

Effect of Boric Acid Treatment Method on the Characteristics of Poly(vinyl alcohol)/Iodine Polarizing Film

Eun Joo Shin,¹ Won Seok Lyoo,² Yang Hun Lee³

¹Research Institute of Human Ecology, Dong-A University, Busan 604-714, South Korea

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

³Department of Textile Industry, Dong-A University, Busan 604-714, South Korea

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ABSTRACT: Four types of polyvinyl alcohol (PVA)/iodine complex films were made using different boric acid treatments to prepare polarizing films having high durability under humid and warm atmospheres and to identify the effects of the boric acid treatment method on the formation of the PVA/iodine polarizing film. The four types of films were a PVA iodinated film(I), a PVA film that was iodinated and then treated with boric acid(I-B), a PVA film that was treated with boric acid and then iodinated(B-I), and a PVA film that was simultaneously treated with iodine and boric acid(I+B). The concentrations of I₂/KI were 0.03, 0.05, and 0.07 mol/L, and the concentrations of boric acid were 0.1, 0.3, and 0.5 mol/L. Comparing four type films treated

with 0.05 mol/L I₂/KI and 0.5 mol/L boric acid, the conformation of PVA/iodine complexes for I-B film were larger than the others. The degrees of polarization (ρ) of all of the films increased to very high levels (99.9% \uparrow). The durability of I-B was superior to B-I or I+B, and the change in the ρ was below 5% because the boric acid treated after iodine treatment reduced the molecular mobility of the PVA/iodine complex chains through intracrosslinking, so that the PVA/iodine complex could not easily collapse. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 672–681, 2012

Key words: drawing; films; Raman spectroscopy; UV–vis spectroscopy; X-ray

INTRODUCTION

Polyvinyl alcohol (PVA) molecules form complexes with iodine, because the polyiodide ions interrupt the intermolecular hydrogen bonds. Iodine forms blue colored complexes with many substances, such as starch, nylon 6, poly(vinyl pyrrolidone), and PVA.¹ From the application point of view, the blue PVA/iodine complex is the most important among them, for it is widely used for film polarizers. The polarizers are prepared by soaking PVA films in a solution of iodine and potassium iodine (KI) and subsequent drawing to cause the high degree of uniaxial orientation.^{2–5}

In the commercial process, boric acid has been added to the solution used in the film stretching, promoting the formation of PVA–iodine complexes in the film. Boric acid plays the crucial role on the production of high-performance polarizers.⁶ Boric acid forms either an intramolecular crosslinking

covalent bond or an intermolecular crosslinking hydrogen bond in the PVA resin.^{7–9} The intermolecular crosslinking contributes to the formation of the PVA hydrogel. The intramolecular crosslinking contributes to the formation of an extended PVA chain segment, which is helpful to form the aggregate model type PVA/iodine complex. Furthermore, in helical model type complexes, the formation of an intrachain bridge enhances the stability of the complex.^{10,11} Therefore, boric acid is believed to stabilize the PVA/iodine complexes through crosslinking, but a systematic investigation to conform the role of boric acid in the stabilization of the PVA/iodine complex has not been established yet. A few studies have been conducted on PVA/iodine complexes in the presence of boric acid in the soaking media. Miyazaki et al.⁶ investigated the role of boric acid penetrated into the PVA film is immersed in boric acid aqueous solutions and resulted that boric acid plays an important role on the effective orientation of a large amount of PVA molecular chains without strain-induced crystallization as the crosslinking agent during film stretching, as the crosslinkers inhibit recrystallization of the PVA chains.

In our previous studies, we have estimated the effect of boric acid on durability of PVA–iodine polarizing sheet film^{12,13} in the iodination at solution

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

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before casting (IBC); boric acid combined with the PVA chain to form intramolecular crosslinking segments that were regarded as a defect in the crystal, which decreased the melting temperature of PVA. The formation of I_3^- and I_5^- increased with increasing boric acid content in IBC state. In the next state, the IBC film was immersed in I_2/KI aqueous solution, the strength of the peak corresponding to I_3^- decreased, and that for I_5^- increased due to the formation of a new PVA/iodine complex, which is the reason for higher durability under a humid and warm atmosphere compared with a commercial polarizing film. In study of examination of the role of boric acid and the effect of heat treatment on PVA-iodine polarizing films prepared IBC of PVA/iodine/boric acid films, the transmittance and degree of polarization for the films increased and decreased with increasing heat treatment time under heat and a humid atmosphere, respectively. However, this tendency decreased with increasing boric acid concentration and heat treatment.¹² These results indicate that boric acid on preparing IBC PVA/iodine polarizing sheet film enhances the formation of I_3^-/I_5^- ions and increases the durability under heat and humid atmosphere.

In this study, we tried the effect of the boric acid on preparing commercial PVA/iodine polarizing sheet film and investigated the boric acid treatment method on the characteristics of the polarizing film. That is, we were wondering about which step of boric acid treatment was most effective on formation of I_3^-/I_5^- ions and increasing the durability under heat and humid atmosphere. Therefore, four types of PVA/iodine complex films were prepared using different boric acid treatment methods. These films included a PVA iodinated film (I), a PVA film that was iodinated and then treated with boric acid (I-B), a PVA film that was treated with boric acid and then iodinated (B-I), and a PVA film that was simultaneously treated with iodine and boric acid (I+B). The effects of the boric acid treatment method and the concentrations of iodine and boric acid on the characteristics of the PVA/iodine complex films were investigated through Raman spectrometry, differential scanning calorimetry (DSC), X-ray diffraction (XRD), and UV-vis absorption spectrometry. The effects on the durability and the polarizing efficiency of the four types of PVA/iodine polarizing films were also investigated.

EXPERIMENTAL

Material

A PVA films with a thickness of about 80 μm were obtained from Kuraray (Japan). The degree of polymerization of the films was 2400, and the s-diad con-

tent and the degree of saponification values of 54.5% and 99.0%, respectively, were measured using H-NMR with a Bruker Advance 500 at 500 MHz using DMSO- d_6 .

Preparation of PVA/iodine complex film

The films were soaked in aqueous solutions of 0.03, 0.05, and 0.07 mol/L I_2/KI and 0.1, 0.3, and 0.5 mol/L boric acid for 1 min, washed with water, and dried at room temperature for over 1 week to completely evaporate the water and sublimate the excess iodine. The PVA/iodine complex films were prepared using four different types of boric acid treatment methods. These films included a PVA iodinated film (I), a PVA that was iodinated and then treated with boric acid (I-B), a PVA film that was treated with boric acid and then iodinated (B-I), and a PVA that was simultaneously treated with iodine and boric acid (I+B). The boric acid- and I_2/KI -induced weight gains were determined from the weight difference between the dried film before and after soaking.

Wet drawing of film

The films were wet-drawn four times of the initial length using a 2-wt % boric acid solution at 40°C and a speed of 10 mm/min using a hand-made drawer. The drawn films were subsequently dried at 60°C for 30 min. There was scarcely any difference of thickness among four types drawn films, of which was about $45 \pm 5 \mu\text{m}$.

Characterization

The transmittance (T) and the degree of polarization (ρ) of the films were estimated using UV-visible spectrometry (UV-2401PC, Shimadzu) with the following eq. (1).^{3,14,15}

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

In this equation, T_{\parallel} and T_{\perp} are the transmittances of the film that superimposed on each other parallel and perpendicular to the elongation direction of the films, respectively.

The polarizing films were stored in a constant temperature and humidity chamber (relative humidity of 80% and temperature of 70°C). The durability with respect to the heat and humidity of the polarizer was evaluated from the change in the degree of polarization.

Measurements

The resonance Raman spectra were measured using a Nicolet Almega XR Dispersive Raman spectrophotometer with 780-nm lines.

TABLE I
The Variations in the Weight Gain of I₂/KI and Boric Acid in the PVA Films with I₂/KI and Boric Acid Concentration According to the Boric Acid Treatment Methods

I	Conc. of I ₂ /KI (mol/L)	Weight gain by I ₂ /KI (wt %)			
	0.03	2.44			
	0.05	3.07			
	0.07	3.59			
I-B	Conc. of I ₂ /KI (mol/L)	Weight gain by I ₂ /KI (wt %)	Conc. of boric acid (mol/L)	Weight gain by boric acid (wt %)	Weight gain by I ₂ /KI and boric acid (wt %)
	0.03	2.44	0.1	1.55	3.99
			0.3	2.85	5.29
			0.5	3.10	5.54
	0.05	3.07	0.1	2.27	5.34
			0.3	2.49	5.56
			0.5	2.75	5.82
	0.07	3.59	0.1	2.45	6.04
			0.3	2.48	6.07
			0.5	2.64	6.23
B-I	Conc. of boric acid (mol/L)	Weight gain by boric acid (wt %)	Conc. of I ₂ /KI (mol/L)	Weight gain by I ₂ /KI (wt %)	Weight gain by I ₂ /KI and boric acid (wt %)
	0.1	0.93	0.03	1.86	2.79
			0.05	2.22	3.15
			0.07	2.46	2.29
	0.3	2.28	0.03	1.40	3.68
			0.05	1.45	3.73
			0.07	2.18	4.46
	0.5	2.80	0.03	0.99	3.79
			0.05	1.40	4.20
			0.07	2.12	4.93
I+B	Conc. of I ₂ /KI (mol/L)	Conc. of boric acid (mol/L)	Weight gain by I ₂ /KI and boric acid (wt %)		
	0.03	0.1	2.55		
		0.3	3.28		
		0.5	3.41		
	0.05	0.1	3.24		
		0.3	3.65		
		0.5	3.71		
	0.07	0.1	4.47		
		0.3	4.49		
		0.5	5.22		

The DSC was performed using a TA DSC 2910 at a heating of 20°C/min in a N₂ atmosphere.

The XRD was measured using a Rigaku D/MAX-2500 with nickel-filtered Cu-K_α radiation (40 kV and 30 mA). The diffraction scans curves were measured at room temperature over a range of 2θ = 5°–40° with a scan rate of 5°/min. The molecular orientation was characterized by XRD pole figures. The data was obtained using a goniometer by rotating the films with scanning angle φ of 0° ≤ φ ≤ 360°.

The UV–vis absorption spectra of the iodinated PVA films were measured in the wavelength range from 200 to 800 nm using a Shimadzu spectrophotometer.

RESULTS AND DISCUSSIONS

The effect of boric acid on the characteristics of the PVA/iodine complex films was very important on formation of I₃⁻/I₅⁻ ions and improving the durability under heat and humidity. Therefore, four

types of boric acid treatment methods (I, I-B, B-I, and I+B) were used on the manufactured PVA/iodine complex films to investigate which step of boric acid treatment was most effective on formation of I₃⁻/I₅⁻ ions in polarizing sheet film and increasing the durability under heat and humid atmosphere.

Characteristics of undrawn PVA/iodine complex films

I₂/KI and boric acid-induced weight gain

Table I and Figure 1 show the variations in the weight gain of iodine and boric acid in the PVA films with increasing I₂/KI and boric acid concentrations for the boric acid treatment methods. The weight gain of I increased with I₂/KI concentration as shown in Figure 1(a).

In case of I-B films, the boric acid-induced weight gain increased with boric acid concentration at same concentration of I₂/KI; however, it decreased at

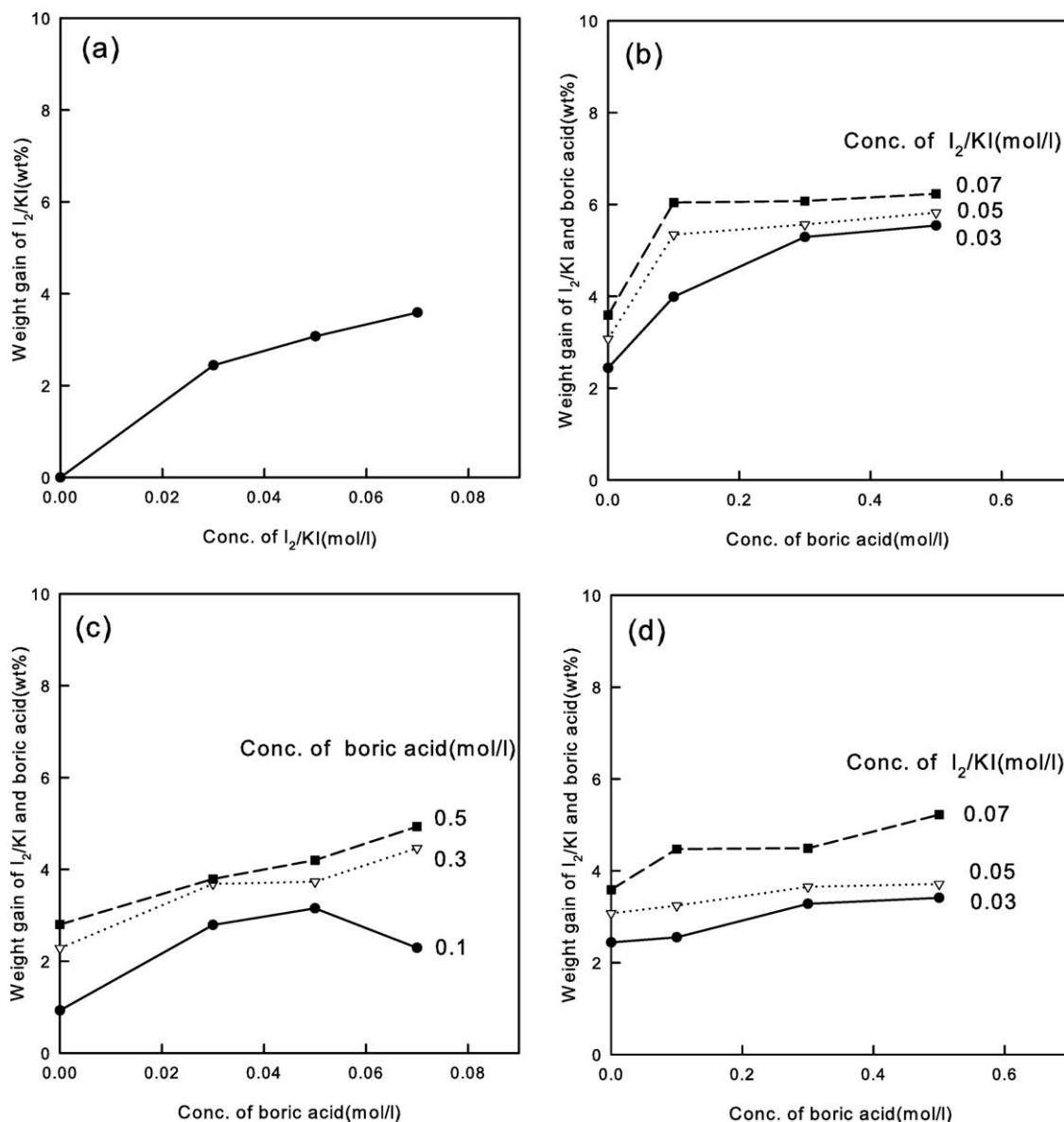


Figure 1 The variations in the weight gain of I₂/KI and boric acid in the PVA films with I₂/KI and boric acid concentration according to the boric acid treatment methods. (a: I, b: I-B, c: B-I, and d: I+B).

higher concentration of boric acid (0.3 and 0.5 mol/L) with increasing concentration of I₂/KI. When the PVA/iodine film could be immersed at a lower concentration of boric acid (0.1 mol/L), the boric acid could easily enter into PVA film inside during relatively short time, but this tendency was reversed at higher concentration of boric acid (0.3 and 0.5 mol/L). The adsorption time of the PVA/iodine film in the boric acid aqueous solution was estimated not enough to intrude into the film inside. This adsorption time was limited within 1 min with commercial processing in mind. A preliminary experiment said when the soaking time was over 1 min, the transmittance of film was very low, and it could not be used for polarizing film. The total weight gain by I₂/KI and boric acid increased with concentration of boric

acid and I₂/KI, which tendency is shown in Figure 1(b). At lower concentration of I₂/KI, the total weight gain increased gradually, but it increased markedly with boric acid concentration to 0.1 and levels off.

In case of B-I, the boric acid-induced weight gain increased with the concentration of boric acid, and the I₂/KI-induced weight gain also increased at same concentration of boric acid, but the I₂/KI-induced weight gain decreased with concentration of boric acid at same concentration of I₂/KI. When the iodine intrudes into the PVA chains created a boric acid bridge between the PVA chains, the formation of the PVA/iodine complex was more difficult than without boric acid because of the decreasing the number of -OH groups in PVA. Generally,

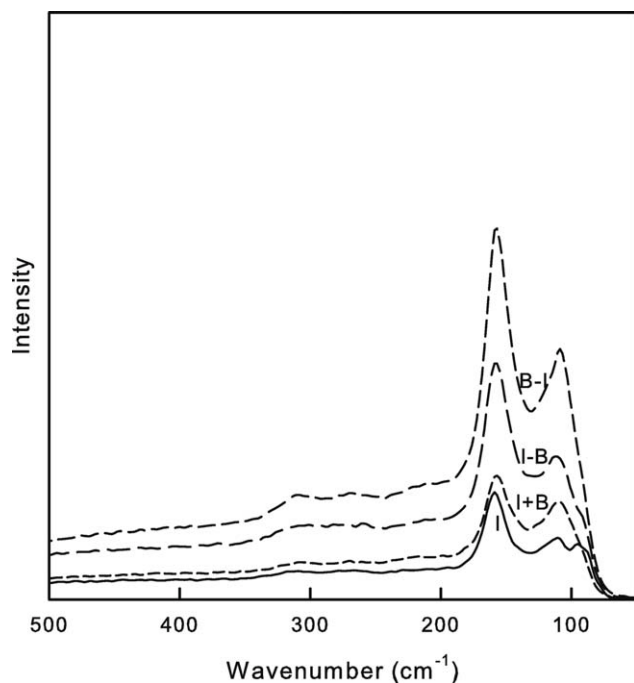


Figure 2 The Raman spectra of the four types of PVA/iodine complex films (I_2/KI : 0.05 mol/L and boric acid: 0.5 mol/L).

the I_3^- and I_5^- types of polyiodine have been reacted as the PVA/iodine complex,^{16,17} especially with $-OH$ groups in PVA chains. The boric acid forms an intramolecular crosslinking with covalent bond type with $-OH$ groups in the PVA amorphous region, which increase the orientation of PVA chains and can accelerate formation of the PVA/iodine complex and enhance its stability. However, in this study, the boric acid forms an intramolecular crosslinking with $-OH$ groups in PVA, and then the iodine ions were intruded in short time, which was the reason of decreasing the I_2/KI -induced weight gain. This is for the lack of iodine ions to complex with PVA in compound I_5^- or over. The total weight gain by I_2/KI and boric acid is shown in Figure 1(c). The total weight gain of I_2/KI and boric acid for B-I were lower than I-B [Fig. 1(b)].

In case of I+B, the total weight gain of I_2/KI and boric acid increased with concentration of boric acid and I_2/KI as shown in Figure 1(d), which was lower than I-B or B-I because of the conflict between boric acid and iodine in PVA molecules forming either a bridge or a complex within 1 min. In this work, the optimal soaking time for the PVA films in I_2/KI and boric acid was 1 min for polarizing films.

From those results, the total weight gain of I_2/KI and boric acid of I-B was larger than those of other cases. When preparing the polarizing sheet film from these samples by measuring transmittance and degree of polarization, which will be discussed in the following, the adequate concentration of I_2/KI and

boric acid for comparing four types (I, I-B, B-I, and I+B) were 0.05 mol/L and 0.5 mol/L, respectively.

Raman spectra

Figure 2 shows the Raman spectra of the four types of PVA/iodine complex films that were treated with I_2/KI 0.05 mol/L and boric acid 0.5 mol/L. These spectra exhibited strong band at 160 cm^{-1} and weaker scattering at around 108 cm^{-1} . The latter peak that was caused by the Raman active symmetric stretching vibration mode depended on the structure of the I_3^- species. The former peak at 160 cm^{-1} has been found in compounds containing I_5^- species,⁷ which indicates that symmetric and linear I_5^- was formed. Yokota and Kimura¹⁸⁻²¹ also reported that the polyiodine with a linear configuration is I_5^- and with a distorted configuration is I_3^- .

In this figure, the intensity of peaks followed the order of B-I > I-B > I+B > I, which appears that not only the addition of boric acid but also the order of the boric acid addition in I_2/KI aqueous solution affected the formations of the PVA/iodine complexes. I+B had little effect on the complex formation, but others increased the formation of I_3^- and I_5^- ions. Moreover, adding boric acid before iodine (B-I) was the most effective method of forming polyiodine in the PVA film because the complex that formed in the amorphous phase containing either linear polyiodine I_5^- or I_3^- , which was enveloped by the four PVA segments of the syndiotactic configuration with the extended conformation.⁹ Therefore, the

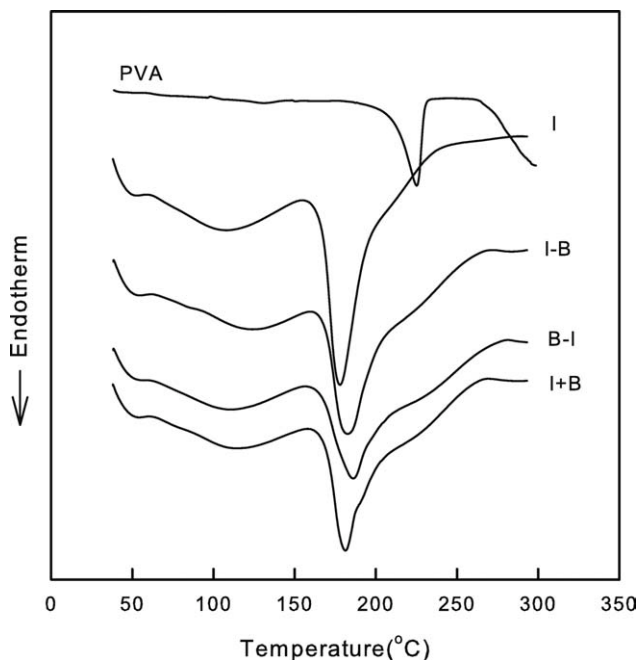


Figure 3 The DSC curves of the four types of PVA/iodine complex films (I_2/KI : 0.05 mol/L and boric acid: 0.5 mol/L).

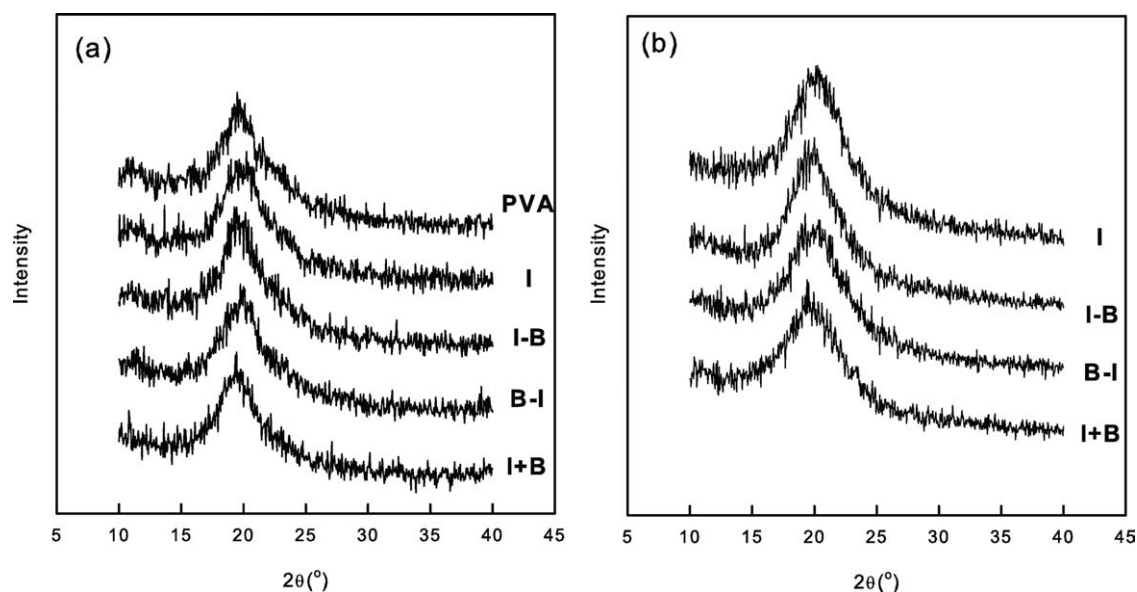


Figure 4 The XRD spectra of the four types PVA/iodine complex films (I_2/KI : 0.05 mol/L and boric acid: 0.5 mol/L). a: Undrawn films and b: drawn films.

extended conformation of PVA formed the complex more effectively. That is, the boric acid formed an intramolecular crosslinking covalent bond, which contributed to the formation of the extended PVA chain segment and formed the aggregate model type PVA/iodine complex. In I-B, the boric acid decreased the freedom of the PVA/iodine aggregated complex chains, which was formed early, and provided a higher stability to the complex, which will be the reason of good durability to heat and humidity described in the next section.

DSC analysis

Figure 3 shows the DSC curves of the untreated PVA and four types of complex films. The DSC thermograms of the untreated PVA films show the endothermic peak at 230°C and starting endothermic peak at around 280°C, corresponding to the melting of crystals and the partial decomposition of —OH side groups, respectively. However, the PVA/iodine or PVA/iodine/boric acid complex films indicated a new broad peak at the lower temperature zone (60°C–150°C), which was probably assigned to melting of the quasicrystalline phase.¹² The peak temperature increased with adding the boric acid (I-B, B-I, and I+B), especially that of I-B film highest. The quasicrystalline phase can be regarded as defects in the pure PVA crystalline phase: the adding of iodine and boric acid multiplied such defects in the PVA crystalline phase and brought about the decrease of melting temperature and weakening of the pure PVA crystal, melting peak on the DSC curves. Therefore, the endothermic peaks at around 180°C and 220°C, corresponding to the melting pure PVA and

degradations of —OH side groups, decreased as DSC curves of pure PVA. Additional DSC experiments were done to elucidate the peak at 60°C–150°C as three successive steps: involving heating to 120°C and holding at that temperature for 5 min, slow cooling to 30°C, and heating again to 300°C were carried out to examine the peak. As a result, the board peak (60°C–150°C) disappeared, and the size of the melting peak increased because of the formation of a more perfect crystal. In comparing four types of films, the temperature of three peaks of I-B, B-I, and I+B film higher than those of I film, especially those of I-B, were highest. This may result from the effect of boric acid, which conformed the intramolecular crosslinking on the PVA chain and stabilized the PVA/iodine complex.

X-ray analysis

Figure 4(a) shows the WAXD profiles of the films that were soaked in different solutions and then dried. The diffraction peaks at around $2\theta = 19.5^\circ$ and $2\theta = 22.5^\circ$ were assigned to the (101) + (10 $\bar{1}$) and (200) planes of the PVA crystals. The spectrum of I film exhibited almost the same shape as the PVA crystal, indicating that the PVA crystallites were not affected. However, the peak of I-B, B-I, and I+B films was broader than that of I film, because of the addition of boric acid in the swelling media. Ohishi et al. also reported to elucidate the effect of boric acid in swelling media on the crystallinity and resulted like that the effect of boric acid on the WAXD intensity was negligibly small under this experimental conditions (our experimental condition was same).²²

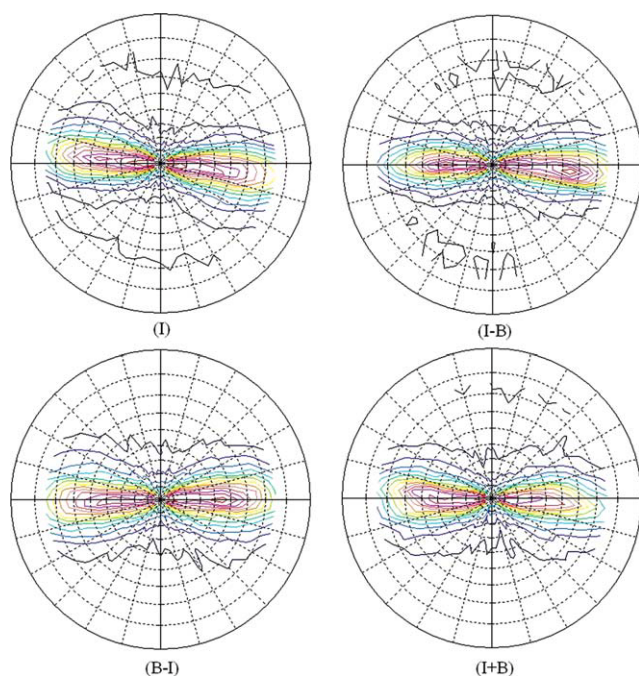


Figure 5 Contour plots X-ray pole figures for the (101) diffraction planes of the four types of films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The WAXD profiles of the four types of drawn films were measured in Figure 4(b) to elucidate the effect of drawing on the crystallinity. The peak at $2\theta = 19.5^\circ$ shift to higher angle 19.9° (in case of boric acid contained: I-B, B-I, and I+B) and 20.3° (in case of I). This indicates that recrystallization during the drying process may be suppressed by crosslinking with boric acid because of strain-induced complex formation, which is enhanced with boric acid decreasing of entropy of the PVA chains.⁶ Although, a significant difference in the intensity and width was not observed among the four types of films, the diffraction peak at $2\theta = 20^\circ$ shift to lower scattering, which might be resulted from the some broadening of original PVA unit cell owing to intrusion of $-B$ between PVA chains by crosslinking.²³

Characteristics of drawn PVA/iodine complex films

The PVA/iodine films have been used as high-quality polarizer because of their ability to form PVA/iodine complexes and their dichromatic performance. The preparation of a PVA polarizing sheet film is a two-step process, where the film is soaked in the I_2/KI aqueous solution, uniaxially drawing them with a solution containing boric acid. However, few studies have examined the boric acid exposure times in the soaking media. The main role of boric acid is stabilizing the PVA/iodine complexes through crosslinking. Therefore, the soaking method of boric acid in

the soaking media is important in the preparation of high-quality PVA polarizer.

XRD pole figures

Figure 5 shows the contour plots X-ray pole figures for the (101) diffraction planes of the four types of films. This pole figures measured to identify the molecular orientation and density of PVA and iodine or boric acid among these films. The orientation and density for PVA molecular of I-B film was higher than those of other films.

UV-vis absorption spectra

Figure 6 shows the absorption spectra of the PVA/iodine films that were drawn in water at $30^\circ C$. The five absorption peaks that appeared at $\sim 200, 310, 370, 480,$ and 650 nm were assigned to I^- , I_3^- , $I_2 \cdot I_3^-$, I_3^- , and I_5^- ions, respectively. The first three peaks were confirmed by the experiment for PVA dissolved in the I_2/KI solution, and the last two peaks were attributed to the formation of the PVA/iodine complexes.^{6,13} The strength of the first three peaks was greater than the last two peaks, indicating that mostly the iodine ions (I^- , I_3^- , and $I_2 \cdot I_3^-$) existed in the PVA films, but a few PVA/iodine complex ions (PVA- I_3^- and PVA- I_5^-) were also present. Comparing the four types of films, the conformation of the iodine ions and the PVA/iodine complexes in the I-B film was larger than the others, indicating that boric acid accelerated the formation of the iodine complexes. In Figure 2, the formation of the PVA/iodine complex was most effective in B-I, but after drawing (Fig. 6), B-I was not as effective as I-B. The strain-induced complex formation and the effect of boric acid after soaking in the I_2/KI solution enhanced the complex formation by extending the PVA chain conformation. This effect was much more noticeable for the films drawn in boric acid aqueous solution than the water.

Figure 7(a-c) shows the absorption spectra of the four PVA/iodine films that were drawn in the 2-wt % boric acid aqueous solution at $40^\circ C$ with concentration of I_2/KI . Generally, the intensity of peaks increased with concentration of I_2/KI , and the first two peaks (corresponding to 290 and 360 nm) decreased, and the last two peaks (corresponding to 470 and 650 nm) increased after drawing in boric acid aqueous solution, comparing films drawn in water. All of the spectra for the films (I, B-I, and I+B) except for I-B exhibited weak peaks at ~ 650 nm, clearly indicating that the boric acid treatment after immersion in the I_2/KI solution affected the formation of the complex I_5^- ions in the PVA film. Therefore, boric acid was necessary for the formation of the PVA/iodine complexes, and the boric

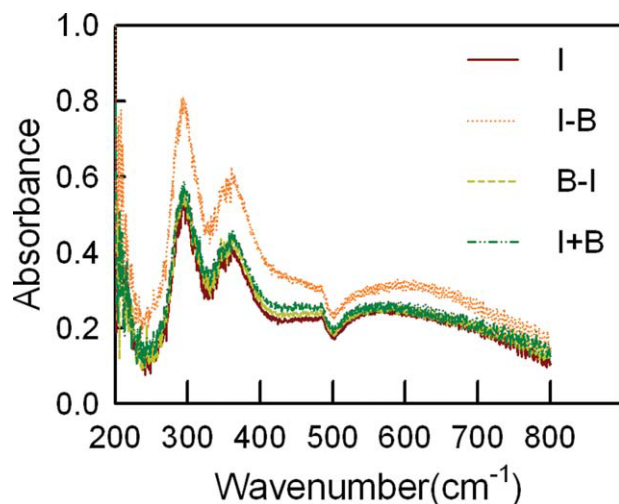


Figure 6 The UV-visible spectra of the four types of PVA/iodine complex films that were drawn in water at 30°C (I_2/KI : 0.05 mol/L and boric acid: 0.5 mol/L). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

acid treatment method was also an important condition in the formation of the complexes in the films.

Transmittance and degree of polarization

The transmittance (T) and degree of polarization (ρ) of films were very important factors of the polarizing sheet films. Table II shows the T and ρ of the PVA/iodine films with increasing I_2/KI and boric acid concentrations and different boric acid treatment methods. These films were drawn in a 2 wt % aqueous boric acid solution. As the concentration of I_2/KI increased, the T and ρ of I film decreased and increased, respectively, because the iodine molecules entered into the PVA chains, and aggregates formed to yield polyiodine. The T decreased more for the I-B films than B-I or I+B. The ρ of all of the films increased to a very high level (99.9% \uparrow). The overall trends of T and ρ results I-B, B-I, and I+B were the same as I, but absolute values decreased with increasing concentration of boric acid. Therefore, I-B type more effectively formed and sustained the PVA/iodine complex than the other types of films.

Durability on heat and humidity

In commercial polarizing films, the sublimation of iodine under humid and warm atmospheres is a serious problem, because the polyiodine molecules are easily deformed and released from the PVA. To measure the durability of polarizing film, the general condition of experimental is the humid at 80% and the warm at 50°C for 120 h. Most of polarizing films could be endured in this condition. So, we chose the humid at 80% and the warm at 70°C for discrimina-

tion among films. Generally, the commercial polarizing PVA/iodine complex film cannot endure until 15 h because of iodine evaporation under humid and heat atmosphere. Figure 8 shows the change of the ρ for the four types of PVA/iodine polarizing films at a relative humidity of 80% and a temperature of 70°C. The change in the ρ increased with increasing treatment time for all of the films. The polyiodine molecules easily deformed and were released from the PVA because of the high sublimation characteristics of iodine. These results elucidated the effect of boric acid in the swelling solution on the durability under heat and humidity. Therefore, boric acid was not only necessary for the formation of the PVA/iodine complex in the undrawn films but also the complex sustainment under heat and humidity. The effect varied boric acid addition methods in the swelling solution, the durability of I-B was superior to B-I or I+B, and the change in the ρ was below 5% because the boric acid reduced the molecular mobility of the PVA chains through crosslinking, so that the PVA/iodine complex could not easily collapse.

CONCLUSIONS

Four types of PVA/iodine complex films (I, I-B, B-I, and I+B) were prepared using different boric acid treatment methods, and the PVA/iodine films were

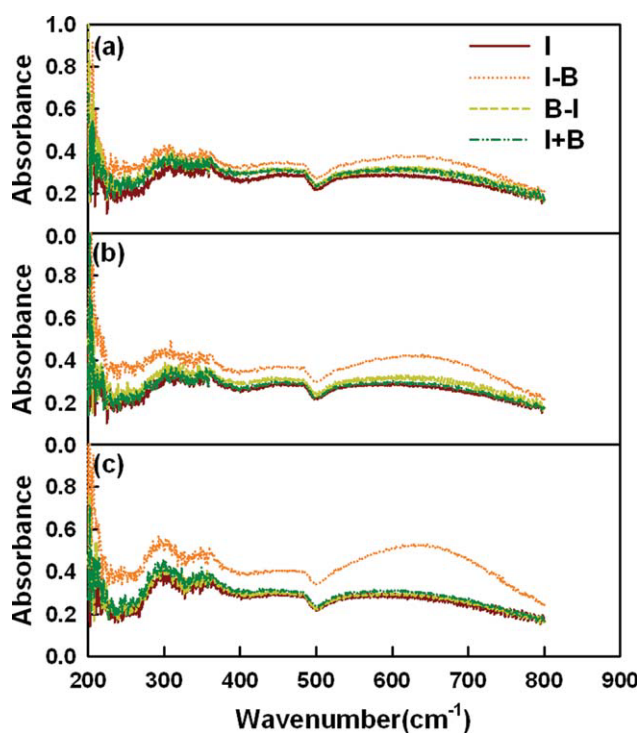


Figure 7 The UV-visible spectra of the four types of PVA/iodine complex films that were drawn in the 2-wt % boric acid aqueous solution at 40°C. (a: 0.03, b: 0.05, and c: 0.07 mol/L I_2/KI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
The Variation of Transmittance and Degree of Polarization According to the Boric Acid Treatment Methods of the PVA/Iodine Films with I₂/KI and Boric Acid Concentrations

I	Conc. of I ₂ /KI (mol/L)		Transmittance (%)	Degree of polarization (%)
	0.03		55.91	99.96
	0.05		51.77	99.98
	0.07		44.35	99.99
I-B	Conc. of I ₂ /KI (mol/L)	Conc. of boric acid (mol/L)		
	0.03	0.1	53.89	99.98
		0.3	52.67	99.98
		0.5	52.19	99.98
	0.05	0.1	42.24	99.99
		0.3	38.15	99.99
		0.5	33.88	99.99
	0.07	0.1	35.56	99.96
		0.3	35.11	99.99
		0.5	34.70	99.99
B-I	Conc. of boric acid (mol/L)	Conc. of I ₂ /KI (mol/L)		
	0.1	0.03	54.26	99.98
		0.05	48.22	99.99
		0.07	40.03	99.99
	0.3	0.03	55.31	99.96
		0.05	47.91	99.97
		0.07	40.93	99.99
	0.5	0.03	56.16	99.96
		0.05	48.11	99.97
		0.07	41.44	99.97
I+B	Conc. of I ₂ /KI (mol/L)	Conc. of boric acid (mol/L)		
	0.03	0.1	56.98	99.96
		0.3	55.83	99.96
		0.5	55.78	99.96
	0.05	0.1	50.45	99.99
		0.3	50.39	99.98
		0.5	48.59	99.98
	0.07	0.1	46.78	99.99
		0.3	45.31	99.99
		0.5	42.13	99.99

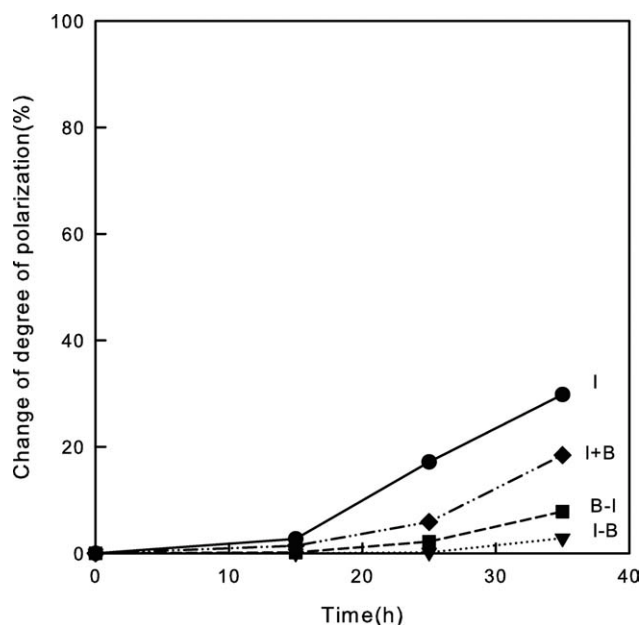


Figure 8 The change of the degree of polarization for the four types of PVA/iodine polarizing films at a relative humidity of 80% and a temperature of 70°C (I₂/KI: 0.05 mol/L and boric acid: 0.5 mol/L).

successively drawn in an aqueous solution of 2 wt % boric acid to polarize the films. The concentrations of I₂/KI were 0.03, 0.05, and 0.07 mol/L, and the concentrations of boric acid were 0.1, 0.3, and 0.5 mol/L. The characteristics of the undrawn and drawn PVA/iodine films were investigated.

The I₂/KI-induced and boric acid-induced weight gain of the four types of PVA films increased about 2.5%–3.6% and 0.9%–2.8%, respectively, with increasing boric acid and I₂/KI concentration. The adequate concentration of I₂/KI and boric acid for polarizing film were 0.05 and 0.5 mol/L, respectively. The XRD spectrum of I exhibited almost the same profile as the PVA, indicating that the PVA crystallites were not affected. The degrees of polarization (ρ) of all of the films increased to very high levels (99.9% \uparrow).

However, the melting temperature, the PVA molecules orientation, and the conformation of PVA/iodine complexes of I-B film were higher than those of other films by DSC, XRD pole figures, and UV analyses, respectively. The durability of I-B film also was superior to B-I or I+B at a relative humidity of 80% and a temperature of 70°C, and the change in the ρ was below 5% because the boric acid treated

after iodine reduced the molecular mobility and higher molecular orientation of PVA chains through intracrosslinking, so that the PVA/iodine complex could not easily collapse.

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