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ORIGINAL PAPER

Effect of boric acid treatment on the crystallinity and drawability of poly(vinyl alcohol)–iodine complex films

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Abstract A film iodinated at solution state before casting (BIBC film) and a film iodinated after casting (BIAC film) were prepared by casting an aqueous solution of poly(vinyl alcohol) (PVA) including I_2/KI and boric acid, and by successively soaking the PVA film in aqueous solutions of boric acid and I_2/KI, respectively. The boric acid-induced and I_2/KI-induced weight gains relative to the PVA were 3, 5, 7, and 10%, and 3, 5, 10, and 20%, respectively. The effects of boric acid and iodine on the crystallinity and drawability of the films were investigated. Although the crystalline structure of the BIAC films was not affected by boric acid, the boric acids in the PVA solution containing I_2/KI may have formed intra-molecular cross-links on the PVA chain to accelerate the formation of the PVA–iodine complex evenly, and subsequently interrupt the PVA crystallization through the BIBC film formation to render the resultant film slightly crystalline or practically amorphous. This occurred even at a much lower I_2/KI-induced weight gain (20%) than the minimum weight gain (125%) at which the iodinated at solution state before casting film without boric acid indicated a practically amorphous state. The maximum draw ratio of the films generally decreased with increasing boric acid content, which was mainly attributed to the increase of the extended segments of the PVA chains in the amorphous region due to the cross-links formed with the boric acids. The maximum draw ratios of the BIBC films tended to decrease more severely than those of the BIAC films.

Keywords Polyvinyl alcohol · Film · Crystallinity · Drawability · Cross-linking

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Introduction

A large number of researches on the poly(vinyl alcohol) (PVA)–iodine complex have been carried out. They can be divided roughly into three classes, as researches on the formation mechanism and structure of the complex [1–26], the application of the complex formation to the improvement of processability [27–38], the direct use of the complex such as a hydrogel, sheet polarizer etc. [39–46].

It is supported by a large majority of the researchers that the polyiodide ions (I_3^-, I_5^-) form complexes with –OH on PVA chains in not only amorphous region but also crystalline region. When the iodine sorption was over 12 wt%, the iodination in crystalline region was occurred [2, 32].

The models of the PVA–iodine complex in the amorphous and crystalline regions were proposed, respectively. Two models in the amorphous region were proposed, that is, the aggregate model by Miyasaka [44] and the helical model by Zwick [11]. Several PVA segments with extended conformation are surrounding a polyiodide ion in the aggregate model which is for the complex forming in water-swollen film, whereas one PVA chain forms a helical conformation surrounding a polyiodide ion in the helical model which is for the complex forming in the solution.

Miyasaka et al. [32, 44] proposed two models in crystalline region, the intercalation model and the substitution model. In the intercalation model, a polyiodine intercalates between two PVA chains on the *a*-axis, which indicates the X-ray diffractions peaks at $2\theta = 6.6$, 13.5, and 19.4°. In the substitution model, one of the two PVA chains in Bunn's PVA crystal cell is substituted by a polyiodine, and therefore the *c*-axis is about twice as long as that of Bunn's cell, which indicates the X-ray diffractions peaks at $2\theta = 8.5$, 14.5, and 20.5°. They confirmed the intercalation and substitution models with X-ray diffractions patterns of iodinated PVA films whose iodinated sorption were relatively low (14 wt%) and high (100 wt%), respectively.

The most part of those researches were carried out for the iodination of PVA in solution state [11, 19–22, 30, 31] or in film state [29, 32, 33, 35–39, 41–44]. However, we prepared a new type of PVA–iodine complex film by casting a PVA solution previously iodinated with I_2/KI, and referred to it as IBC (iodinated at solution state before casting) film. The outstanding physical characteristic of the IBC film was that its crystallinity decreased with increasing the iodine sorption and came to amorphous state when the iodine sorption was over 125 wt% [37, 38].

On the other hand, the boric acid has been occasionally used as cross-linking agent in PVA or used to accelerate formation of the PVA–iodine complex and enhance its stability. It has been known that the boric acid forms an intra-molecular cross-linking with covalent bond type or an inter-molecular cross-linking with hydrogen bond type in the PVA resin [13, 30, 44, 45]. The inter-molecular cross-linking can contribute to the formation of PVA hydrogel. The intra-molecular cross-linking can contribute to making extended segment of PVA chain which is helpful to form the aggregate model type PVA–iodine complex. Furthermore, intra-chain bridge forming on the helical PVA chain in the helical model type complex can contribute to enhancement of its stability [11, 12].

However, the effects of boric acid on the characteristics of the PVA–iodine complex films have not been studied. In this research, therefore, we investigated the effect of boric acid added in the PVA–iodine complex films on their crystallinity and drawability. Furthermore, we paid special attention to the procedure for adding the I_2/KI and the boric acid. Therefore, two types of film were prepared for study: a film boric acid treated and iodinated at solution state before casting (BIBC film) and one boric acid treated and iodinated after casting (BIAC film). The BIBC film was produced by casting an aqueous solution of PVA including boric acid and I_2/KI, and the BIAC film was prepared by successively soaking a PVA film in aqueous solutions of boric acid and I_2/KI. The concentrations of I_2/KI and boric acid were varied.

The crystallinity of the films was examined with X-ray diffraction (XRD) and differential scanning calorimetry (DSC), and the drawability of the films was investigated by measuring the maximum draw ratio.

Experimental

Material

The PVA powder from Sigma-Aldrich Company in Japan was used to prepare films. The reported degrees of saponification and M_w were 99.9% and 89000–98000, respectively.

Film preparation

BIBC film

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 the film shape, and then drying them at room temperature for 48 h. The weight ratios of boric acid to PVA (boric acid-induced weight gain) were 3, 5, 7, and 10%, and those of I_2/KI (I_2/KI-induced weight gain) were 3, 5, 10, and 20%.

BIAC film

A PVA film was prepared by casting an aqueous solution of 10 wt% PVA. The film was soaked in aqueous solutions of 0.05, 0.1, and 0.3 M boric acid for 1, 30, 60, 360, and 1440 min, washed with water, and dried at room temperature. The films treated with boric acid were soaked in aqueous solutions of 0.01, 0.05, and 0.1 M I_2/KI (1:2) for the same times as those used in the boric acid treatment, rinsed with water, and air-dried at room temperature for over 1 week, as this was the necessary duration for complete water evaporation and excess iodine sublimation. The boric acid- and I_2/KI-induced weight gains were determined from the weight difference between the dried film before and after soaking. The samples which had same boric acid- and I_2/KI-induced weight gains with the BIBC films were selected for the subsequent experimental procedures. The sample whose I_2/KI-induced weight gain was 3% without boric acid could not be obtained, and was therefore excluded from the following procedures.

Drawing

The maximum draw ratio was determined through the following drawing examination. The films of 5 mm width and 10 mm length were drawn by a hand-operated drawer at 90 °C in a silicon oil bath up to the film fracture. The extension speed was fixed to with 10 mm/min.

Measurements

XRD was performed by Rigaku D/max-III-A with Cu K_α radiation. DSC was performed by a TA DSC 2910 at a heating rate of 20 °C/min in an N_2 atmosphere.

Results and discussion

Crystallinity of the films

It was reported that the influence of the iodine on the crystal structure of PVA is varied with the quantity of iodine sorption with three types: (1) no influence with iodine sorption ~12 wt%, (2) altering to the intercalation type with relatively low iodine sorption, and (3) altering to the substitution type with relatively high iodine sorption [32, 44]. Our samples have 3–20 wt% of iodine sorption, and are applicable to the type of (1) or (2).

It has been known that the XRD peaks for pure PVA crystal appear at $2\Theta = 11.3$, 19.0, and 28.0°, and those for the iodinated PVA crystal with the intercalation type structure applicable to this experimental, appear at $2\Theta = 6.5$, 13.5, and 19.4° [32].

Figure 1a–d shows the XRD scans for the BIAC films according to the I_2/KI-induced weight gain. There were two peaks at $2\Theta = 11$ and 19°, which revealed a PVA crystal structure in the case of the very low I_2/KI-induced weight gain (Fig. 1a). This indicated that no iodine was penetrated into the crystalline region of the PVA. With increasing I_2/KI-induced weight gain, however, the peaks were gradually shifted toward $2\Theta = 13$, and 20°, indicating a PVA–iodine complex crystal. There were no remarkable differences in the position and intensity of the peaks according to the boric acid-induced weight gain in each figure. This indicated that boric acid did not affect the crystalline structure of the BIAC films because the boric acid could not permeate into the crystal region constituted in the PVA film prior to the boric acid treatment.

Figure 2a–d shows the XRD scans for the BIBC films according to the I_2/KI-induced weight gain. The BIBC films with no boric acid presented two obvious peaks in all the figures. Merely, they gradually shifted toward a higher Bragg angle and their intensity decreased a little with increasing I_2/KI-induced weight gain, as in

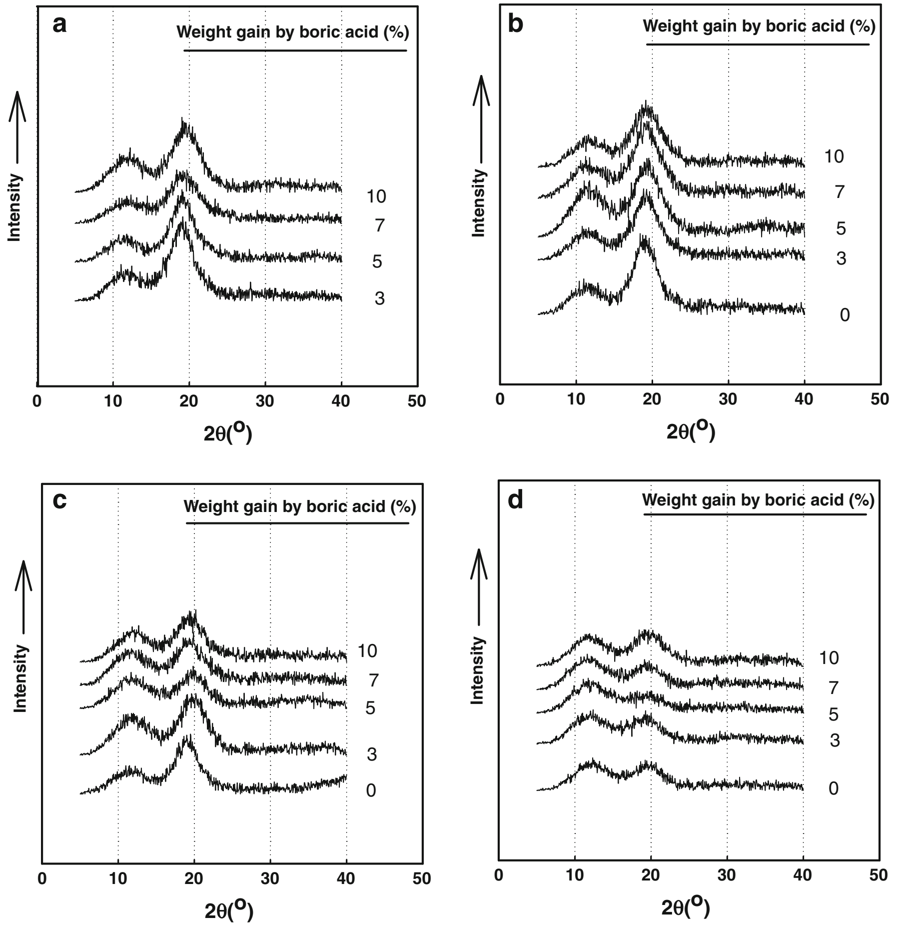

Fig. 1 X-ray diffraction scans of the BIAC films with I_2/KI-induced weight gain (I_2/KI-induced weight gain (%) **a**: 3, **b**: 5, **c**: 10, **d**: 20%)

the case of the BIAC films. However, the films containing boric acid presented a very weak peak at $2\Theta = 20°$ or no peak, which suggested that the films were slightly crystalline or practically amorphous. This may have resulted from the unusual process of the BIBC film preparation. That is, the boric acids and iodine ions react with the PVA molecules in a solution state to form intra-molecular cross-linking and to form complexes evenly within the PVA chain, which would interrupt the crystallization in the solidifying procedure of the film.

This result of achieving a practically amorphous film state with only low I_2/KI-induced weight gain (below 20%) was very significant, because the IBC film without boric acid indicated a practically amorphous state in the film with much higher I_2/KI-induced weight gain (more than 125%) [37]. To investigate whether this significant result was caused by the effect of the boric acid alone or the combined effect of the boric acid and iodine, extra films were prepared from

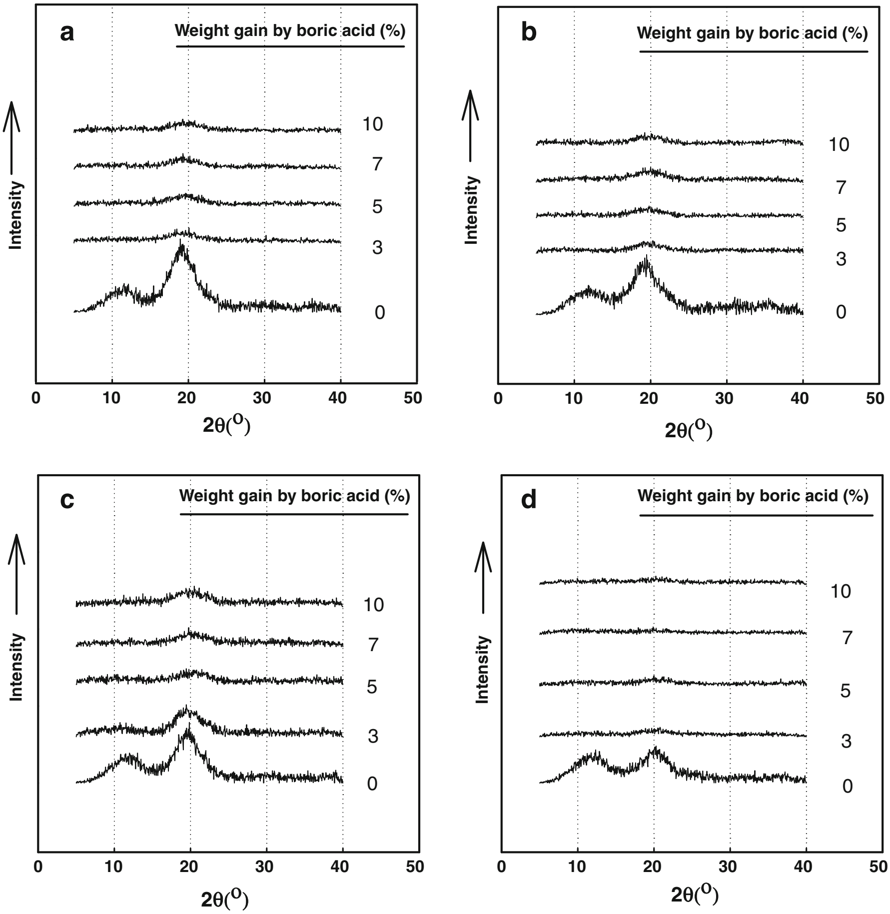

Fig. 2 X-ray diffraction scans of the BIBC films with I_2/KI-induced weight gain (I_2/KI-induced weight gain (%) **a**: 3, **b**: 5, **c**: 10, **d**: 20%)

aqueous solutions of PVA containing boric acid alone, and were examined with XRD and DSC. Figure 3 shows the XRD scans for the PVA films containing boric acid alone. In general, there were no remarkable differences in the XRD scans between the pure PVA film and the boric acid-induced films. But the diffraction peak appreciably became broader toward the wide angle side with increasing boric acid content. Ohishi et al. [47] studied the role of boric acid in PVA film. They concluded that the boric acid suppressed the recrystallization of the PVA chains in drying process and reduced the molecular mobility, probably due to cross-linking among PVA chains which were produced by the partial dissolution of smaller crystallites and the surficial parts of larger crystallites when the films were pre-swollen with water. In addition, Okada et al. [48] deduced the XRD peak at $2\theta = 22.1°$, which was about 2° wider than the main peak, was attributed to the extended PVA chains cross-linked with boric acid. These previous studies regarded

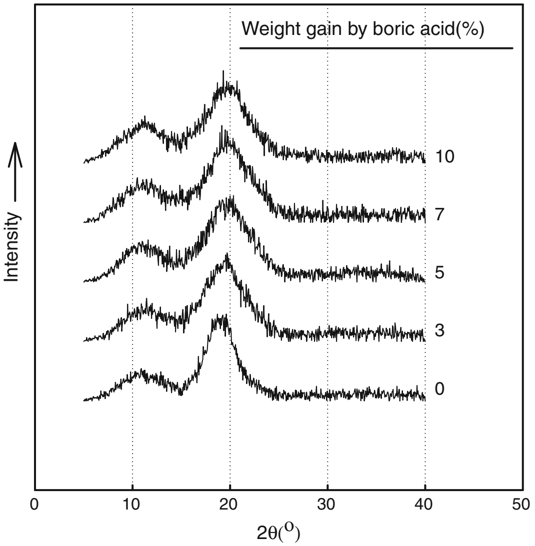

Fig. 3 X-ray diffraction scans of the PVA films containing boric acid

a quasi-crystalline phase composed of boric acid cross-linked chains which made the XRD main peak broader or indicated and additional peak at 2° wider Bragg angle than that of the main peak. In our experimental, the broadening of the main peak ($2\theta = 19°$) toward the wider angle side could be distributed to the growth of the additional peak reported by Okada et al. [48]. This result suggested that there may be not only pure PVA crystalline phase but also the quasi-crystalline phase in the boric acid-induced films. We deduced that the tiny quasi-crystalline phases corresponding to the chain segments combining the cross-linking may be dispersed within the PVA crystalline phase matrixes in the films. That is, the PVA chain segments combining the boric acid cross-linking must be embraced in the crystalline phase of the films because the boric acids had been uniformly distributed in the PVA solutions for preparing the films.

This eduction can be supported by the DSC curves shown in Fig. 4. The pure PVA film indicated a strong and sharp crystal melting peak at about 220 °C. However, the boric acid-induced films indicated a new broad peak at the lower temperature zone ($80 \simeq 180$ °C), which was probably assigned to melting of the quasi-crystalline phase. This peak inevitably intensified, in contrasts the existing peak assigned to the pure PVA crystalline phase was weakened and its temperature was decreased, with increasing the boric acid content. The quasi-crystalline phase can be regarded as defects in the pure PVA crystalline phase: the increase of the boric acid content 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. On the other hand, the new broad peak could also be interpreted to have resulted from the melting of another quasi-crystals composed of pure PVA chains. If so, those peaks will disappear after adequate drawing. To confirm this possibility, the DSC for drawn films by four times was performed and

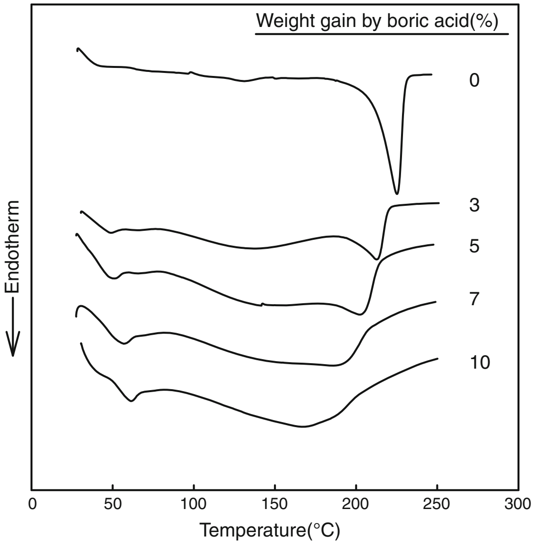

Fig. 4 DSC thermograms of the PVA films containing boric acid

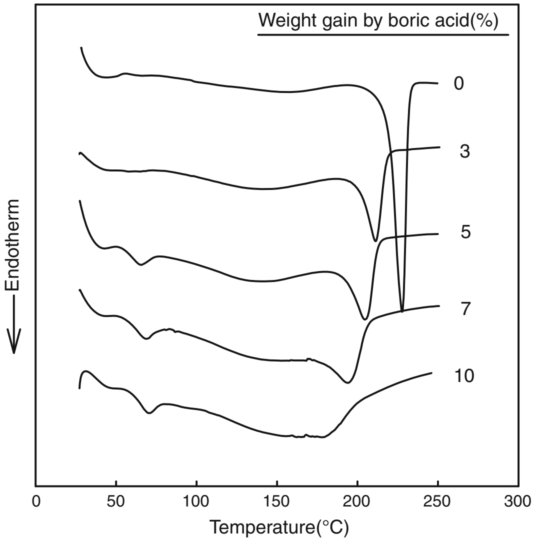

Fig. 5 DSC thermograms of the drawn PVA films containing boric acid

the results were shown in Fig. 5. There were no remarkable changes in the appearances of the peaks other than the increase in their intensity by drawing. This result paradoxically supports our interpretation that the new broad peak in Fig. 4 may have resulted from the melting of the defect portions in crystalline region due to boric acid. To conclude, although the boric acids alone within the PVA resin cannot influence the PVA crystallization, they form intra-molecular cross-links on the PVA chain to accelerate the formation of the PVA–iodine complex in the presence of iodine ions, which interrupt the PVA crystallization.

Maximum draw ratio

Figures 6 and 7 show the variation of the maximum draw ratios of the BIAC and BIBC films, respectively, with increasing boric acid-induced weight gain. The increase of the maximum draw ratios with increasing I_2/KI-induced weight gain was reasonable result due to the destruction of the intermolecular hydrogen bonds by I_2/KI [36].

In the figures, the maximum draw ratio of the films generally decreased with increasing boric acid-induced weight gain. The influence of the boric acid within the

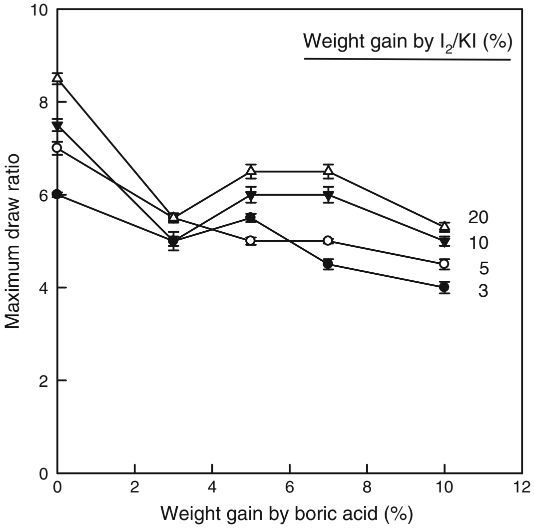

Fig. 6 Change of the maximum draw ratio of the BIAC films with boric acid-induced weight gain

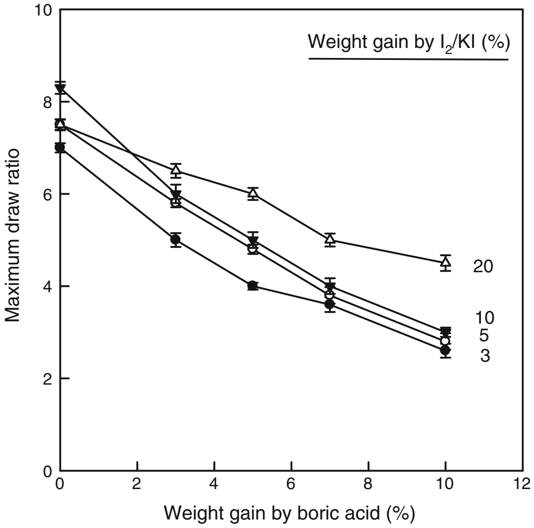

Fig. 7 Change of the maximum draw ratio of the BIBC films with boric acid-induced weight gain

PVA resin on the drawability of the films may be generally attributed to three factors. (1) The intra-molecular cross-linking type on the PVA chain segment extends the segment, thereby decreasing the drawability. (2) The inter-molecular cross-linking type is also a decreasing factor of drawability. (3) The intra-molecular cross-linking type, on the other hand, decreases the number of hydroxyl groups on the PVA molecule, subsequently decreasing the intermolecular hydrogen bonds, which increases the drawability. The decreasing tendencies of the maximum draw ratio in this experimental may have resulted mainly from the first and second factors above. Nevertheless, the slight lack of consistency in the decreasing tendency of the maximum draw ratio for the BIAC films may have been caused by the influence of the third factor.

Although the difference between the BIAC and BIBC films was not significant, the decreasing tendencies for the BIBC films were appreciably greater than those for the BIAC films. Here, we cautiously brought up the structure of the PVA–iodine complex in the amorphous region of PVA as another factor associated with the influence of the boric acid on the drawability of the iodinated PVA films. As stated above, two types of complex structure in amorphous region have been proposed: the aggregate model [26, 44, 46] and the helical model [4, 11, 12]. In the BIAC film, the tie chains, whose mobility is highly restricted by the crystal interfaces, can hardly form a helical conformation to create the helical model but can form the aggregate model with polyiodine. In the case of the BIBC film, however, the PVA chains with high mobility in the solution state before the film formation can easily form a helical conformation to create the helical model [11]. Therefore, the BIBC films may have both the aggregate and helical model type complexes, while the BIAC films may have only the former. These helical model type complexes in the BIBC films probably reduce the straight length of the tie chain and hence probably decrease the drawability even more. This role of the helical type complex in the drawability of the iodinated film is just an assumption and necessary to be investigated experimentally in future.

Conclusions

Two types of PVA–iodine complex films—BIBC and BIAC—were prepared by casting an aqueous solution of PVA including I_2/KI and boric acid, and by successively soaking the PVA film in aqueous solutions of boric acid and I_2/KI, respectively. The boric acid-induced weight gains relative to the PVA were 3, 5, 7, and 10%, and the I_2/KI-induced weight gain were 3, 5, 10, and 20%. The effects of boric acid and iodine on the crystallinity and drawability of the films were investigated.

The crystalline structure of the BIAC films was not affected by boric acid treatment because the boric acid could not permeate into the crystal region in the PVA film prior to the boric acid treatment. However, in the BIBC films, the boric acids may have formed intra-molecular cross-links on the PVA chain to accelerate the formation of the PVA–iodine complex evenly in the solution state, and then interrupted the PVA crystallization through film formation. Consequently, the films presented a slightly crystalline or practically amorphous state, even though their I_2/KI-induced weight gains (below 20%) were much lower than the minimum weight gain (125%) at which the IBC film without boric acid indicated a practically amorphous state.

The maximum draw ratio of the films generally decreased with increasing boric acid-induced weight gain, which was attributed mainly to the increase of the extended segments of the PVA chains in the amorphous region due to the cross-links formed with the boric acids. The maximum draw ratios of the BIBC films tended to decrease more severely than those of the BIAC films, which was attributed to the additional effects of the reduction of the straight length of the tie chain owing to the formation of the helical model type PVA–iodine complexes in the amorphous region and very low crystallinity of the BIBC films.

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