

Effects of Lignin as a Filler on Properties of Soy Protein Plastics. II. Alkaline Lignin

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ABSTRACT: Blend plastics based on soy protein isolate (SPI) strengthened with alkaline lignin (AL) in the weight ratio of 10:0 to 5:5 were prepared with 40 wt % glycerol as a plasticizer by compression molding. The structure and mechanical properties of the blends were investigated by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), dynamical mechanical thermal analysis (DMTA), and tensile tests. The results indicated that the introduction of AL could effectively increase the tensile strength and Young's modulus, thermal stability, and elongation of the composite plastics when the AL content ranged from 10 to 20 parts. Moreover, the blend plastics

containing 50 parts AL exhibited maximum tensile strength (1.98 MPa) and much higher than that with the SP-AL0 sheet with AL alone (0.89 MPa). In addition, tests of water absorption proved that the introduction of hydrophobic AL effectively reduced water absorption and, hence, decreased water sensibility. Therefore, AL, a relatively low-cost filler, plays a major role in enhancing the strength and water resistivity of soy protein plastics. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3291–3297, 2003

Key words: mechanical properties; blends; biodegradable

INTRODUCTION

The development of plastics based on soy protein (SPI) has attracted the attention of researchers due to its low-cost, abundant, renewable, biodegradable, and environmental-friendly features.^{1–6} However, the application of soy protein plastics is limited because they are brittle and water-sensitive. Many chemical and physical modifications have been used to improve the shortcomings of the materials. A blend has been widely evaluated as an effective and simple way to modify the properties of polymeric materials for specific needs. Soy protein/modified polyester blends have been prepared by injection molding, and they exhibit good miscibility, resulting in improvement of the mechanical strength and moisture sensitivity of soy protein plastics.⁷ Therefore, soy protein/polycaprolactone (PCL) blends compatibilized by methylene diphenyl diisocyanate (MDI) were obtained by compression molding, and the introduction of PCL and MDI can effectively modify the mechanical properties and restrict the water absorption of the materials.⁸ The blend plastics from starch and soy protein have been

largely developed by screw-extrusion and injection molding.⁹ Cellulose, as a filler, has been blended into soy protein plastics to increase the rigidity of the plastics.¹⁰ In addition, polyphosphate filler was introduced into soy protein plastics to enhance the stiffness, strength, and water resistivity.¹¹ In our previous work,^{12,13} a series of graft-interpenetrating polymer networks (graft-IPNs) were synthesized from castor oil-based polyurethane and nitrolignin. The study showed that 2.8 wt % nitrolignin played an important role in simultaneously enhancing the tensile strength and elongation. In addition, lignosulfonate (LS), a rigid polyelectrolyte containing ionic, hydrophilic, and hydrophobic groups, and many polar groups, was introduced into soy protein plastics and interacted with the SPI molecules to form networks, improving the mechanical properties and water resistance.¹⁴

It is noted that alkaline lignin (AL), a by-product from the alkaline pulping process of papermaking, is an abundant and low-cost material. Baumberger et al.^{15,16} investigated the behaviors of starch–lignin blends prepared by the compression-molding method and indicated that the products made from a relatively hydrophobic lignin obtained from the alkaline kraft pulping process exhibited a lower water sensitivity than those made from LS. Therefore, it is worth investigating the use of AL to improve the properties of soy protein plastics. In this work, blended plastics based on SPI and AL were prepared by the compression-molding method and their properties were measured by wide-angle X-ray diffraction, differential scanning calorimetry, dynamical mechanical thermal analysis,

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tensile tests, and tests of water sensitivity. The effects of AL as a filler on the properties of soy protein plastics were investigated and compared with those of LS.

EXPERIMENTAL

Materials and preparation of samples

SPI with a moisture content of 6.8% was provided by the Yunmeng Protein Technologies Co. (Hubei, China) and used without further treatment. AL was supplied by the Guangzhou Chemistry Institute of China (Guangzhou, China). Analytical-grade glycerol (GL) was purchased from the Shanghai Chemical Co. (Shanghai, China).

Mixtures of SPI and AL (60 wt %, with SPI of 0, 10, 20, 30, 40, and 50 parts) and 40 wt % GL were mechanically mixed at room temperature, followed by melt blending with an intensive mixer (Brabender Instruments Co., Germany) at 140°C and 75 rpm for 10 min. Subsequently, the blend was placed in a mold covered with two polished stainless-steel plates and then compression-molded using a hot press according to a previous method.⁵ The specimen was molded at 160°C and 20 MPa for 3 min and then air-cooled to about 50°C for 0.5 h under constant pressure before removal from the mold. By changing the AL content from 0 to 50 parts, the obtained sheets were coded as SP-AL0—SP-AL5.

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 CuK 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⁻¹. The tensile strength (σ_b), elongation at break (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⁻¹ 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 rate of 10°C min⁻¹ from -150 to 100°C. Prior to the test, the samples were heated from room temperature to 100°C to remove moisture and other volatile components in the sheets and then cooled to -150°C at a cooling rate of 20°C min⁻¹.

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 to 120°C with a heating rate of 3°C min⁻¹. Thermogravimetric

analysis (TGA) curves of the sheets were recorded on a TG 209 thermoanalyzer (Netzsch Co., Germany) under a nitrogen atmosphere from 20 to 800°C at a heating rate of 10°C min⁻¹.

Tests of water sensitivity

Water absorption was measured according to ASTM D570-81 with minor modification. The samples 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 then submerged in distilled water at room temperature for 2 and 26 h. The extra water on the surface of the specimen after water soaking was removed with a paper towel and the specimen then was weighed again. The container without the soaking specimen 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 of the container weight. The water absorption (Ab) was calculated by the following equation:

$$Ab = (W_1 - W_0 + W_{sol})/W_0 \quad (1)$$

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

To study the water resistance (R) of the materials, the sheets were immersed in water at room temperature for 1 h. The R values of the sheets was calculated by the following equation:

$$R = \sigma_b(\text{wet})/\sigma_b(\text{dry}) \quad (2)$$

where $\sigma_b(\text{wet})$ is the tensile strength of the specimen immersed in water for 1 h and $\sigma_b(\text{dry})$ is the tensile strength of the specimen tested in the dry state.

RESULTS AND DISCUSSION

Mechanical properties

The effects of the AL contents on the tensile strength (σ_b), elongation at break (ε_b), and Young's modulus (E) for the sheets are shown in Figures 1 and 2. The σ_b of the SP-AL sheets in dry and wet states increased with an increase of the AL content, suggesting that the addition of AL can effectively enhance the σ_b of the plastics. At the same time, the ε_b of the sheets containing AL decreased with an increase of the AL content. However, SP-AL1 and SP-AL2 exhibited a higher ε_b than that of SP-AL0. The results suggested that the added AL with a moderate content from 10 to 20 parts simultaneously enhanced the σ_b and ε_b . The changes of the E values were opposite those of ε_b , and the E

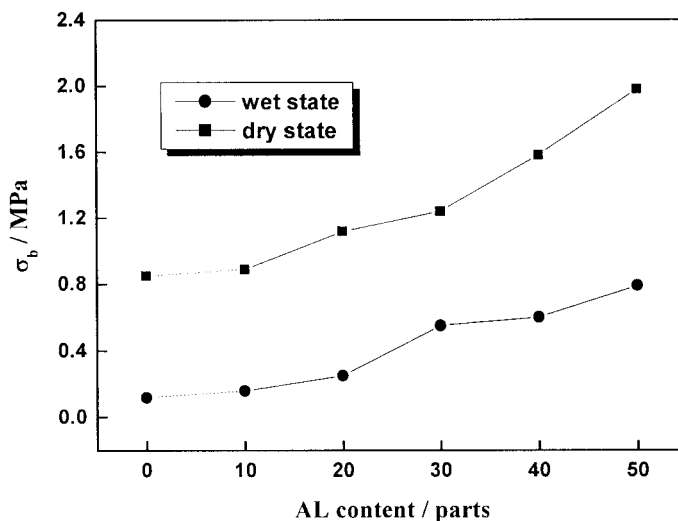


Figure 1 Dependence of tensile strength (τ_b) on AL content of SP-AL sheets in dry and wet states.

value of SP-AL1 was slightly lower than that of SP-AL0.

Compared with the effects of calcium LS on the mechanical properties of soy protein plastics,¹⁴ AL was more effective in enhancing the strength and rigidity. When the AL content was 50 parts, σ_b was achieved to 1.98 MPa, higher than the maximum value for the SP-LS sheets (1.62 MPa). However, the introduction of AL decreased the elongation of the AP-AL sheets. Although AL is mainly hydrophobic, it was blended into the hydrophilic SPI to improve the mechanical properties of the soy protein plastics. Compared with LS, AL has fewer active groups and did not promote physical crosslinks. Therefore, AL can be used as a filler for soy protein plastics to reinforce the materials because of its rigidity and strong interaction with SPI, such as hydrogen bonding and other physical forces.

Thermal properties

DSC thermograms of the SP-AL sheets are shown in Figure 3, and the glass transition temperature (T_g) and the change of heat capacities (ΔC_p) are listed in Table I. Similar to the sheets based on SPI and LS (SP-LS), the combination of the plasticization of GL and the compression-molding process resulted in an obvious glass transition attributed to SPI. Except for SP-AL1, the SP-AL sheets exhibited a lower T_g than that of SP-AL0, suggesting an increase of microphase separation due to the introduction of incompatible AL. The slightly higher T_g observed for the SP-AL1 sheet indicated that blends with a low concentration of AL did not result in an obvious microphase separation between SPI and AL. However, this behavior resulted in a slightly enhanced ε_b of the materials.

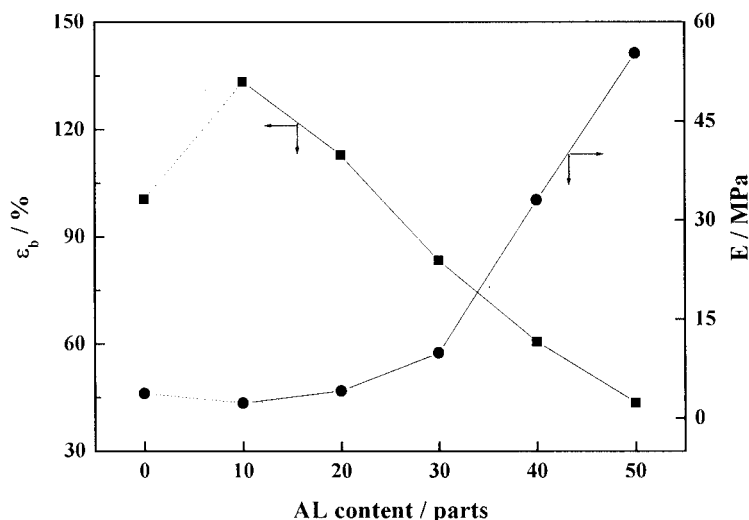


Figure 2 Dependence of (■) elongation at break (ε_b) and (●) Young's modulus (E) on AL content of SP-AL sheets.

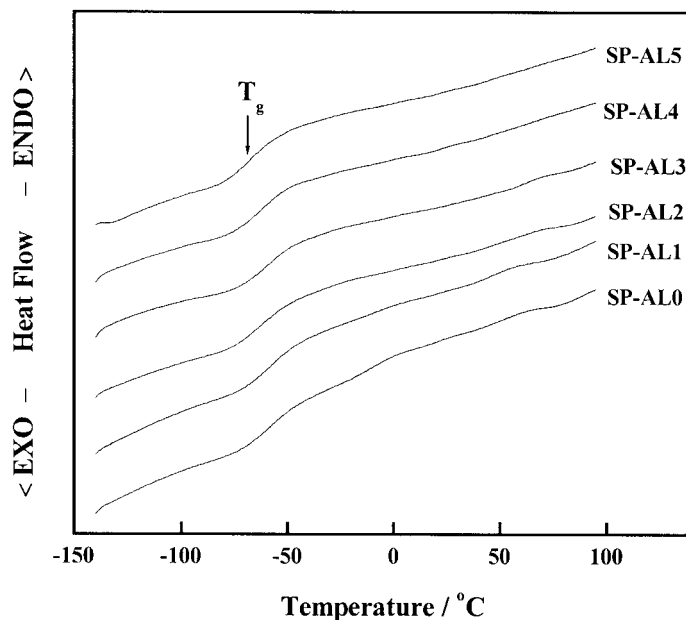


Figure 3 DSC thermograms of SP-AL sheets.

DMTA curves of the SP-AL sheets are shown in Figure 4, and the related data are summarized in Table I. The storage modulus ($\log E'$) for the sheets first increased with an increase of the temperature and then gradually decreased. The higher $\log E'$ at low temperature for all the sheets resulted mainly from the antiplasticization of SPI by GL, which stiffened the SPI molecules. The loss modulus ($\log E''$) as function of temperature was the same as $\log E'$ (graphs not shown), but two obvious loss peaks, which were in the range of -66 to -75 and 55 – 85°C , respectively, appeared in $\tan \delta$ - T curves for every sheet. The peaks at low temperature were assigned as the α -transition of the SPI molecules in the materials. As usual, the T_g values for the SP-AL sheets from the relaxation temperature corresponding to the α -transition (T_α) in $\tan \delta$ - T curves were higher than those measured from DSC because of the nature of the dynamic test.¹⁷ The $\tan \delta$ - T curves can be utilized to reveal information concerning molecular- and/or segmental-scale motions in polymers, which include the effects of molec-

ular interaction and the chemical environment. The T_α of the SP-AL sheets was lower than that of SP-AL0 with SPI alone, suggesting that the addition of AL prevented interaction among the SPI molecules, and the immiscibility with a certain degree between hydrophobic AL and hydrophilic SPI provided more space for motion for the SPI segments or chains. Similar to the results of the DSC, the T_α of SP-AL1 was also slightly higher than that of SP-AL0.

In addition, the loss peak at a high temperature could result from the thermodynamic relaxation of the materials. Combined with the TGA curves shown in Figure 5, the T_{\max} of the SP-AL sheets shifted to a higher temperature with an increased AL content while the height of the loss peak increased, suggesting that the thermal stability of the materials increased with increase of the AL content.

Similar to LS, the introduction of AL resulted in microphase separation in the SP-AL sheets, as proven by the T_g data. However, this was different from the increase of T_α in the SP-LS sheets, in which the forma-

TABLE I
DSC and DMTA Data and the Degree of Crystalline (χ_c) for the SP-AL Sheets and SPI

Sample No.	Glass transition		α -Relaxation		Loss peak		χ_c
	T_g (onset) ($^\circ\text{C}$)	ΔC_p ($\text{J g}^{-1} \text{K}^{-1}$)	T_α ($^\circ\text{C}$)	$\tan \delta$	T_{\max} ($^\circ\text{C}$)	$\tan \delta$	
SPI	—	—	—	—	—	—	0.31
SP-AL0	-70.4	0.27	-66.58	0.278	55.39	0.404	0.35
SP-AL1	-70.0	0.31	-66.30	0.263	61.94	0.432	0.34
SP-AL2	-75.2	0.39	-70.57	0.261	68.50	0.477	0.34
SP-AL3	-72.5	0.42	-71.99	0.265	75.05	0.508	0.33
SP-AL4	-75.0	0.37	-68.29	0.249	79.61	0.609	0.32
SP-AL5	-79.2	0.42	-74.27	0.233	84.17	0.692	0.34

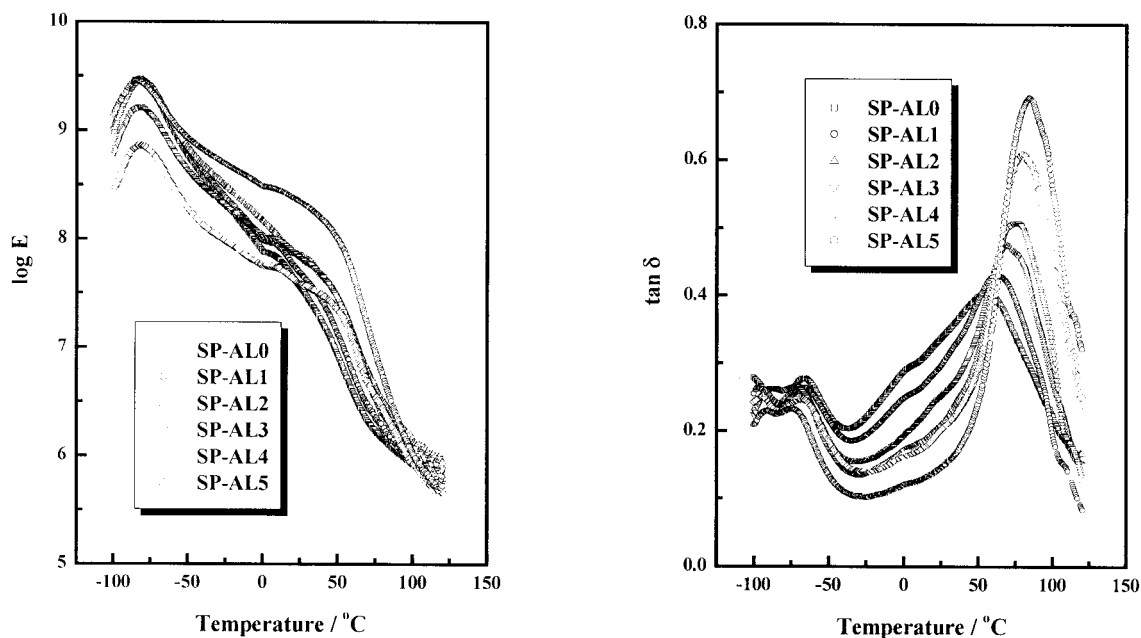


Figure 4 Storage modulus ($\log E'$) and $\tan \delta$ of SP-AL sheets as a function of temperature.

tion of the physical crosslinks restricted the molecular motion. In this work, a certain degree immiscibility between hydrophobic AL and hydrophilic SPI provided more space for molecular motion, resulting in a decrease of the T_{α} . In addition, the T_{\max} 's of the loss peaks for the SP-AL sheets were higher than those for the SP-LS sheets, suggesting that the thermal stability of the materials can benefit more from AL than from LS.

Degree of crystalline

The degree of crystalline (χ_c) and WAXD patterns for SPI and the SP-AL sheets are shown in Table I and Figure 6, respectively. Usually, a miscible blend could

result in a decrease of the χ_c . In spite of the addition of amorphous AL, the χ_c values of the sheets containing AL were close to those of SP-AL0 with SPI alone, suggesting the existence of a certain degree of microphase separation in the materials. The conclusion from the WAXD results was consistent with the DSC data.

Water absorption and water resistance

The dependence of the water absorption and water resistivity on the AL content in the SP-AL systems is shown in Figures 7 and 8. The introduction of AL efficiently restricted the water absorption (A_b) and the

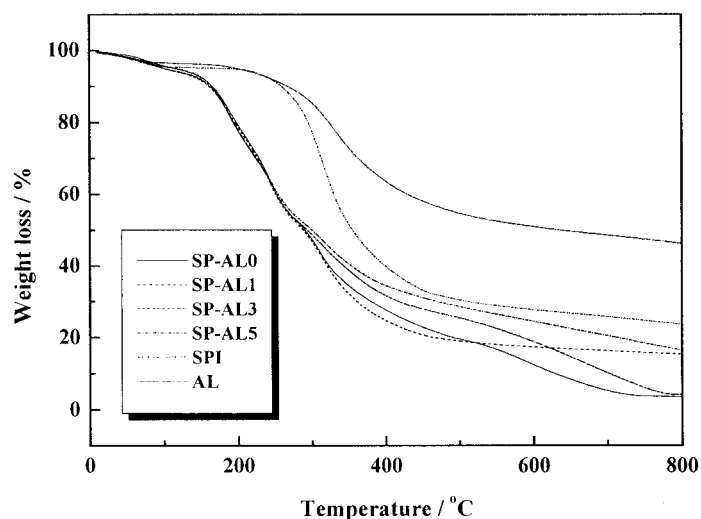


Figure 5 TGA curves of the SP-AL sheets, AL, and SPI.

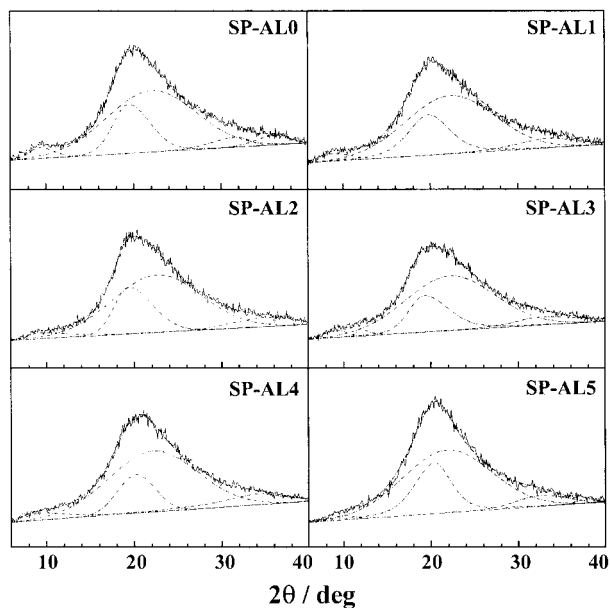


Figure 6 WAXD patterns of the SP-AL sheets. AL was amorphous as proven by WAXD.

swelling of the soy protein plastics. The water absorption of the SP-AL sheets decreased with an increase of AL content from 240 to 85%. At the same time, the water resistance (R) of the SP-AL sheets first increased with an increase of LS content up to 30 parts to reach 0.45 and then slightly decreased. It is well known that AL is more hydrophobic than is LS, but had fewer active groups and no ionic ones. Therefore, the lower water absorption of the SP-AL sheets was attributed to the hydrophobic nature of AL. Compared with the SP-LS sheets, the lower water resistance of the SP-AL sheets resulted from the absence of physical crosslinks which occurred in the SP-LS sheets.

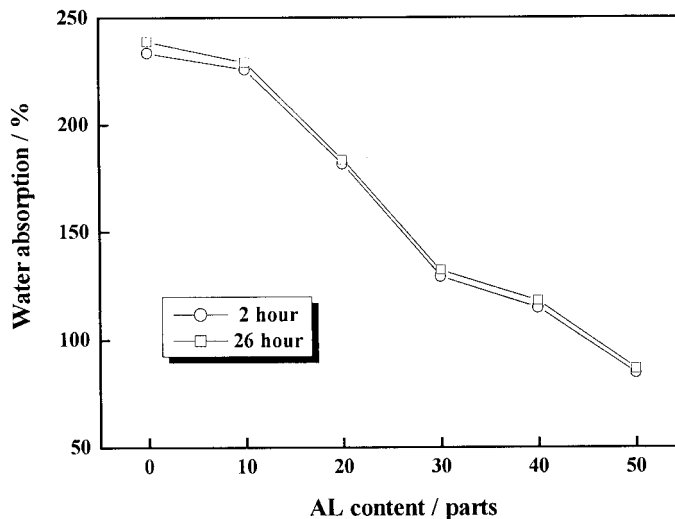


Figure 7 Dependence of water absorption on AL content of the SP-AL sheets immersed in water for 2 and 26 h.

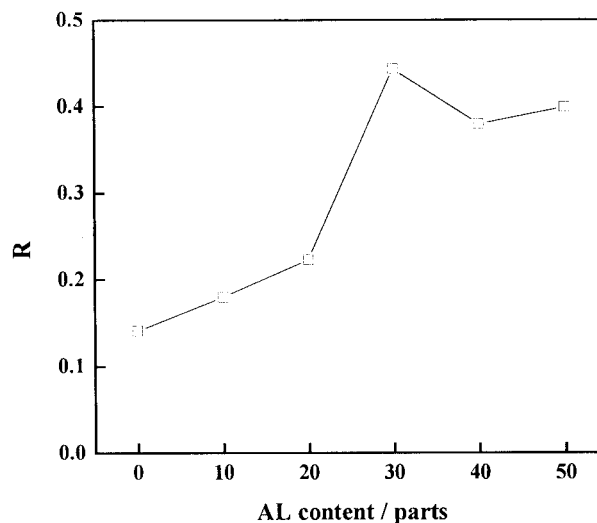


Figure 8 Dependence of water resistance (R) on AL content of the SP-AL sheets immersed in water for 1 h.

CONCLUSIONS

Blend plastics based on SPI-strengthened with AL were prepared with glycerol as a plasticizer using the compression-molding method. The SP-AL sheets exhibited higher thermal stability, tensile strength, and Young's modulus than those of SP-AL0 with SPI alone. It was noted that at a moderate concentration of 10–20 parts AL could simultaneously enhance the tensile strength and elongation of the blends. When the AL content was 50 parts, the σ_b value was 1.98 MPa, much higher than that of the sheet without AL (0.89 MPa). The improvement of the mechanical properties of the SP-AL plastics was attributed to the reinforcement of the rigid AL and strong intermolecular interaction between SPI and AL. In addition, the hydrophobic nature of AL effectively reduced the water absorption of the materials and,

hence, enhanced the water resistance. Compared with calcium LS, AL exhibited a greater reinforcement effect on the compositive soy protein materials.

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