

Polarizer Effect and Structure of Iodinated Before and After Casting Poly(vinyl alcohol) 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: Poly(vinyl alcohol) (PVA)/iodine polarizing film was manufactured as follows: PVA iodinated in solution before casting (IBC film) and iodinated again after casting (IBC + IAC film) and then the IBC + IAC film was drawn in boric acid aqueous solution (IBC + IAC polarizing film), to improve the durability of the polarizing film under a humid and warm atmosphere. These effects were examined by investigating the structural and optical properties of the IBC, IBC + IAC, and IBC + IAC polarizing films. In the IBC state, the PVA chain segments that combined boric acid and iodine were regarded as defects of the crystal, the formation of I_3^- decreased with respect to weight gain of boric acid. In the IBC + IAC state, the strength of the peak corresponding to I_3^- decreased and the I_5^- peak increased. The iodine ions

penetrated into crystal of the IBC state during the IAC process and formed a new PVA/iodine complex crystal at the $2\theta = 20^\circ$ in the X-ray diffraction curves. In the IBC + IAC polarizing film state, another type of polarizing film (IBC + IAC polarizing film-H) containing I_3^- ions mainly was manufactured as well as the IBC + IAC polarizing film to compare the effects of the I_3^- and I_5^- ions on the durability of the polarizing films. The durability of the I_3^- ions that were complexed with the PVA chain was higher than the I_5^- ions, which could possibly be separated to I_3^- and I_2 . © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 397–405, 2011

Key words: durability; Raman spectra; film; draw; polarizer

INTRODUCTION

Iodine forms blue-colored complexes with many substances, such as starch, nylon6, poly(vinyl pyrrolidone), and poly(vinyl alcohol) (PVA).¹ The blue PVA–iodine complex is the most applicable complex among them because it is widely used for film polarizers.^{2,3} These polarizers are prepared by soaking PVA films in a solution of iodine and potassium iodide (KI) with boric acid and subsequent drawing to create a high degree of uniaxial orientation. However, commercial polarizing films have some serious problems, such as poor water stability and easy iodine desorption under a warm and humid atmosphere. To overcome these shortcomings, Lyoo and coworkers⁴ prepared a polarizing film with a high molecular contents of syndiotactic diad PVA to enhance the durability of the PVA–iodine polarizing film. Yamaura et al.⁵ determined that the PVA–iodine complex formation increased with increasing syndiotactic diad content to 56–58% from poly(vinyl

trifluoroacetate). Murajashi and coworkers^{6,7} also reported that the irregular tacticity necessarily causes faults in the hydrogen bonding, decreasing the stability of the complex. High syndiotactic PVA is a superior configuration for the complex formation over atactic PVA.¹ However, the various difficulties that are involved with these films include obtaining high syndiotactic diad PVA content, adsorbing iodine in the film because of the high crystallinity, and overcoming the high cost. Therefore, efforts have been made to overcome these problems.

The effects of the addition of boric acid on the complex formation have also been studied by many researchers. Recently, Ohishi et al.⁸ confirmed that boric acid is necessary for the formation of the complexes in the films, and the intermolecular hydrogen bonds of PVA are broken by boric acid, which increases the intramolecular hydrogen bonds and increases the less mobile component. However, when boric acid is used during the manufacturing of polarizing sheet film in a wet-drawn process, the films exhibit problems, such as poor durability under a hot and humid atmosphere and easy iodine desorption. Therefore, in our study, the boric acid was added in the PVA aqueous solution and the I_2 /KI soaking solution before and after PVA casting step, respectively.

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

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In previous reports,^{9–11} we have been submitted papers about “Iodinated in the solution before casting (IBC) PVA film.” First, we reported the paper⁹ “Structure of films iodinated in solution before casting,” which was investigated mostly about the structure of IBC film. Second, we reported the paper¹⁰ “Making IBC PVA films and its application,” which was about the application of IBC PVA film to polarizing film. Third, we submitted the paper¹¹ recently about “Effect of boric acid and heat treatment of IBC PVA films,” which was about the improved method of durability for IBC PVA polarizing film. In this article, we tried that the IBC PVA film could be connected with the commercial preparation method for improved durability of polarizing film. Therefore, each of the papers^{9–11} were tightly correlative with the industrial production of polarizing film and the materials (a PVA solution containing I₂/KI, I₂/KI/boric acid, and in relation to contents of I₂/KI and boric acid) for preparing polarizing film in each of paper were different. Actually, the resistance to heat and humidity was higher for the IBC PVA polarizing films than commercial polarizing films because the interaction between the polyiodine molecules and the PVA chains was higher in the IBC state than the commercial iodinated after casing (IAC) PVA film. Although the process of IBC PVA polarizing film is better than that of commercial polarizing film from a durability point of view, the oxidation of plant machine is worried due to iodine in processing of making IBC PVA film.

In this study, the polarizing sheet film was manufactured using the following method. First, the PVA/iodine/boric acid film was mixed in the PVA solution state before casting and this solution was cast (IBC film), and then iodinated again after casting (IBC + IAC film), and finally, IBC + IAC film was drawn in boric acid aqueous solution and dried (IBC + IAC polarizing film). From this method, the iodine and boric acid content was minimized in the solution state and included in the complex crystal during IBC + IAC processing, which enhanced the complex formation and provided the complex with a higher stability. The iodine and boric acid that were included in the complex crystal were not easily volatilized from film and were expected to increase the durability of the polarizing sheet film. Actually, the PVA polarizing containing PVA–iodine complexes are prepared in the following four steps: making PVA films and soaking the films in an I₂/KI aqueous solution, uniaxially drawing them there, and treating them with a solution containing boric acid. The difference point with industrial production is the first process of making PVA films. Instead of making PVA films, we produced IBC PVA film, which was containing a small amount of iodine and boric acid. The next processes for production of

polarizing film were similar to that of the industrial process. We also paid attention to compare the effects of I₃[−] and I₅[−] ions on the durability of the polarizing films. For this reason, we manufactured another type of polarizing film (IBC + IAC polarizing films-H) containing I₃[−] ions mainly by heating process as well as the IBC + IAC polarizing film.

EXPERIMENTAL

Material

The PVA powder was purchased from the Sigma-Aldrich Company in Japan and used in the film preparation. The reported degree of saponification and M_w were 99.9% and 89,000–98,000, respectively.

Preparation of IBC films

The films were prepared by casting aqueous solutions of 7 wt % PVA containing boric acid and I₂/KI on a glass plate at 60°C and then drying them at room temperature for 48 h. The weight ratios of boric acid to PVA (boric acid-induced weight gain) were 0.5, 1, 2, and 3%, and the ratios of I₂/KI (I₂/KI-induced weight gain) were 0, 1.5, and 3%. These films shall be called “IBC film.”

Preparation of IBC + IAC films

The IBC films were soaked in an aqueous solution of 0.025 mol/L I₂/KI (1 : 2) for 60 s, rinsed with water, and air-dried at room temperature for over 1 week. These films shall be called “IBC + IAC film.”

Preparation of IBC + IAC polarizing films

The IBC + IAC complex films were drawn four times using a hand-operated drawer at 40°C in a 2 wt % boric acid aqueous solution at a drawing speed of 10 mm/min. The drawn films were subsequently dried at 60°C for 30 min. These films shall be called “IBC + IAC polarizing film.”

Another type of the IBC + IAC polarizing films were manufacture as follows: the IBC films were iodinated again at 0.05 mol/L I₂/KI aqueous solution for 60 s, dried, heated at 130°C for 20 min, and then drawn as same as IBC + IAC polarizing film processing to compare the effects of I₃[−] and I₅[−] ions on the durability of the polarizing films. These films shall be called “IBC + IAC polarizing film-H.” To compare IBC + IAC polarizing film and IBC + IAC polarizing film-H, the concentrations of I₂/KI aqueous solution in state of preparing IBC + IAC film were adjusted to 0.025 and 0.05 mol/L, respectively, to have similar transmittances.

Characterization

Transmittance (T) and degree of polarization (ρ): the films were analyzed using UV–visible (UV–vis) spectrometry (UV-2401PC, Shimadzu) with the following eq. (1)

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

In this equation, T_{\parallel} and T_{\perp} are the transmittances of the film that were superimposed on each other parallel and perpendicular to the direction of the elongation of the film, respectively. The sensitivity of UV–vis spectroscopy was two decimal places. Therefore, the data for the film transmittance was rounded off to three decimal places. Generally, the degree of polarization of a sample is reported as two decimal places.

Durability: The polarizing films were stored in a constant temperature and humidity chamber (relative humidity of 80% and temperature of 70°C for 40 h). The durability of the polarizing films to heat and humidity was evaluated with respect to 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.

The XRD was measured using D/MAX-2500 with nickel-filtered Cu-K α radiation (40 kV and 30 mA) from Rigaku. The diffraction scans curves were measured at room temperature over the range $2\theta = 5^{\circ}$ – 40° with a speed rate of $5^{\circ}/\text{min}$.

The UV–vis ray spectra of the iodinated PVA films were measured in for wavelengths from 200 to 800 nm using a Shimadzu spectrophotometer.

The differential scanning calorimetry (DSC) was performed using a TA DSC 2910 at a heating of $20^{\circ}\text{C}/\text{min}$ in a N_2 atmosphere.

The dynamic mechanical thermal analysis (DMTA) was performed using a DMA Q800 V7.5 at a heating of $5^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Structural analysis of IBC, IBC + IAC, and IBC + IAC polarizing films

A previous report¹² showed that iodine does not have an influence on the crystal structure of PVA with an iodine sorption less than 12 wt %. However, the influence depends on the PVA iodinated method, IBC or IAC.

Figure 1 shows the DSC thermograms of the PVA and IBC films with respect to the weight gain of boric acid and I_2/KI . Pure PVA exhibited three endo-

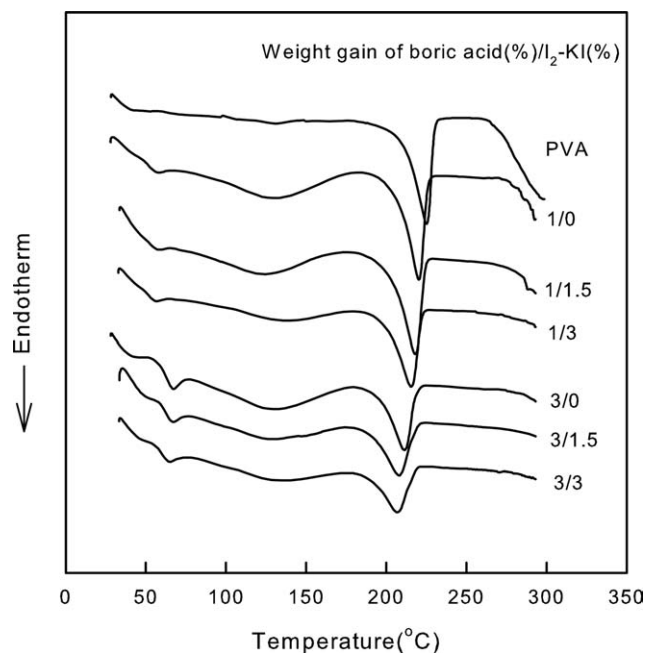


Figure 1 The DSC thermograms of the PVA and IBC films.

thermic peaks at 50°C , 120 – 170°C , and 220°C . The lowest and highest temperature peak corresponds to the glass transition temperature (T_g) and the melting point of a crystal (T_m), respectively. The small and broad peak was attributed to the melting of a semi-crystal of pure PVA. Additional DSC experiments involving three successive steps: involving heating to 180°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 small peak at 120 – 170°C . As a result, the small and broad peak (120 – 170°C) disappeared and the size of the melting peak increased due to the formation of a more perfect crystal.

However, the films containing boric acid showed two peaks in the lower temperature zone (60 – 70°C and 100 – 150°C). In addition, the strong peak (at 230°C) weakened and its temperature decreased gradually with increasing weight gain of boric acid and I_2/KI .

The peak at $\sim 60^{\circ}\text{C}$ was assigned to the T_g of PVA resulting from the intramolecular crosslinking caused by boric acid, which increased with increasing boric acid content. These intramolecular crosslinking PVA–boric acid segments associated with a chemical reaction restrained the molecular motion and increased the T_g of PVA with increasing boric acid content. These results will be discussed again in the following DMTA analysis. Another broad peak at approximately 100 – 150°C was assigned to the melting of the crystalline portions at which the PVA chain segment was combined with boric acid via intramolecular crosslinking, making the intermolecular distance greater. This can be regarded as a defect

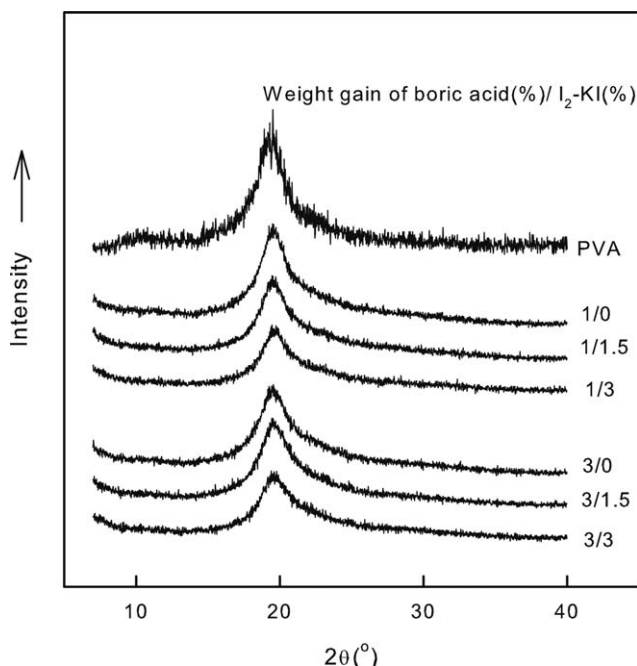


Figure 2 The XRD scans of the IBC films.

in the crystal, which caused a decrease in the melting temperature with increasing boric acid content.¹³ The peak became broader with increasing I_2/KI content. The intramolecular crosslinking PVA–boric acid segments were favorable to complex formation with I_2/KI . With these PVA–boric acid– I_3^- or I_5^- segments, the distance between the PVA segments was longer due to the absorption of boric acid and iodine ions, which could be destroyed by heating during the DSC experiment. The melting temperature (approximately 210–220°C) also decreased with increasing I_2/KI and boric acid content, which is inevitable due to the increase in those defects in the crystalline region. Figures 2 and 4 show the XRD patterns and DMTA curves indicating the effect of the crosslinks of the complex, respectively.

Figure 2 shows the XRD scans of the PVA and IBC films with respect to the weight gain of boric acid and I_2/KI . The diffraction peak at around $2\theta = 19.5^\circ$ was assigned to the (101)/(10i) planes of the PVA crystal. The spectra exhibited almost the same profile regardless of boric acid and I_2/KI content, but the peak at $2\theta = 19.5^\circ$ was weaker and broader with increasing boric acid and I_2/KI content because the crystallite sizes perpendicular to the chain axis became smaller through the addition of boric acid and iodine ions in the swelling media.⁸ The combined effect of the boric acid and iodine on the X-ray results was more significant than the effect of boric acid alone. Figure 3 shows the XRD scans of the IBC, IBC + IAC, and IBC + IAC polarizing films with respect to the weight gain of boric acid. The intensity of the $2\theta = 19^\circ$ peak decreased and slightly

shifted toward a higher angle through the iodine adsorption during the IAC process with increasing weight gain of I_2/KI in the IBC + IAC films. The intensity of the $2\theta = 19^\circ$ peak for the 3/3 and 3/5 IBC + IAC films prominently decreased. Therefore, the iodine ions penetrated into crystal of the IBC film during the IAC process and formed a PVA/iodine complex crystal at $2\theta = 20^\circ$. The intensity of the PVA/iodine complex crystal peak increased with drawing during the polarizing film synthesis. The strain-induced complex formation strongly suggested that the extended conformation of the PVA chains was favorable to the complex formation, implying that the conformation in the complex was extended.¹

Figure 4 shows the DMTA for the pure PVA, IBC, and IBC + IAC films. For the untreated films, the α_a dispersion peak at 60°C was assigned to the glass transition temperature (T_g) of PVA. The peaks in both the IBC and IBC + IAC films were observed at about 130°C, which was higher than the untreated film. This increase in the T_g resulted from the intramolecular crosslinking caused by boric acid. The T_g of PVA decreased in the PVA/iodine complex film because the intermolecular hydrogen bonds were ruptured by iodine.¹⁴ The effects of iodine were investigated by comparing the IBC + IAC films to the IBC films. From these results, the effects of boric acid were more significant than iodine on the

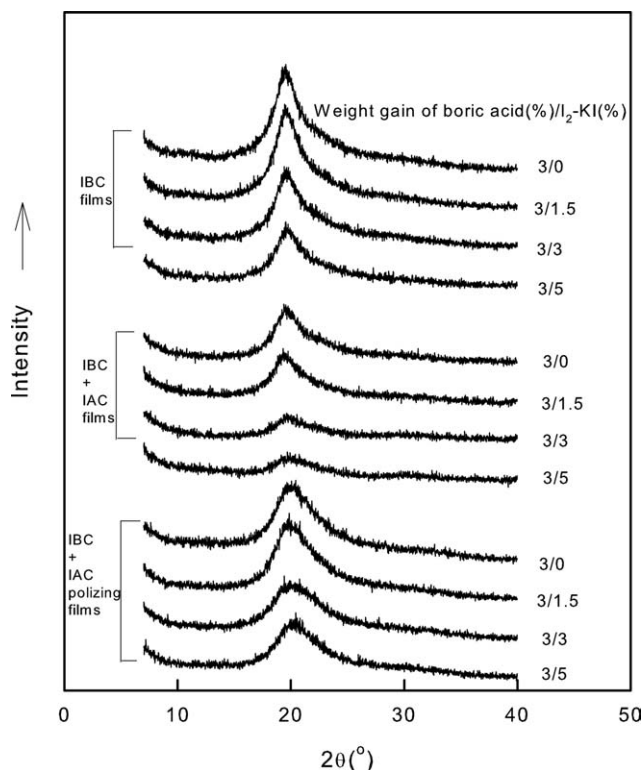


Figure 3 The XRD scans of the IBC films, IBC + IAC films, and IBC + IAC polarizing films.

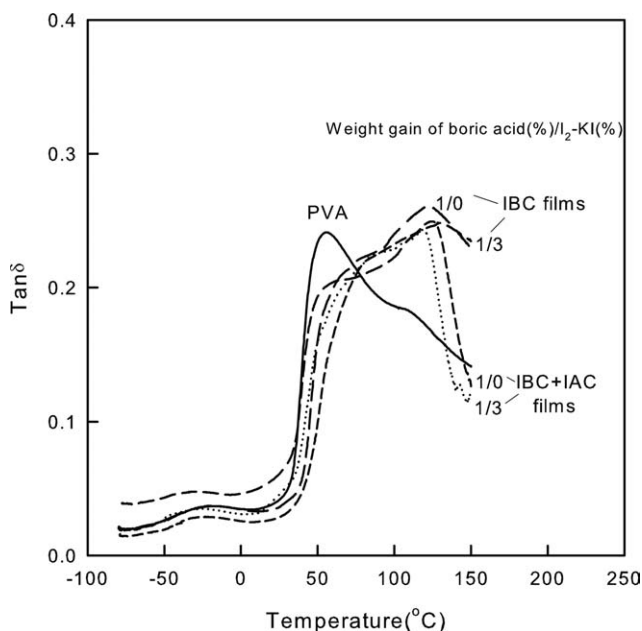


Figure 4 The DMTA for the pure PVA, IBC films, and IBC + IAC films.

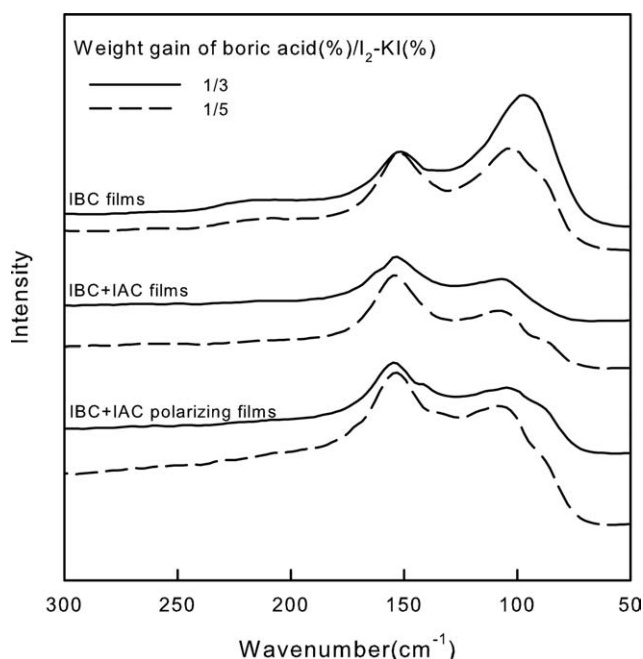


Figure 6 Raman spectra of the IBC films, IBC + IAC films, and IBC + IAC polarizing films.

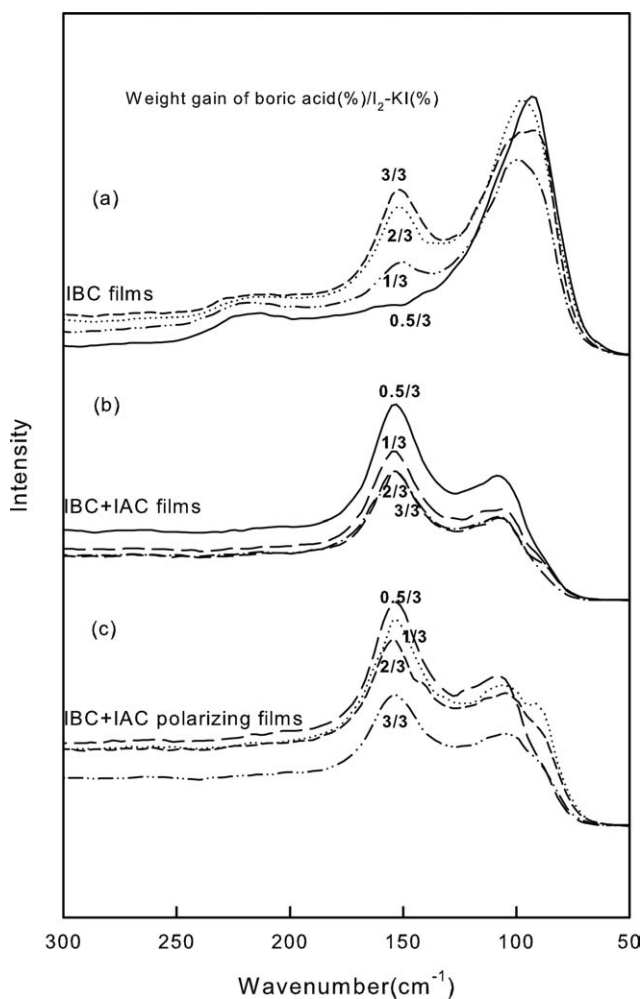


Figure 5 The Raman spectra of the IBC films (a), IBC + IAC films (b), and IBC + IAC polarizing films (c).

thermal properties, and the crosslinking caused by boric acid in the PVA chain was confirmed.

Figure 5(a) shows the Raman spectra of the IBC containing 3 wt % I_2/KI with respect to the weight gain of boric acid. These spectra exhibited weak scattering at 160 cm^{-1} and stronger scattering at around 108 cm^{-1} . The latter peak was caused by the Raman active symmetric stretching vibration mode and 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,¹⁵ which means that symmetric and linear I_5^- was formed. Yokota and Kimura¹⁶ also reported that I_5^- is the linear configuration of polyiodine, and I_3^- is the distorted configuration. The formation of I_3^- decreased with increasing weight gain of boric acid in the IBC film, and the I_5^- , which was not appeared at a low weight gain of boric acid (0.5%), also increased with respect to the weight gain of boric acid. These results confirmed that boric acid reduced the molecular mobility of the PVA chains by causing crosslinking.⁸ The intramolecular crosslinking that was caused by boric acid contributed to the formation of the extended segment of PVA chain, which led to the formation of I_5^- with a linear configuration. Figure 5(b) shows the Raman spectra of the IBC + IAC films with respect to the weight gain of boric acid. Generally, the strength of the peak corresponding to I_3^- decreased, and the I_5^- peak increased after the IAC process compared to Figure 5(a). Soaking the film in the I_2/KI aqueous solution aggravated the iodine ions that formed, especially the

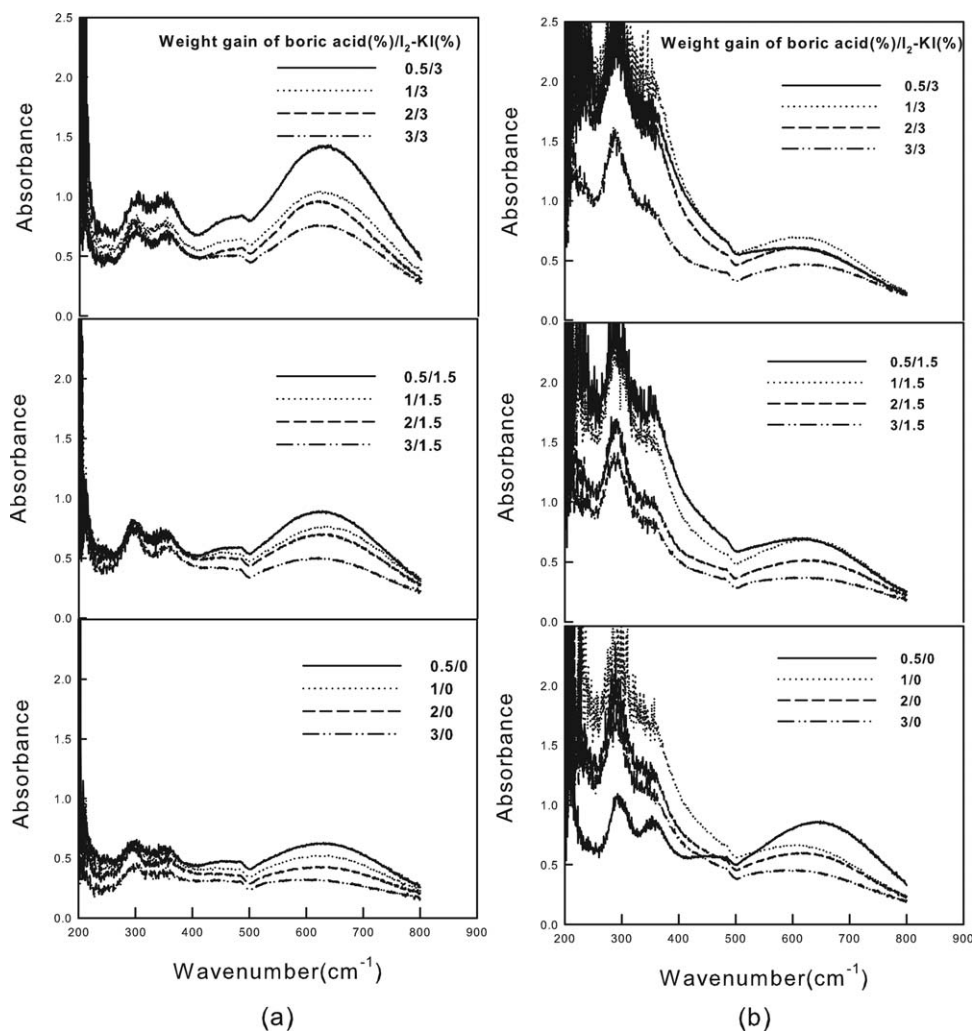


Figure 7 The UV-vis absorption spectra of the IBC + IAC polarizing films (a) and IBC + IAC polarizing films-H (b).

I_5^- ions. This tendency was higher at lower concentrations of boric acid. Figure 5(c) shows the Raman spectra of the IBC + IAC polarizing films. The strength of the peaks increased after the drawing process because of the strain-induced complex formation. Therefore, the extended conformation of the PVA chains was favorable to complex formation, implying that the conformation of the chain in the complex was extended.¹

Figure 6 shows the Raman spectra of the IBC, IBC + IAC, and IBC + IAC polarizing films, respectively, at 1% boric acid with respect to the weight gain of I_2/KI . As the weight gain of I_2/KI increased, the I_3^- peak decreased and the I_5^- peak increased.

Optical properties of IBC + IAC polarizing films

Figure 7 shows the UV-vis absorption spectra of the IBC + IAC polarizing films and standard polarizing film. In the spectra, the five absorption peaks that appeared at ~ 200 , 310, 370, 480, and 650 nm were assigned to the I^- , I_3^- , $I_2 \cdot I_3^-$, I_3^- , and I_5^- ions, respec-

tively. The first three peaks were confirmed by the experiment for PVA that was dissolved in the I_2/KI solution and the last two peaks were attributed to the formation of the PVA-iodine complexes.^{8,16} The absorbance of the films increased with decreasing boric acid and increasing weight gain of I_2/KI in the PVA films. The I_3^- or I_5^- ions (during the next IAC process) could not easily intrude the IBC film with increasing boric acid concentration because the additional boric acid created a bridge between the PVA chains during the film casting process (IBC process). The films in Figure 7(a) formed more I_5^- ions than I_3^- ions. The effects of the I_3^- and I_5^- ions on the durability of the polarizing films were compared through the fabrication of another type of polarizing film (IBC + IAC polarizing film-H) with conformed I_3^- ions mainly by heating process and shown in Figure 7(b), the films underwent the same IBC process, and then the films were soaked in a 0.05 mol/L I_2/KI aqueous solution during the IAC process and heated at 130°C for 20 min. These experimental heating conditions

TABLE I
The Transmittance (T) and Degree of Polarization (ρ) of the IBC + IAC Polarizing Films, and IBC + IAC Polarizing Films-H

IBC film		IBC + IAC films	IBC + IAC polarizing films	
Weight gain of I ₂ /KI (%)	Weight gain of boric acid (%)	Concentration of I ₂ /KI (mol/L)	Transmittance (%)	Degree of polarization (%)
1.5	0.5	0.025	13.61	99.991
	1.0		19.17	99.993
	2.0		23.34	99.995
	3.0		31.91	99.996
			IBC + IAC polarizing films-H	
	0.5	0.05 (heated at 130°C for 20 min)	18.65	99.994
	1.0		20.93	99.994
	2.0		30.74	99.996
	3.0		41.59	99.997

were determined by examining the transmittance and degree of polarization in Table I and were suitable for the polarizing films. In Figure 7(b), the intensity of the peak at 650 nm corresponding to I₅⁻ decreased, whereas the peaks at 310, 370, and

480 nm increased because I₅⁻ ions were divided into bound I₃⁻ (310 nm), I₂·I₃⁻ (370 nm), and complex I₃⁻ (480 nm).^{15,17,18} Finally, excess I₃⁻ ions were observed in the heated PVA/iodine complex films. Among these films, the most adequate polarizing

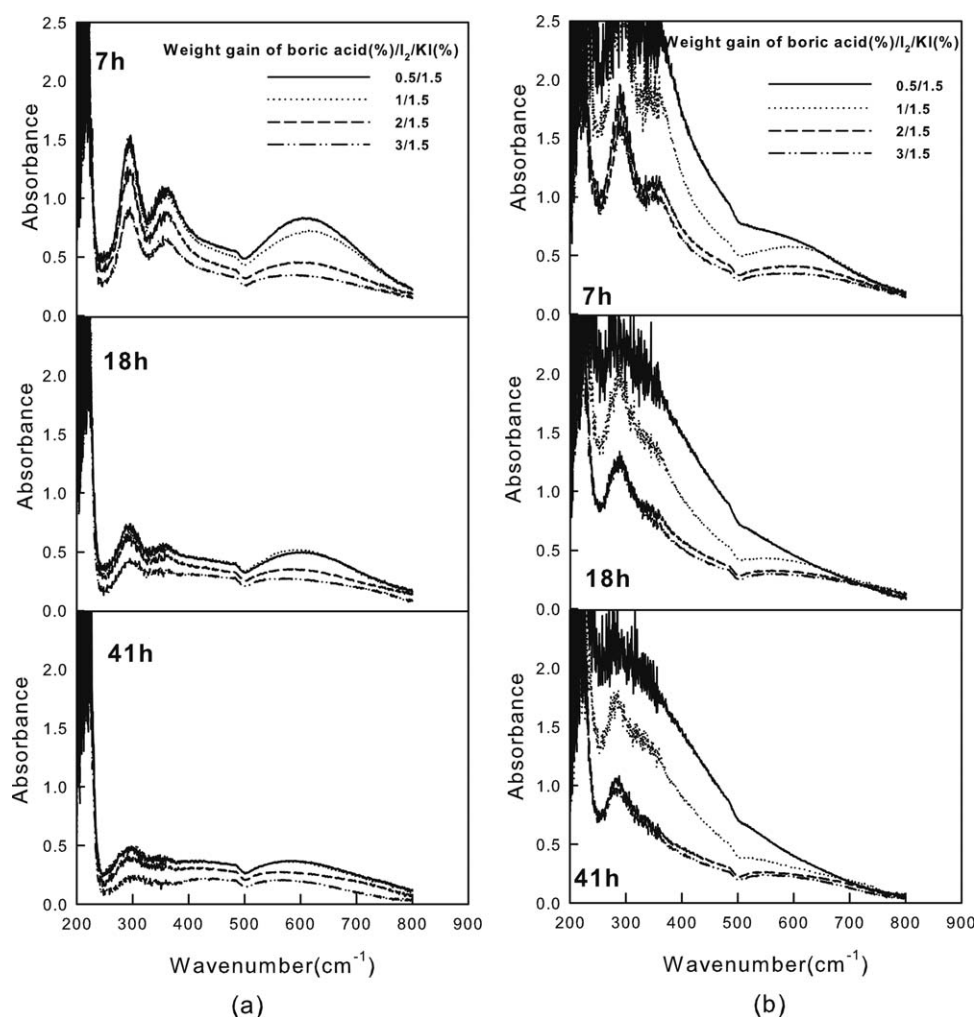


Figure 8 The UV-vis spectra of the change in the I₃⁻ and I₅⁻ ions in a warm and humid atmosphere at a relative humidity of 80% and a temperature of 70°C of the IBC + IAC polarizing films (a) and IBC + IAC polarizing films-H (b).

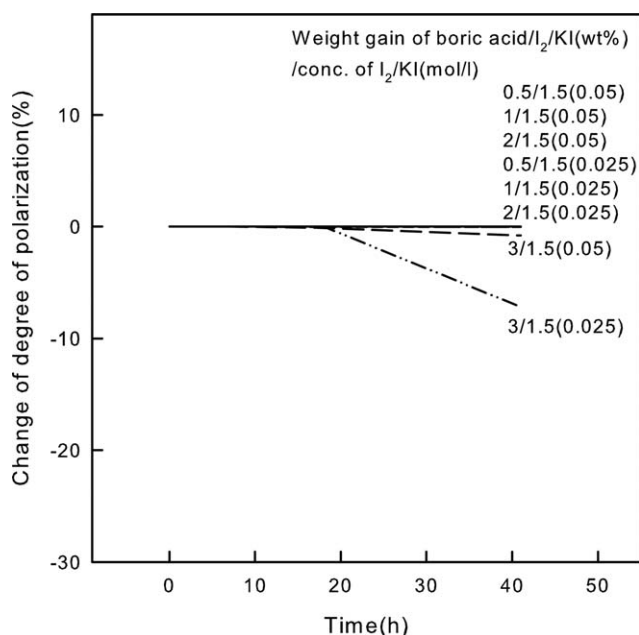


Figure 9 The change in the degree of polarization (ρ) for IBC + IAC polarizing films and IBC + IAC polarizing films-H at 70°C/80% for 40 h.

sheet film is shown in Table I. The transmittance (T) and degree of polarization (ρ) of the films were very important factors for the polarizing sheet films. As the concentration of boric acid increased, the T increased and the ρ of all of the films increased to a very high level (99.9% ↑). In commercial polarizing films, the sublimation of iodine under humid and warm atmosphere is a serious problem because the polyiodine molecules easily deform and are released from the PVA. Therefore, the two types of films (IBC + IAC polarizing film and IBC + IAC polarizing film-H) were prepared to compare the effects of the I_3^- and I_5^- ions on the durability of the polarizing films. These films were expected to be promising materials of high durability on heat and humidity. The general conditions for measuring the durability of the polarizing film were 50°C and 80% relative humidity for 120 h. Most of the films endured in this condition. Therefore, the conditions used to discriminate the films in this study were 70°C at 80% relative humidity.

Figure 8(a,b) shows the UV-vis spectra of the change in the I_3^- and I_5^- ions in a warm and humid atmosphere at a relative humidity of 80% and a temperature of 70°C. The intensity of the corresponding I_3^- and I_5^- ion peaks decreased with time. After 7 h, the I_5^- complex ion peak (600 nm) decreased, whereas the I_3^- and $I_2 \cdot I_3^-$ free ion peaks increased. After that, all of the peak intensities decreased over time. Figure 9 shows the change in the degree of polarization (ρ) for the two types of films, the heated IBC + IAC polarizing films-H and normal IBC +

IAC polarizing films at 70°C/80% for 40 h. Commonly, the PVA/iodine polarizing film has a low durability under a 70°C/80% atmosphere because of the high sublimation characteristics of iodine, but most of the IBC + IAC films were sustained until 40 h. The durability of the IBC + IAC polarizing films-H was higher than the normal films. As mentioned above, the IBC + IAC polarizing films-H contained mostly I_3^- ions, whereas the normal IBC + IAC polarizing films formed a complex with I_5^- ions. From the durability results, the durability of the I_3^- ions that were complexed with PVA chain was higher than the I_5^- ions because the possibility of I_5^- separating into I_3^- and I_2 was high. Overall, the synthesis of PVA/iodine polarizing films containing I_3^- ions could be adequate from the durability point of view, if possible.

CONCLUSIONS

An IBC and polarizing film IAC (IBC + IAC) was manufactured to improve the durability of the PVA/iodine polarizing film under a humid and warm atmosphere as well as to determine the effect of I_3^- and I_5^- ions on the polarizing efficiency and durability. These effects were investigated by determining the structural and optical properties of the IBC, IBC + IAC, and IBC + IAC polarizing films. 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 the IBC state. In the IBC + IAC state, 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. Another polarizing film (IBC + IAC polarizing films-H) containing I_3^- ions was manufactured mainly by a heating process to compare the effects of the I_3^- and I_5^- ions on the durability of the polarizing films, which was higher than normal IBC + IAC polarizing films. Overall, the durability of I_3^- ions complexed with the PVA chain was higher than that complexed with I_5^- ions.

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