

Crosslinking of Poly(vinyl alcohol) *via* Bis(β -hydroxyethyl) Sulfone

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ABSTRACT: Poly(vinyl alcohol) (PVA) was crosslinked *via* bis(β -hydroxyethyl) sulfone (BHES) at elevated temperatures to improve the water resistance. The best conditions for the crosslinking such as temperature, heat-treatment period, and amount of BHES or catalyst were screened out. Water resistance of the crosslinked PVA was characterized in terms of swelling and weight loss in water. The addition of BHES into PVA followed by heating at elevated temperature resulted in successful formation of crosslinking structure. The crosslinking occurs above 160 °C and takes shorter period at high temperature than low temperature. The crosslinking catalyst, sodium carbonate, acts more effectively at 160 °C than at 200 °C. The results from thermal analysis using a differential scanning calorimetry revealed that the catalyst functions against BHES to lower the temperature for the crosslinking reaction and that even the crosslinked films have the PVA crystalline. The crosslinking procedure using BHES and sodium carbonate is applicable to form ion-exchange fibers based on PVA with high water resistance. [DOI 10.1295/polymj.36.472]

KEY WORDS Poly(vinyl alcohol) / Crosslinking / Thermal Post-treatment / Bis(β -hydroxyethyl) Sulfone /

PVA is a typical hydrophilic polymer and can be readily blended with additives such as particles or other polymers. Therefore, PVA has potential feasibilities to be matrices forming functional products with strong hydrophilicity. However, PVA sometimes requires crosslinking formation for practical applications in water since PVA is a water-soluble polymer.

Industries conventionally heat-treat PVA products to enhance water-resistance. Such heat-treated PVA has only physical crosslinking based on crystalline structure. So formed physical crosslinking may lose in hot water. When PVA is blended with other substances or has insufficient degree of saponification, the crystallization by the heat-treatment may fail to form; PVA can be dissolved in water even at room temperature. Chemical modifications are also employed to improve the water resistance of PVA. The modifications involve the acetalization of the hydroxyl group in PVA by mono-aldehyde like formaldehyde to enhance hydrophobicity and by di-aldehyde such as glutaric aldehyde or glyoxal to form intermolecular crosslinking. The chemical crosslinking is effective to improve the water resistance of PVA.^{1,2} However, the acetalization processes require heavy-duty equipment since the post-treatment for the crosslinking uses strong acid and volatile reagents. If the crosslinking of PVA by a simple heat-treatment is viable, then the processes to obtain PVA-based products with high water resistance become industrially valuable. However, little information on such methods and their effectiveness has been open to public. Ding *et al.* ap-

plied heat-treatment methods to crosslinking PVA *via* glyoxal.³ In this case, the process requires an acidic catalyst. Another case using heat-treatment to crosslink PVA deals with water-soluble isocyanates or isocyanates in an emulsion form.⁴ The isocyanates react with hydroxyl group in PVA to form urethane bonds. Our previous study used poly(acrylic acid) as a crosslinking reagent for PVA to produce crosslinking network *via* ester bonds.⁵ The PVA crosslinked by heat-treatment exhibited strong water resistance. However, this crosslinking method is inapplicable to PVA used as a matrix for cationic materials.

In this study, we investigate the crosslinking of PVA *via* bis(β -hydroxyethyl) sulfone (BHES) by means of thermal post-treatment. BHES is known as a shape-stabilizer for cotton.⁶ The reaction of BHES with the hydroxyl groups in cotton was extensively studied by Tesoro *et al.*⁷ BHES is non-ionic, water-soluble, and miscible with PVA. This reagent seems to have feasibilities as a crosslinking reagent in wide range of applications. BHES is expected to react with the hydroxyl group in PVA. However, there are few reports regarding the reaction with PVA and its applications.⁸ Therefore, we conducted fundamental research on the crosslinking conditions of PVA *via* BHES to enhance the water resistance. Finding proper conditions may result in practical use for functional materials such as ion-exchange fibers.

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EXPERIMENTAL

Materials

A completely saponified PVA (DENKA F12) was used after sufficient washing with water. The degree of saponification and the degree of polymerization were more than 99.9 mol % and 1,200, respectively. Bis(β -hydroxyethyl) sulfone (BHES) solution in water (47%) for film preparation and solid BHES for thermal analysis were kindly supplied from Meisei Chemical Works, Ltd. Sodium carbonate, Na₂CO₃, obtained from Wako Pure Chemical Industries, Ltd. was used as a crosslinking catalyst. Ion-exchange resin (IER DIAION SK-116) was pulverized with a ball mill before use.

Film Preparation

Blend ratios of PVA/BHES in films were 100/0, 99/1, 95/5, 90/10, 85/15, and 80/20. The amount of catalyst added, sodium carbonate, was 0, 0.1, 0.2, and 0.4 wt % based on solid films. PVA aqueous solution and BHES aqueous solution were mixed to prepare 8 wt % solution of solid in water. Desired amount of the catalyst was added into the solution if necessary. The solution was cast onto a glass plate to form 100 μ m films in solid form and dried under ambient conditions. The resulting films were thermally treated in an air oven at a fixed temperature in the range of 120 to 200 °C for a certain period up to 60 min. Figure 1 represents an expected reaction between PVA and BHES.

Preparation of Ion-exchange Fiber

The ratio of components in spinning dope, PVA/IER/BHES/Na₂CO₃/H₂O, was 19/19/3.6/0.07/60 by weight. The spinning dope was prepared with a kneading machine and extruded from a nozzle into hot air at 130 °C to obtain fibrous samples. A control spinning dope solution without BHES and sodium carbonate was also prepared by the same manner. The fi-

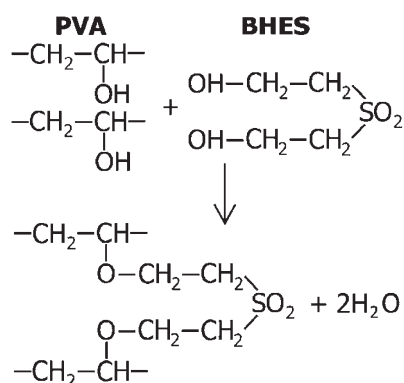


Figure 1. Expected reaction between PVA and BHES.

brous samples were post-treated at 200 °C for 10 min.

Characterization

Thermal analysis for BHES, sodium carbonate, and PVA was performed with a differential scanning calorimetry, DSC, (Shimadzu DSC60) at a scanning rate of 10 K/min.

The effectiveness of crosslinking was evaluated in terms of swelling and weight loss of the PVA films in water at 30 and 98 °C. A heat-treated film was initially weighed (w_{ini}) and immersed in water at 30 °C over night or in hot water at 98 °C for 5 h, followed by weighing (w_{wet}). The water was chilled to room temperature to weigh the swollen film (w_{wet}). The film was again dried on a hot plate for 5 min to measure the weight (w_{dry}). Degree of swelling, *SR*, and weight loss were defined as follows, respectively. The *SR* and weight loss reflect the degree of crosslinking and the gel fraction for crosslinked film.

$$SR = w_{\text{wet}}/w_{\text{dry}} \quad (1)$$

$$\text{Weight loss (\%)} = (1 - w_{\text{dry}}/w_{\text{ini}}) \times 100 \quad (2)$$

Heat-treated ion-exchange fibers with and without BHES were subjected to the above mentioned measurements for swelling and weight loss in hot water at 98 °C. Ion-exchange capacity of the fibers was also determined before and after the immersion in the hot water. We employed a general method to determine the capacity of strong cation-exchange resins.⁹ Degree of swelling, *SR*, and weight loss of the ion-exchange fiber were determined using the same procedure for films mentioned above.

RESULTS AND DISCUSSION

Heat-treatment Conditions

Figure 2 shows plots of degree of swelling, *SR*, and weight loss, respectively, for PVA films with BHES (10 wt %) and without BHES as a function of heat-treatment temperature from 120 to 200 °C. The samples were exposed to the heat for 10 min. There is no significant difference in the *SR* values against the heat-treatment temperature between these two films when the films were equilibrated to the water at 30 °C. The *SR* values decrease with the temperature. Generally, the crystallinity of PVA increases with the heat-treatment temperature.¹⁰ Therefore, no difference in the *SR* values between these two films implies that the water resistance of PVA at 30 °C depends mainly on the amount of crystalline structure in the films. On the other hand, the PVA films without BHES completely dissolved in the hot water at 98 °C except for a sample cured at 200 °C. However, the weight loss of the film containing BHES starts to drop between the temperatures from 140 to

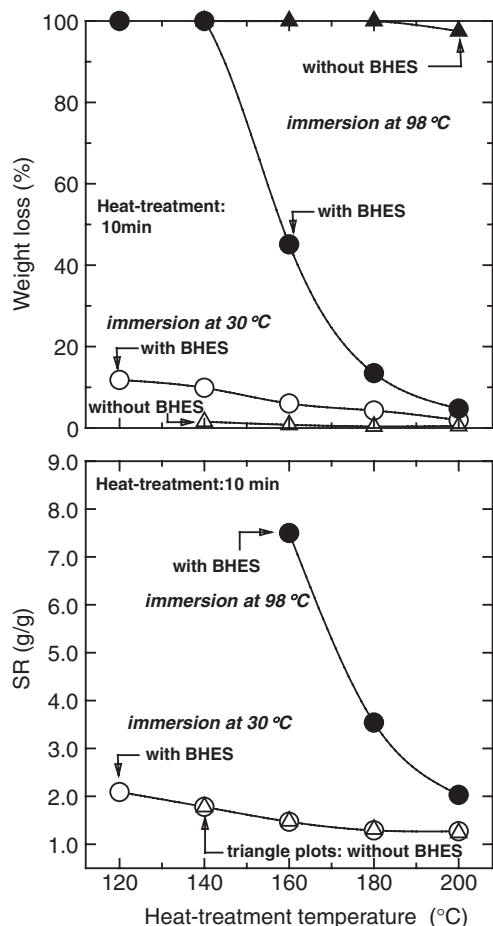


Figure 2. Degree of swelling, SR, and weight loss for PVA films with 10 wt% BHES and without BHES at 30 and 98 °C vs. heat-treatment temperature.

160 °C and keeps decreasing up to 200 °C. This significant change in the weight loss coincides with that in the SR value. The relatively high weight loss of the film containing BHES during the immersion in the water at 30 °C compared to the film without BHES is due to the extraction of BHES from the film into the equilibrated water.

Figure 3 shows plots of the weight loss at 98 °C for the film containing BHES as a function of the period exposed to the heat. The effect of the period on the weight loss is small when the temperature is high; the weight loss of the film heated at 200 °C is almost constant against the period examined whereas that for the film heated at 160 °C decreases with the time exposed to the heat. The same trend is seen for the SR values at 30 °C and 98 °C. However, the values at 30 °C were lower than that at 98 °C. The difference in the effect of the cured period between the tests at two different immersion temperatures on the swelling is owing to the existence of crystalline in PVA at 30 °C. No crystalline structure in PVA is supposed to remain during the equilibrium in hot water at 98 °C. Therefore, the SR value at 98 °C depends only

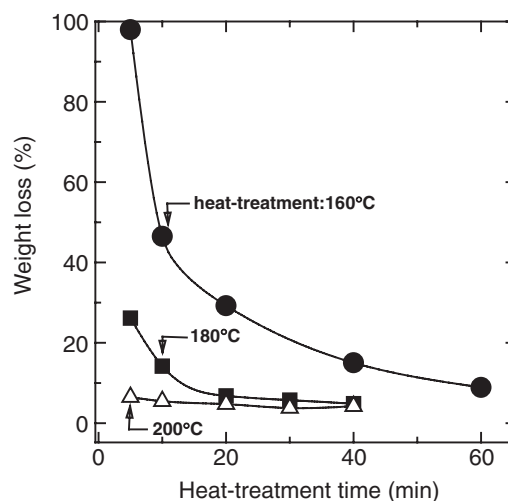


Figure 3. Weight loss of PVA film with 10 wt% BHES at 98 °C vs. heat-treatment time.

on degree of the crosslinking whereas that at 30 °C involves the effect of the amount of crystalline structure. As far as the crosslinking of PVA is estimated in terms of swelling and weight loss, we may conclude that the crosslinking reaction is completed in 10 min at 200 °C or 20 min at 180 °C.

Figure 4 represents the effect of BHES amount con-

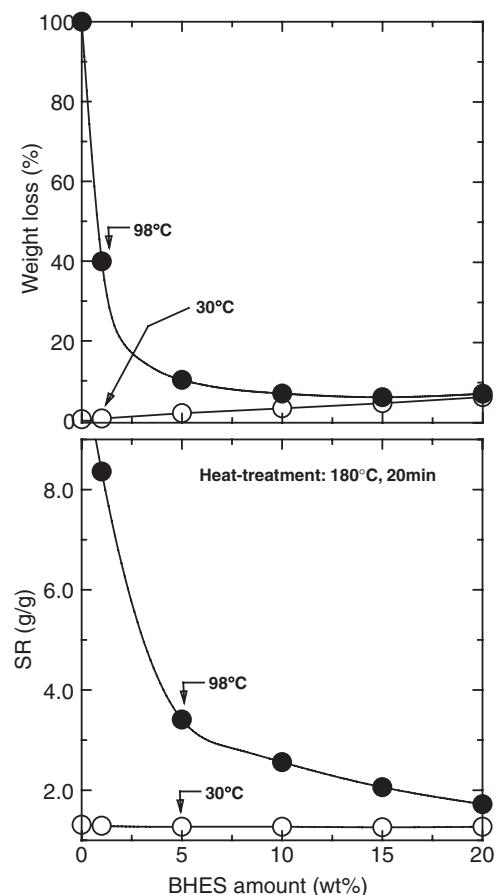


Figure 4. Degree of swelling, SR, and weight loss for PVA films at 30 and 98 °C vs. BHES amount.

tained in PVA films on the swelling and insolubility. The sample films were treated at 180 °C for 20 min. The SR value at 30 °C is constant against the BHES amount. This is again due to the dominant effect of crystalline structure in PVA on the water resistance. On the other hand, the SR value at 98 °C decreases with the increase in the amount of BHES, implying that the degree of crosslinking increases as the amount of BHES in PVA becomes large. The weight loss at 30 °C increases with the amount of BHES in PVA. This is due to the increase in the extraction of unreacted BHES. The weight loss at 98 °C is minimized when the amount of BHES loaded to PVA is more than 5 wt%. However, the efficiency of the crosslinking becomes high as the BHES amount increases since the difference in the values of weight loss between the films equilibrated to the water at 30 and 98 °C, the amount of extracted PVA, becomes small.

Addition of Catalyst

Varying the amount of crosslinking catalyst, sodium carbonate, in PVA films containing 10 wt% of BHES leads to the result for the weight loss shown in Figure 5. There is no significant influence of the loaded amount on these values at 180 and 200 °C. On the other hand, the changes in the weight loss is large in the range of the amount from 0 to 0.1 wt% for the film heated at 160 °C and in the range of the amount from 0.1 to 0.4 for the film heated at 140 °C. The film heated at 120 °C, even the catalyst is added, is soluble in the hot water at 98 °C. The change in the values of the weight loss as a result of catalyst loading becomes small as the amount of catalyst in PVA films increases; the catalyst loading has a small effect on crosslinking at high temperature heat-treatment. The trend is the same for the swelling. In

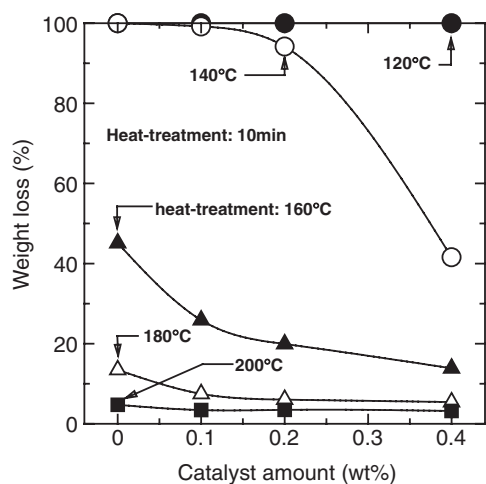


Figure 5. Weight loss of PVA films containing 10 wt% BHES at 98 °C vs. catalyst amount.

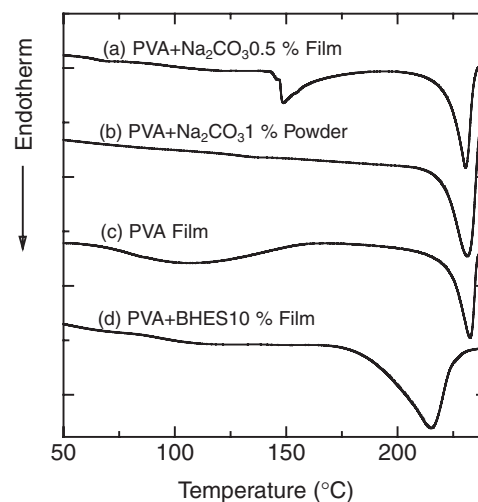


Figure 6. DSC curves of the first heating run for PVA film and PVA films containing BHES or catalyst.

other words, loading catalyst can be an effective method to enhance water resistance of PVA when the crosslinking conditions like heat-treatment temperature are limited to apply.

Thermal Analysis

Figure 6 shows the DSC curves of PVA films containing BHES or sodium carbonate. The on-set temperature of endothermic change on the curve (d) of PVA film containing 10 wt% of BHES is about 170 °C and is lower than that of the PVA film without additives, indicating that BHES plasticizes PVA.¹¹ On the other hand, loading sodium carbonate has no significant effect on the DSC curve of PVA film. The endothermic peak around 150 °C on the curve (a) seems to be attributed to the vaporization of carbon dioxide from sodium hydrogen carbonate produced during film preparation. DSC curves of BHES mixed with different amount of sodium carbonate are shown in Figure 7. An endothermic peak on the curve of BHES (e) around 170 °C is probably attributed to degradation of BHES.^{12,13} The on-set temperature of this endothermic change shifts to 140 °C as a result of adding 1 wt% of sodium carbonate. Further addition of sodium carbonate has no significant effect on the on-set temperature of the endothermic peak. The results shown in Figures 6 and 7 indicate that the catalyst functions only to depress the activation temperature of BHES for the crosslinking reaction.

DSC curves of PVA films mixed with different amount of BHES (PVA/BHES = 100/0, 95/5, 90/10, 80/20) were also measured. The DSC measurement was performed after heat-treating the films for 20 min at 180 °C. The endothermic peak attributed to the melting of the PVA crystalline appeared on the crosslinked films (see Figure 8). The melting peak

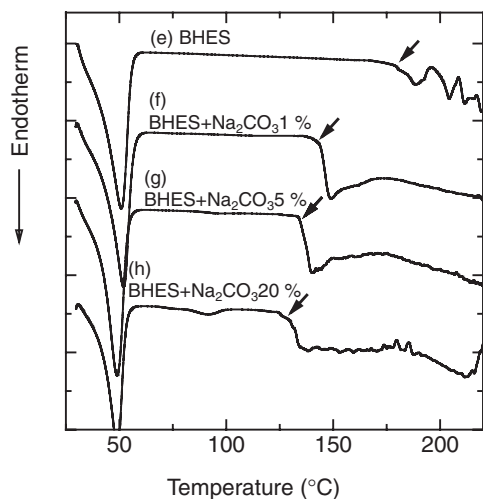


Figure 7. DCS curves for BHES and BHES with catalyst.

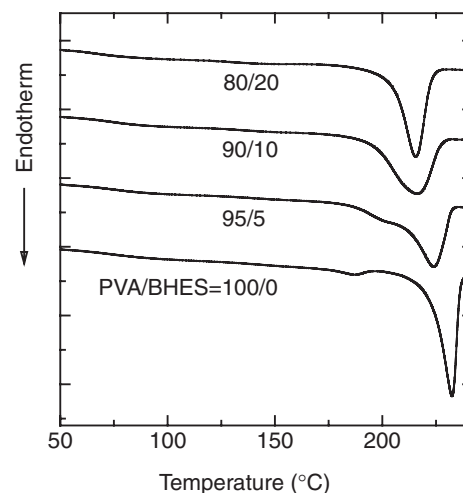


Figure 8. DSC curves of the first heating run for heat-treated PVA film and PVA films containing BHES. Sample films had been heat-treated at 180 °C for 20 min already.

Table I. Characteristics of ion-exchange fiber

Ion-exchange fiber	Before immersion ^a			After immersion ^a		
	Cross section ^b (μm)	Ion-exchange capacity (meq/g-net fiber)	SR ^c (g/g)	Ion-exchange capacity (meq/g-net fiber)	SR ^c (g/g)	Weight loss (%)
Crosslinked by BHES	ca. 100 × 50	2.2	1.6	2.2	2.1	3.4
Uncrosslinked	ca. 100 × 50	2.2	1.6	—	—	broken

^aImmersed in hot water at 98 °C for 5 h. ^b“dog bone” shape. ^cDegree of swelling.

of the heat-treated films with different amount of BHES shifted to low temperature side as the amount of BHES increased. The heat of fusion is almost identical, indicating that the degree of crystallinity is independent of the BHES amount. The result suggests that the PVA film with BHES forms not only the crosslinking structure *via* covalent bonds but also the physical crosslinking *via* PVA crystalline formed by heat-treatment. The similar degree of crystallinity on the PVA films with different amount of BHES and the swelling behavior at 30 °C on Figure 4 suggest that the physical crosslinking of crystalline structure dominates the water resistance around room temperature.

Application of Crosslinking to Ion-exchange Fiber

Table I summarizes the ion-exchange capacity, swelling, and weight loss of an ion-exchange fiber before and after the immersion in water at 98 °C. The fiber without BHES can not hold its structure in the hot water. On the other hand, no significant loss of the weight and the ion-exchange capacity of the fiber containing BHES were confirmed. Therefore, the method using BHES for crosslinking PVA has a possibility to manufacture ion-exchange fibers used for applications like a hot water disinfection process to produce deionized water.

CONCLUSIONS

Conditions for crosslinking of poly(vinyl alcohol), PVA, *via* bis(β -hydroxyethyl) sulfone, BHES, were explored. The crosslinking procedure was applied to produce ion-exchange fibers with high water resistance. The following conclusions were obtained.

- Heating PVA containing BHES at certain temperatures leads to the improvement in the water resistance.
- The crosslinking reaction occurs above 160 °C when PVA contains only BHES.
- The effect of catalyst loading on the crosslinking of PVA is remarkable at low temperature.
- Na₂CO₃ catalyst functions against BHES to decrease the reaction temperature.
- PVA crystalline exists after crosslinking formation with BHES and dominates the water resistance at 30 °C.
- Ion-exchange fibers composed of PVA and pulverized ion-exchange resin exhibit fair water resistance.

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