

# Structure and Properties of Casting Films Blended with Starch and Waterborne Polyurethane

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**ABSTRACT:** A series of casting films blended from starch and waterborne polyurethane (STPU) in aqueous solution were prepared. The structure and properties of the films were investigated by infrared spectroscopy, ultraviolet spectroscopy, scanning electron micrography, strength test, thermogravimetric analysis, and different scanning calorimetry. The results showed that the tensile strength and modulus of air-dried STPU blend films increased with the increase of starch content, while elongation decreased. When starch content was in the range from 80 to 90 wt %, the blend films showed significantly higher tensile strength, breaking elongation, water resistivity, and light transmittance than that of pure starch film, resulting from the miscibility between starch and waterborne polyurethane. Moreover, the STPU films containing 90 wt % starch have higher thermal stability than pure waterborne polyurethane film, and their light transmittance was close to the polyurethane, due to the existence of a strong intermolecular hydrogen bonding between starch and polyurethane. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2006–2013, 2001

**Key words:** starch; waterborne polyurethane; blend; biodegradable polymer

## INTRODUCTION

Recently, the environmentally friendly materials from natural and renewable resources have been paid much attention.<sup>1</sup> Starch, as an abundant raw material with low cost, has been applied in the field of degradable plastics, and the blend films containing starch are potential materials in agriculture, medicine, and packaging industry. However, the wide applications are limited by the lack of water resistivity and the brittle property of starch casting films. To improve the mechanical

properties of materials, blending starch with other polymers, such as poly(vinyl alcohol),<sup>2</sup> methylcellulose,<sup>3</sup> and low density polyethylene<sup>4</sup> is regarded as a simple way.

Polyurethane (PU) materials have been generally used in the automobile, paint, furniture and textile industries, etc. Waterborne polyurethane (WBPU), as a nontoxic, nonflammable, and environment-friendly material,<sup>5</sup> is a polymer expected to improve properties of starch films by using a blend in view of the hydrophilic groups and its partial hydrophobe caused by soft segments. Soy protein and corn starch were incorporated into a flexible polyurethane foam formulation, owing to reaction between residual NCO groups in PU and hydrogen groups in starch.<sup>6,7</sup> Interestingly, the polyurethane sheets and foams, prepared by making a reaction of a mixture of poly(ethylene glycol) and molasses with diphenylmethane diisocyanate, were biodegradable in soil.<sup>8</sup> Recently, it has

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been proved that the polyurethane in the polyurethane / natural polymers interpenetrating polymer network coating was slowly decomposed to convert into aromatic ethers by the microorganism in soil.<sup>9</sup> Therefore, a study on new biodegradable material prepared from starch and WBPU in water system favors both protection of environment and consuming the limited petroleum.

In our laboratory, the miscibility, structure, and properties of blend membranes of cellulose with other polymer such as casein, alginate, and konjac glucomannan were investigated, and they have excellent mechanical properties and some functions.<sup>10–13</sup> In this work, the WBPU was synthesized, and blended with starch in water system to prepare a new material. The effect of starch content on miscibility, tensile strength, water resistivity, thermal stability, and morphology of blended films were investigated by strength test, thermogravimetric analysis (TGA), different scanning calorimetry (DSC), IR spectroscopy, UV spectroscopy, and scanning electron micrography (SEM).

## EXPERIMENT

### Materials

Commercial 1,4-toluene diisocyanate (TDI; supplied by Shanghai Chemical Co.) was vacuum dried at 80°C for 2 h, and used as hard segments. Commercial polyoxypropylene glycol (PPG; supplied by Nanjing Chemical Factory) was vacuum dried at 105°C for 5 h, and used as soft segments. 2,2-bis(hydroxyl methyl) propionic acid (DMPA; supplied by Chengdu Polyurethane Co.), as chain extender and anionic center, was vacuum dried at 110°C for 2 h. Triethylamine (TEA) and ketone as neutralized reagent and solvent, respectively, were immersed in 4 Å molecular sieves for more than a week to dehydrate before use. The DMPA, TEA, and ketone all were of analytical grade. Cornstarch containing 23.5% amylose and 75% amylopectin was purchased from Wuhan Starch Co. in China, and vacuum dried at 105°C for 5 h before use.

### Preparation of WBPU

Anionic WBPU was synthesized according to the prepolymer mixing process.<sup>14,15</sup> The ratio of NCO/OH in this case was 1.75. A four-necked flask was fitted with a thermometer, a stirrer, an

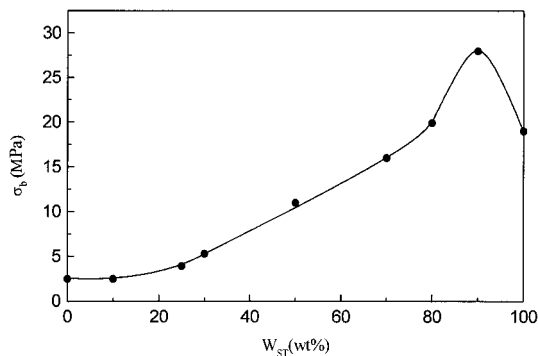
inlet, and an outlet of dry nitrogen. The amount of 47.3 g of PPG2000 and 3.17 g of DMPA were added into the flask and stirred at 120°C for 15 min to dissolve DMPA easily, then cooled to 85°C. The amount of 14.4 g of TDI was introduced into the flask under dry nitrogen, and the reaction was carried out for 2–3 h until the NCO groups content reached a given value, determined by dibutylamine back titration.<sup>16</sup> Fifty milliliters of ketone was added to reduce the viscosity of prepolymer. Finally, the product was cooled to 60°C, and neutralized with TEA for 30 min. The WBPU was formed by the drip adding water for a period of 20 min. The solid content of the WBPU was 20% and its viscosity measured by using a rotation viscosity meter (NDJ-4, Shanghai Balance Factory) was 6.9 MPas.

### Preparation of Blend Films

Two grams of starch and 40 g of water were added to a three-necked flask, and heated slowly to 80°C, stirring vigorously for 1 h to obtain a 5 wt % starch translucent paste. The WBPU was mixed with desired starch paste at 85°C for 30 min with stirring. The mixture was vacuum degassed, and then cast on a teflon plate mold (120 × 200 mm<sup>2</sup>) with a groove deep of 1 mm. The mold was dried at 40°C in an oven for 10 h to obtain a transparent film. The thickness of the films was controlled by the concentration of paste and the thickness of the casting paste to be from 0.05 to 0.1 mm. The drying temperature should be controlled to below 40°C in order to make water in paste evaporating slowly. All films were stored at room temperature and 75% relative humidity [controlled by saturated salt method according to ISO/R483-1966(E)] for a week to give moisture content of the film to be constant to about 5–13 wt %. By changing the weight ratio of starch in the dried film weight such as 10, 30, 50, 70, 80, and 90 wt %, a series of starch/polyurethane (STPU) films were prepared, coded as STPU10, STPU30, STPU50, STPU70, STPU80, and STPU90, respectively. Films prepared from pure starch and pure WBPU were coded as ST and PU, respectively.

### Characterization

IR spectra of the vacuum-dried films were recorded with a Fourier transform infrared (FTIR) 3000 spectrometer (Shimadzu Co.). The optical transmittance of the films in the wavelength range of 400–800 nm was measured by using a



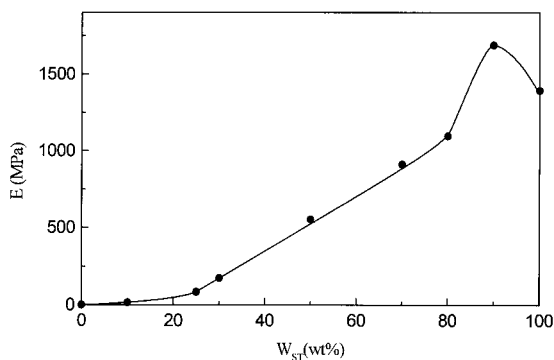
**Figure 1** Effect of starch content ( $W_{ST}$ ) on stress at break ( $\sigma_b$ ) of STPU films.

UV-160A Spectroscop (Shimadzu Co.), according to the Beer–Lambert law to give percent light transmittance for the films with thickness of 0.05 mm. The cross sections of the films were observed by a scanning electron microscope (S-570 SEM, Hitachi). The samples were frozen under liquid nitrogen, then fractured, mounted on a stub and coated with gold.

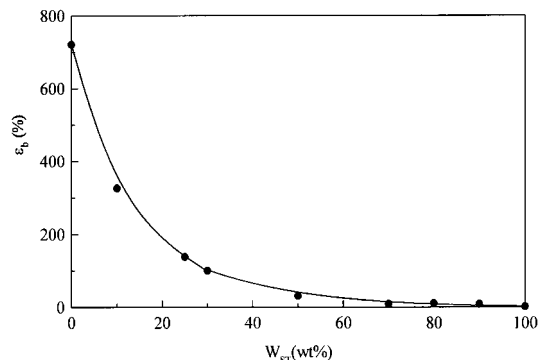
#### Measurement of Mechanical Properties

The mechanical properties of the films [ $100 \times 10 \times (0.1-0.05)\text{mm}^3$ ] were measured on an universal testing machine (CMT6503, Shenzhen SANS Test Machine Co., Ltd.) according to ISO6239-1986 (E) with tensile speed to at a constant speed 5mm/min to obtain tensile strength ( $\sigma_b$ ), modulus ( $E$ ), and breaking elongation ( $\epsilon_b$ ). The mean values of  $\sigma_b$ ,  $E$ , and  $\epsilon_b$  were obtained from three replications, respectively.

The films [ $70 \times 40 \times (0.05-0.1)\text{mm}^3$ ] with weight of 150–200 mg were immersed in water at room temperature for 30 min, and then used for



**Figure 2** Effect of starch content ( $W_{ST}$ ) on Young's modulus ( $E$ ) of STPU films.



**Figure 3** Effect of starch content ( $W_{ST}$ ) on breaking elongation ( $\epsilon_b$ ) of STPU films.

the measurement of their water resistivity.<sup>17</sup> The water resistivities ( $R$ ) of the films were evaluated from  $\sigma_{b(\text{dry})}$  value in the dry state and  $\sigma_{b(\text{wet})}$  in the wet state by the following equation:

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

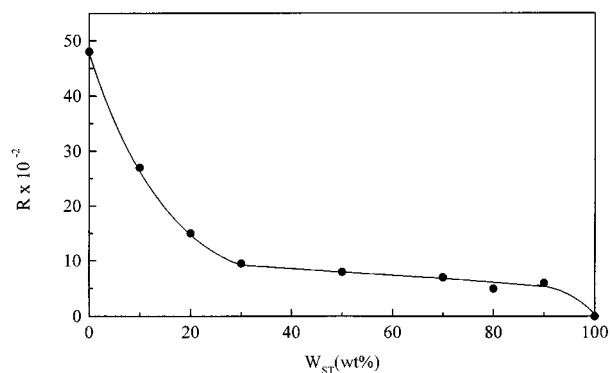
More than three replications were conducted. The absorbed water content ( $W_{\text{H}_2\text{O}}$ ) in the films was measured according to ISO62-1980 (E), the films were required to be immersed in water at 25°C for 24 h. The  $W_{\text{H}_2\text{O}}$  value was calculated by the following equation:

$$W_{\text{H}_2\text{O}} = [(W_2 - W_1)/W_1] \times 100 \quad (2)$$

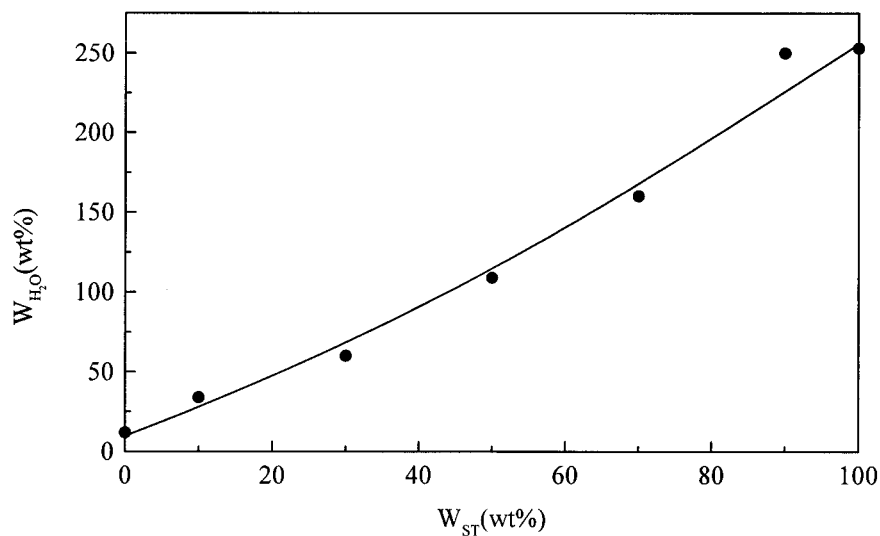
where  $W_1$  and  $W_2$  are, respectively, the weights of dry and swollen membrane.

#### Thermal Analysis

Ten milligrams of vacuum-dried samples were weighed accurately in an aluminum pan, and



**Figure 4** Effect of starch content ( $W_{ST}$ ) on water resistivity of STPU films.



**Figure 5** Effect of starch content ( $W_{ST}$ ) on absorbed water content ( $W_{H_2O}$ ) of STPU films.

sealed hermetically. The DSC analysis for the samples was performed with a thermal analyzer (DSC-204, Netzsch Co.) under nitrogen atmosphere at a heating rate of 20°C/min from -100 to 400°C. The TGA of STPU50 film was measured by using a thermal analyzer (TG209, Netzsch Co.) with a heating rate of 20°C/min from room temperature to 700°C.

## RESULTS AND DISCUSSION

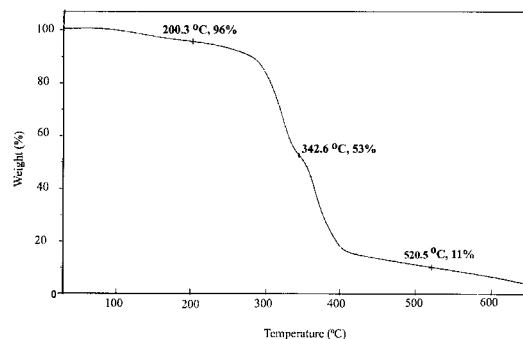
### Effects of Starch Content on Mechanical Properties

Figures 1, 2, and 3 show the effects of the starch content ( $W_{ST}$ ) on tensile strength ( $\sigma_b$ ), Young's modulus ( $E$ ), and breaking elongation ( $\epsilon_b$ ), respectively. It indicated that with the increase of starch content, both strength and modulus of the STPU films increased, and elongation decreased quickly, resulting from the toughness of starch. When starch content was lower than 30%, strength and modulus of STPU films hardly changed with the increase of starch content; meanwhile, breaking elongation reduced, suggesting weak intermolecular interaction between two polymers. However, the films STPU90 and STPU80 showed higher tensile strength ( $\sigma_b$ ) and higher breaking elongation ( $\epsilon_b$ ) than that of the pure starch film, suggesting the formation of strong interaction between the WBPU and starch. Wolff et al.<sup>18</sup> have reported that air-dried starch film showed lower tensile strength (5.5 MPa) and

lower breaking elongation (5%). The  $\sigma_b$  and  $\epsilon_b$  values of the ST film were given to be 19 MPa and 2%, which were much lower than that of the STPU90 (28 MPa, 9%) and STPU80 (20 MPa, 11%).

Figure 4 shows the effect of the starch content ( $W_{ST}$ ) on the water resistivity of the STPU films. With the increase of the starch content, the  $R$  values of the films containing starch decreased from 0.49 to 0.07. The  $R$  values of the blend films were all much higher than that of starch film (0.002), suggesting that WBPU is beneficial to improve the water resistivity of starch film.

Figure 5 shows the effect of the starch content ( $W_{ST}$ ) on the absorbed water ( $W_{H_2O}$ ) in the films. It indicated that the water content in STPU films increased with the increase of  $W_{ST}$ , due to hydrophobic soft segments of WBPU.



**Figure 6** The TGA curve for the film STPU50.

**Table I Results of TGA for Films STPU50**

No.	$T_i^a$ (°C)	$T_e^b$ (°C)	Loss Weight (%)	Residue at $T_e$	Composition
Stage 1	25	200	4	96	Moisture, TEA
Stage 2	200	342	42	53	WBPU
Stage 3	342	520	42	11	TEA, starch

<sup>a</sup> Initial decomposition temperature.

<sup>b</sup> Ending decomposition temperature.

### Effects of Starch Content on Thermal Properties

Figure 6 shows the TGA curve of the film STPU50, and the corresponding values were exhibited in Table I. A three-step degradation included a relatively short stage with a very small percent of weight loss ending at 200°C, a much higher thermal-resistant stage with 42.16% weight loss at 342°C, where WBPU almost decomposed, and the final stage mainly corresponding to the decomposition of starch.<sup>19</sup>

The experimental results of DSC for the STPU films were summarized in Table II. There was no peak in the range from 250 to 320°C for the pure starch film, while the pure WBPU film has sharp peak in the same temperature range. This implies that the peak appeared from 250 to 320°C belonged to the thermal degradation of WBPU in STPU films. Interestingly, the decomposition temperatures in the blend films of STPU30–STPU90 are higher than that of pure WBPU, implying that greater thermal stability for the STPU films. The conclusion is supported by the stronger mechanical properties of the STPU90 film than that of ST film. The blend film had three kinds of  $T_g$ : the first  $T_g$  for wet starch, the second  $T_g$  for the hard domains of WBPU, and the third  $T_g$  for the soft segment of

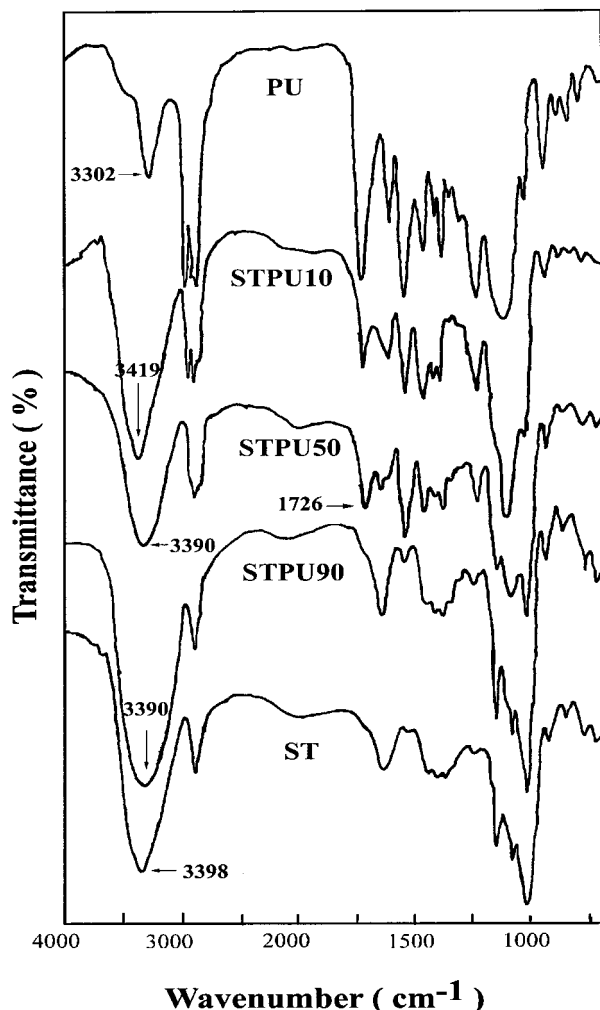
WBPU.<sup>20</sup> The first  $T_g$  was about 5°C for starch contained 13 wt % water, but it was hard to be detected due to the existence of much water; the change for the second  $T_g$  was too weak to be detected, which ranged from 100–200°C<sup>21</sup>; the third  $T_g$  was listed in Table II. It is worth noting that the  $T_g$  values of soft segments of STPU films decreased from –45.7 to –55.7°C with the increase of starch. This indicated that the miscibility between soft segments and hard segment domains decreased with the increase of starch content. The microphase separation between soft segments and hard segments in the blend films favored their flexibility,<sup>22</sup> resulting in low value of  $T_g$  of soft segments in WBPU for the films STPU80 and STPU90. The hard segment domains with many N–H groups, C=O groups, and COOH groups easily formed hydrogen bonding with starch, so that the interaction force between starch and WBPU increased with the increase of WBPU content, leading to relatively weak intermolecular force in the starch itself.

### Structure and Miscibility

The IR spectra of ST, STPU90, STPU50, STPU10, and PU are shown in Figure 7. The absorption peak at 3390 cm<sup>-1</sup> for STPU90 broadened and

**Table II Experimental Results of DSC for STPU Films**

Code	$T_g$ of Soft Segments (°C)			Decomposition Peaks	
	Onset Point	Midpoint	End Point	Midpoint (°C)	Endotherm (cal/g)
PU	–53	–46	–39	274	6.6
STPU10	–49	–42	–35	305	5.8
STPU30	–53	–46	–40	301	7.9
STPU50	–55	–47	–40	301	5.6
STPU70	–55	–49	–40	293	26
STPU80	–58	–50	–41	298	8.5
STPU90	–66	–56	–41	292	85
ST	—	—	—	—	—



**Figure 7** IR spectra of the films ST, STPU90, STPU10, and PU.

shifted to lower wavenumber than that for ST ( $3398\text{ cm}^{-1}$ ), indicating that strong intermolecular hydrogen bonding occurred between starch and WBPU. Interestingly, the peak at  $1726\text{ cm}^{-1}$  for STPU90, attributed to the  $\text{C}=\text{O}$  groups of WBPU in STPU90, almost disappeared, implying a good miscibility. But there was obvious difference between STPU10 and STPU90, where the peak at  $3419\text{ cm}^{-1}$  for STPU10 became narrower and shifted to higher wavenumber, indicating the decrease of the intermolecular hydrogen bonding. Moreover, all peaks for the STPU10 were almost simply overlapped from those of ST and PU, similar to the result from two polymers mechanically mixing, suggesting immiscibility between the WBPU and starch in STPU10.

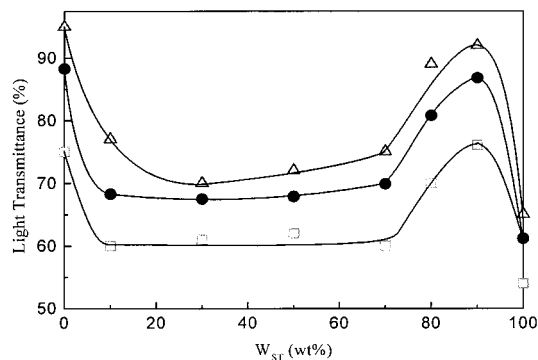
The light transmittances of the STPU films as functions of starch content ( $W_{\text{ST}}$ ) are shown in

Figure 8. Interestingly, the light transmittance of STPU90 achieved 88% at 600 nm, similar to that of PU, implying a good miscibility. The miscibility of STPU films increased with the increase of starch content in the range from 70 to 90%.

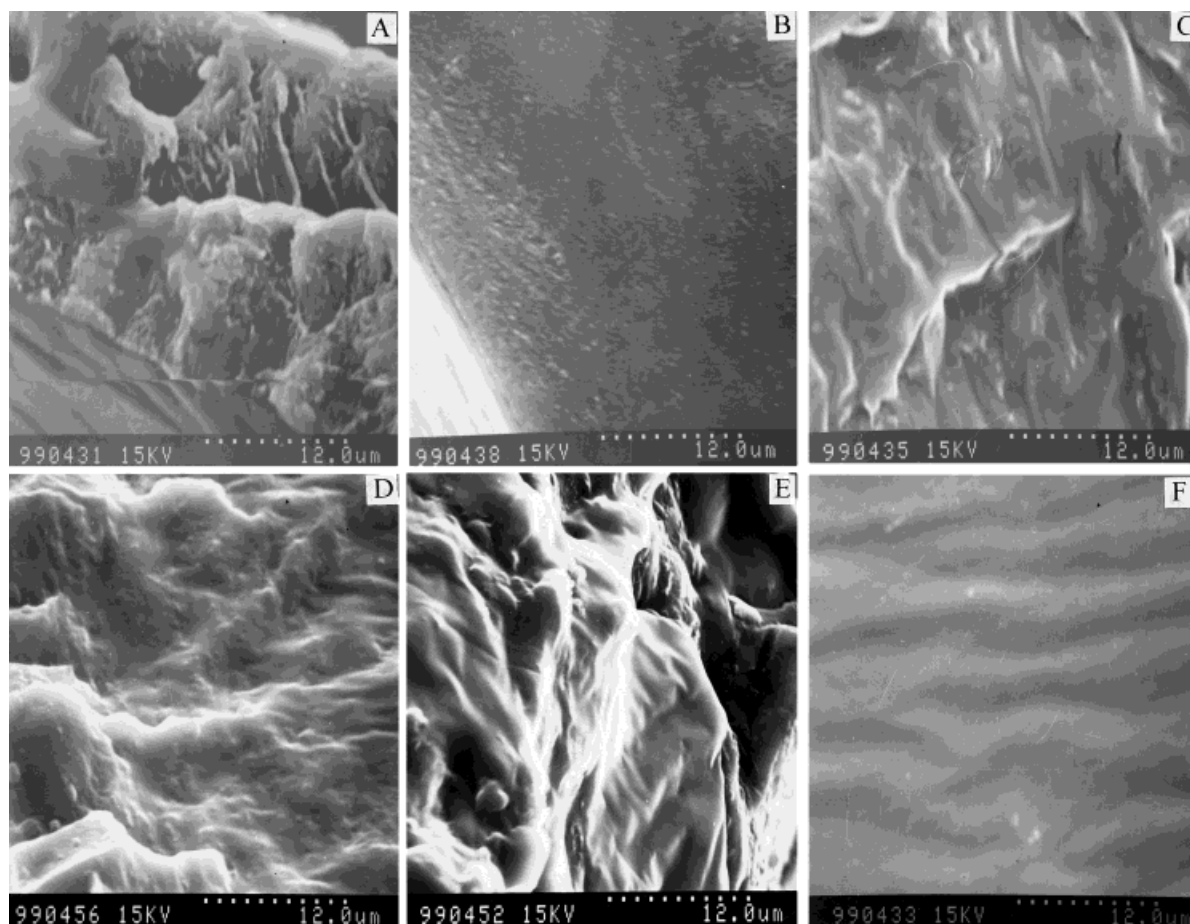
Figure 9 shows SEM of the cross sections of the films ST, STPU90, STPU80, STPU30, STPU10, and PU, respectively. The film ST from pure starch (A) shows a very rough structure with globules and holes, because aqueous gelatinized starch was a suspension of swollen particles,<sup>23, 24</sup> so that parts of water-insoluble particles exist in the pure starch film. The cross sections of films STPU90 (B) and STPU80 (C) have smooth morphology, namely dense architectural structure, indicating good miscibility between starch and WBPU. In this case, a little WBPU was distributed in the continuous phase of starch to produce strong adhesion force and homogenous systems. The films of STPU30 (D) and STPU10 (E) all exhibited rough structures, suggesting the phase separation. This is in good agreement with their low transparence shown in Figure 8.

## CONCLUSION

The casting films blended with starch and waterborne polyurethane were successfully prepared. When starch content was in the range from 80 to 90%, the blend films showed significantly higher tensile strength, breaking elongation, water resistivity, thermal stability, and light transmittance than that of pure starch film, due to the strong interaction between starch and waterborne polyurethane. When



**Figure 8** Effect of starch content ( $W_{\text{ST}}$ ) on light transmittance of the films at 400 nm ( $\square$ ), 600 nm ( $\bullet$ ), and 800 nm ( $\triangle$ ).



**Figure 9** SEM of the sections of the films ST (A), STPU90 (B), STPU80 (C), STPU30 (D), STPU10 (E), and PU (F).

starch content was 90 wt %, the blend film has a good miscibility. Waterborne polyurethane is beneficial to improve the water resistivity of starch film. However, when WBPU content was more than 30%, the blend is immiscibility. When 10–20 wt % WBPU was dispersed in the continuous phase of starch, the strong adhesion force and a homogenous system can be produced, resulting in a dense architectural structure. In this case, the interaction force between the two polymers reached a maximum; so that the properties of the films STPU90 and STPU80 were improved. IR results indicated the strong hydrogen bonds exist between starch and waterborne polyurethane in the blend films.

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