50 min to obtain a water-resistant NPU-GSD-3 sheet.

Characterization

The infrared (IR) spectra of the sheets were measured on a Fourier-transform infrared (FTIR) spectrometer (Spectrum One, Perkin-Elmer Company) using the accessory of attenuated total reflection (ATR) pool and a KBr plate with a resolution of 4 cm⁻¹. The scanning ranges were 400–4000 cm⁻¹ for FTIR and 650–4000 cm⁻¹ for ATR-FTIR.

X-ray diffraction (XRD) was measured with an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Japan) with Cu K α at 40 KV and 30 mA. The diffraction angle (2 θ) ranged from 6° to 40°.

Scanning electron microscope (SEM) micrographs were taken on a S-570 microscope (Hitachi, Japan). The sheets were frozen in liquid nitrogen, snapped immediately, and then vacuum-dried. The surface and cross-section of the sheets were coated with gold for SEM measurement.

Dynamic mechanical thermal analysis (DMTA) was carried out using a DMTA-V dynamic mechanical analyzer (Rheometric Scientific Company) at a frequency

of 1 Hz. The temperature ranged from -100 to 250°C , and the heating rate was $5^{\circ}\text{C}/\text{min}$.

Measurement of mechanical properties

The tensile strength (σ_b) and breaking elongation (ε_b) of the samples were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Company Ltd., China) according to ISO6239-1986 (E) with a tensile rate of $5\text{ mm}/\text{min}$. To study the water resistance of materials, the sheets were immersed in water at 25°C for 1 h. The water resistance (R_σ) of sheets were evaluated from $\sigma_{b(\text{dry})}$ value in dry state and $\sigma_{b(\text{wet})}$ in wet state by the following equation:

$$R_\sigma = \sigma_{b(\text{wet})} / \sigma_{b(\text{dry})} \quad (1)$$

Biodegradation test in medium

Biodegradation tests were carried out according to our previous work.¹⁷ *Fusarium moniliforme* (AF 93017, AF 93018), *Chaetomium divaceum* (AF 93119), and *Trichoderma viride* (AF 93252) were supplied by China Center for Type Culture Collection (CCTCC) at Wuhan University. A mineral salts medium was prepared containing $0.7\text{ g}/\text{L}^{-1}$ of KH_2PO_4 , $1.0\text{ g}/\text{L}^{-1}$ of NH_4NO_3 , $0.002\text{ g}/\text{L}^{-1}$ of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $0.002\text{ g}/\text{L}^{-1}$ of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and $0.005\text{ g}/\text{L}^{-1}$ of NaCl , with pH adjusted to 6.5 by the addition of a $0.01\text{ mol}/\text{mL}^{-1}$ NaOH aqueous solution. The medium was sterilized by autoclaving at 120°C for 20 min. The agar media were prepared by adding 15 wt % of the mineral salts medium to a sterilized Petri plate to provide a solidified agar layer. The autoclaved sheets ($6 \times 4\text{ cm}^2$) were placed on the surface of the agar, and then the strain pore suspension ($0.2\text{ mL}/\text{dish}$, 10^6 pore mL^{-1}) was spread on the surface of the sheets. Both the agar plate and beaker containing 50 mL of $0.03\text{ mol}/\text{mL}^{-1}$ $\text{Ba}(\text{OH})_2$ solution as the CO_2 absorbent was placed into a 2500-mL desiccator. The desiccator was closed and incubated at 30°C for 28 days. The CO_2 absorbent was titrated with 0.025 mol mL^{-1} of oxalic acid. Blanks for these trials were prepared identically except for the sheet addition. The experimental values of net CO_2 evolution ($\text{CO}_{2,\text{EXP}}$) were calculated according to the volume of consumed oxalic acid in titration of a sample and a blank control. The theoretical values of CO_2 evolution ($\text{CO}_{2,\text{THE}}$) were obtained from element analysis. The extent of biodegradation (R) was given by:¹⁷

$$R = (\text{CO}_{2,\text{EXP}} / \text{CO}_{2,\text{THE}}) \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

Comparison of GSD and GSPI sheets

ATR-FTIR spectra of the PSD, GSD-3, and GSPI-2 sheets are shown in Figure 1. The N—H bending and

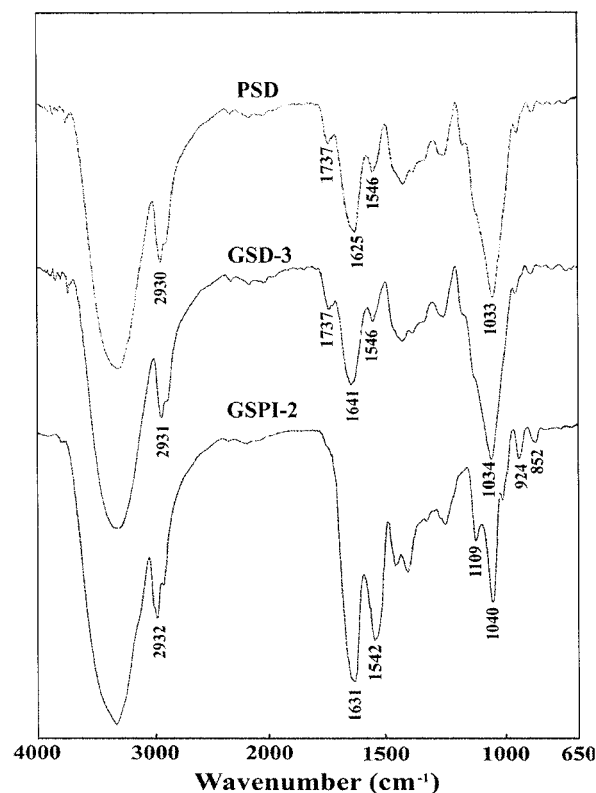


Figure 1 ATR-FTIR spectra of PSD, GSD-3, and GSPI-2.

C—N stretching vibration of peptide bands at 1542 cm^{-1} were attributed to SPI in the GSPI-2 sheet, and the strong stretching vibration of C=O was at 1631 cm^{-1} . The peak at 1546 cm^{-1} for the GSD-3 and PSD sheets significantly decreased because of the relatively low protein content. Moreover, the relatively high peak at 1034 cm^{-1} is assigned to C—OH of cellulose in the PSD and GSD sheets, suggesting that they were mainly composed of cellulose. The band at 1737 cm^{-1} was assigned to ester bonds formed by cellulose and polysaccharide with protein in the GSD-3 and PSD sheets, which is absent in GSPI sheet. This result suggests that the esterification took place in the surface of the GSD-3 and PSD sheets during heating compression.

SEM images of the surface and cross-section for the GSD-3 and GSPI-2 sheets are shown in Figure 2. Although the GSD-3 sheet contained cellulose, soy protein, and polysaccharide, its surface and cross-section exhibited smooth and homogeneous structure similar to that of the GSPI-2 sheet prepared from mostly pure protein. The SEM results supported the conclusion from IR data that indicate that the chemical reaction in the GSD-3 sheet enhanced the miscibility among the different components.

The dependencies of σ_b and ε_b on the GA content of the GSD and GSPI sheets are shown in Figures 3 and 4, respectively. On the whole, the σ_b values of the GSD sheets were higher than those of GSPI, but ε_b values

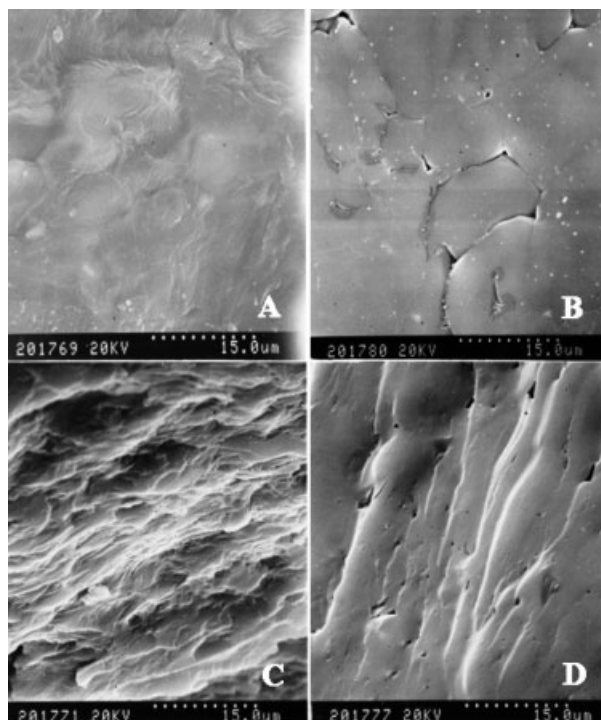


Figure 2 SEM images of the surfaces of (A) GSD-3 and (B) GSPI-2, and the cross-sections of (C) GSD-3 and (D) GSPI-2.

were lower than those of the GSPI. This difference can be explained by the presence of the cellulose component, which is a kind of relatively rigid molecule that plays a role in enhancement of the strength.

Effect of glycerol and glutaraldehyde

Glycerol is usually used as plasticizer of natural polymers, such as cellulose, starch, and protein plastics, etc., and its content in materials directly relates to the properties of the materials. The effects of glycerol content on σ_b and ϵ_b of the PSD sheet are shown in Figure 5. With an increase of glycerol content, σ_b

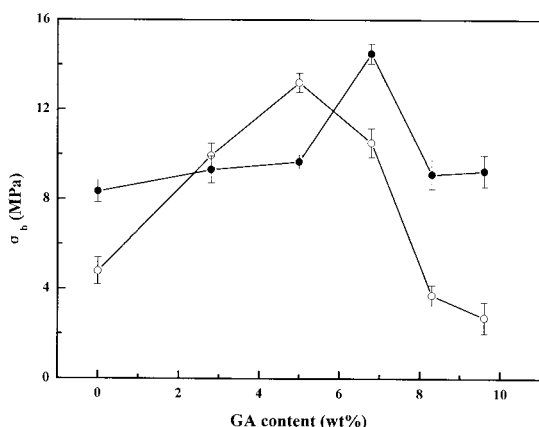


Figure 3 Effect of GA content on tensile strength (σ_b) of (●) GSD and (○) GSPI sheets.

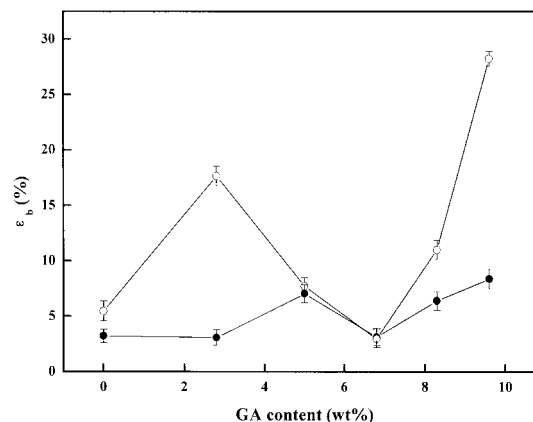


Figure 4 Effect of GA content on breaking elongation (ϵ_b) of (●) GSD and (○) GSPI sheets.

decreased but ϵ_b increased. Therefore, the glycerol content from 33 to 40% was determined to be the most suitable content.

As shown in Figures 3 and 4, the σ_b values of the GSD sheets were significantly higher than those of the PSD sheets due to the cross-link effect of GA, but ϵ_b values of the GSD sheets were close to those of the PSD sheets. With an increase of GA content, the σ_b of the GSD-3 and GSPI-2 sheets reached the maximum values of 14.5 and 13.2 MPa, respectively, and then decreased. In this case, the cross-link reaction was not complete, so that unreacted GA in the sheets containing higher GA content plays a role in plasticization, resulting in lower strength. The ϵ_b of two kinds of sheets increased with an increase of GA content, indicating that a cross-linking network was formed.

DMTA curves of the GSD-3, PSPI, and PSD sheets are shown in Figure 6. The $\tan \delta$ loss peak at -64°C for the PSPI sheet was attributed to the glass transition of soy protein, and its peak intensity was higher than those of the GSD-3 and PSD sheets. There were multiple peaks from 75 to 175°C in the DMTA curve of the

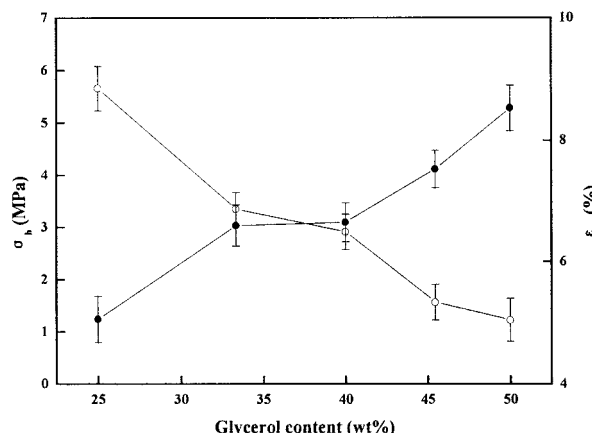


Figure 5 Effects of glycerol content on tensile strength (σ_b , ○) and breaking elongation (ϵ_b , ●) of PSD sheets.

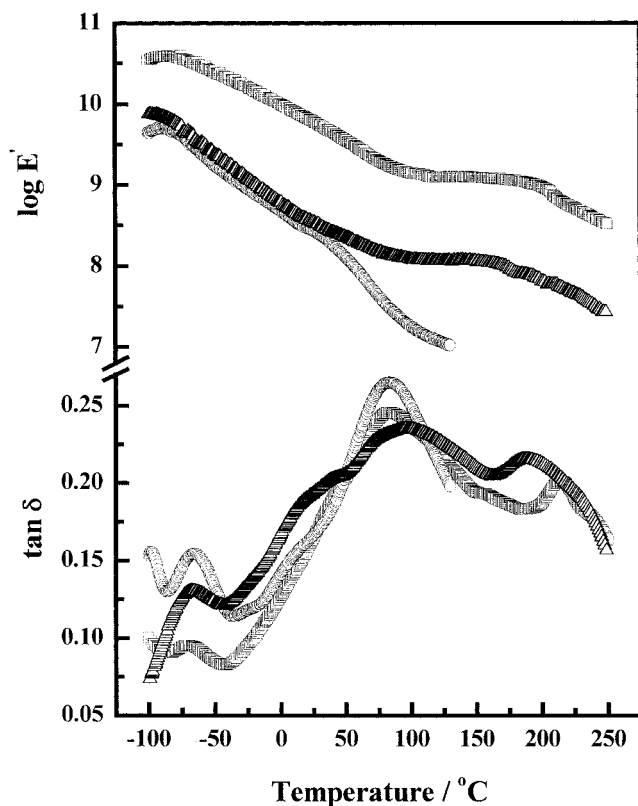


Figure 6 DMTA curves of the (□) GSD-3, (○) PSPI-2, and (△) PSD.

PSD due to the different components. However, the DMTA curve of the GSD-3 sheet showed obvious peaks at 82 and 214°C, corresponding to the moisture loss⁷ and thermal decomposition of the cellulose, respectively. Obviously, the thermal stability and storage modulus (E') of the GSD-3 sheet was higher than that of PSD due to the effects of cross-linking structure.

The XRD patterns of the GSD-3 and PSD sheets and SD powder are shown in Figure 7. A new crystal peak appeared at 24°, which is absent from the XRD patterns of protein¹⁵ and cellulose¹⁸ and may be caused by the polysaccharide component. The peak intensity at 24° for the GSD-3 sheet decreased because of the breaking of crystal due to the cross-linking of GA.

The incubation time dependence of CO₂ evolution for the PSD and GSD-3 sheets is shown in Figure 8. The extent of biodegradation of the GSD-3 sheet was slightly lower than that of the PSD sheet, indicating that the GSD-3 sheet cross-linked with GA also exhibited good biodegradability. The leveling off of the curves at 70% R is believed to indicate that total degradation results in conversion of 70% of the carbon to CO₂ and the other 30% to microorganism mass, etc.

Effect of IPN coating

The IR spectra of the NPU-GSD-3 sheet and the mixture of PU/NC coating and GSD-3 sheet are shown in

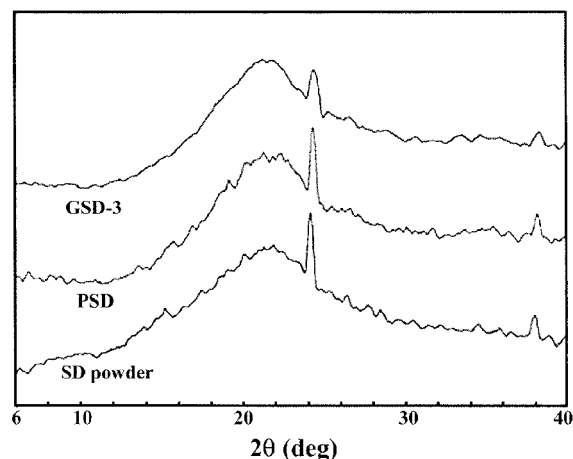


Figure 7 X-ray diffractograms of GSD-3, PSD sheets, and SD powder.

Figure 9. The absorption band at 2290 cm⁻¹ assigned to the residue of —NCO groups of the PU/NC coating almost disappeared in the NPU-GSD-3 sheet because of the reaction between PU and cellulose or polysaccharide. At the same time, a new band at 1740 cm⁻¹, assigned to aromatic esters, occurred in this case. Thus, it is deduced that chemical bonds exist between PU/NC coating and SD, resulting in the strong bonding of the coating layer and GSD-3 sheet.

As shown in Table I, the mechanical properties of the NPU-GSD-3 sheet were significantly higher than those of the GSD-3 sheet, indicating that the IPN coating plays an important role in enhancement of the strength and water resistance of the protein plastics. When the GSD-3 sheet was soaked in water for long time, the water directly attacked the surface layer and then penetrated into inner of the GSD-3 sheet. In this case, in the absence of esterification between cellulose,

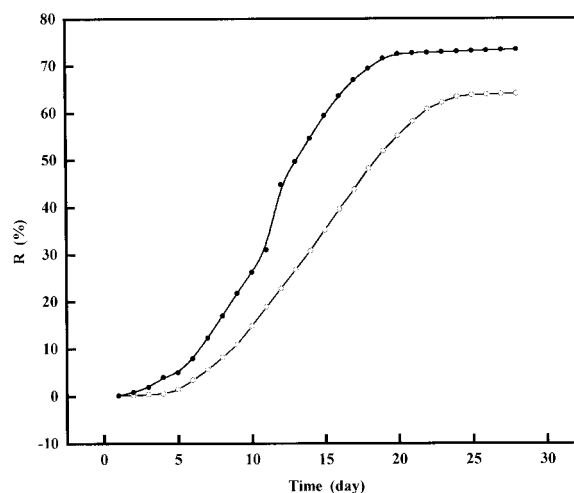


Figure 8 CO₂ evolution (R) dependence on incubation time from the (●) PSD and (○) GSD-3 sheets in an aqueous medium at 25°C.

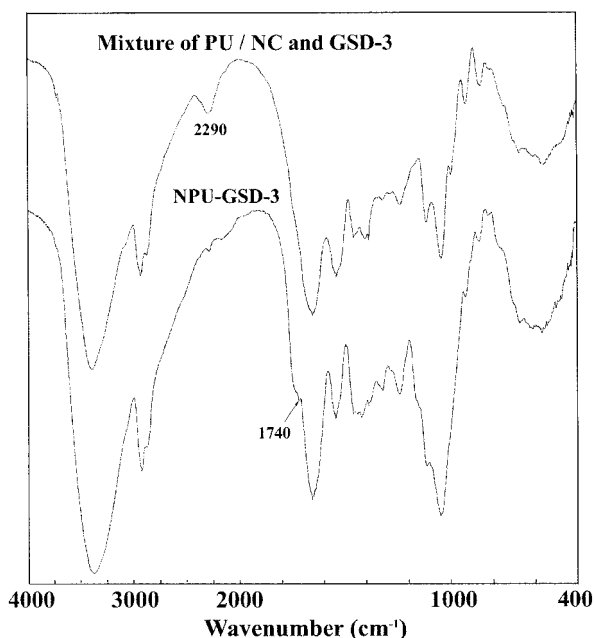


Figure 9 IR spectra of the NPU-GSD-3 sheet and the mixture of PU/NC coating and GSD-3 sheet.

polysaccharide, and soy protein, the water penetration led to a rapid decrease in the strength. As shown in Figure 9, there is no band at 1737 cm^{-1} in the IR spectrum but only in the ATR-IR spectra of the GSD-3 sheet, indicating esterification on the surface.

In our previous work,¹⁷ the regenerated cellulose films coated with PU/natural polymers IPN coating can be degraded by microorganisms in the soil. These microorganisms directly attack the IPN coating layer and then penetrate into the cellulose to speedily metabolize the plastic. This process is accompanied by the production of CO_2 , H_2O , glucose cleaved from

TABLE I
Mechanical Properties of the NPU-GSD-3 and GSD Sheets

Sheet	Coating Content (mg/cm^2)	σ_b (MPa)		R_σ
		Dry	Wet	
NPU-GSD-3	0.27	24.6	9.8	0.40
GSD-3	no	14.5	0.3	0.02

cellulose, and small molecules decomposed from the coatings, such as aromatic ether, glucopyranose derivatives, nitrate, etc. Therefore, the PU/NC coating layer on the NPU-GSD-3 sheet should be biodegradable.

CONCLUSION

Biodegradable plastics GSD-3 were prepared from SD with 25% glycerol as the plasticizer and 6.8% glutaraldehyde as the cross-linker under a pressure of 20 MPa at 120°C . Like the sheets based on SPI, the GSD-3 sheets exhibited good tensile strength, breaking elongation, and thermostability because of the strong interaction between cellulose, polysaccharide, and protein in the SD. Moreover, the GSD-3 sheets were fully biodegraded by strains of *Fusarium moniliforme*, *Chaetomium divaceum*, and *Trichoderma viride*. The strength and water resistance of the NPU-GSD-3 sheet coated with castor-oil-based PU/nitrochitosan IPN coating were significantly improved. The IPN coating plays an important role in forming a strong interfacial bonding between the GSD-3 sheet and the coating layer by chemical reaction, resulting in enhancement of the mechanical properties.

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