Effect of Boric Acid and Heat Treatment for the Formation of Poly(vinyl alcohol)/Iodine Complex Films Iodinated at Solution Before Casting

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ABSTRACT: This study examined the role of boric acid and the effect of heat treatment on PVA-iodine polarizing films prepared in the solution state before casting (IBC) of PVA/iodine/boric acid films. The films were prepared by casting aqueous solutions of 10 wt % poly(vinyl alcohol) (PVA) containing boric acid with 0, 0.1, 0.3, and 0.5 mol/l of I_2/KI aqueous solution, and I_2/KI(1 : 2) with 5 wt % of PVA. The effect of boric acid and heat treatment on the durability of the IBC PVA polarizing sheet films was investigated by UV–vis absorption spectroscopy. Boric acid was found to be essential for the complex formation in PVA/iodine solutions at relatively low I_2/KI concentrations and high temperatures. The strength of the complex peak at ~ 600 nm in UV–vis absorption spectra increased with increasing boric acid concentration. With increasing heating temperature over 90°C the intensity of the peak at 600 nm corresponding to the complex decreased due to the evaporation of I_2 decomposed from I_5^-, but the peak at 355 nm corresponding to free $I_2{\cdot}I_3^-$ was remained unchanged. From heat treatment at 150°C, the intensity of the peak at 600 nm decreased but the intensity of the complex peak (600 nm) of the sample with 0.5 mol/l boric acid was unaffected. 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. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1950–1956, 2011

Key words: film; drawability; crosslinking; processing; UV–vis spectroscopy

INTRODUCTION

The most important application of the PVA/iodine complex is the use of a sheet polarizer as a high quality form of dichroism in liquid crystal display systems.[1–5] The polarizer is the PVA/iodine complex film soaked in an I_2/KI solution and stretched unidirectional. However, commercial polarizing films have serious problems, such as poor water stability and easy iodine desorption under a warm and humid atmosphere. Several methods have been attempted to produce syndiotactic PVA(s-PVA) with higher tacticity and increase the molecular weight to resolve these problems with the preparation of polarizing films.[6–8] A subsequent treatment of the polarizing films with boric acid was reported to be effective in stabilizing the PVA/iodine complex. The effect of boric acid is also apparent in the complex formation of partially-saponified PVA in solutions. The addition of boric acid results in a large amount of the blue complex in addition to the red one in a solution but only the red complex forms in the absence of boric acid. Boric acid is believed to make a bridge between the PVA chains, which will decrease the freedom of chains and improve the stability of the complex. Boric acid forms intramolecular crosslinking with the covalent bond type or an intermolecular crosslinking with the hydrogen bond type in the PVA resin, which can accelerate the formation of the PVA/iodine complex and enhance its stability.[9–11] However, there are no reports of the effects of boric acid addition to the aqueous PVA solution containing I_2/KI on the PVA polarizing sheet film.

In a previous report,[12] polarizing films were prepared with PVA iodinated at the solution before casting (IBC), and the properties were good for the polarizer. However, there are no reports on the role of boric acid and heat treatment in the stabilization of the PVA/iodine complex, particularly manufacture in the PVA solution state.

In this study, a film was manufactured with PVA iodinated in the solution state before casting (IBC),[12,13] which was produced by casting an aqueous PVA solution, including I_2/KI and boric acid. The I_2/KI and

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boric acid concentrations were varied. The effect of boric acid and heat treatment on the durability of the IBC PVA polarizing sheet films was examined by UV–vis absorption spectroscopy.

EXPERIMENTAL

Material

The PVA powder was purchased from Sigma-Aldrich Company (Seoul, Korea) and used as received. The reported degrees of saponification and M_w were 99.9% and 89,000–98,000, respectively.

Film preparation

The films were prepared by casting aqueous solutions of 10 wt % PVA containing boric acid and I_2/KI on a glass plate at 60°C to form a film shape, followed by drying at room temperature for 48 h. The weight ratios of boric acid and I_2/KI to PVA were 0, 1.7, 5.1, and 8.6%, and 3, 5, and 7%, respectively. The boric acid content is reported as mol/l to I_2/KI aqueous solution (0, 0.1, 0.3, and 0.5 mol/l) in the tables and figures.

Drawing

The IBC films were drawn 4 times using a hand-operated drawer at 60°C in methyl alcohol. The width, length, and thickness of the samples were 5, 10, and 0.15–0.2 mm, respectively, and the drawing speed was 10 mm/min. After drawing, the width and thickness of the 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 spectroscopy (UV-2401PC, Shimadzu) using the following eq. (1).[14,15]

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

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

Heat treatment

The polarizing films were heat treated in an oven at 60, 90, 120, 150, and 180°C for 5 min. The durability of the heat treated polarizing film was evaluated by heat-treating the films at 100°C for 0.5 h.

Durability

The polarizing films were kept in a constant temperature and humidity chamber (relative humidity of 80% and temperature of 50 and 70°C). The durability of the films to the heat and humidity of the polarizer was evaluated from the change in transmittance and degree of polarization.

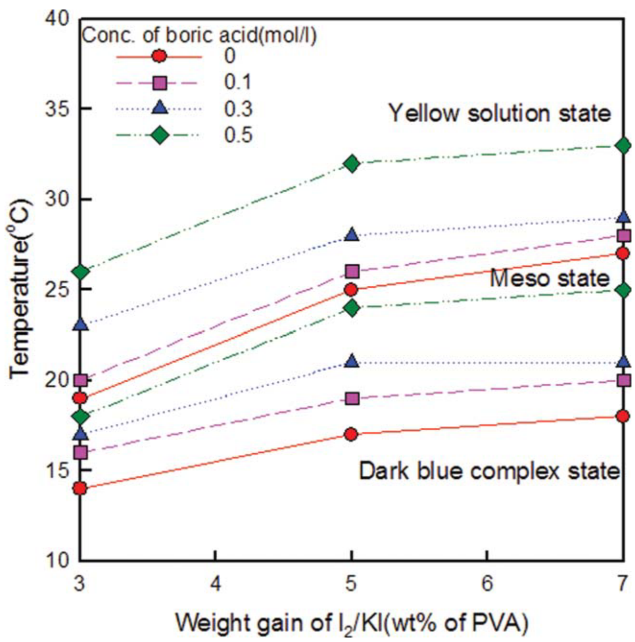

Figure 1 Phase diagram of PVA/iodine/boric acid aqueous mixtures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Measurement

The ultraviolet and visible (UV–vis, Shimazu UV-2401PC, Tokyo, Japan) absorption spectra of the films were recorded at wavelengths ranging from 200 to 800 nm.

RESULTS AND DISCUSSION

Phase diagram of PVA/iodine/boric acid aqueous mixtures

Figure 1 shows the phase diagram of the PVA/boric acid/iodine aqueous solution. A PVA/iodine/boric acid complex solution was prepared evaluate the effect of boric acid and iodine. To prepare the undrawn IBC film, the PVA/iodine/boric acid aqueous solution was poured onto a glass plate. At that time, the color of the solutions changed from yellow to greenish-yellow, green, bluish green, and finally to dark blue, which suggests that the gradual formation of PVA/iodine complexes from a homogeneous solution upon cooling. Figure 1 shows photographs of the color change in the complex upon cooling. The trend of the color change varied with the iodine and boric acid concentration, in which the characteristic temperatures for complex formation strongly depend on the iodine and boric acid concentration. The temperature for complex formation increased with increasing

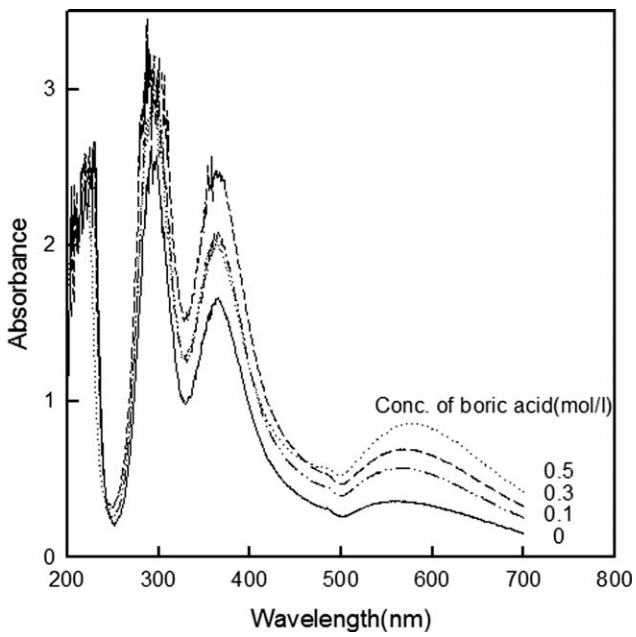

Figure 2 UV–vis absorption spectra of PVA/iodine/boric acid polarizing films with various boric acid.

iodine and boric acid concentration. Generally, the formation of a PVA/iodine complex is favorable at low temperatures but the temperature for complex formation increased with increasing iodine and boric acid concentration. In Figure 1, a dark blue complex state of 5 wt % I_2/KI was accomplished under 16°C, but the addition of 0.5 mol/l boric acid, the complex formation temperature increased to 23°C. Complex formation of 3 wt % I_2/KI was made possible at 15°C by adding 0.1 mol/l boric acid, even though it was impossible without boric acid. However, complex formation was possible at the same temperature with 5 wt % I_2/KI without boric acid. It was confirmed that boric acid is necessary for complex formation in a PVA/iodine solution at relatively low I_2/KI concentrations and high temperatures.

UV–vis absorption spectrum of PVA/iodine/boric acid polarizing films

Before heat treatment

Figure 2 shows the UV–vis absorption spectra of PVA/iodine/boric acid polarizing films containing 5 wt % of I_2/KI with boric acid. In the spectra, five peaks appear at approximately 226, 290, 355, 470, and 600 nm, which correspond to the I^-, I_3^-, free $I_2{\cdot}I_3^-$, bound I_3^- and complexed I_5^- ions, respectively. The first three peaks were confirmed by the experiment on PVA dissolved in an I_2/KI solution, and the last two peaks were attributed to the formation of PVA-iodine complexes.[10,11,16,17]

The strength of each peak at the absorptions was increased with the addition of boric acid. The strength of the complex peak at ~ 600 nm increased with increasing boric acid concentration, even though the strength of the first three peaks increased to 0.3 mol/l boric acid and then decreased because the ionic species produced originally from iodine were consumed to form a complex with PVA molecules.

After heat treatment

Figure 3(a–d) show the absorbance of the various iodine species in the PVA/iodine/boric acid films by heat treatment. The decrease in peak intensity with increasing temperature is reasonable due to the evaporation of I_2 molecules, I_2 molecules from I_5^-, and I_2 from I_3^-.[18] The formation of the complex was not affected by heating the sample to 90°C. Therefore, heat treatment of iodinated film at this temperature is necessary to evaporate the excess I_2, which causes oxidation in the polymer, for later use. From heat treatment at 120°C, the intensity of the peak corresponding to the complex peak at 600 nm decreased due to the evaporation of I_2 decomposed from I_5^- but the peak at 355 nm was either unchanged or increased. However, in the case of untreated boric acid, both 355 and 600 nm peaks decreased after heat treatment at 120°C. After heat treatment at 150°C, the intensity of the peak corresponding to the complex peak at 600 nm decreased, but the intensity of the complex peak (600 nm) of 0.5 mol/l boric acid was unaffected. This suggests that boric acid had formed intramolecular crosslinks on the PVA chains, which must decrease the freedom of the chains and impart higher stability to the complex. The heat stability of film containing boric acid must be strong.

Transmittance and degree of polarization of PVA/iodine/boric acid polarizing films

Table I shows the change in the transmittance (T) and degree of polarization (ρ) of PVA/iodine/boric acid polarizing films with various boric acid concentrations before and after heat treatment. The T and ρ without boric acid were 48.56 and 97.5%, respectively. T decreased with increasing boric acid concentration but ρ increased. This was attributed to boric acid increasing the content of the PVA/iodine complex. As above mentioned, the boric acid remarkably enhances complex formation, and the effect on complex formation is so great that the effect of stereoregularity of the PVA chains almost disappears in the presence of large amount of boric acid.[2] The most suitable film for the polarizing films was prepared using 0.3 mol/l boric acid with a 36.07 T and 99.9 ρ, respectively. After heat treatment, T increased but ρ decreased, due to the

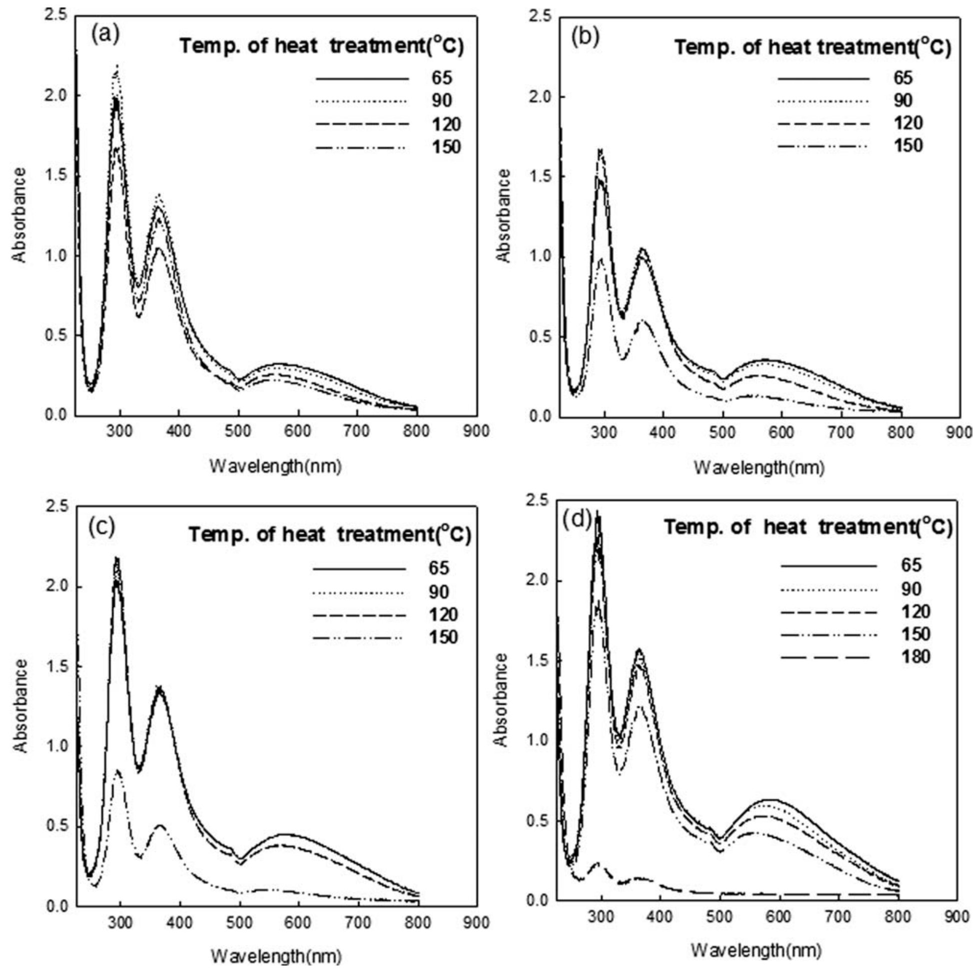

Figure 3 UV–vis absorption spectra of PVA/iodine/boric acid polarizing films containing 5 wt % of I_2/KI and heat treated with various temperatures.(a: 0, b: 0.1, c: 0.3, d: 0.5 mol/l of boric acid).

evaporation of I_2 from I_5^- and I_3^-. In the film not containing boric acid, heat treatment at 90°C decreased ρ but the heating temperature sustaining a $\rho > 95\%$ increased with increasing boric acid concentration. Heat treatment of a PVA/iodine/boric acid polarizing film containing 0.5 mol/l boric acid at 150°C resulted in a $\rho > 99\%$. The optimal heat temperatures at 0, 0.1, 0.3, and 0.5 mol/l boric acid were 0, 90, 120, and 150°C, respectively.

TABLE I
Transmittance (T) and Degree of Polarization (ρ) of PVA/Iodine/Boric Acid Polarizing Films with Various Heat Treatment Temperature and Concentration of Boric Acid

Temp (°C)	0		90		120		150	
	T (%)	ρ (%)	T (%)	ρ (%)	T (%)	ρ (%)	T (%)	ρ (%)
Conc. of boric acid (mol/l)								
0	48.56	97.4	51.21	93.4	55.31	88.1	62.73	73.3
0.1	45.26	98.1	48.37	95.3	58.90	80.0	77.03	47.6
0.3	36.07	99.9	36.71	99.9	41.49	99.5	80.42	44.1
0.5	24.08	99.9	26.98	99.9	30.96	99.9	41.13	99.3

Durability of PVA/iodine/boric acid polarizing films

The PVA/iodine polarizing films have a weak point in use under a warm and humid atmosphere. Therefore, a study of the behavior for iodine ions is necessary to take complementary measures for polarizing films. Heat treatment at 90°C is necessary to eliminate the excess iodine to prevent oxidation.

Figure 4 shows the T and ρ of PVA/iodine/boric acid polarizing films before (a) and after (b) heat treatment at 90°C for 0.5 h and placed under heat and humidity conditions (50°C, 80%). In case of film before heat treatment [Fig. 4(a)], the T and ρ of the films increased and decreased, respectively, due to the sublimation of iodine and the polyiodine molecules easily deformed and released from PVA. However, this tendency decreased with increasing boric acid concentration and heat treatment, which may be strengthened for improved resistance to heat and humidity. The heat-treated films [Fig. 4(b)] showed better resistance to heat and humidity than the non-heat treated films. With time, the T

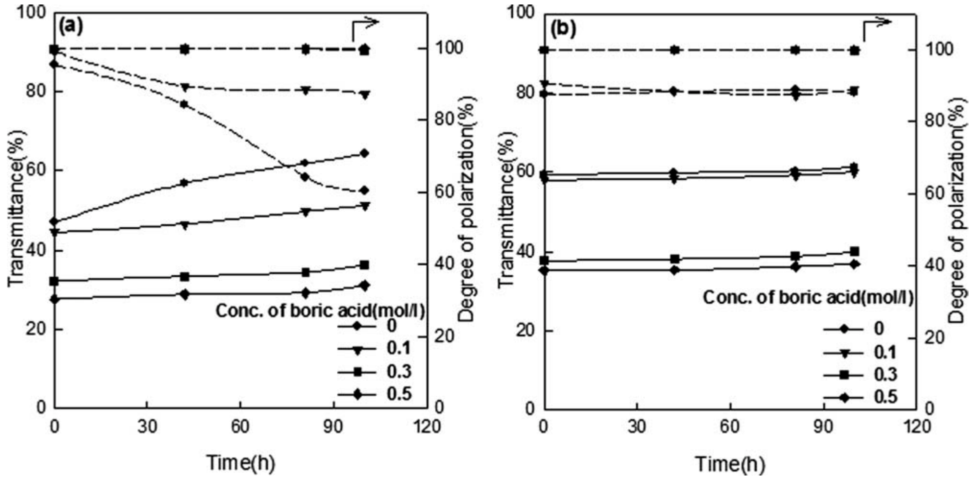

Figure 4 Transmittance (*T*) and degree of polarization (ρ) of PVA/iodine/boric acid polarizing films before (a) and after (b) heat treatment at 90°C for 0.5 h and placed under heat and humidity conditions (50°C, 80%).

and ρ of the films remained unchanged for 100 h. The T and ρ of the untreated and 0.1 mol/l boric acid polarizing films after heat treatment were approximately 59 and 80%, respectively, due to iodine sublimation, which was an unsuitable condition for polarizing a film. However, boric acid

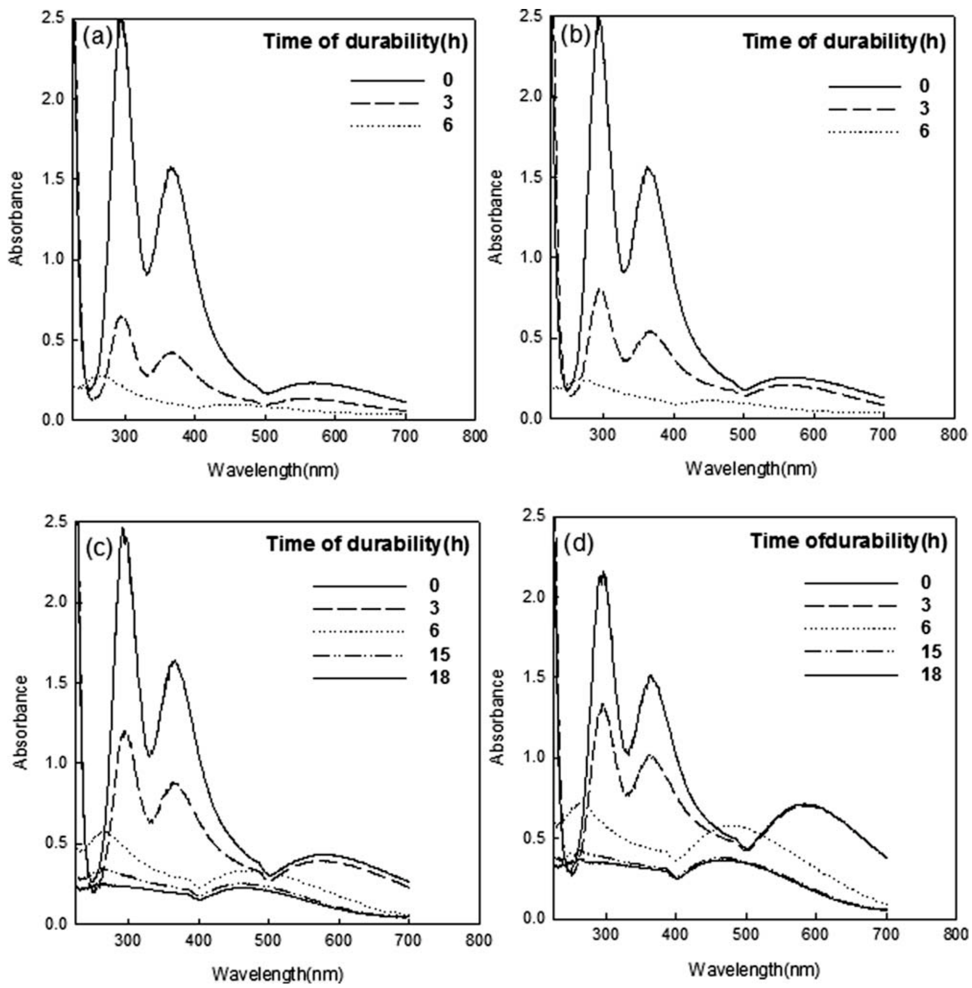

Figure 5 Variation of UV–vis absorption spectra of PVA/iodine/boric acid polarizing films treated at 100°C for 0.5 h and placed under heat and humidity (70°C, 80%).

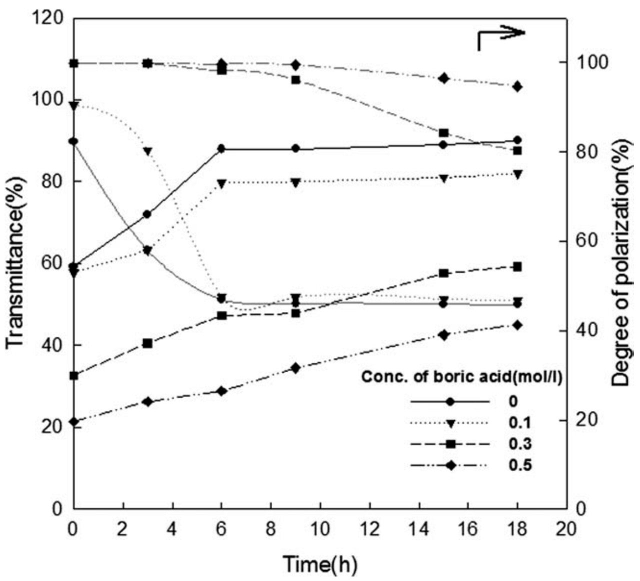

Figure 6 Transmittance (T) and degree of polarization (ρ) of PVA/iodine/boric acid polarizing films treated at 100°C for 0.5 h and placed under heat and humidity (70°C, 80%).

concentrations of 0.3 and 0.5 mol/l were suitable for polarizing the film. This shows that the boric acid content and heat treatment stabilizes the complex in a PVA/iodine film.

Figure 5 shows the resistance to heat and humidity (70°C, 80%) of polarizing films according to the heating length at 100°C for 0.5 h and different boric acid concentrations. Generally, the intensity of each peak decreased with time in a warm and humid atmosphere, but this was a slow and steady progress with boric acid. Over 0.3 mol/l boric acid, the films have an endurable complex at 70°C and 80% relative humidity for 18 h. With time under the warm and humid atmosphere, the wavelength of each peak showed a red shift. This is different from the result of heat treatment. The peak at 600 nm corresponding to the complex shifted to 480 nm corresponding to bound I_3^-, which means that the blue I_5^- complex had separated into I_2 and I_3^- and I_2 had evaporated in the warm and humid atmosphere to leave I_3^- and the complex with PVA molecules.

Figure 6 shows the T and ρ of the PVA/iodine/boric acid polarizing films, which were heat treated at 100°C for 0.5 h and placed under heat and humidity conditions (70°C, 80%). Although the ρ of the films containing 0, and 0.1 boric acid decreased immediately, those of the films containing 0.3 and 0.5 mol/l boric acid had better stability. Generally, stability under high temperatures and humidity are important. To solve this problem, syndiotactic PVA with higher tacticity and higher molecular weight might be needed to prepare good polarizing film.

CONCLUSIONS

This discussion examined the role of boric acid and heat treatment of PVA/iodine polarizing films prepared in the solution state of PVA/iodine/boric acid. The PVA iodinated in the solution state before casting the (IBC) film was produced by casting an aqueous PVA solution containing I_2/KI and boric acid. The effect of boric acid and heat treatment on the durability of IBC PVA polarizing sheet films was examined by UV–vis absorption spectroscopy.

The effect of boric acid

It was confirmed that boric acid is necessary for complex formation in a PVA/iodine solution at relatively low I_2/KI concentrations and high temperatures. The intensity of the complex peak in the UV–vis absorption spectrum at approximately 600 nm increased with increasing boric acid concentration. And, the intensity of each peak decreased with time in a warm and humid atmosphere, but this was a slow and steady progress in the presence of boric acid.

The effect of heat treatment

Heat treatment of an iodinated film at 90°C is necessary to evaporate the excess I_2. From heat treatment at 120°C, the intensity of the peak corresponding to the complex peak at 600 nm decreased and the peak at 355 nm was relatively unaffected or increased. From heat treatment at 150°C, the intensity of the peak corresponding to the complex at 600 nm decreased but the intensity of the complex peak (600 nm) of 0.5 mol/l boric acid was unchanged. The optimal heat temperatures at 0, 0.1, 0.3, and 0.5 mol/l boric acid were 0, 90, 120, and 150°C, respectively. The resistance to heat and humidity of the heat treated films were better than that of the non-heat treated films.

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