

Making Polyvinyl Alcohol Films Iodinated at Solution State Before Casting and Its Application

Eun Joo Shin,¹ Won Seok Lyoo,² Yang Hun Lee¹

¹Division of Clothing and Textiles, Dong-A University, Pusan 604-714, South Korea

²Division of Advanced Organic Materials, School of Textiles, Yeungnam University, Gyeongsan 712-749, South Korea

Received 27 July 2007; accepted 14 January 2008

DOI 10.1002/app.28181

Published online 15 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This research focused on the manufacture a polarizing film with PVA iodinated at solution before casting (IBC) film, which was prepared by casting aqueous solutions of 10 wt % poly(vinyl alcohol) (PVA) containing boric acid with 0, 0.1, 0.5, and 1.0 mol/L of I₂/KI aqueous solution, and I₂/KI(1:2) with 0, 5, and 10 wt % of PVA. The lights of wavelengths between 450 and 700 nm were polarized in UV analysis. The degree of polarization and transmittance of the IBC polarizing film (10 wt % I₂/KI and 0.5 mol/L boric acid) are 99.9% and 43.2%, respectively. The resistance of the heat and humidity of IBC polarizing films was higher than that of commercial polarizing films, which were elucidated by changing the transmittance of the films. This can be explained by the fact

that the interaction between polyiodine molecules and PVA chains as the state of IBC is higher than that of the commercial state. The effect of boric acid may be strengthened for the resistance of heat and humidity. Crosslinking by boric acid improved thermal properties of the IBC polarizing films, resulting from the increases of degradation temperature in DSC and TG analysis. And the unit cell broadening occurred, which was caused by the intrusion of boric acid into PVA chains in X-ray analysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1143–1149, 2008

Key words: film; polyvinyl alcohol; crystal structure; crosslinking

INTRODUCTION

As the fact was found that iodine interrupts intermolecular hydrogen bonds and makes complex polymer chains not only in the crystalline but also in the amorphous regions of several polar polymers, the study about polyvinyl alcohol (PVA)/iodine complex has been accelerated.^{1–7} They have been studied about the role of adsorbed iodine into PVA film, and recently reported that the iodine form the PVA/iodine complexes and considered to play a role of structure the microfibrillar network as junction points between the microfibrils.⁸ Chetri et al.⁹ and Bin et al.¹⁰ reported that iodine act as a catalyst for dehydration of PVA.

Previous studies of the formation of PVA/iodine complex in potassium iodide(KI) aqueous solutions focused on the dilute regime.^{11,12} Recently, Yang et al.¹³ studied about concentrated PVA/I₂/KI aqueous mixture by ¹H and ¹³C NMR spectroscopy as well as rheometry according to their phase diagram.

In our laboratory,^{14,15} the structure of the iodinated PVA films possessing various quantities of io-

dine through thermal analyses and drawability tests have been studied. On the other hand, we have tried the preparation of the PVA films iodinated at solution before casting (IBC films),^{16,17} where iodine adsorption has no limit unlike the PVA films iodinated after casting (IAC films), wherein the film is sunk as a solid state in the I₂/KI aqueous solution. The IBC PVA film has possibility of the minimum of entanglements between intermolecular chains as well as the disturbance of PVA crystallization, and the film with weight gain of I₂/KI 117% was almost amorphous. But the crystallinity of that film increased by drawing regardless of crystallinity before drawing. And the process of film preparation by IBC method is simpler than that of IAC method. That is, we were able to prepare the iodinated PVA film immediately from blended PVA aqueous solution state with I₂/KI and boric acid except for the process of PVA film casting.

The most important application of the PVA-iodine complex is the use of a sheet polarizer as a high quality of dichroism in liquid crystal display systems. The polarizer is the PVA-iodine complex film soaked in an I₂/KI solution and stretched unidirectionally. However, commercial polarizing films have serious problems like poor water stability and easy iodine desorption under warm and humid atmosphere. To resolve these problems, several methods to produce syndiotactic PVA(s-PVA) with higher tacti-

Correspondence to: Y. H. Lee (leeyh@daunet.donga.ac.kr).

Contract grant sponsor: Korean Government (MOEHRD); contract grant number: KRF-2005-037-C00065.

city as well as to increase molecular weight have been tried in the preparation of polarizing films.^{18–21} The polarizing films with s-PVA have high water-resistance quality and fastness of iodine, but there were difficulties of manufacturing s-PVA and adsorbing iodine in the film due to high crystallinity. Recently, Song et al.²² prepared polarizing films using diachronic dyes and reported that the polarizing efficiency of PVA/dye polarizing films reached almost full contrast but their single-piece transmittances were rather low. The subsequent treatment with boric acid for the polarizing films reported that it is effective to stabilize the PVA-iodine complex. But the exact mechanism of this in relation to the nature of the iodine species present is uncertain.

In the present article, therefore, we focused on the manufacture a polarizing film with PVA iodinated at solution before casting (IBC) film, which was saved the processing course of PVA film casting as compare with commercial method, and we able to control the weight gain of iodine in PVA films for adequate transmittance. And then the combined effect of boric acid in IBC polarizing film was investigated mainly in terms of structure and optical properties of the polarizing films by using thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), X-ray diffractometry, and UV-vis absorption spectrometry.

EXPERIMENTAL

Preparation of PVA films containing boric acid

The films were prepared by casting 10 wt % PVA (polymerization of 2300 and 99.9% hydrolyzed, Kolon Chem. Co., Korea) solution containing boric acid of 0.47, 2.35, and 4.65 wt % to the PVA (weight gain), which were poured on a glass plate at 60°C and were put in air at 30°C for 48 h. The three kinds of weight gain of boric acid were controlled in the same quantities with IBC PVA films as details are given later. So we will mark the content of boric acid as concentration of mol/L to I₂/KI aqueous solution (0.1, 0.5, and 1.0 mol/L) in tables and figures.

Preparation of IBC polarizing films

The films were prepared by casting 10 wt % PVA solution containing I₂/KI of 5 and 10 wt % to the PVA, which were poured on a glass plate at 60°C and were put in air at 30°C for 24 h. The boric acid contained 0.1, 0.5, and 1.0 mol/L of I₂/KI aqueous solution.

Drawing

The PVA/boric acid film and IBC PVA films were drawn to 3.5 times by a hand-operated drawer at 65

~ 80°C in *n*-propanol. The width, length, and thickness of samples were 5 mm, 10 mm, and 0.15 ~ 0.2 mm, respectively, and the drawing speed was 10 mm/min. After drawing, the width and thickness of samples were changed to 1 mm and 0.09 ~ 0.11 mm, respectively.

Transmittance and degree of polarization (ρ)

The films were estimated by UV-visible spectrometry (UV-2401PC, Shimadzu) using the following eq. (1).^{23,24}

$$\rho (\%) = [(Y_{\parallel} - Y_{\perp}) / (Y_{\parallel} + Y_{\perp})]^{1/2} \times 100 \quad (1)$$

where Y_{\parallel} and Y_{\perp} are the transmittances of the film superimposed on each other parallel and perpendicular to the direction of the elongation of the film, respectively.

Durability

Polarizing films were kept in a constant temperature and humidity chamber (relative humidity of 80% and temperature of 50°C). Durability for the heat and humidity of the polarizer was evaluated from the change of transmittance.

Measurements

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed by a TA TGA 2950 and a TA DSC 2910, respectively. Both tests were conducted at the heating rate of 20°C/min in the atmosphere of N₂. X-ray diffractometry was performed using Rigaku D/max-III-A with Cu-K α radiation. ¹H NMR analyses were carried out with a Bruker DPX 300-Hz spectrometer in DMSO-d₆ at room temperature.

RESULTS AND DISCUSSION

Structure of PVA/boric acid films

It has long been known that the reaction of boric acid with PVA yields boric acid esters, which link the polymeric chains and fix iodine in the film. But the mechanism of PVA-iodine-boric acid has been scarcely found. Therefore, we have investigated the behavior of the PVA-boric acid film before studying PVA-iodine-boric acid. The boric acid is presumed to form monodiol-type bonds as shown by the eq. (2). The structure indicated is the simplest form of intramolecular bonding as eq. (2), and crosslinking is also possible by hydrogen bonding between the diol complex and PVA chains such as eq. (3), although its bonding force is weak and its participation will be minor.^{25–27}

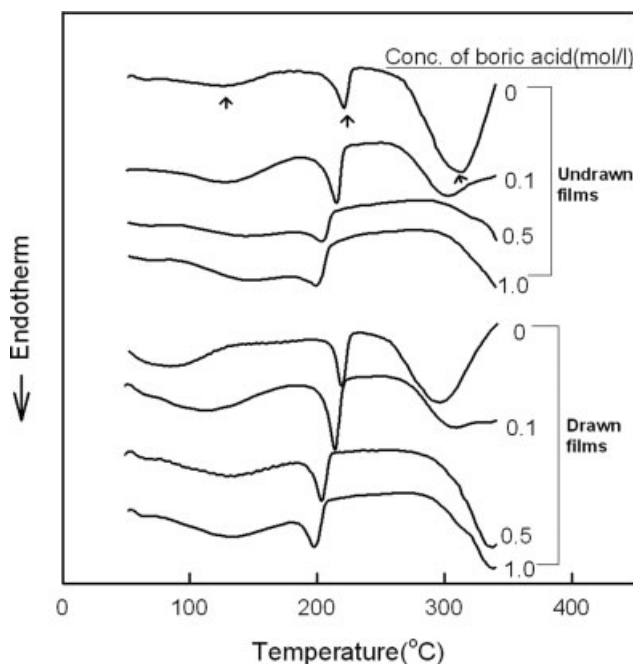
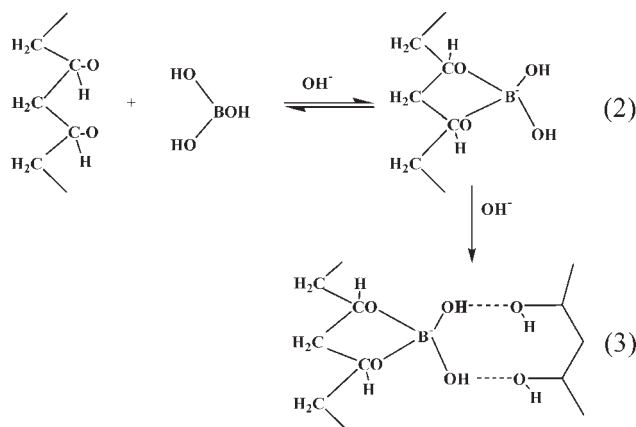


Figure 1 DSC thermograms of the untreated PVA film and undrawn and drawn PVA/boric acid films.



DSC analysis

Figure 1 shows DSC thermograms of the undrawn and drawn PVA/boric acid films. There are three kinds of endothermic peaks at around 130, 220, and 310°C in undrawn PVA/boric acid films. The sharp peak at 220°C must correspond to the melting of crystal. As the later-mentioned TG results, the component at 310°C was estimated to be associated with the degradation of —OH side groups and the partial degradation of main chains. It was estimated to be the broad peak at around 130°C as quasicrystal of PVA, which was conformed in endothermic process. To support this estimation, we performed additional experiments of DSC undergoing three successive steps of heating up to the maximum peak temperature followed by an isothermal abiding for 1 min, slow cooling to ambient, and then heating again to

350°C. The results are indicated in Figure 2. There is an exothermic peak at 130°C on the cooling step, which was estimated as a recrystallization of quasicrystal and to be cleared at 150°C associated with quasicrystal on the cooling step. And the melting peak at round 230°C was larger due to formation more perfect crystal.

With boric acid increasing, the melting temperature of quasicrystal and crystal increased and decreased, respectively. It can be explained that the unperfected crystal was conformed by the addition of boric acid and the regularity of PVA crystal decreased during the crystallizing course from aqueous solution state. And the temperature of the peak related to the degradation of PVA/boric acid film increased due to the intercrosslinking of high concentration of boric acid. It is believed that, as the boric acid used a crosslinking agent in the PVA, it can form a didiol complex with PVA by hydrogen bonding.²⁷ These facts appeared more clearly in the drawn films.

X-ray analysis

Figure 3 shows the X-ray diffraction scans of the undrawn and drawn PVA films containing boric acid before iodination. The main peak at $2\theta = 19.5^\circ(101)$ shifted to a lower scattering angle with boric acid increasing, which might result from the some broadening of original PVA unit cells owing to the intrusion of —B of boric acid between PVA chains

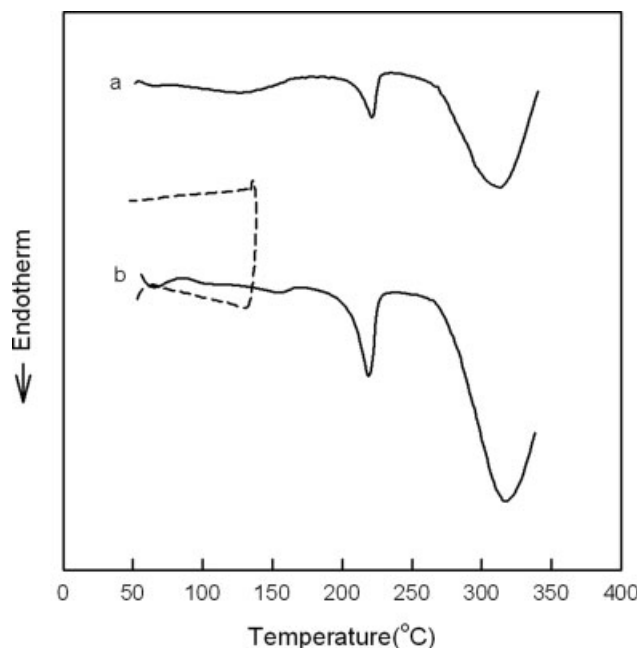


Figure 2 (a) DSC thermograms of untreated PVA film (b) DSC thermograms of untreated PVA film (heating to 130°C → cooling to room temperature → heating to 350°C).

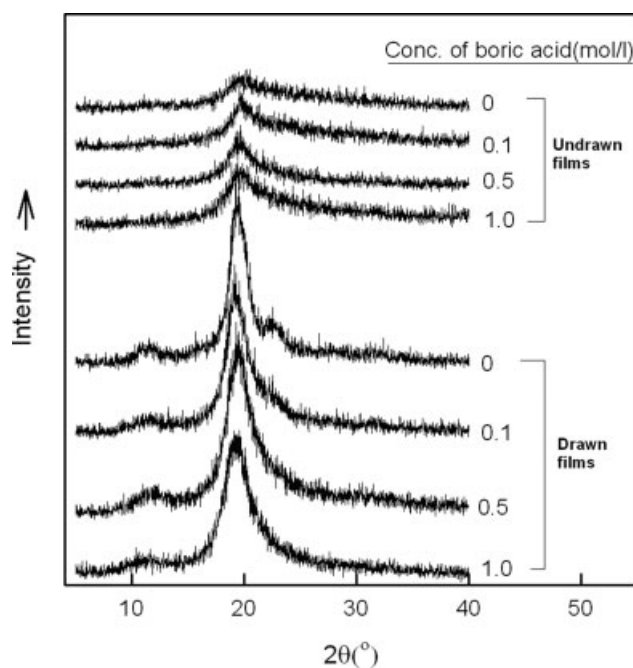


Figure 3 X-ray diffraction scans of the undrawn and drawn PVA films containing boric acid before iodination.

by crosslinking.^{28,29} The overall appearance of the diffraction scans is similar to but the intensity of the peak was clearer than that of the unoriented films. The X-ray diffractometer scans of the untreated drawn films along the equatorial direction through the 100, 001, 10 $\bar{1}$, 101, and 200 reflections were broadened by boric acid.

TG analysis

Figure 4 shows the TG curves of the undrawn PVA films containing boric acid before iodination. In this study, thermal degradation of the PVA/boric acid film was compared with that of the untreated PVA film. The reports on the TG analysis for the untreated PVA were described in our previous work.¹⁴ The first weight loss of films (Zone I) happened at 160°C, which must be associated with moisture in films. The second weight loss of films (Zone II) happened between 240 and 320°C, followed by third weight loss (Zone III) from 320 to 460°C, and then the last weight loss (Zone IV) from 460 to 540°C, associated with partial side groups, the residue side groups and partial polymer backbone and then remaining polymer backbone, respectively, and a very small amount of a residue from films at a higher temperature. For the PVA/boric acid film, similar ranges of the weight loss were observed, the first from 260 to 340°C, followed by a further weight loss between 340°C and approximately 480°C, and the last weight loss from 480°C and then leaving a residue. Consequently, the set-on temperatures of

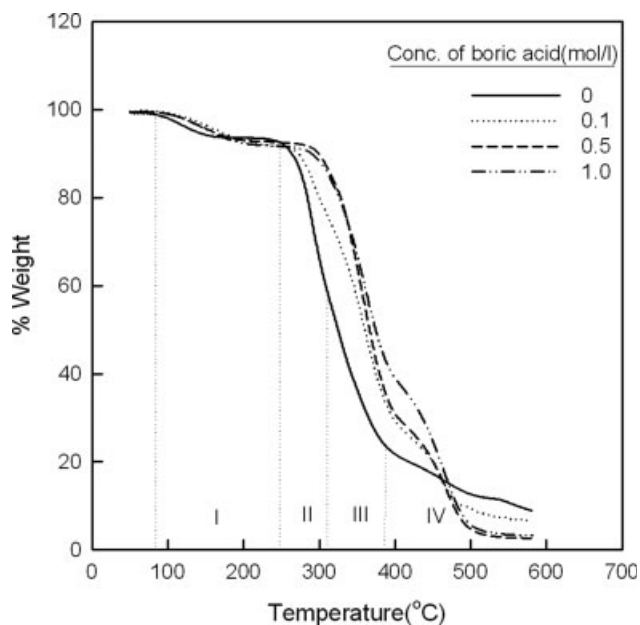


Figure 4 TG curves of the undrawn PVA films containing boric acid before iodination.

PVA/boric acid films at each stage were 20 ~ 30°C higher than those of untreated PVA films, indicating that PVA/boric acid film has a better thermal stability than untreated PVA films due to the crosslinking of B—O bonds. With boric acid increasing, the set-on temperature of each steps increased.

Optical properties of IBC films

Table I shows the variation of the transmittance and degree of polarization of films with various concentration of boric acid. Because of the high weight gain of I₂/KI, the value of the transmittance of films iodinated was very low. Over 10 wt % I₂/KI films, the values of DP reached 100 but the films were not suitable for polarizing films due to the low transmittance (>10%) of films. In the case of 5 wt % I₂/KI for films, transmittance increased to about 40% but

TABLE I
Transmittance and Degree of Polarization of IBC Films with Various Concentration of Boric Acid

| Weight gain of I ₂ /KI (wt %) | Conc. of boric acid (mol/L) | Transmittance (%) | Degree of polarization (%) |
|--|-----------------------------|-------------------|----------------------------|
| 5 | 0 | 47.78 | 94.72 |
| | 0.1 | 43.15 | 94.63 |
| | 0.5 | 42.05 | 94.01 |
| | 1.0 | 17.96 | 99.99 |
| 10 | 0 | 27.86 | 99.85 |
| | 0.1 | 31.71 | 99.87 |
| | 0.5 | 43.20 | 99.95 |
| | 1.0 | 0.42 | 99.99 |

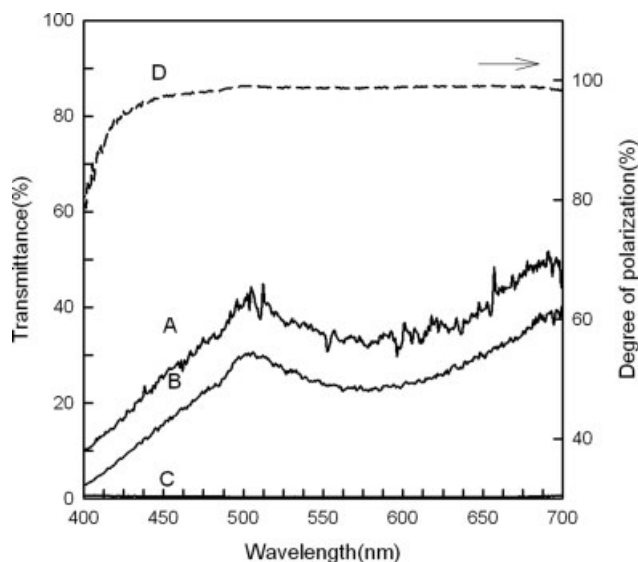


Figure 5 Behavior as a polarizer of the film weight gain of I_2/KI 10% and 0.5 mol/L boric acid. (a) Transmittance of a sheet of the film parallel (b) and vertical (c) arrangement in direction of elongation (d) degree of polarization.

DP decreased due to the low absorption of I_2/KI . The most adequate film for polarizing films was prepared by 10 wt % I_2/KI film. With the concentration of boric acid increasing, the transmittance and DP increased to 0.5 mol/L and then decreased due to the increasing crosslinking in the film, which can decrease the quantities of the effective iodine molecules. For high quality polarizing films, the concentration of 0.5 mol/L boric acid may be reasonable.

Figure 5 shows the behavior as a polarizer of the film weight gain of I_2/KI 10% and 0.5 mol/L boric acid. The lights of wavelengths between 450 and 700 nm are polarized. The DP and transmittance of this film are 99.9% and 43.2%, respectively. As compared with commercial polarizing films, this IBC film also has good property for polarizing films.

Figure 6 shows the resistances for the heat and humidity of polarizing films. As time increased, the transmittance of the films increased due to the sublimation of iodine and polyiodine molecules easily deformed and released from PVA. The change of transmittance for commercial films was faster than that of IBC films. This can be explained by the fact that the interaction between polyiodine molecules and PVA chains as state of IBC is higher than that of the commercial state. The effect of boric acid may be strengthened for the resistance of heat and humidity.

Structure of IBC polarizing films

For analysis the IBC polarizing films, we selected the films of 10 wt % weight gain of I_2/KI , of which films contained high degree of polarization.

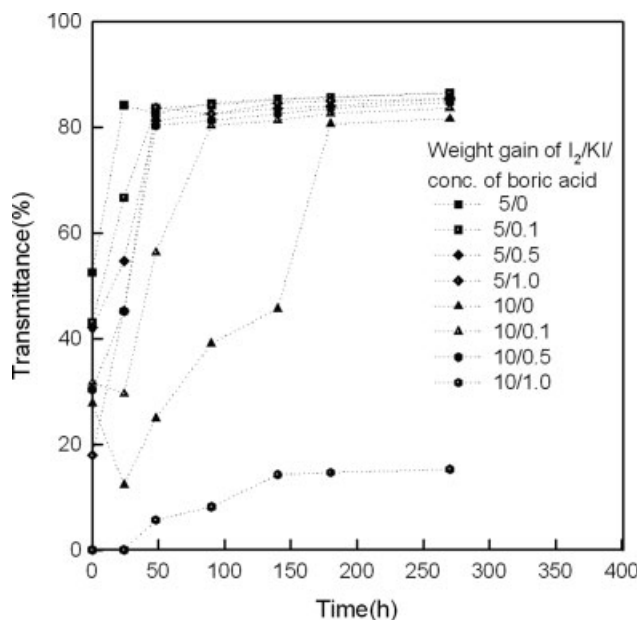


Figure 6 Change of transmittance of IBC films at 50°C and relative humidity 80% for 270 h with time.

DSC analysis

Figure 7 shows the DSC thermograms of the untreated IBC polarizing film and treated films with boric acid. There are two kinds of endothermic peaks at around 120 and 200°C. As compared with PVA/boric acid films, the temperature of the peaks decreased due to the addition of I_2/KI (10 wt % of PVA), which is associated with I_2 of oxidation. The

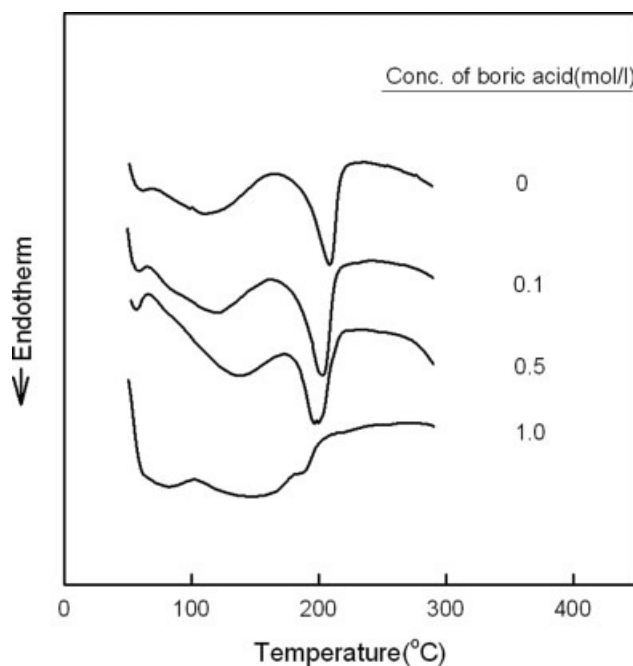


Figure 7 DSC thermograms of IBC polarizing film treated with various conc. of boric acid.

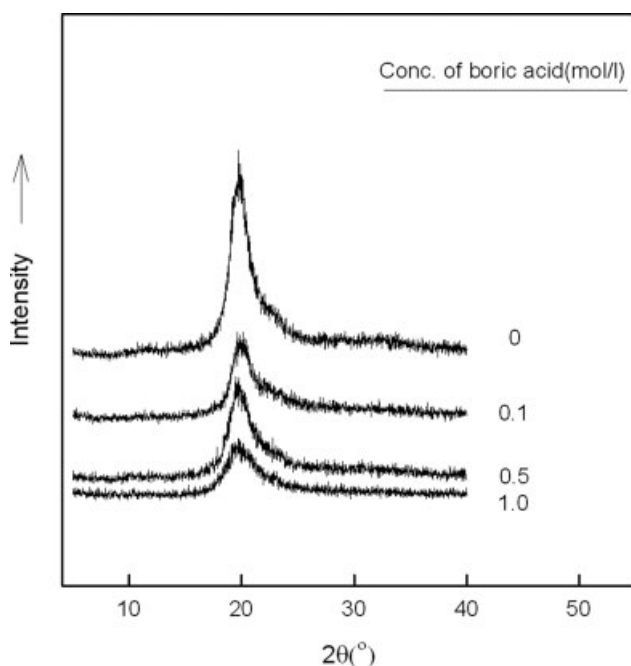


Figure 8 X-ray diffraction scans of IBC polarizing films treated with various conc. of boric acid.

sharp peak at 200°C of the untreated IBC polarizing film, corresponding to the overlapped peak of crystal melting and decomposition of side groups, divided to double peaks and decreased the temperature of peaks with the treated boric acid. As mentioned of our previous report,¹⁶ there was PVA original crystal, not combined with iodine (in case of low weight gain of I₂/KI) but relaxed in IBC state. With conc. of boric acid increasing, the temperature of peaks decreased owing to the intrusion of boric acid between PVA chains by crosslinking and then lost crystal, which remained quasicrystal state and appeared at lower temperature as a broad peak. But the temperature of quasicrystal peak increased with conc. of boric acid due to the increase of crosslinking in the IBC polarizing film. In the case of 1.0 mol/L boric acid, there was a broad triple peak from 120 ~ 190°C corresponding to the melting of quasicrystal, melting of crystal and decomposition of side groups, respectively.

X-ray analysis

Figure 8 shows the X-ray diffraction scans for IBC polarizing films. The intensity of main peaks decreased with boric acid as compared with the untreated film because of the relaxation of crystal by the intrusion of boric acid, which supported the DSC results as mentioned earlier. As compared with PVA/boric acid films (Fig. 3), the main peak of which shifted to a higher angle and broadened due to the intrusion of iodine.

TG analysis

Figure 9 shows the TG curves for IBC polarizing films. In the case of IBC films, the set on the temperature of Zone II decreased than that of PVA/boric acid due to the oxidation of I₂, but this temperature increased with boric acid. This may be a result of a special crosslinking quality associated with the better thermal resistance of B—O compared to C—O bond.³⁰ With the increase of boric acid, the contents of crosslinking increased and then the set-on temperature of Zone III decreased and was separated into two steps. This fact is clearly shown in 1.0 mol/L boric acid.

Tacticity of films after deiodination

The change of PVA configuration is rare, but its probability existed due to the complex role of iodine and boric acid. In our laboratory, we were interested in the modification of the PVA crystal by the sorption of some agents. Moreover, in the IBC method, which was manufactured as a PVA-iodine aqueous solution state, the molecular chain of PVA can be changed easily. In this state, the inter- and intracrosslinking of boric acid can accelerate the change of PVA configuration. So we wondered what happened in the change of PVA configuration.

Table II shows the tacticity of IBC films after deiodination through ¹H NMR spectrometry. For this measure, IBC polarizing films put in oven at 70°C, 80% of relative humidity for 360 h for completely deiodination. And then the films were dried in vacuum oven at 40°C for 24 h. The original syndiotactic

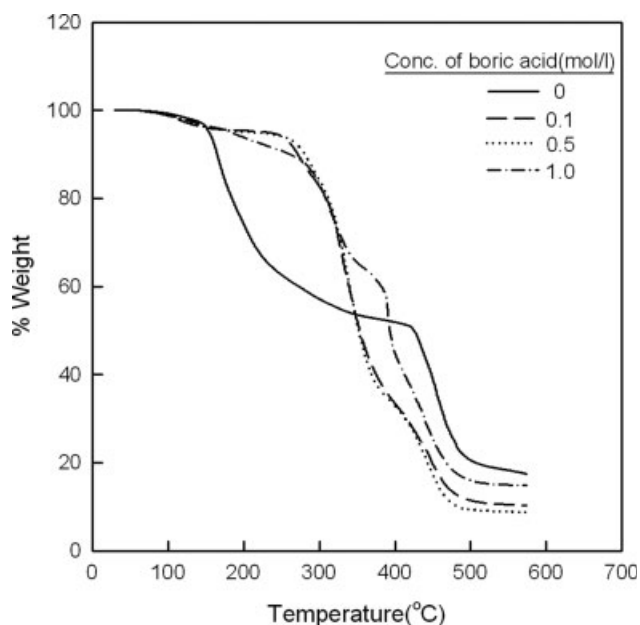


Figure 9 TG curves of IBC polarizing films treated with various conc. of boric acid.

TABLE II
Tacticity of IBC PVA Films after Deiodination by ^1H NMR Spectrometer

| Samples | Tacticity in triad | | | Tacticity in diad | |
|-----------------------------|--------------------|-------|-------|-------------------|-------|
| | mm | mr | Rr | m | r |
| Untreated | 0.210 | 0.490 | 0.300 | 0.445 | 0.544 |
| Conc. of boric acid (mol/L) | 0 | 0.180 | 0.524 | 0.296 | 0.442 |
| | 0.5 | 0.186 | 0.505 | 0.309 | 0.439 |

diad (s-diad) content of PVA was 54.4%, but the content of s-diad increased by iodination and the addition of boric acid. Especially, the IBC film containing 0.5 mol/L boric acid had higher s-diad content than any other film. It certainly showed that the configuration of PVA changed and their syndiotacticity increased with iodine and boric acid. However, the studies on enhancing the deformation of PVA will be performed.

CONCLUSIONS

We manufactured PVA films iodinated at solution state before casting (IBC) and examined its application of polarizing film. On the other hand, the crosslinking effects by boric acid on the structure and properties also considered. The IBC polarizing films were prepared by casting solutions of 10 wt % PVA containing selected quantities of boric acid (0.1, 0.5, 1.0 mol/L of I_2/KI solution) and 5, 10 wt % I_2/KI . The lights of wavelengths between 450 and 700 nm are polarized in UV analysis. The degree of polarization and transmittance of the film (10 wt % I_2/KI and 0.5mol/L boric acid) are 99.9% and 43.2%, respectively. As compare with commercial polarizing film, this IBC polarizing film also has good property for polarizing film. The change of transmittance for commercial film was faster than that of IBC polarizing film. This can be explained by the fact that the interaction between polyiodine molecules and PVA chains as state of IBC is higher than that of commercial state. The effect of boric acid may be strengthened for resistance of heat and humidity. Crosslinking by boric acid improved thermal properties of the PVA film, resulting from increases of degradation temperature in DSC and TG analysis. In the case of PVA/boric acid film, it was found that the unit cell broadening

occurred, which was caused by the intrusion of boric acid into PVA chains in X-ray analysis.

References

1. Sakurada, I. *Polyvinyl Alcohol Fibers*, Marcel Dekker: New York and Basel, 1985, p 147.
2. Zwick, M. M. *J Appl Polym Sci* 1965, 9, 2393.
3. Haas, H. C. *Polyvinyl Alcohol-Properties and Applications*; Wiley: London, 1973, p 503.
4. Takamiya, H.; Tanahashi, Y.; Matsuyama, T.; Tanigami, T.; Yamaura, K.; Matsuzawa, S. *J Appl Polym Sci* 1993, 50, 1807.
5. Choi, Y. S.; Miyasaka, K. *J Appl Polym Sci* 1993, 48, 313.
6. Oishi, Y.; Miyasaka, K. *Polym J* 1986, 18, 307.
7. Oishi, Y.; Miyasaka, K. *Polym J* 1987, 19, 331.
8. Miyazaki, T.; Katayama, S.; Funai, E.; Tsuji, Y.; Sakurai, S. *Polymer* 2005, 46, 7436.
9. Chetri, P.; Dass, N. N.; Saram, N. S. *Polym Bull* 2007, 58, 489.
10. Bin, Y.; Chen, Q.; Nakamura, Y.; Tsuda, K.; Matsuo, M. *Carbon* 2007, 45, 1330.
11. Tebelv, L. G.; Kikul'skii, G. F.; Korchagina, Y. P.; Glikmm, S. A. *Vysokomol Soecin Ser A* 1965, 7, 123.
12. Noguchi, H.; Jalai, H.; Matsuzawa, S. *J Polym Sci Polym Phys* 1997, 35, 1701.
13. Yang, H.; Watanabe, H.; Horii, F. *Polym Repr Jpn* 2005, 54, 1250.
14. Shin, E. J.; Lee, Y. H.; Choi, S. C. *J Appl Polym Sci* 2004, 91, 2407.
15. Shin, E. J.; Lee, Y. H.; Choi, S. C. *J Appl Polym Sci* 2005, 95, 1209.
16. Shin, E. J.; Lee, Y. H.; Choi, S. C. *J Appl Polym Sci* 2006, 101, 3497.
17. Shin, E. J.; Lee, Y. H.; Choi, S. C. *J Appl Polym Sci* 2008, 108, 34.
18. Lyoo, W. S.; Yeum, J. M.; Choi, J. H.; Ji, B. C.; Ghim, H. D.; Kim, J. P.; Noh, T. H.; Yoon, W. J. *Polym Test* 2001, 20, 503.
19. Lyoo, W. S.; Yeum, J. M.; Choi, J. H.; Song, H. C.; Ji, B. C.; Kim, J. P.; Noh, T. H.; Yoon, W. J.; Cheong, T. S. *J Appl Polym Sci* 2001, 82, 108.
20. Ghim, H. D.; Kim, J. P.; Kwon, I. C.; Lee, C. J.; Lee, J. W.; Kim, S. S.; Lee, S. M.; Yoon, W. S.; Lyoo, W. S. *J Appl Polym Sci* 2003, 87, 1519.
21. Yeum, J. H.; Kwak, J. W.; Han, S. S.; Kim, S. S.; Ji, B. C.; Noh, S. K.; Lyoo, W. S. *J Appl Polym Sci* 2004, 94, 1435.
22. Song, D. H.; Yoo, H. Y.; Lee, J. J.; Kim, J. P. *Mol Cryst Liq Cryst* 2006, 445, 65.
23. Tanizaki, Y. *Bull Shem Soc Jpn* 1957, 30, 935.
24. Fillipovich, L. N.; Ariko, N. G.; Agabekov, V. E.; Malashko, P. M. *J Appl Spec* 2005, 72, 617.
25. Mitsushiro, S.; Masahiro, S.; Yoshiharu, K.; Hiroshi, F.; Shunji, N. *Polymer* 1988, 29, 336.
26. Mitsushiro, H. Y.; Hidenobu, K.; Shunji, N. *Polymer* 1988, 29, 2066.
27. Wang, H. H.; Shyr, T. W.; Hu, M. S. *J Appl Polym Sci* 1999, 73, 2219.
28. Cho, J. D.; Lyoo, W. S.; Chvalun, S. N. *J Blackwell Macromol* 1999, 32, 6236.
29. Lyoo, W. S.; Chvalun, S.; Ghim, H. D.; Kim, J. P.; Blackwell, J. *Macromolecules* 2001, 34, 2615.
30. Gao, J.; Liu, Y.; Yang, L. *Polym Degrad Stab* 1999, 63, 19.