Starch Crosslinked with Poly(vinyl alcohol) by Boric Acid

Yeping Yin, Jianfang Li, Yingchun Liu, Zhong Li

Science College, Huazhong Agricultural University, Wuhan, 43007 China

Received 22 September 2004; accepted 17 November 2004
DOI 10.1002/app.21569
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Starch was crosslinked with poly(vinyl alcohol) (PVA) by boric acid. A suitable plasticizer and defoamer were added to obtain the brei. A film from the starch and PVA (SP film) was prepared by casting. The effects of various factors, such as the crosslinking temperature, the PVA content, and the amounts of glycerol and boric acid, on the tensile strength and breaking elongation were studied. The results showed that the SP film prepared by boric acid crosslinking had excellent mechanical properties. The film-forming properties, transmittance, and water resistance of the SP film were also investigated. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1394–1397, 2005

Key words: crosslinking; films; compatability; mechanical properties; infrared spectroscopy

INTRODUCTION

During the past 50 years, the study of the film from starch and poly(vinyl alcohol) (PVA; SP film) has progressed significantly.[1–7] Previous studies have proved that the SP film is biodegradable.[2–9] In the preparation of the SP film, formaldehyde is usually used as a crosslinking agent.[6] The results have shown that formaldehyde is a good crosslinking agent, but it presents undesirable effects because of its environmental pollution. Among the various tested crosslinking agents, boric acid has finally been selected because it is a good crosslinking agent and produces no pollution in the environment. Moreover, boric acid is beneficial to the growth of plants.

The seven kinds of trace elements that plants require are Fe, Mn, Zn, Cu, B, Mo, and Cl. The lack of B is the most common fact among the trace elements.[10] The boron fertilizers usually used are borax and boric acid. In this study, boric acid was used as a crosslinking agent. The hydroxyl group in boric acid and starch/PVA can react to form an ester linkage.

EXPERIMENTAL

Materials

Cornstarch (Kelong Chemical Apparatus Co., Wuhan, China) was kiln-dried at 110°C for 2 h. PVA (molar mass = 77.000 g/mol; Xilong Chemicals Group, Wuhan, China), boric acid, glycerol, and Tween 80 (defoamer; Helian Chemical Apparatus Co.) were used without further purification.

Crosslinking reaction and film preparation

PVA and pure water were placed in a three-necked flask equipped with a thermometer and stirrer. PVA was dissolved at 90°C. Then, the brei of starch and glycerol (plasticizer) were added. The mixture was gelatinized at 80°C, and boric acid was added after 2 h with a constant-pressure dropping funnel. After 2 h at 80°C, Tween 80 was added, and the brei was obtained after 30 min. The SP film was prepared with a casting process.

Characterization

The viscosity of the reaction mixture was measured with an NDJ-95 viscometer (Balance Instruments Factory, Shanghai, China). The tensile strength and breaking elongation of the SP film were determined with a mechanical tester (RGT-2, Reger Instrument Co., Ltd., Shenzhen, China). The rate of extension was 500 mm/min. The transparency of the film was determined with a spectrophotometer (SP-1102, Shanghai Spectrum Instruments Co., Ltd., Shanghai, China) with a working wavelength of 500 nm. We determined the water absorption of the film by placing the film samples in a constant-temperature (30°C) water bath and weighing them at regular intervals. Infrared spectra were obtained with a Nicolet Instruments (Warwick, United Kingdom) 750 spectrophotometer.

RESULTS AND DISCUSSION

Viscosity of the reaction solution after crosslinking

The viscosity of the brei showed the extent of the crosslinking reaction. It also had an influence on the

Correspondence to: Y. Yin (yinyeping@mail.hzau.edu.cn).

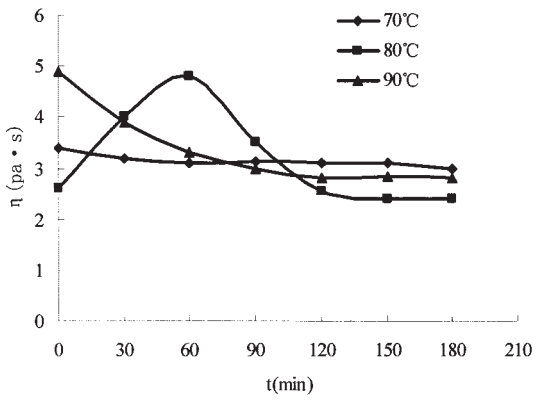

Figure 1 Viscosity (η) of the SP brei at different temperatures and times.

film-forming ability of the brei and the properties of the formed film. When the viscosity of the brei was too high, the fluidity of the brei was too small to form a film. However, when the viscosity was too low, the film-forming ability was also poor, and the film's strength was low. The viscosity of the reaction mixture was determined at different temperatures and is reported as a function of time (Fig. 1).

The viscosity of the reaction system changed slightly with time at 70°C. At 90°C, the viscosity of the reaction system gradually dropped at first and then changed only slightly after 100 min. It is likely that two reactions occurred simultaneously: crosslinking between PVA and starch and hydrolysis of starch itself. The crosslinking reaction caused an increase in the viscosity, whereas hydrolysis reduced it. At a lower temperature, both the crosslinking reaction and hydrolysis were slow, so the viscosity of the reaction system changed only slightly with time. The activation energy of the crosslinking reaction was larger than that of hydrolysis. Therefore, the rate of crosslinking increased with the temperature more quickly than that of hydrolysis. At 90°C, the viscosity was highest at first, but as the concentration of the crosslinking agent decreased with time, the rate of crosslinking gradually decreased, and the hydrolytic reaction of the starch became significant; therefore, the viscosity dropped. At 80°C, the rate of crosslinking was greater than that of hydrolysis before 60 min. After 60 min, hydrolysis dominated. The optimum conditions for crosslinking were 60 min and 80°C, but under these conditions, the viscosity was too high for the brei to form a good film. The best reaction time, therefore, was 90 min.

Influence of the quantity of the crosslinking agent on the mechanical properties of the SP film

The effect of the quantity of the crosslinking agent on the mechanical properties of the SP film is shown in Table I. With an increase in the dosage of boric acid, the tensile strength of the film rose at the beginning but fell when the dosage was up to 2.0%, whereas the breaking elongation dropped continuously. Increasing the quantity of boric acid improved the extent of crosslinking between PVA and starch and thus strengthened the bonding of the two kinds of molecules; this led to an increasing tensile strength of the film. However, when the quantity of boric acid was too high, the film became brittle, and the tensile strength and elongation of the film dropped.

Effect of the quantity of the crosslinking agent on the transmittance of the SP film

Table II shows the transmittance of the SP film with different amounts of boric acid. Increasing the quantity of boric acid increased the transmittance of the SP film initially and then reduced it at longer times. These results can be explained if we assume that the compatibility of PVA and starch was poor. When the crosslinking agent was added, crosslinking occurred between PVA and starch, and the compatibility of PVA and starch improved, as did the transmittance.

TABLE I
Mechanical Properties of the SP Film with Different Amounts of the Crosslinking Agent

	H_3BO_3 (%)							
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Tensile strength (MPa)	2.68	8.85	10.57	12.15	9.13	10.11	—	—
Breaking elongation (%)	75	60	22	15	10	8	—	—

TABLE II
Transmittance of the SP Film with Different Amounts of the Crosslinking Agent

	H_3BO_3 (%)							
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Transmittance (%)	39.0	85.2	81.8	85.4	42.4	46.1	—	—

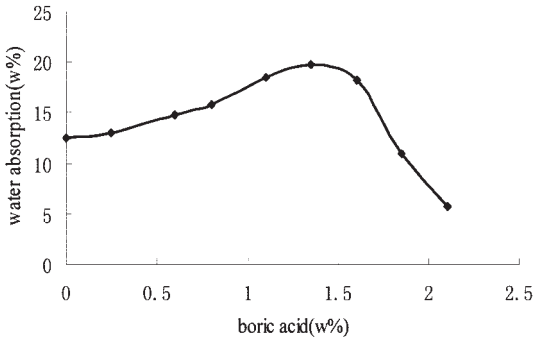

Figure 2 Water absorption (w) of the SP film with different amounts of the crosslinking agent.

However, when the dosage of boric acid was too high, crosslinking occurring among the same kinds of molecules was more likely to happen, and this led to increasing molecular weight. Then, the entropy of mixing (ΔS_{mix}) decreased. According to the Gibbs–Helmholtz formula ($\Delta G_{mix} = \Delta H_{mix} - T \times \Delta S_{mix}$), ΔG_{mix} increased, where ΔG_{mix} is mixing free energy and ΔH_{mix} mixing enthalpy at temperature T. Therefore, the compatibility of PVA and starch became poor, and the transmittance of the SP film dropped.

Influence of the quantity of the crosslinking agent on the water absorption of the SP film

The curve of the water absorption of the SP film versus the quantity of the boric acid is shown in Figure 2. The curve indicates that the water absorption of the SP film rose at first and then fell after some time. This can be explained as follows: when the quantity of boric acid was low, the extent of crosslinking was small. In comparison with the total number of hydroxyl groups of the SP blends, only a small number of the hydroxyl groups reacted, and a large number of the hydroxyl groups remained free. Partial crosslinking and branching in the molecules caused the degree of crystallinity to drop. The free volume thus increased, and the water absorption increased. When the quantity of boric acid reached a certain level, the water absorption dropped

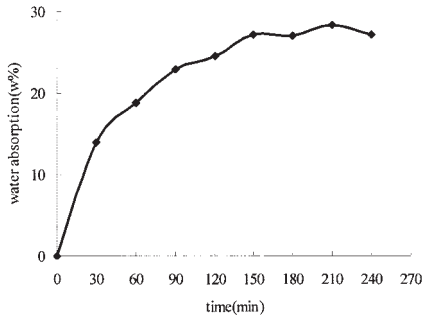

Figure 3 Water absorption (w) of the SP film with the time.

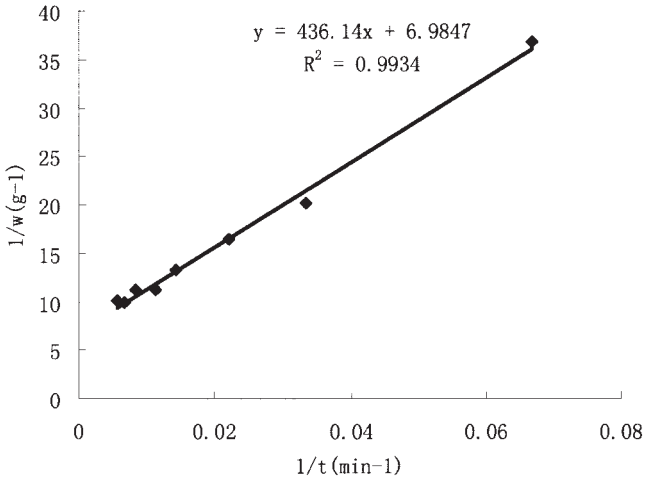

Figure 4 Water absorption (w) of the SP film with the immersion time.

because of excessive crosslinking, which made the bonding of the starch and PVA molecules stronger and stronger. At the same time, the quantity of remaining hydroxyl groups decreased, and this improved the water resistance of the SP film.

The relationship of the water absorption of the SP film and the immersion time is shown in Figure 3. The curve rises at first and then levels, and this suggests that the water absorption gradually reached saturation. The reciprocal of water absorption ($1/w$) of the SP film showed a good linear correlation with the reciprocal of time ($1/t$; the square of correlation coefficient (R^2) = 0.993; Fig. 4). It can be written as a linear relationship in the form of the following equation:

$$1/w = 430 \times 1/t + 7.23$$

The point at which the straight line intersects the ordinate is the saturation value of water absorption.

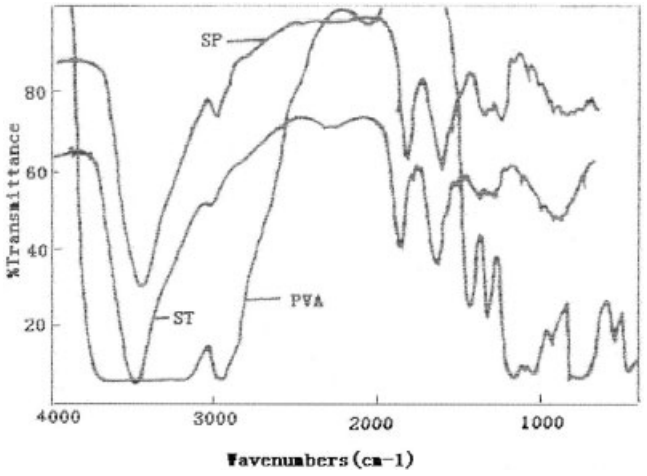

Figure 5 Infrared spectra of the samples.

Infrared spectral analysis of the SP film

Infrared spectra of samples of the starch, PVA, and SP film are presented in Figure 5. The main characteristic peaks of starch can be identified as follows. The high and wide flexible vibration peak of —OH occurred at 3435 cm^{-1}. The weak and mid-strength flexible vibration peak of —CH_2 occurred at 2931 cm^{-1}. The wide flexible vibration peak of C—O in associating hydroxyl groups appeared at 1637 cm^{-1}. A group of peaks occurring from 1384 to 1450 cm^{-1} was the deformed vibration peak of —CH_2 in —CH_2OH. Asymmetric flexible vibrational peaks of C—O—C occurred at 1115 and 1008 cm^{-1}.

The main characteristic peaks of PVA can be identified as follows. The peaks in the Fourier transform infrared spectra at 3504 and 2945 cm^{-1} represented flexible vibrations of —OH and —CH_2, respectively. Because of the influence of hydrogen bonds, a flexible vibration peak of C—O in associating hydroxyl groups occurred at 1564 cm^{-1}; the deforming vibration peaks of —CH_2 in —CH_2OH appeared from 1236 to 1419 cm^{-1}. Asymmetrical flexible vibration peaks of C—O—C occurred at 1143 and 1095 cm^{-1}; the rocking vibration peaks of —CH_2 appeared at 917 and 853 cm^{-1}.

Infrared spectra of the SP film obviously changed in comparison with those of starch and PVA. First, the flexible vibration peak of —OH occurred at 3411 cm^{-1}, and the width and shape of the peak were similar to those of starch. This illustrates that the structure of hydrogen bonding in the blends was similar to that in starch. At the same time, a new structure of hydrogen bonding resulted from the crosslinking reaction. The peak of —OH therefore moved to a lower wave number. Second, the similarity of the spectra of SP and starch proved that during the crosslinking reaction, crosslinking among the PVA molecules exceeded that between PVA and starch.

CONCLUSIONS

Boric acid is an excellent crosslinking agent for starch with PVA. The SP film was obtained through the proper design of the crosslinking reaction conditions and component formulation. The obtained SP film had good transmittance, mechanical properties, and water resistance.

References

1. Yang, H. D. China Plast 1996, 10(7), 1.
2. Li, Y. F.; Dou, Z. China Plast Ind 1990, 3, 44.
3. Qiu, W. Y.; Qiu, X. H. Prog Mater Sci 1993, 7, 157.
4. Gao, X. H. J Sci Teach College Univ 1998, 18, 31
5. Wu, J.; Xie, B. J. Fine Chem 2001, 18, 423.
6. Ji, Y. Y.; et al. Fine Chem 1994, 11, 52.
7. Wang, X. C.; et al. Mod Plast Process Appl 1999, 11, 44.
8. Shogren, R. L.; Thompson, A. R.; Felker, F. C.; Harry-Okuru, R. E.; Gordon, S. H.; Greene, R. V.; Gould, J. M. J Appl Polym Sci 1992, 44, 1971.
9. Iwamoto, A.; Tokiwa, Y. J Appl Polym Sci 1994, 52, 1357.
10. Bao, B. J. Phosphate Compd Fertil 1997, 12(6), 69.