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Post-crosslinking modification of thermoplastic starch/PVA blend films by using sodium hexametaphosphate

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ABSTRACT

Thermoplastic starch (TPS)/poly (vinyl alcohol) (PVA) blend films were post-treated by crosslinking through soaking the films in sodium carbonate aqueous solution and sodium hexametaphosphate aqueous solution sequentially and then heating. The effects of the concentrations of the sodium carbonate aqueous solution and the sodium hexametaphosphate aqueous solution, soaking time, heating temperature and time on the properties of the TPS/PVA blend films were investigated. It was found that the crosslinking modification significantly reduced the moisture sensitivity of the TPS/PVA blend films, i.e., lowered the equilibrium moisture content of the blend films, increased the tensile strength and Young's modulus but decreased the elongation at break of the blend films. The described method could be used for post-treating TPS/PVA based products to optimize their properties.

1. Introduction

Starch is a natural polymer of D-glucose containing amylose and amylopectin. The development of thermoplastic starch (TPS) has received considerable attention over the last two decades due to its biodegradability, renewability and low cost (Averous, 2004; Gandini, 2008; Mohanty, Misra, & Hinrichsen, 2000; Yu, Dean, & Li, 2006). However, the hydrophilic nature of starch causes the moisture content in TPS to change with environment and leads to the mechanical properties of TPS to be jeopardized in damp environment, which renders TPS unsuitable for many high humidity applications (Gandini, 2008).

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 (Follain, Joly, Dole, & Bliard, 2005; Shogren, Lawton, Tiefenbacher, & Chen, 1998; Solaro, Corti, & Chiellini, 2000; Sreedhar, Chattopadhyay, Karunakar, & Sastry, 2006; Yun & Yoon, 2010). Although TPS/PVA blends presented a lower water uptake compared to TPS, due to existence of the hydroxyl groups on the molecules of starch and PVA, the hydrophobic characteristics of the TPS/PVA blends still need to be improved.

Crosslinking modification is an efficient and commonly used approach to increase the water resistance of starch and PVA. Research results showed that surface photo-crosslinking modification of TPS sheets and TPS/PVA films significantly reduced the surface hydrophilic characteristics and improved the water resistance of the materials (Zhou, Zhang, Ma, & Tong, 2008; Zhou et al., 2009). The photo-crosslinking modification needs a UV source to initiate and finish the crosslinking reaction. Alternatively, the crosslinking modifications of both TPS and PVA can be also implemented by heating, and heating seems easier and more convenient for practice applications. For the crosslinking modification of starch or PVA through heating, glutaraldehyde (El-Tahlawy, Venditti, & Pawlak; Parra, Tadini, Ponce, & Lugao, 2004; Ramaraj, 2007; Wang & Hsieh, 2010; Yoon, Chough, & Park, 2007), epichlorohydrin (Jiang, 1992; Rioux, Lspas-Szabo, Ait-Kadi, Mateescu, & Juhasz, 2002; Sreedhar et al., 2006), citric acid (Reddy & Yang, 2010; Shi et al., 2008), boric acid (Yin, Li, Liu, & Li, 2005), borax (Sreedhar, Sairam, Chattopadhyay, Rathnam, & Rao, 2005), sodium trimetaphosphate (Mao, Wang, Meng, Zhang, & Zheng, 2006) and trisodium trimetaphosphate (Li et al., 2009) were used as crosslinking agent to react with the hydroxyl groups in starch or PVA.

In this paper, the crosslinking modification of TPS/PVA blend films was carried out through heating after the films were soaked in sodium carbonate aqueous solution and sodium hexametaphosphate aqueous solution sequentially. Unlike other crosslinking modifications for TPS/PVA blend system (Ramaraj, 2007; Yoon et al., 2007), the method used in this study is a post-crosslinking technique that could be applied after the products were formed instead of during the products formation. Some of the physical properties of the crosslinking modified TPS/PVA films were characterized to investigate the influences of the post-crosslinking modification.

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2. Experimental

2.1. Materials

Corn starch was obtained from Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China). PVA with polymerization degree of 1750 ± 50 was supplied by Shenyang Dongxing Reagent Factory (China). Sodium hexametaphosphate (SHMP) was purchased from Xilong Chemicals Co. Ltd. (China). Glycerol and sodium carbonate (Na_2CO_3) were from Beijing Beihua Fine Chemicals Co. Ltd. (China). All these chemicals were reagent grade and used as received without any further purification.

2.2. Film preparation

TPS/PVA blend films were prepared by a solution casting method. First, PVA solution was prepared by adding 7.5 g of PVA into 500 g of distilled water and heating with stirring at 95 °C till dissolution. 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 heated with stirring at 95 °C for 60 min to gelatinize the starch. Afterward, the prepared PVA solution was added. The mixture was kept at 95 °C and maintained stirring for 40 min to get 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 amount into PMMA trays for casting and dried at 50 °C. The dried films with thickness about 0.21 mm were peeled off and stored at room temperature (20 ± 2 °C) and 59% relative humidity (RH) for experimental use.

2.3. Crosslinking modification

After conditioned at 59% RH to moisture equilibrium, small pieces (25 mm × 20 mm) of the TPS/PVA blend film were first soaked in Na_2CO_3 aqueous solutions (with different concentrations for various periods of time) then in SHMP aqueous solutions (with different concentrations for various periods of time). When the films were taken out from the solutions, filter papers were used to absorb the excess solution on the surfaces. The films treated with the Na_2CO_3 solution and SHMP solution were placed in an oven with temperatures ranging from 25 °C to 50 °C for various periods of time to finish the crosslinking reaction.

2.4. Swelling degree and gel mass

The extent of crosslinking was characterized by the measurement of the film's swelling degree (SD) in DMSO and gel mass (GM). The determination of SD and GM was carried out according to the procedure described in the literature (Delville, Joly, Dole, & Bliard, 2002). The specimens were conditioned at 59% RH for moisture equilibrium, and the weighed mass were referred to as m_0. Then, the specimens were immersed in DMSO, in which the intact TPS/PVA blend film is completely soluble. After 48 h, the insoluble part (swollen film) was filtered out and weighed (the amount was referred to as 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 constant weight (the amount was referred to as m_d). The SD normalized by surface area and GM normalized by total mass were calculated from the following formula:

$$\text{Normalized SD} = \frac{m_s - m_d}{m_d \times A}$$

$$\text{Normalized GM} = \left(\frac{m_d}{m_0}\right) \times 100\%$$

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

2.5. Moisture absorption measurement

Moisture absorption was measured by storing the specimens at room temperature (20 ± 2 °C) in desiccators with controlled relative humidities (11, 33, 59, 75 and 95% RH); these were maintained by saturated salt solutions (Zhou et al., 2008). 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. The equilibrium moisture content (EMC) was calculated with the measured wet weight (w_w) and the dry weight (w_d) by:

$$\text{EMC} = \frac{w_w - w_d}{w_d}$$

2.6. Mechanical properties

Dumbbell-shaped specimens with 50 mm long and 4 mm neck width were cut from the prepared films. After the crosslinking modification, all of the specimens were conditioned at a given relative humidity and room temperature (20 ± 2 °C) until moisture equilibrium was reached. The tensile tests were carried out with an universal testing machine (Model QJ-210, Shanghai Qingji, China) with a 100 N loading cell at 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.

3. Results and discussion

3.1. Crosslinking reaction

Because the intact TPS/PVA blend films are soluble in DMSO, therefore, the GM of the crosslinking modified TPS/PVA blend films is related to the amounts of starch and PVA macromolecules involved in formation of the crosslinking networks. The SD of the modified TPS/PVA blend films is related to the crosslink density of the newly created networks. The lower the normalized SD was, the higher the crosslink density was.

Fig. 1 showed the values of the normalized SD and normalized GM of the specimens soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and in 1.0% SHMP aqueous solution for 30 s sequentially, and heating 2 h at different temperatures; while Fig. 2 showed the normalized SD and normalized GM as a function of reaction time for the specimens soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and in 1.0% SHMP aqueous solution for 30 s sequentially, and heating at 50 °C. It can be seen that, within the investigated temperature, ranging from 25 °C to 50 °C, higher temperature gave rise to lower SD and higher GM, which indicated that more macromolecules were crosslinked with higher crosslink density. This could be attributed to the increase of effective collision frequency of starch, PVA and SHMP at a higher temperature. Although higher temperature gave an advantage to the crosslinking reaction, if the temperature was too high, the evaporation of moisture in the films would be accelerated, which, in turn, decreased macromolecular mobility of starch and PVA. It was also found in Fig. 2 that the normalized SD decreased and normalized GM increased with increasing reaction time and the changing rates were initially fast and then slowed down. Beyond

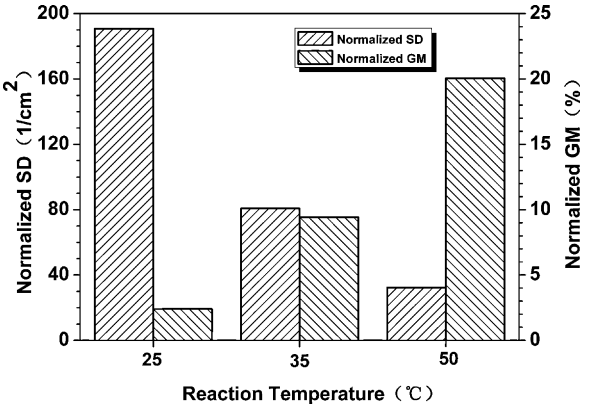

Fig. 1. Normalized SD and normalized GM for the TPS/PVA blend films soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and in 1.0% SHMP aqueous solution for 30 s sequentially, and heating 2 h at different temperatures.

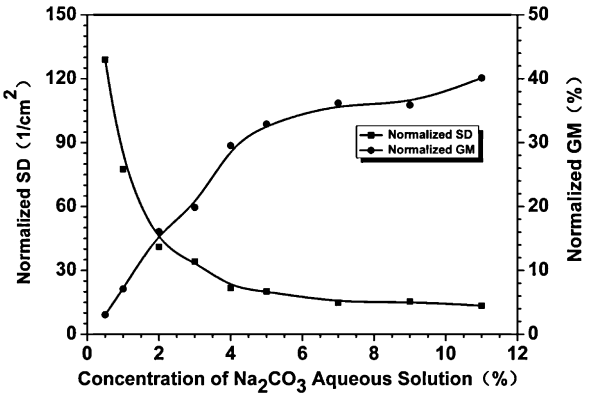

Fig. 3. Effect of the concentration of Na_2CO_3 aqueous solution on the normalized SD and normalized GM of the TPS/PVA blend films soaked in Na_2CO_3 aqueous solutions for 30 s and then in 1.0% SHMP aqueous solution for 30 s and heated at 50 °C for 2 h.

the initial fast changing regions, the curves leveled off and reached stable values which were less-dependant on the reaction time. This is understandable, because the intermolecular bridges created by the crosslinking and the moisture evaporation during the reaction led to decrease of macromolecular mobility of starch and PVA, which hindered the crosslinking reaction.

During the crosslinking reaction between starch and SHMP, SHMP reacts with the hydroxyl groups on starch molecules, forming intra and inter ester linkages which crosslink starch molecules. Alkaline environment is advantageous to the hydroxyl groups of starch becoming oxygen anions and keeping the reaction toward the crosslinking (Lim & Seib, 1993; Fang et al., 2008). Therefore, the crosslinking modification of TPS/PVA blend films with SHMP would profit from the alkaline treatment such as soaking the films in Na_2CO_3 aqueous solution. Fig. 3 presented the normalized SD and normalized GM as a function of concentration of Na_2CO_3 aqueous solution for the specimens soaked in Na_2CO_3 aqueous solutions for 30 s and then in 1.0% SHMP aqueous solution for 30 s and heated at 50 °C for 2 h. It can be seen from Fig. 3 that the normalized SD decreased and normalized GM increased rapidly with increase of Na_2CO_3 aqueous solution concentration when the concentration was lower than 4.0%, afterward both SD and GM curves turned into level and were less dependent on the concentration of Na_2CO_3 aqueous solution. These results indicated that the alkaline treatment with Na_2CO_3 aqueous solution could promote the crosslinking reaction in the TPS/PVA blend films when using SHMP as the crosslinking agent, but over high concentration of Na_2CO_3 aqueous solution would not make more contribution.

The effect of concentration of SHMP aqueous solution on the normalized SD and normalized GM of the TPS/PVA blend films soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and then in SHMP aqueous solutions for 30 s and heated at 50 °C for 2 h was showed in Fig. 4. The normalized SD decreased and normalized GM increased significantly with increase of the concentration of SHMP aqueous solution when the concentration was lower, but both SD and GM curves gradually turned into level when the concentration was higher. This is understandable, because, for a given soaking time, higher concentration of SHMP aqueous solution would yield a higher content of SHMP in the films, which could cause more macromolecules to participate the crosslinking and create a network with higher crosslink density, giving rise to higher GM and lower value of SD. However, because the formation of the intermolecular bridges due to crosslinking would decrease macromolecular mobility of starch and PVA, which, in turn, reduces the crosslinking reaction kinetics, therefore, further increase of the concentration of SHMP aqueous solution would not yield lower SD and higher GM as shown in Fig. 4.

The soaking times in Na_2CO_3 and SHMP aqueous solutions determine the thickness of the surface layer containing Na_2CO_3 and SHMP, which will affect the depth where the macromolecular network can be formed. Fig. 5 showed the normalized SD and normalized GM as function of soaking time in Na_2CO_3 aqueous solution for the specimens soaked in 3.0% Na_2CO_3 aqueous solutions and then in 1.0% SHMP aqueous solution for 100 s and heated at 50 °C for 2 h. As can be seen that, for the given soaking time in

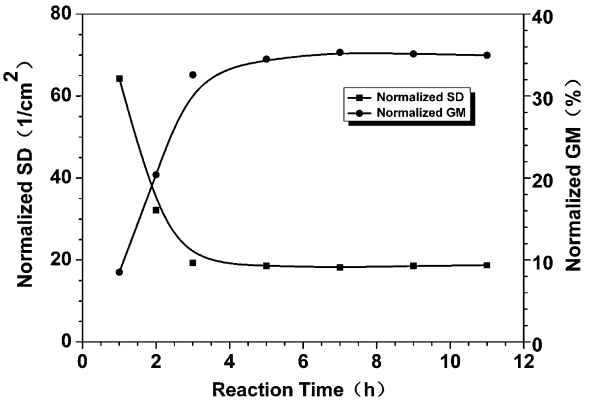

Fig. 2. Normalized SD and normalized GM as function of reaction time for the TPS/PVA blend films soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and in 1.0% SHMP aqueous solution for 30 s sequentially, and heating at 50 °C.

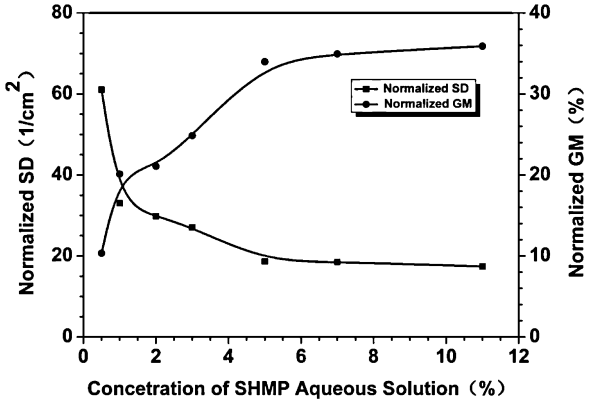

Fig. 4. Effect of the concentration of SHMP aqueous solution on the normalized SD and normalized GM of the TPS/PVA blend films soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and then in SHMP aqueous solutions for 30 s and heated at 50 °C for 2 h.

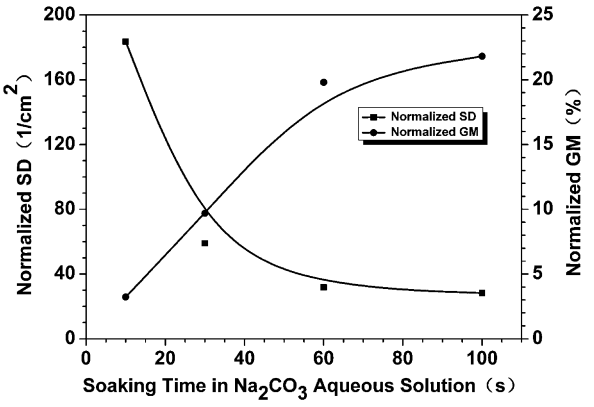

Fig. 5. Normalized SD and normalized GM as function of soaking time in Na_2CO_3 aqueous solution for the TPS/PVA blend films soaked in 3.0% Na_2CO_3 aqueous solution and then in 1.0% SHMP aqueous solution for 100 s and heated at 50 °C for 2 h.

SHMP aqueous solution (100 s), longer soaking in Na_2CO_3 aqueous solution (the longest was 100 s) gave rise to a lower value of normalized SD and a higher value of normalized GM. Actually, the influence of soaking time in Na_2CO_3 aqueous solution and SHMP aqueous solution is quite complex. It can be imagined that there is a gradient distribution of both Na_2CO_3 and SHMP along the depth of the films, longer soaking time could result in not only a thicker surface layer containing Na_2CO_3 or SHMP but also a higher content of Na_2CO_3 and SHMP in the surface layer even the concentration of aqueous solution was kept as constant, therefore, longer soaking time could lead to higher GM and lower SD when soaking time was short. However, if soaking time was long enough, the contents of Na_2CO_3 and SHMP in the films might reach saturation, this could decrease the influence of the concentration of aqueous solution on SD and GM.

3.2. Moisture absorption

The purpose of the crosslinking modification for the TPS/PVA blend films is to lower their moisture sensitivity. Moisture absorption is an index which can be used to characterize the moisture sensitivity. Theoretically, moisture absorption of TPS/PVA blend films is related to the amounts of the hydroxyl groups in the specimens, the more the hydroxyl groups are, the higher the EMC is.

The specimens soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and in 1.0% SHMP aqueous solution for 30 s sequentially were used to investigate the influence of reaction temperature and time on the EMC at different RHs. Table 1 presented the EMC at different RHs for the control and the crosslinking modified TPS/PVA blend films. Compared to the control one, the data in Table 1 indicated the crosslinking modification significantly lowered the EMC of the TPS/PVA blend films especially in the high RH range, but the influence of reaction temperature (ranging from 25 °C to 50 °C) and heating time (ranging from 1 h to 5 h) on the EMC was not notable. It should be pointed out that when the crosslinking modified specimens were conditioned at room temperature and various RHs for moisture equilibrium, the crosslinking reaction was supposed to continue during this period of time. The influence of reaction temperature and time on the EMC could be concealed by the conditioning. The less impact of reaction temperature and time on the EMC of the crosslinking modified TPS/PVA blend films as shown in Table 1 may be attributed to this.

Table 1
Effect of reaction temperature and time on the EMC at different RHs of the TPS/PVA blend films soaked in 3.0% Na_2CO_3 aqueous solution for 30 s and in 1.0% SHMP aqueous solution for 30 s.

Treating conditions			RH (%)				
Temp (°C)	Heating time (h)		11	33	59	75	95
–	–	Control	0.49	5.44	9.89	15.83	46.43
25	2		0.35	4.28	8.04	13.20	27.65
35	2		0.21	4.03	7.86	12.30	26.94
50	2		0.24	4.06	7.88	11.94	26.67
50	1		0.32	4.12	7.92	12.67	28.56
50	3		0.22	4.05	7.67	11.94	25.50
50	5		0.23	4.08	7.60	11.68	24.94

Table 2
Effect of the concentration and soaking time in Na_2CO_3 and SMHMP aqueous solutions on the EMC at different RHs for the TPS/PVA blend films heating at 50 °C for 2 h.

Treating conditions			RH (%)				
Na_2CO_3	SHMP		11	33	59	75	95
–	–	Control	0.49	5.44	9.89	15.83	46.43
0.5%, 30 s	1.0%, 30 s	–	0.09	4.19	7.65	12.57	30.78
1.0%, 30 s	1.0%, 30 s	–	0.10	4.01	7.50	12.54	29.70
2.0%, 30 s	1.0%, 30 s	–	0.15	3.98	7.59	12.18	33.03
4.0%, 30 s	1.0%, 30 s	–	0.16	4.03	7.66	12.09	33.44
7.0%, 30 s	1.0%, 30 s	–	0.19	4.07	7.77	11.75	33.58
11.0%, 30 s	1.0%, 30 s	–	0.17	3.97	7.94	12.08	36.32
3.0%, 10 s	1.0%, 100 s	–	0.29	4.23	7.80	12.13	23.92
3.0%, 30 s	1.0%, 100 s	–	0.26	4.04	7.66	11.79	23.01
3.0%, 60 s	1.0%, 100 s	–	0.26	4.14	7.66	11.71	22.58
3.0%, 100 s	1.0%, 100 s	–	0.25	4.02	7.54	11.40	22.97
3.0%, 30 s	0.5%, 30 s	–	0.36	4.05	7.74	12.42	33.75
3.0%, 30 s	1.0%, 30 s	–	0.27	4.05	7.73	12.25	31.49
3.0%, 30 s	3.0%, 30 s	–	0.21	3.92	7.53	12.09	29.59
3.0%, 30 s	5.0%, 30 s	–	0.16	3.96	6.99	11.66	28.36
3.0%, 30 s	9.0%, 30 s	–	0.15	3.87	7.04	11.60	28.54
3.0%, 100 s	1.0%, 10 s	–	0.35	4.28	8.09	12.02	24.91
3.0%, 100 s	1.0%, 30 s	–	0.29	4.30	7.82	11.73	23.25
3.0%, 100 s	1.0%, 60 s	–	0.25	4.16	7.59	11.75	19.88
3.0%, 100 s	1.0%, 100 s	–	0.21	3.99	7.56	11.65	19.59

Heating at 50 °C for 2 h was chosen for investigating the effect of soaking time and the concentration of Na_2CO_3 and SMHMP aqueous solutions on the moisture absorption. The influences of the soaking time and concentration of Na_2CO_3 and SMHMP aqueous solutions on the EMC were presented in Table 2. It can be seen that, after the crosslinking modification, the TPS/PVA blend films showed a much lower moisture uptake compared to the control one at various relative humidities, especially in the high RH range. In other words, the crosslinking modification under the described conditions did dramatically reduce the moisture uptake ability of the TPS/PVA blend films. The data in Table 2 also indicated that the influence of the concentration of Na_2CO_3 aqueous solution and the soaking time in Na_2CO_3 aqueous solution were not notable, but the effect of the concentration of SHMP aqueous solution and the soaking time in SHMP aqueous solution were remarkable. The specimens treated with higher concentration of SHMP aqueous solution gave rise to lower EMC in the high RH range and longer soaking time in SHMP aqueous solution yielded lower EMC at a given relative humidity. This may be attributed to the fact that Na_2CO_3 just played a role of a catalyst, while SHMP is crosslinking agent. Therefore, either using higher concentration of SHMP aqueous solution or soaking the films in SHMP aqueous solution for longer time would introduce more SHMP into the films, and higher content of SHMP could cause more hydroxyl groups in the films were consumed, giving rise to lower values of EMC.

3.3. Mechanical properties

Because the mechanical properties are important criterion for many practical applications of materials, it was necessary

Table 3
Mechanical properties of the control and modified TPS/PVA blend films by soaking them in 3.0% Na_2CO_3 aqueous solutions for 100 s and then in 1.0% SHMP aqueous solution for different periods of time and heated at 50 °C for 2 h.

Mechanical properties	Control	Soaking time (s)			
		10	30	60	100
Tensile strength (MPa)	2.30 ± 0.12	4.95 ± 0.19	5.94 ± 0.24	6.60 ± 0.26	5.66 ± 0.28
Young's modulus (MPa)	14.28 ± 0.91	31.98 ± 2.79	44.00 ± 3.22	86.65 ± 4.93	69.89 ± 3.49
Elongation at break (%)	72.78 ± 2.50	63.45 ± 2.09	59.88 ± 1.86	43.47 ± 4.47	41.76 ± 5.39

to investigate the effect of the crosslinking modification on the mechanical properties of the TPS/PVA films.

Table 3 presented the tensile strength, Young's modulus and elongation at break of the control TPS/PVA blend films and the crosslinking modified ones through soaking them in 3.0% Na_2CO_3 aqueous solutions for 100 s and then in 1.0% SHMP aqueous solution for different periods of time and heated at 50 °C for 2 h. It should be mentioned that, before the testing, all of the specimens were conditioned at room temperature (20 ± 2 °C) and 75% RH for moisture equilibrium. The data in Table 3 indicated that, compared to 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 can be seen that the soaking time in SHMP aqueous solution had a remarkable impact on the mechanical properties of the TPS/PVA blend films. The values of the tensile strength and Young's modulus increased with the increase of the soaking time and reached the highest value at 60 s, then declined with further prolongation of the soaking time, while the trend of the elongation at break against the soaking time was monotonic decreasing. As showed in Table 2, the EMC of the modified films at 75% RH were very close, the differences in the mechanical properties should be mainly due to the difference in the crosslink density of the macromolecular networks created under the different conditions.

4. Conclusions

The TPS/PVA blend films can be post-modified by crosslinking through soaking the films in sodium carbonate and sodium hexametaphosphate aqueous solutions, sequentially, and then heating in an oven. The results of the moisture absorption measurements indicated that the post-crosslinking modification significantly reduced the equilibrium moisture content of the TPS/PVA blend films, i.e., lowered the hydrophilic characteristic of the films. The results of the mechanical properties measurements showed that the crosslinking modification 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 post-treating TPS/PVA based products to optimize their properties.

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