

# Crosslinking Reaction of Poly(vinyl alcohol) with Poly(acrylic acid) (PAA) by Heat Treatment: Effect of Neutralization of PAA

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**ABSTRACT:** The crosslinking reaction of poly(vinyl alcohol) (PVA) by esterification using poly(acrylic acid) (PAA) as a crosslinking reagent was investigated to obtain highly insoluble PVA materials. Blend films of PVA and PAA (PVA/PAA = 8/2) were prepared to examine the effect of degree of neutralization (DN) in PAA and heat-treatment conditions on the degree of crosslinking reaction. The degree of crosslinking reaction varied significantly when the DN of PAA changed. The optimum DN for the crosslinking reaction was in the range of 5 to 10 mol %. In the case of unneutralized PAA, the degree of crosslinking reaction was at most 15 mol % by heat treatment for 20 min at 200°C. Applying partially neutralized PAA (DN = 10 mol %) raised

the degree to about 40 mol % under the same heat-treatment conditions. FTIR analysis revealed that the hydroxyl group of PVA in the film blended with unneutralized PAA was degraded to a greater degree than that with partially neutralized PAA as a result of heat treatment. It was found that heat treatment at a low pH condition enhances the degradation of the hydroxyl group of PVA, resulting in a decrease of the number of crosslinking sites by esterification. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2420–2427, 2003

**Key words:** poly(vinyl alcohol); poly(acrylic acid); degradation; crosslinking; blends

## INTRODUCTION

Poly(vinyl alcohol) (PVA) is a typical water-soluble polymer. Because insolubility is required for the application of PVA as fibers or films, it is necessary to enhance the insolubility of PVA in water. Acetalization by a monoaldehyde such as formaldehyde is one of the practical methods to introduce an insoluble structure against water to PVA. In this case, insolubility is obtained by substituting hydrophobic groups for the hydroxyl group. Intermolecular crosslinking by acetalization is also practically carried out using a dialdehyde such as glutaric aldehyde or glyoxal. The PVA thus treated forms a strong covalent bond between the hydroxyl and aldehyde groups to exhibit high water resistance. However, the acetalization process must be carried out at a relatively high cost because it is a heavy-duty process involving volatile and acidic reagents. On the other hand, heat treatment is conventionally applied to introduce water resistance to PVA with some forms. The resistance can be achieved by a physical crosslinking network among small crystals of PVA formed by heat treatment. When

heat-treated with drawing, PVA fibers become insoluble even in boiling water. However, the insolubility of PVA thus obtained cannot last for extended periods of time.

In this study, insolubilization of PVA using dry heat treatment was attempted after mixing a crosslinking reagent and PVA to obtain a high degree of crosslinking reaction. Application of such a simple and convenient technique is essentially important for the industrial production process. Poly(acrylic acid) (PAA) was selected as a crosslinking reagent because it has a functional carboxyl group in every monomer unit to react with PVA and characteristics including high solubility in water as a solvent for the casting solution and high miscibility with PVA. In addition, it is one of the typical commercialized polymers available. Strong crosslinking by ester linkage can be formed between the hydroxyl group of PVA and the carboxyl group of PAA.

Concerning blend materials of PVA and PAA, a number of investigations were published especially for separation membrane materials.<sup>1–5</sup> In other studies, PVA/PAA hydrogels as an actuator-sensor system<sup>6</sup> and miscibility of PVA/PAA blends<sup>7</sup> were also studied. Kawakami and Kawashima<sup>8–10</sup> investigated the intermolecular crosslinking between PVA and PAA with esterification by dry heat treatment. According to these studies, the degree of crosslinking

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reaction was relatively low. The maximum degree was at most 14 mol % of PAA monomer unit even at the best heat-treatment conditions. However, such a low degree of reaction often causes practical problems such as a high level of swelling in water. When a water-soluble additive is used, a large number of unreacted PVA chains and the additive can leak out into water if the PVA network is highly swollen. In some cases (e.g., ion-exchange fibers) about 40 mol % of degree of crosslinking reaction is required to suppress such swelling and leakage. Therefore, this study focuses on the modification of heat-treatment conditions along with the degree of neutralization of PAA to improve the crosslinking reaction.

## EXPERIMENTAL

### Materials

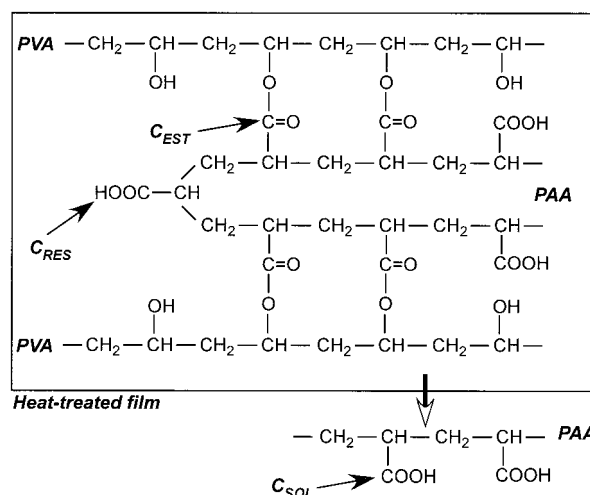
A completely saponified PVA (Denka F12, Tokyo, Japan) was used after sufficient washing with water. The degree of saponification was more than 99.9 mol % and the degree of polymerization was 1200. PAA (average molecular weight 5000) was purchased from Wako Pure Chemicals (Osaka, Japan) and used without further purification. Partially neutralized PAA (0–15 mol % based on monomer unit) was prepared by adding a predetermined amount of aqueous sodium hydroxide solution to aqueous PAA solution at room temperature.

### Film preparation

The blend ratio of PVA/PAA film was 8/2 by weight; the molar ratio of the hydroxyl group of PVA to the carboxyl group of PAA was about 6.5/1. Deionized water was used for the preparation of polymer solution. Blend films were prepared as follows. An aqueous solution of blend polymer (8–10 wt %) was cast onto a glass plate to obtain a 100- $\mu\text{m}$ -thick film. The cast film was dried, followed by heat treatment at a fixed temperature in the range of 140 to 210°C for up to 40 min in an oven.

### Characterization

The pH of the casting solution for PVA/PAA blends and PAA was measured at 24°C using a glass electrode-type pH meter (DKK IOL-30). FTIR spectra were measured on a Shimadzu (Kyoto, Japan) FTIR-8300. PVA and blend films (thickness < 10  $\mu\text{m}$ ) were prepared for the IR measurement. After being cast and dried, the films were heat-treated on aluminum foil at 200°C for 30 min or 4 h. In the case of PAA, potassium bromide was mixed with PAA to make a thin disk for the IR measurement because the prepared PAA film was quite brittle.



**Figure 1** Expected crosslinking structure of heat-treated PVA/PAA blend film.

### Degree of swelling and weight loss

The degree of swelling ( $SR$ ) was defined as follows:

$$SR = (\text{weight of swollen film}) / (\text{weight of dry film}) \quad (1)$$

A heat-treated film was immersed in water at 30°C overnight, and then immersed again in water at 95°C for 4 h. After measuring the weight of swollen film for the immersion at both 30 and 95°C, the film was dried at 180°C on a hot plate for 3 min, after which the dried film was weighed (immersion test). The  $SR$  value at 30°C was calculated based on the dry weight of the film after the heat treatment. The  $SR$  value at 95°C was calculated based on the dry weight of the film after the immersion test. Weight loss was calculated from the difference in the weight of the film between just after the heat treatment for crosslinking and after the immersion test. To compare the  $SR$  values between the H- and the Na-form of residual carboxylic group in the PVA/PAA blend film, the weight of swollen samples was measured after an ion-exchanging process using an aqueous solution of hydrochloric acid or sodium hydroxide.

### Degree of crosslinking reaction

An expected crosslinking network structure of PVA/PAA blend is presented in Figure 1. The degree of crosslinking reaction  $X$  was calculated from the amount of carboxyl group of PAA in a blend film before and after the reaction:

$$X = C_{EST} / C_{INI} \times 100 - R_{PAA} \quad (2)$$

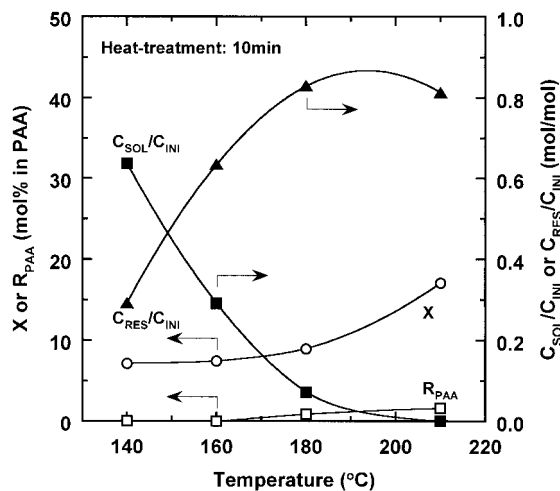
where  $C_{EST}$  is the concentration of carboxyl group consumed in the esterification between PVA and PAA,  $C_{INI}$  is the initial concentration of carboxyl group in the blend, and  $R_{PAA}$  is the degree of degradation of carboxyl group by the heat treatment.  $C_{EST}$  is calculated using the following equation:

$$C_{EST} = C_{INI} - C_{RES} - C_{SOL} \quad (3)$$

where  $C_{RES}$  is the concentration of residual carboxyl group after the heat treatment and  $C_{SOL}$  is the concentration of carboxyl group extracted out of the blend film during the process to determine the  $C_{RES}$ . A trace amount of carboxyl group contained in the commercial PVA was ignored here.<sup>11</sup>  $C_{INI}$  was calculated from the blend ratio of PVA and PAA, degree of neutralization, film weight, and results for acid-base titration of the aqueous PAA solution. The amount of extracted PAA ( $C_{SOL}$ ) was also determined by acid-base titration. A sample film was immersed in 200 mL of water at 30°C overnight (17–24 h). The water containing extracted PAA was poured into a strong cation-exchange resin column to convert all the PAA content into H-form, after which it was titrated.

The  $C_{RES}$  was determined by use of the following steps. After determining  $C_{SOL}$ , the sample film (0.5 g) was shaken in 25 mL of aqueous solution of sodium hydroxide (0.1N) at room temperature overnight (16–20 h) to convert the residual carboxyl group (–COOH) in the film to the sodium carboxylate form (–COONa). The amount of consumed sodium hydroxide corresponding to the quantity of residual carboxyl group in the film was determined by acid-base titration. In the case of partially neutralized PAA, the blend film was shaken in 25 mL of aqueous solution of hydrochloric acid (0.1N) at room temperature overnight to convert all the COONa form to the COOH form. After the above-mentioned processes followed by sufficient rinsing, titration was carried out to determine the  $C_{RES}$  in the film. The titration applied here to the films is a general method to determine the ion-exchange capacity of weak cation-exchange resin.<sup>12</sup>

It is known that a very small amount of PAA degrades during the heat treatment.<sup>13</sup> According to the literature,<sup>7</sup> the degradation of PAA in a blend film during heat treatment was estimated to be less than that of a film made of pure PAA. The degradation of pure PAA itself, however, was measured to correct the value of the degree of crosslinking reaction. Amounts of carboxyl group in PAA before and after the heat treatment were determined by acid-base titration to estimate the degree of PAA degradation. Partially neutralized PAA film was dissolved in water after the heat treatment. The solution was poured into a cation-exchange resin column. The content of the carboxyl group in the film before and after the heat treatment was determined in the same way as mentioned. The



**Figure 2** Degree of crosslinking reaction  $X$ , degree of PAA degradation  $R_{PAA}$ , leakage of PAA  $C_{SOL}/C_{INI}$ , and residual carboxyl group  $C_{RES}/C_{INI}$  in the blend film of PVA and unneutralized PAA versus heat-treatment temperature.

degree of pure PAA degradation  $R_{PAA}$  by heat treatment was calculated using the following equation:

$$R_{PAA} = 1 - \frac{\text{Content after heat treatment}}{\text{Content before heat treatment}} \times 100 \quad (4)$$

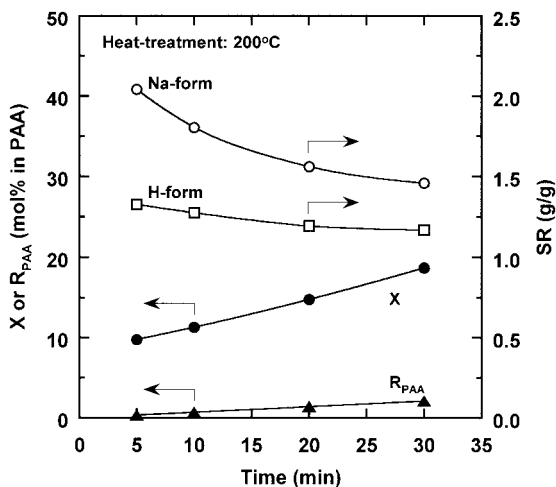
where Content is measured in meq/g.

## RESULTS AND DISCUSSION

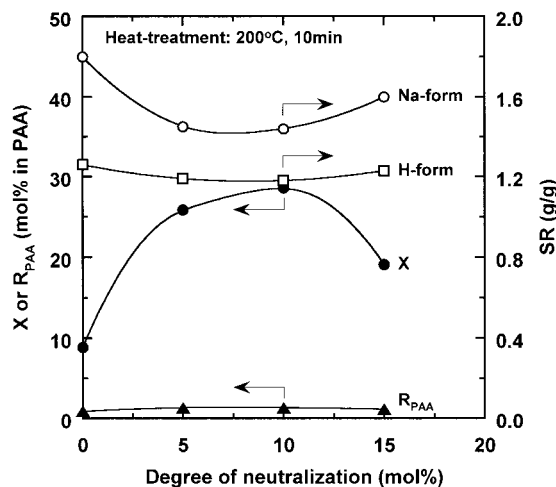
### Crosslinking conditions

The optimum heat-treatment temperature and period were screened out using a blend film of PVA and unneutralized PAA. The relative amount of carboxyl group in the extracted PAA and the residual carboxyl group to that initially loaded in the blend film,  $C_{SOL}/C_{INI}$  and  $C_{RES}/C_{INI}$ , along with the  $X$  and the  $R_{PAA}$ , are plotted as a function of heat-treatment temperature in Figure 2. The amount of the extracted carboxyl group decreases with the temperature, indicating that the PAA chains are effectively fixed in the blend film by high-temperature treatment. This is the reason that the amount of the residual carboxyl group increases as the temperature increases. The other reason is that the degree of crosslinking is not high enough to compensate for the increase in the residual free carboxyl group; that is, the degree of crosslinking is about 17 mol % even at 210°C, where the film color is brown. The coloration implies the decomposition of PVA and/or PAA chains. Therefore, the heat-treatment temperature was fixed at 200°C in the subsequent sections.

Figure 3 shows the changes in the degree of reaction  $X$  and the degree of pure PAA degradation  $R_{PAA}$  with the time of heat treatment at 200°C along with the



**Figure 3** Degree of crosslinking reaction  $X$ , degree of PAA degradation  $R_{PAA}$ , and degree of swelling  $SR$  for Na- and H-forms of PAA in the blend films of PVA and unneutralized PAA versus heat-treatment time. The Na- and H-forms of the films were prepared after the heat treatment.



**Figure 4** Degree of crosslinking reaction  $X$ , degree of PAA degradation  $R_{PAA}$ , and degree of swelling  $SR$  for Na- and H-forms of PAA in the blend films of PVA and PAA versus degree of neutralization.

swelling results for blend films with the H-form and the Na-form of PAA. The  $X$  value increases with the increase in the heat-treatment time, reaching about 18 mol % at 30 min. The color of the film gradually becomes brown as the heat-treatment time increases. The difference in the  $SR$  values between the H-form and the Na-form is sufficiently large to suggest that a substantial number of free carboxyl groups in the film remain as unreacted. The value of  $X$  is not significantly different from that in the literature.<sup>10</sup>

As a conclusion for the crosslinking reaction of the PVA/unneutralized PAA blend film, there was not sufficient improvement in the degree of crosslinking reaction even by high temperature or long-term heat treatment. In the subsequent sections, therefore, a different approach to improve the degree of crosslinking reaction was attempted; crosslinking using PAA with different degrees of neutralization was investigated.

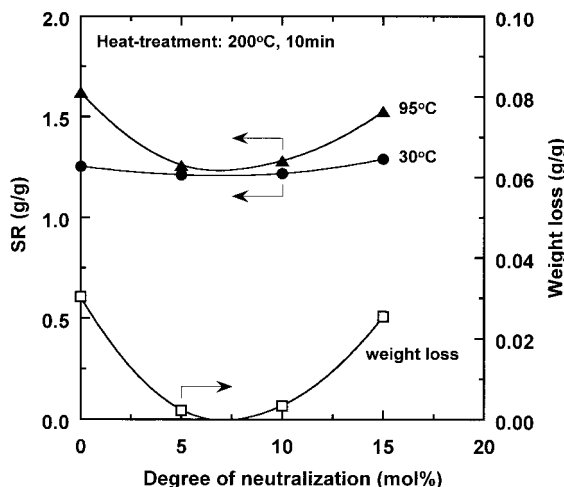
**Crosslinking reaction using partially neutralized PAA**

pH values of the casting solution for the PVA/PAA blend film were 2.6 at 0 mol % of the degree of neutralization (DN), 3.3 at 5 mol %, 3.8 at 10 mol %, and 4.2 at 15 mol %. The heat treatment was carried out at 200°C for 10 min. The blend film formed from PVA and neutralized PAA with 15 mol % of DN was slightly opaque. Clear phase separation of the blend film was observed on an image taken by an optical microscope.

Figure 4 shows the effect of DN in PAA on the degree of degradation  $R_{PAA}$ , the degree of crosslinking reaction  $X$ , and the degree of swelling  $SR$  for the blend films with both the H-form and the Na-form of PAA,

which were prepared after the heat treatment for the crosslinking reaction. The  $R_{PAA}$  shows no significant change throughout the DN range studied, whereas the  $X$  exhibits a maximum value about 30 mol % between 5 to 10 mol % of DN. The  $SR$  for the Na-form is greater than that for the H-form. This is a well-known behavior for crosslinked polymers possessing carboxyl groups.<sup>10</sup> The difference in the  $SR$  value between the H-form and the Na-form in the range of 5 to 10 mol % of DN was smaller than that at 0 and 15 mol % of DN. The small difference in the  $SR$  value is attributed to the reduced content of the carboxyl group in the blend films as a result of high consumption of the carboxyl group by the crosslinking reaction.

Figure 5 shows the  $SR$  of the PVA/PAA blend film equilibrated with water at 30 and 95°C along with the

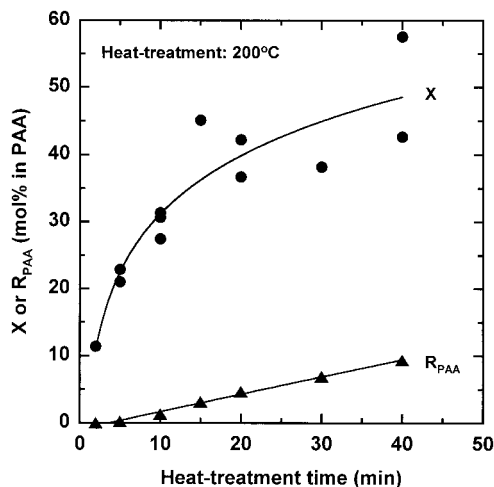


**Figure 5** Degree of swelling at 30 and 95°C and weight loss of the heat-treated PVA/PAA films versus degree of neutralization.

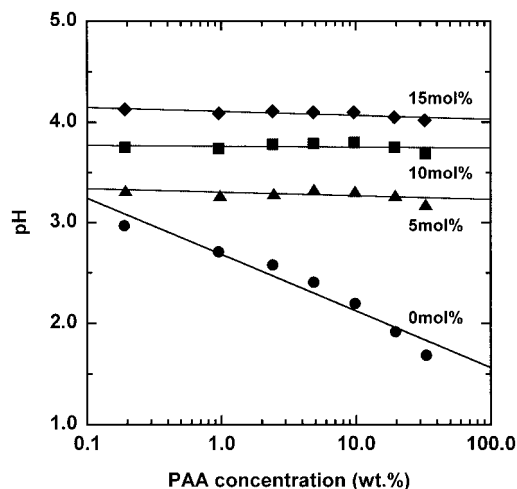
weight loss as a function of the DN. The *SR* value at 30°C is almost constant against the DN, which is the result of suppression of swelling by the crystalline structure formed by PVA polymer. On the other hand, the PVA crystals melt in water at 95°C. In this case, the obtained *SR* value simply corresponds to the degree of crosslinking reaction. As shown in Figure 5, the *SR* value at 95°C exhibits a minimum in the DN range of 5 to 10 mol %, indicating that the crosslinking reaction proceeds effectively in this DN range.

### Heat-treatment time

As a comparison of the effect of the heat-treatment time on the crosslinking reaction at 200°C between the two blend films consisting of partially neutralized or unneutralized PAA with PVA, the degree of crosslinking reaction *X* is plotted along with the degree of pure PAA degradation  $R_{PAA}$  as a function of heat-treatment time in Figure 6 (DN = 10 mol %). Although  $R_{PAA}$  increases with the heat-treatment time, especially for the partially neutralized PAA, degradation of PAA in an actual blend film during heat treatment is estimated to be less than that of a film made of pure PAA as described above.<sup>7</sup> The *X* value calculated from eq. (2), therefore, is not overestimated. The *X* value increases with the heat-treatment time, reaching about 40 mol % at 20 min heat treatment in Figure 6. The coloration of the blend film containing partially neutralized PAA was clearly less than that of the blend film with unneutralized PAA, implying that the degradation of polymers composing the film is less in the partially neutralized PAA compared to that in unneutralized PAA. Partial neutralization of PAA on the crosslinking reaction with PVA in the dry state was found to be valid even in terms of the heat-treatment time.



**Figure 6** Degree of crosslinking reaction *X* and degree of PAA degradation  $R_{PAA}$  for the blend film of PVA and neutralized PAA (10 mol %) versus heat-treatment time.



**Figure 7** pH of unneutralized and neutralized PAA (0, 5, 10, and 15 mol %) aqueous solutions versus PAA concentration.

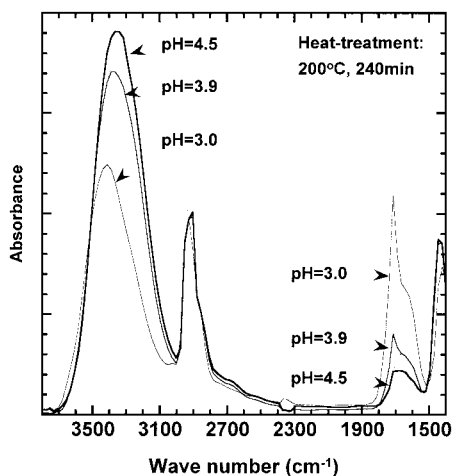
### pH of PAA solution

As mentioned previously, the pH of the casting solution for the PVA/PAA blend film changes largely with the degree of neutralization of the PAA. It is considered that there might be some effects of hydrogen ion concentration or status on the crosslinking reaction. Therefore, the change in the pH with the concentration of aqueous PAA solution for each degree of neutralization was examined. The results are presented in Figure 7. In the case of the solution containing unneutralized PAA (DN = 0 mol %), the pH value decreases with the increase in the PAA concentration; pH = 3.0 at 0.2 wt % to pH = 1.9 at 20 wt %. On the other hand, the pH value of aqueous solution for PAA in the DN range of 5 to 15 mol % hardly depends on the PAA concentration, indicating that partially neutralized PAA has a buffer effect on the solution. The water content in the film at the end of the water evaporation from the cast solutions is very low; the PAA concentration is almost 100 wt %; the hydrogen ion concentration in the unneutralized PAA is significantly high. The final pH value is estimated to be about 1.6 by extrapolating the pH curve to 100 wt % of PAA concentration in Figure 7. This unstable condition of the hydrogen ion produced from PAA might have an influence on the crosslinking reaction of the blend film even under dry condition. On the other hand, the buffer effect of neutralized PAA seems to cause a favorable condition for the crosslinking reaction.

### IR spectra

#### Model heat-treated PVA films

Model heat-treated PVA films were prepared to obtain a better understanding of the effect of acidity on the



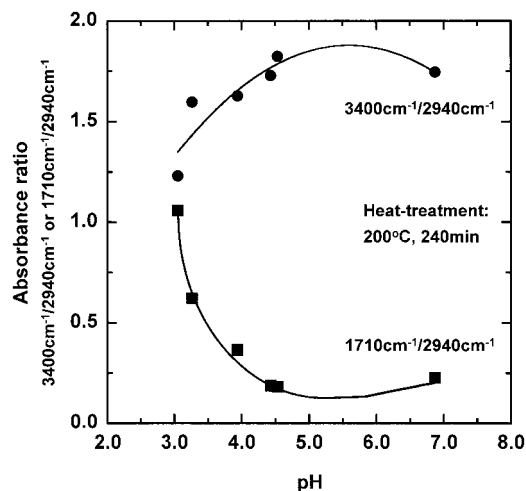
**Figure 8** IR spectra of heat-treated PVA films prepared from 5 wt % of aqueous PVA solutions with pH values of 3.0, 3.9, and 4.5.

PVA chemical structure from IR spectra. The PVA films were fabricated from 5 wt % of PVA solutions in water with a pH value controlled by the addition of dilute aqueous sulfuric acid solution. The maximum quantity of the added sulfuric acid was less than 0.1 mol % based on the concentration of the hydroxyl group in the PVA. The films were heated at 200°C for 4 h.

Figure 8 shows the IR spectra of the heat-treated PVA films prepared from the solutions with pH values of 3.0, 3.9, and 4.5. The absorbance peaks attributed to the hydroxyl group (stretching) and the ketone group (stretching) can be seen around 3400 and 1710  $\text{cm}^{-1}$ , respectively. Nagai et al.<sup>14</sup> reported similar differences in IR spectra of PVA heat-treated above 210°C. The ketone group was produced by the oxidative degradation of the hydroxyl group in PVA. The absorbance of these two peaks is normalized by the absorbance at 2940  $\text{cm}^{-1}$  attributed to the stable methylene group in PVA to plot as a function of the pH value of the casting solution in Figure 9. The relative value of the absorbance for the hydroxyl group (3400/2940  $\text{cm}^{-1}$ ) decreases, whereas that for the ketone group (1710/2940  $\text{cm}^{-1}$ ) increases as the pH value decreases. The results suggest that the hydroxyl group degrades easily and that the crosslinking reaction between PVA and PAA is inhibited when the pH value is low. When the pH value of the PVA solution is less than 4, significant changes in the structure take place, as seen in Figure 9. The results are consistent with the low degree of crosslinking reaction for a blend film prepared from the casting solution with a low pH value such as PVA/unneutralized PAA film.

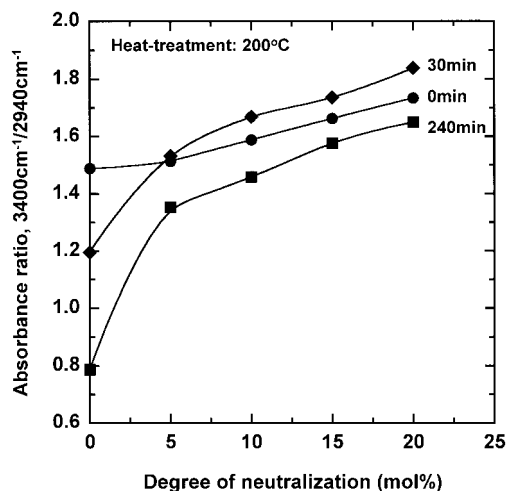
#### PVA/PAA blend and pure PAA films

The relative absorbance of hydroxyl group (3400  $\text{cm}^{-1}$ ) and carbonyl groups (1710  $\text{cm}^{-1}$ ) to the absor-

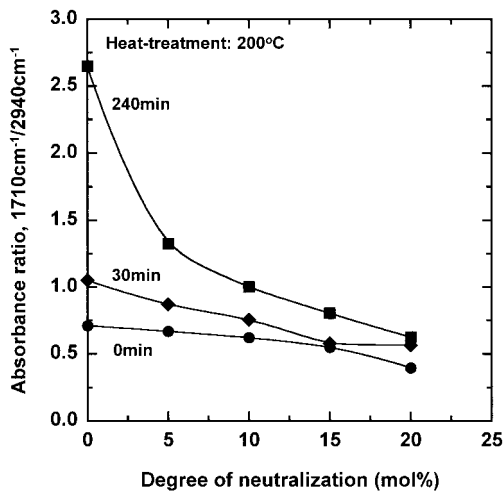


**Figure 9** Absorbance ratios for 3400/2940 and 1710/2940  $\text{cm}^{-1}$  in the IR spectra of heat-treated PVA films prepared from 5 wt % of aqueous PVA solutions with pH controlled by a small amount of  $\text{H}_2\text{SO}_4$ .

bances attributed to the methylene group of the PVA/PAA blend film heat-treated at 200°C for 0, 30, and 240 min are plotted as a function of the degree of neutralization in Figures 10 and 11, respectively. The carbonyl groups include the ketone produced by the degradation of the hydroxyl group in PVA, the carbonyl in the carboxyl group in PAA, and the carbonyl in the ester linkage formed as a result of crosslinking. The relative absorbance for the hydroxyl group (3400/2940  $\text{cm}^{-1}$ ) of both films heat-treated for 30 and 240 min is smaller in the DN range of 0 to 5 mol % than that of the unheated film, whereas the relative absorbance for the carbonyl groups (1710/2940  $\text{cm}^{-1}$ ) is greater. The results indicate that the hydroxyl group in the blend film formed by PVA and unneutralized PAA



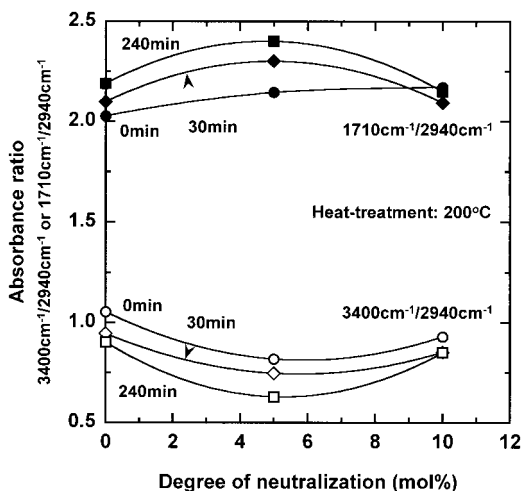
**Figure 10** Absorbance ratios for 3400/2940  $\text{cm}^{-1}$  in the IR spectra of heat-treated PVA/PAA blend films versus degree of neutralization in PAA.



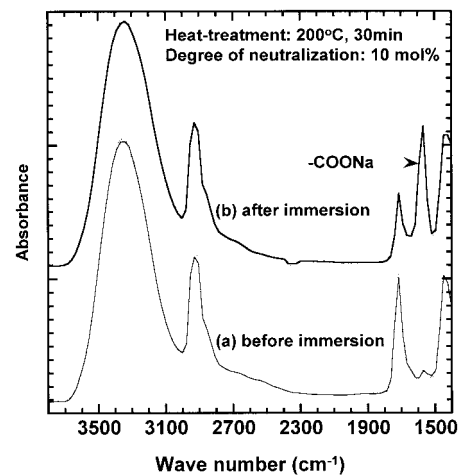
**Figure 11** Absorbance ratios for  $1710/2940\text{ cm}^{-1}$  in the IR spectra of heat-treated PVA/PAA blend films versus degree of neutralization in PAA.

degrades readily as a result of the heat treatment. Thus, this high level of degradation under a low pH condition is fairly consistent with the results obtained from pure PVA films in the previous section. In the case of PAA itself, on the other hand, the relative absorbance for  $3400/2940$  and  $1710/2940\text{ cm}^{-1}$  shows no significant change within the DN range of 0 to 10 mol %, as seen in Figure 12. Therefore, the change in the relative absorbance for the PVA/PAA blend film in Figures 10 and 11 is attributed mainly to the change in the structure of the PVA.

Figure 13 represents the IR spectra of a heat-treated PVA/neutralized PAA (DN = 10 mol %) blend film before [Fig. 13(a)] and after [Fig. 13(b)] immersion in an aqueous sodium hydroxide solution (0.1N) for 4 h. The absorbance peak around  $1570\text{ cm}^{-1}$  is attributed



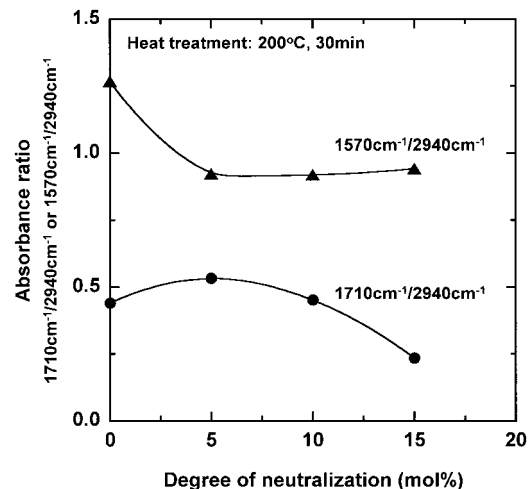
**Figure 12** Absorbance ratios for  $3400/2940$  and  $1710/2940\text{ cm}^{-1}$  in the IR spectra of the heat-treated PAA films versus degree of neutralization in PAA.



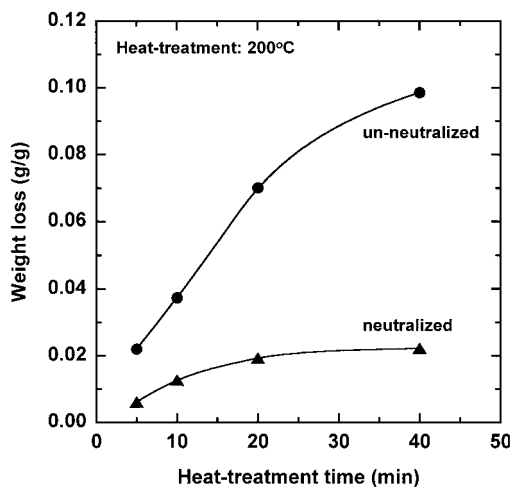
**Figure 13** IR spectra of the heat-treated blend film (a) before and (b) after immersion in an aqueous sodium hydroxide solution.

to the sodium carboxylate formed as a result of ion exchange of the residual carboxyl group in the blend film. The peak around  $1710\text{ cm}^{-1}$  in spectrum (b) is attributed to the carbonyl groups such as the ketone produced by the degradation of PVA and carbonyl of the ester linkage forming the crosslinking. Figure 14 shows the relative absorbance of these two peaks to the absorbance of the methylene group ( $2940\text{ cm}^{-1}$ ) versus the degree of neutralization in PAA. The relative absorbance for sodium carboxylate ( $1570/2940\text{ cm}^{-1}$ ) exhibits the highest value when unneutralized PAA is blended with PVA; the film possesses a larger amount of carboxyl group compared to that of the film formed by partially neutralized PAA and PVA.

In Figure 15, weight loss of PVA/PAA blend films by heat treatment at  $200^\circ\text{C}$  is plotted against the heat-



**Figure 14** Absorbance ratios for  $1710/2940$  and  $1570/2940\text{ cm}^{-1}$  in the IR spectra of the heat-treated PVA/PAA films with Na-form versus degree of neutralization in PAA. The Na-form in the film was prepared after the heat treatment.



**Figure 15** Weight loss of the PVA/unnaturalized PAA and the PVA/neutralized PAA (10 mol %) blend films versus heat-treatment time.

treatment time. The weight loss of the blend film with partially neutralized PAA (DN = 10 mol %) is about 2 wt % after the heat treatment, whereas the loss is about 10 wt % for the case of unneutralized PAA. Application of unneutralized PAA results in serious degradation of PVA.

The results obtained from characterization of the film series support the finding that the esterification reaction (i.e., crosslinking reaction between PVA and PAA) can be enhanced when an appropriately neutralized PAA is used.

### CONCLUSIONS

Poly(vinyl alcohol) was blended with poly(acrylic acid) to fabricate films with high water resistance conferred by a crosslinked structure. The effect of crosslinking conditions including heat-treatment temperature and time, and neutralization of PAA was investigated to obtain greater insight into improvement in the degree of crosslinking reaction. The fol-

lowing conclusions were obtained from the experimental results.

1. The degree of crosslinking reaction was enhanced up to about 40 mol % based on the PAA monomer unit by using partially neutralized PAA.
2. The optimum degree of neutralization in PAA was in the range of 5 to 10 mol %.
3. The hydroxyl group in PVA was consumed for oxidation rather than esterification when unneutralized PAA was used, resulting in the low degree of crosslinking reaction.
4. Phase separation of PVA and PAA domains was observed in the blend film when PAA neutralized more than 10 mol % was used. Insufficient miscibility attributed to the phase separation would lower the probability of the crosslinking reaction.

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