Effect of Postcrosslinking Modification with Glutaraldehyde on the Properties of Thermoplastic Starch/Poly(vinyl alcohol) Blend Films

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ABSTRACT: Thermoplastic starch (TPS)/poly(vinyl alcohol) (PVA) blend films were modified by crosslinking through soaking the films in glutaraldehyde aqueous solution and then heating in an oven. The effects of the concentration of the glutaraldehyde aqueous solution, soaking time, reaction temperature, and time on the crosslinking reaction were investigated. The moisture absorption and mechanical properties of the films were measured to characterize the influence of the crosslinking modification. It was found that the crosslinking modification significantly reduced the moisture sensitivity of the TPS/PVA blend films and increased the tensile strength and Young's modulus but decreased the elongation at break of the TPS/PVA blend films. The described method could be used for posttreating TPS/PVA-based products to optimize their properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3774–3781, 2012

Key words: blends; crosslinking; modification; polysaccharides

INTRODUCTION

Increased awareness of environmental conservation and protection has promoted the presentation of biodegradable materials produced from renewable sources, such as starch, protein, and cellulose.[1–3] Thermoplastic starch (TPS), a biobased material, is a homogeneous melt converted from native starch granules through the disruption of the granular structure with mechanical and thermal energy with presence of water or other plasticizers.[4,5] TPS products already have applications in the plastic market to take the place of nondegradable petrochemical-based products.[6–8] However, the hydrophilic nature of starch causes the moisture content (MC) in TPS to change with environment and leads to the mechanical properties of TPS to be jeopardized in a damp environment, which renders TPS unsuitable for many high-humidity applications.[9]

Poly(vinyl alcohol) (PVA) is well suited for making blends with natural polymer starch because of its biodegradability, good film-forming capability, and water solubility.[10–12] Compared with pure starch films, TPS/PVA blend films present a higher strain value and a lower water uptake, but the hydrophobic characteristics of the blend films still need to be improved.[13]

The hydroxyl groups on starch and PVA molecules are responsible for the hydrophilicity of TPS and PVA. Crosslinking is an efficient way to increase the water resistance of starch and PVA. Crosslinking agents, such as glutaraldehyde,[14–19] sodium trimetaphosphate,[20–22] epichlorohydrin,[3,10,23–25] borax,[2] boric acid,[26,27] citric acid,[28,29] and linear polyol[30] have been used to react with the hydroxyl groups in starch or PVA for modifications. Research results have also shown that surface photocrosslinking modification of TPS sheets and TPS/PVA films significantly reduces the surface hydrophilic characteristics and improves the water resistance of the materials.[31,32] The photocrosslinking modification needs a UV source to initiate and finish the crosslinking reaction. Alternatively, the crosslinking modifications of TPS and PVA can be also implemented by heating, and heating seems easier and more convenient for practice applications.

In this study, the crosslinking modification of TPS/PVA blend films was carried out through heating after the films was treated by soaking in glutaraldehyde aqueous solution for a period of time. Unlike other crosslinking modifications with glutaraldehyde for the TPS/PVA blend system,[14,16,18] the method used in this study was a postcrosslinking technique that could be applied after the products were formed instead of during the product

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formation. Some of the physical properties of crosslinking-modified TPS/PVA films were characterized to investigate the influences of the postcrosslinking modification.

EXPERIMENTAL

Materials

Corn starch was obtained from Changchun Jincheng Corn Development Co., Ltd., Da Cheng Group (Changchun, China). PVA with a polymerization degree of 1750 ± 50 was supplied by Shenyang Dongxing Reagent Factory (Shenyang, China). Glutaraldehyde was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Glycerol and ethanol were from Beijing Beihua Fine Chemicals Co., Ltd. (Beijing, China). Dimethyl sulfoxide (DMSO), from Tianjin Shengao Chemical Reagent Co., Ltd. (Tianjin, China), was used as a solvent for determining the swelling degree (SD) of the surface-crosslinked films. All of these chemicals were reagent grade and were used as received without any further purification.

Film preparation

TPS/PVA blend films were prepared by a solution-casting method. First, PVA solution was prepared by the dissolution of 7.5 g of PVA in 500 g of distilled water through heating at 95°C by a water bath. Then, 35 g of dry corn starch and 7.5 g of glycerol were mixed together and dispersed in 500 g of distilled water to make a suspension. The starch slurry was gelatinized with stirring by heating at 95°C. Afterward, the prepared PVA solution was added. The mixture was kept at 95°C and maintained with stirring for 40 min to get a homogeneous gel-like solution. During this period, distilled water was added to maintain the volume of the mixture. The prepared gel-like solution was distributed in desired amounts into PMMA trays for casting and dried at 50°C. The dried films with a thickness of about 0.21 mm were peeled off and stored at room temperature and 59% relative humidity (RH) for experimental use.

Crosslinking modification

After conditioned at 59% RH to moisture equilibrium, small pieces (25 × 20 mm^2) of the TPS/PVA blend film were soaked in glutaraldehyde aqueous solution with different concentrations for various periods of time. When the films were taken out, the excess solution on the surfaces was absorbed with filter papers. The films treated with the glutaraldehyde aqueous solution were placed in an oven with temperatures ranging from 20 to 50°C for various periods of time to finish the crosslinking reaction.

Characterization

Extent of crosslinking

The extent of crosslinking was characterized by the measurement of the film's SD in DMSO and gel mass (GM). The determination of SD and GM was carried out according to the procedure described by Delville et al.[33] The specimens were conditioned at 59% RH for moisture equilibrium, and the weighed mass was referred to as m_0. Then, the specimens were immersed in DMSO, in which the original TPS/PVA blend film was completely soluble. After 48 h, the insoluble part (swollen film) was filtered out and weighed (m_s) in an analytical balance with a precision of 0.1 mg. Then, the insoluble part was first rinsed in water and then in ethanol to remove the DMSO. The insoluble part was dried at 50°C to a constant weight (m_d). The SD normalized by the surface area and GM normalized by total mass were calculated from the following formula:

$$\text{Normalized SD} = (m_s - m_d)/(m_d A)$$
$$\text{Normalized GM} = (m_d/m_0) \times 100\%$$

where A is the surface area of the specimen before it was immersed in DMSO. Because drying at an elevated temperature will change the crosslink density of the specimens, which will, in turn, influence m_d, the equilibrated mass at 59% RH (m_0) was used as a comparison basis.

Moisture absorption

We measured the moisture absorption by storing the specimens at room temperature in desiccators with controlled RHs (15, 33, 59, 75, and 95% RH); these were maintained by saturated salt solutions.[31] The dried specimens were exposed to the chosen humidity environment and weighed. The moisture equilibrium was considered to be reached when the weight gain was less than 1% since the last weighing. MC was calculated with the measured wet weight (w_w) and the dry weight (w_d) by

$$\text{MC} = (w_w - w_d)/w_d$$

Mechanical properties

Dumbbell-shaped specimens of 50 mm long and with a 4 mm neck width were cut from the prepared films. After the crosslinking modification, all of the specimens were conditioned at a given RH and room temperature until moisture equilibrium was reached. The tensile tests were carried out with a universal testing machine (model QJ-210, Shanghai Qingji, Shanghai, China) with a 100-N loading cell at

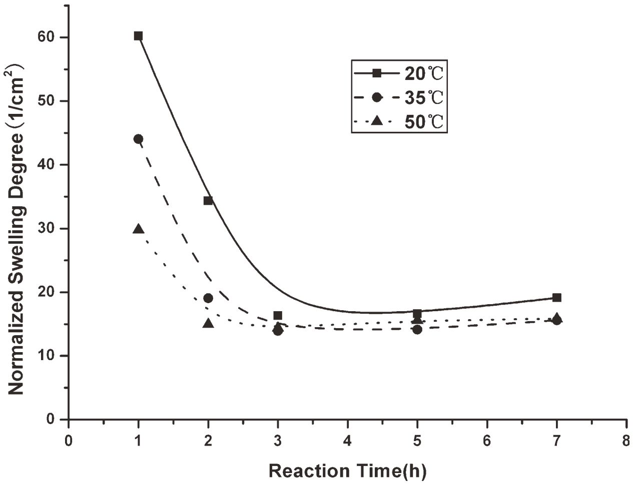

Figure 1 Changes of normalized SD against the reaction time for specimens soaked in 1.0% glutaraldehyde aqueous solutions for 30 s and heated at different temperatures.

a crosshead speed of 5 mm/min. The tensile strength, Young's modulus, and elongation at break were obtained. At least five specimens were measured for each experimental condition, and the average values were taken.

RESULTS AND DISCUSSION

Crosslinking reaction

Glutaraldehyde is a dialdehyde crosslinking agent that has been extensively used to modify starch and PVA.[14,16] The crosslinking of starch and PVA macromolecules with glutaraldehyde is carried out through the nucleophilic addition of a hydroxyl group to the carbonyl group to form hemi–acetal linkages.[15] The normalized SD of the crosslinking-modified TPS/PVA blend films was related to crosslink density of the newly created networks of starch–starch, starch–PVA, and PVA–PVA by glutaraldehyde. The lower the normalized SD was, the higher the crosslink density was. The normalized GM was related to the amounts of starch and PVA macromolecules involved in the formation of the crosslinking networks of starch–starch, starch–PVA, and PVA–PVA.

Effect of the reaction time and temperature

Figures 1 and 2 show the normalized SD and normalized GM as a function of reaction time for the specimens soaked in a 1.0% glutaraldehyde aqueous solution for 30 s and heated at different temperatures. Basically, for all of the investigated temperatures, the normalized SD decreased, the normalized GM increased with increasing reaction time, and the changing rates were initially fast and then slowed down. Beyond the initial fast-changing regions, the curves leveled off and reached stable values that were less dependent on the reaction time. This was understandable because the intermolecular bridges created by crosslinking and moisture evaporation during the reaction led to a decrease in the macromolecular mobility of starch and PVA, which, in turn, hindered the crosslinking reaction.

From Figures 1 and 2, it was noted that the reaction temperature influenced both the kinetics and final values of the normalized SD and GM. The specimens reacting at 20°C needed 3 h to reach the plateaus of normalized SD and GM, whereas the specimens reacting at 50°C needed 2 h to reach the plateaus. This indicated that, within the temperature range of 20–50°C, a higher temperature gave rise to a faster reaction rate. This could have been due to the increase of effective collision frequency of starch, PVA, and glutaraldehyde at a higher temperature. It can be seen from Figures 1 and 2 that the influence of the reaction temperature on the normalized SD and GM was significant in the first 3 h; the normalized SD decreased and normalized GM increased with increasing reaction temperature. However, after 3 h, the influence of the reaction temperature on the final values of the normalized SD and GM was not so remarkable.

It should be pointed out that when the insoluble part of the specimens soaked in DMSO was filtered out, the swollen films divided into two pieces held together by their edges, and the integrity of the pieces depended on the modification conditions, which determined crosslink density. This indicated that the crosslinking reaction took place in the surface layer of the specimens, so the inner part of specimens was dissolved.

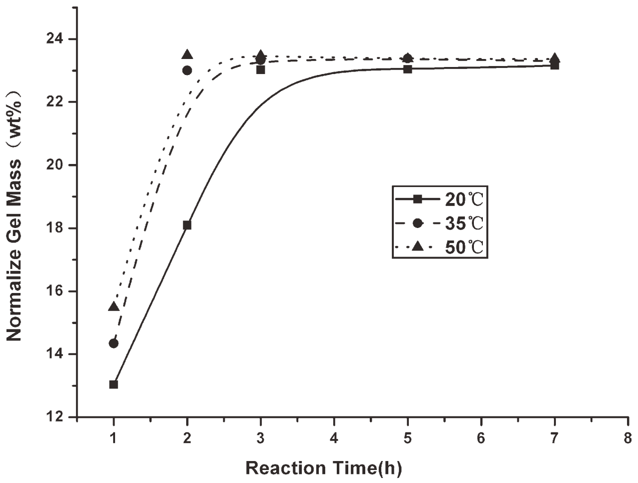

Figure 2 Changes of normalized GM against the reaction time for the specimens soaked in 1.0% glutaraldehyde aqueous solutions for 30 s and heated at different temperatures.

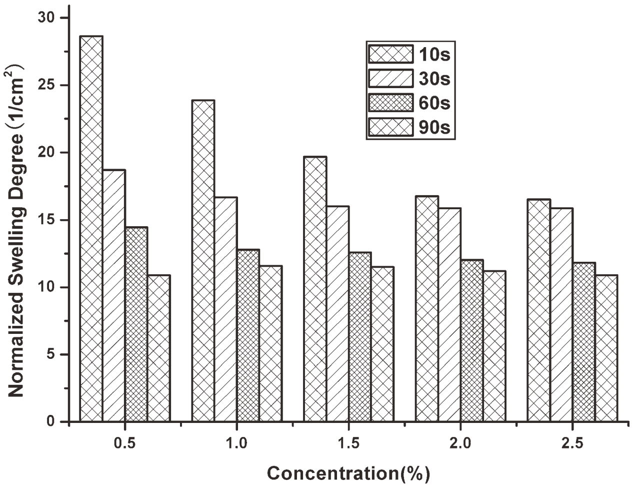

Figure 3 Changes of normalized SD against the concentration of glutaraldehyde aqueous solution for the specimens with different soaking times and heated at 50°C for 2 h.

Effect of the soaking time and concentration of glutaraldehyde aqueous solution

With consideration of the reaction efficiency and economic factor, heating at 50°C for 2 h was chosen to investigate the influences of the soaking time and concentration of glutaraldehyde aqueous solution on the crosslinking reaction. Figures 3 and 4 present the normalized SD and GM as a function of the concentration of glutaraldehyde aqueous solution for the specimens with different soaking times. The soaking time in glutaraldehyde aqueous solution determined the thickness of the surface layer containing glutaraldehyde, which, in turn, affected the depth where the macromolecular network could be formed. As shown in Figures 3 and 4, for a given concentration of glutaraldehyde aqueous solution, a longer soaking time gave rise to a lower value of normalized SD and a higher value of normalized GM. On the other hand, for a given soaking time, normalized SD decreased and normalized GM increased significantly with increasing concentration of glutaraldehyde aqueous solution when the soaking time was short, but when the soaking time was long, the effect of concentration of glutaraldehyde aqueous solution was not notable. This indicated that the effect of the concentration of the glutaraldehyde aqueous solution on the normalized SD and GM was related to the soaking time. Actually, the glutaraldehyde in the surface layer had a gradient distribution along the depth; a longer soaking time could result in not only a thicker surface layer containing glutaraldehyde but also a higher glutaraldehyde content in the surface layer; even the concentration of the glutaraldehyde aqueous solution was the same. A higher content of glutaraldehyde in the surface layer created a network with a higher crosslink density; this gave rise to a lower value of normalized SD. Thus, it was understandable that a longer soaking time led to a higher GM and lower SD when the soaking time was short (<60 s, Figs. 3 and 4). However, when the soaking time was long enough (90 s, Figs. 3 and 4), the glutaraldehyde content in the surface layer might have reached saturation and resulted in a highly crosslinked macromolecular network; this could have caused the influence of concentration of the glutaraldehyde aqueous solution on SD and GM to be not notable, as shown in Figures 3 and 4.

Moisture absorption

The moisture absorption of the TPS/PVA blend films was related to the number of hydroxyl groups in the specimens. Theoretically, the greater the number of hydroxyl groups left after crosslinking modification was, the higher the equilibrium MC was.

Effect of the reaction time and temperature

The specimens soaked in 1.0% glutaraldehyde aqueous solution for 30 s and then heated at different temperatures for different periods of time were used to investigate the influence of the reaction time and temperature on the moisture absorption. Examination results show that the influence of the reaction temperature (ranging from 20 to 50°C) on the moisture absorption was not notable. Figure 5 presents the moisture absorption isotherms of the specimens heated at 50°C for different periods of time. It can be seen that after the crosslinking modification, the TPS/PVA blend films showed a much lower moisture uptake in the high RH range, although this effect was not so obvious in the 15–59% RH region. Figure 6 presents the moisture absorption kinetics at 95% RH of the specimens

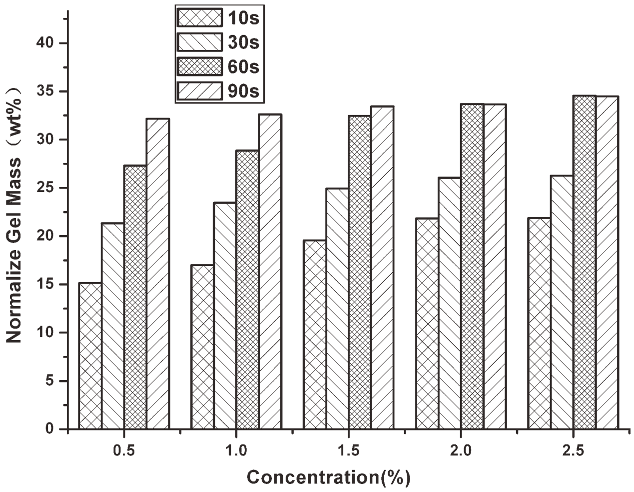

Figure 4 Changes of normalized GM against the concentration of glutaraldehyde aqueous solution for the specimens with different soaking times and heated at 50°C for 2 h.

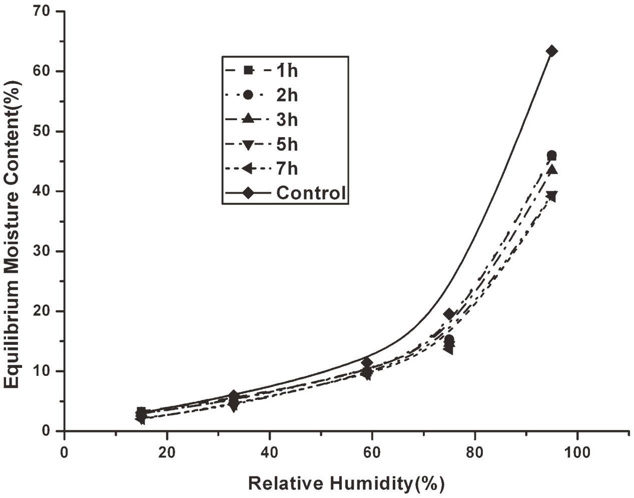

Figure 5 Moisture absorption isotherms at room temperature of the control film and the modified ones soaked in 1.0% glutaraldehyde aqueous solution for 30 s and heated at 50°C for different periods of time.

heated at 50°C for different periods of time. For all of the control and crosslinking-modified films, the moisture absorption was quick in the first 10 h of conditioning; afterward, the curves gradually turned level. The influence of the crosslinking modification on the moisture absorption kinetic curves was notable; the slope of the initial part and the final values of the moisture uptake for the crosslinking-modified films decreased significantly. Moreover, a longer reaction time yielded a lower moisture uptake at a given conditioning time. These results suggest that the crosslinking modification under the described conditions not only reduced the moisture absorption rate but also the moisture-uptake ability of the TPS/PVA blend films.

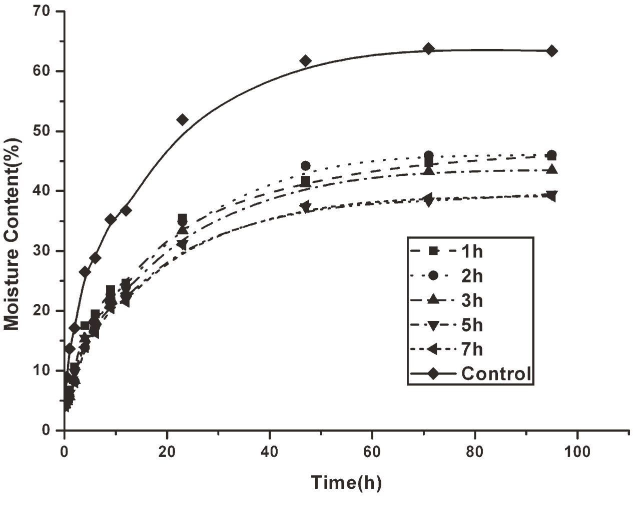

Figure 6 Moisture absorption kinetics at 95% RH and room temperature of the control film and the modified ones soaked in 1.0% glutaraldehyde aqueous solution for 30 s and heated at 50°C for different periods of time.

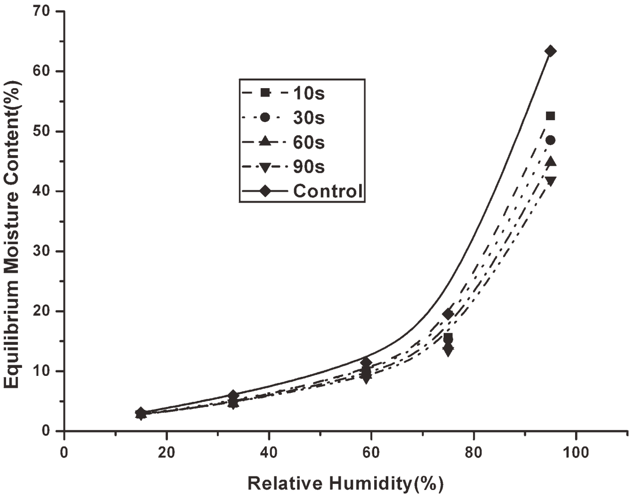

Figure 7 Moisture absorption isotherms at room temperature of the control film and the modified ones soaked in 1.5% glutaraldehyde aqueous solution for different periods of time and heated at 50°C for 2 h.

Effect of the soaking time and concentration of the glutaraldehyde aqueous solution

Heating at 50°C for 2 h was chosen to investigate the effect of the soaking time and concentration of the glutaraldehyde aqueous solution on the moisture absorption. It was found that in the examining ranges of the soaking time (10–90 s) and concentration of the glutaraldehyde aqueous solution (0.5–2.5%), the moisture absorption isotherms for all of the specimens had similar changing trends so did the moisture absorption kinetics at 95% RH and room temperature.

Figure 7 shows the moisture absorption isotherms of the specimens soaked in a 1.5% glutaraldehyde aqueous solution for different periods of time. It could be seen that after the crosslinking modification, the TPS/PVA blend films showed a much lower moisture uptake compared with the control at various RHs, especially in the high-RH range. A longer soaking time yielded a lower equilibrium MC at a given RH, and this was more obvious in the high-RH range. The moisture absorption isotherms of the specimens soaked in a glutaraldehyde aqueous solution with different concentrations (data not shown) indicated that the specimen treated with a higher concentration of glutaraldehyde aqueous solution gave rise to a lower equilibrium MC in the high-RH range.

Compared with that of the control one, the equilibrium MCs of the specimens soaked in 0.5, 1.0, 1.5, 2.0, and 2.5% glutaraldehyde aqueous solutions for 90 s and then heated at 50°C for 2 h decreased about 16, 19, 21, 21, and 22%, respectively, at 95% RH; whereas the equilibrium MCs of the specimens soaked in 2.5% glutaraldehyde aqueous solutions for 10, 30, 60, and 90 s and then heated at 50°C for 2 h decreased about 16, 17, 19, and 22%, respectively, at 95% RH.

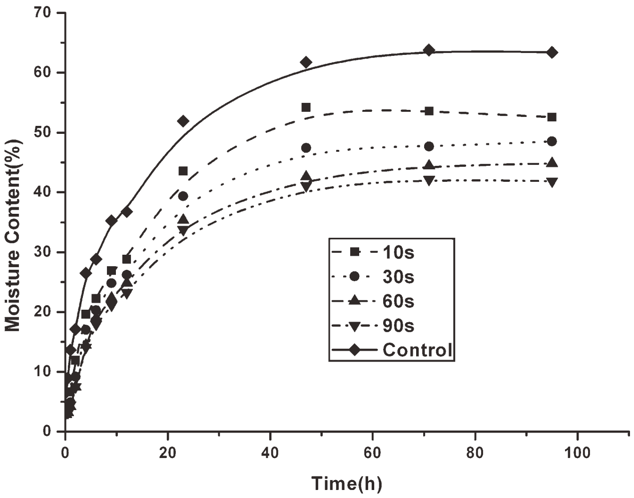

Figure 8 Moisture absorption kinetics at 95% RH and room temperature of the control film and the modified ones soaked in 1.5% glutaraldehyde aqueous solution for different periods of time and reacted at 50°C for 2 h.

Figure 8 depicts the moisture absorption kinetics at 95% RH and room temperature of the specimens soaked in 1.5% glutaraldehyde aqueous solutions for different times. It was found that the influence of the soaking time on the moisture absorption kinetics was remarkable. The specimen soaked for a longer time showed a lower moisture absorption rate and lower MC at a given conditioning time. With regard to the effect of the concentration of the glutaraldehyde aqueous solution, although the concentration of the glutaraldehyde aqueous solution influenced the moisture absorption kinetics, no clear trend was found in the investigated concentration region (0.5–2.5%), the results of moisture absorption kinetics at 95% RH and room temperature indicated that the crosslinking modification under the described conditions did lead to a notable decrease in the moisture absorption rate and dramatically reduced the moisture-uptake ability of the TPS/PVA blend films.

It should be mentioned that crosslinking modification changed the hydrophilic properties of the TPS/PVA film. The measurements of water contact angle showed that the contact angle of the TPS/PVA films increased from 80° (control) to 90–100° after the crosslinking modification.

Mechanical properties

Because the mechanical properties are an important criterion for many practical applications of materials, it was necessary to investigate the effect of the crosslinking modification on the mechanical properties of the TPS/PVA films.

Effect of the reaction time and temperature

Table I presents the effects of the reaction time and temperature on the tensile strength, Young's modulus, and elongation at break of the crosslinking-modified TPS/PVA blend films conditioned at room temperature and 75% RH. Compared with the control film, the crosslinking-modified specimens showed a higher tensile strength and Young's modulus but a lower elongation at break. The data in Table I indicate that a higher reaction temperature gave rise to higher values of tensile strength and Young's modulus and a lower value of elongation at break, and the specimens reacted for 3 h showed better parameters, although the influence of the reaction time on the mechanical properties was dependent upon the reaction temperature. The lower impact of the reaction time on the mechanical properties at 20°C may have been attributed to the fact that when the specimens were conditioned at 75% RH and room temperature for moisture equilibrium before the test; the crosslinking reaction was supposed to continue during this period of time. Thus, the influence of the reaction time at 20°C on the mechanical properties could be concealed by the conditioning.

Effect of the soaking time and concentration of the glutaraldehyde aqueous solution

Table II presents the effect of the soaking time and concentration of glutaraldehyde aqueous solution on

TABLE I
Mechanical Properties of the Crosslinking Modified Films Prepared by Soaking in a 1.0% Glutaraldehyde Aqueous Solution for 30 s and Heating at 20 and 50°C for Different Times

		Reaction time (h)				
Property	Temperature (°C)	0	1	3	5	7
Tensile strength (MPa)	Control	7.3 ± 0.1	—	—	—	—
	20	—	7.5 ± 0.4	8.3 ± 0.5	7.8 ± 0.2	7.8 ± 0.2
	50	—	7.8 ± 0.3	9.5 ± 0.6	8.3 ± 0.7	7.8 ± 0.7
Young's modulus (MPa)	Control	32.5 ± 2.5	—	—	—	—
	20	—	109.4 ± 15.8	142.3 ± 19.9	121.8 ± 22.6	114.5 ± 16.5
	50	—	134.1 ± 19.3	163.9 ± 13.0	130.3 ± 13.6	125.2 ± 15.6
Elongation at break (%)	Control	137.8 ± 8.0	—	—	—	—
	20	—	94.0 ± 13.4	78.6 ± 5.2	82.8 ± 10.1	84.0 ± 11.2
	50	—	74.7 ± 13.0	37.8 ± 8.0	50.8 ± 7.4	50.6 ± 13.8

TABLE II
Mechanical Properties of the Crosslinking Modified Films Prepared by Soaking in Glutaraldehyde Aqueous Solutions with Different Concentrations for Different Times and Heating at 50°C for 2 h

			Soaking time (s)			
Property	Concentration (%)	Control	10	30	60	90
Tensile strength (MPa)	—	7.3 ± 0.1	—	—	—	—
	0.5	—	8.0 ± 0.9	8.4 ± 0.8	11.6 ± 1.1	13.7 ± 1.407
	1.0	—	7.9 ± 0.9	8.5 ± 1.0	11.4 ± 1.0	11.9 ± 1.5
	1.5	—	8.0 ± 0.4	8.5 ± 0.9	11.2 ± 0.7	12.1 ± 1.2
	2.0	—	8.0 ± 0.6	8.2 ± 0.6	9.0 ± 1.1	11.1 ± 0.6
	2.5	—	7.9 ± 1.0	7.8 ± 0.4	8.9 ± 0.3	10.2 ± 1.1
Young's modulus (MPa)	—	32.5 ± 2.5	—	—	—	—
	0.5	—	107.8 ± 13.9	178.1 ± 16.6	257.3 ± 6.6	258.9 ± 2.4
	1.0	—	100.1 ± 3.5	164.1 ± 14.8	230.4 ± 13.3	228.6 ± 16.6
	1.5	—	75.3 ± 12.9	145.2 ± 17.0	209.3 ± 11.1	205.4 ± 16.4
	2.0	—	63.8 ± 4.7	87.0 ± 7.0	182.7 ± 7.0	181.2 ± 18.3
	2.5	—	61.0 ± 9.3	77.1 ± 7.0	178.3 ± 4.7	174.4 ± 4.6
Elongation at break (%)	—	137.8 ± 8.0	—	—	—	—
	0.5	—	119.3 ± 9.0	86.0 ± 10.3	40.5 ± 0.8	33.4 ± 1.9
	1.0	—	106.4 ± 13.3	70.1 ± 17.1	36.0 ± 2.5	35.5 ± 6.5
	1.5	—	106.7 ± 11.5	67.6 ± 7.5	35.3 ± 4.8	21.9 ± 3.1
	2.0	—	115.3 ± 9.5	105.1 ± 14.4	32.9 ± 4.9	23.8 ± 6.3
	2.5	—	119.5 ± 10.1	95.6 ± 12.0	22.1 ± 6.9	23.5 ± 4.7

the mechanical properties of the crosslinking-modified TPS/PVA blend films conditioned at room temperature and 75% RH. Compared with the control one, the crosslinking modification increased the tensile strength and Young's modulus but decreased the elongation at break of the TPS/PVA blend films. It could be seen that the soaking time had a remarkable impact on the mechanical properties of the TPS/PVA blend films. At a given concentration of glutaraldehyde aqueous solution, the tensile strength increased, and the elongation at break decreased with the increase of soaking time. The value of Young's modulus increased with the increase of soaking time and reached the highest value at 60 s; it then declined slightly at 90 s. For a given soaking time, the effect of the concentration of the glutaraldehyde aqueous solution on the tensile strength was not significant, at least in the investigated region, whereas Young's modulus of the modified specimens presented a decreasing trend with increasing concentration of the glutaraldehyde aqueous solution. With regard to the effect of the concentration of the glutaraldehyde aqueous solution on the elongation at break, no clear trend was found in the investigated region.

Effect of RH

Table III presents the effect of RH on the mechanical properties of the crosslinking-modified TPS/PVA blend films. The mechanical properties were measured at room temperature after the specimens were conditioned at different humidities for moisture equilibrium. The mechanical properties of the specimens conditioned at 11%RH were not obtained because of their brittleness.

As shown in Table III, when RH increased from 33 to 95%, the tensile strength and Young's modulus of both the control and crosslinking-modified samples decreased, and the elongation at break of the crosslinking-modified specimens increased, whereas that of control initially increased and then decreased at 95% RH. Because water is a plasticizer for starch and PVA and the MCs of the TPS/PVA blend films

TABLE III
Mechanical Properties at Different RHs of Crosslinking Modified Films Prepared by Soaking in a 1.0% Glutaraldehyde Aqueous Solution for 90 s and Heating at 50°C for 2 h

		RH (%)				
Property	Specimen	11	33	59	75	95
Tensile strength (MPa)	Control	—	34.2 ± 1.1	13.0 ± 0.9	7.3 ± 0.1	2.2 ± 0.1
	Crosslinked	—	20.3 ± 1.5	17.7 ± 1.5	10.1 ± 0.6	4.2 ± 0.1
Young's modulus (MPa)	Control	—	578.3 ± 12.7	321.0 ± 6.1	32.5 ± 2.5	5.1 ± 0.3
	Crosslinked	—	508.5 ± 28.1	417.6 ± 5.7	248.4 ± 11.4	16.1 ± 0.7
Elongation at break (%)	Control	—	12.6 ± 1.0	39.2 ± 3.6	137.8 ± 8.0	88.0 ± 9.3
	Crosslinked	—	5.6 ± 0.2	7.5 ± 0.3	35.5 ± 6.5	75.4 ± 4.2

increased with increasing RH; therefore, the tensile strength and Young's modulus of the specimens decreased, and the elongation at break increased with increasing RH. At 95% RH, the control film was too weak because of the high MC, which led the lower elongation at break.

When RH changed from 33 to 95%, the changing ranges of the tensile strength, Young's modulus, and elongation at break of the control film were 2.16–34.21 MPa, 5.13–578.31 MPa, and 12.62–137.82%, respectively, whereas those for the crosslinking-modified ones were 4.24–20.25 MPa, 16.05–508.45 MPa, and 5.61–75.41%, respectively. Obviously, the crosslinking modification with glutaraldehyde reduced the sensitivity of the mechanical properties of the TPS/PVA blend films to RH.

CONCLUSIONS

The TPS/PVA blend films could be modified by crosslinking through soaking the films in the glutaraldehyde aqueous solution and then heating in an oven. The extent of crosslinking, that is, the thickness of the crosslinked surface layer and the crosslink density of the surface layer, increased with the prolongation of soaking time in a given glutaraldehyde aqueous solution. However, the effect of the concentration of the glutaraldehyde aqueous solution on the extent of crosslinking depended on the soaking time. When the soaking time was shorter than 60 s, the higher concentration of glutaraldehyde aqueous solution gave rise to a higher crosslink density in the surface layer. The results of moisture absorption measurements indicated that the postcrosslinking modification significantly reduced the hydrophilic characteristic of the TPS/PVA blend films; that is, it lowered the equilibrium MC of the films. The results of the mechanical properties measurements showed that the postcrosslinking modification increased the tensile strength and Young's modulus but decreased the elongation at break of the TPS/PVA blend films and also reduced the sensitivity of the mechanical properties of the TPS/PVA blend film to RH as well.

When we compared these glutaraldehyde crosslinking-modified TPS/PVA blend films with those surface-crosslinked through UV irradiation,[32] the water-resistance characteristics were comparable, but the mechanical properties were quite different. The UV surface-crosslinked TPS/PVA blend films showed a much higher tensile strength and Young's modulus but a lower elongation at break. In other words, the TPS/PVA blend films crosslinking-modified with glutaraldehyde in this study were more flexural than the UV crosslinked ones. This was probably due to the higher crosslink density in the surface layer of the UV crosslinked films, which was identified by the much lower SD. Both posttreatment techniques had their own advantages; the adoption should depend on the facilities and performance requirements for the materials.

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