Structure and Processability of Iodinated Poly(vinyl alcohol). IV. Drawability of the Films Iodinated at Solution before Casting

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ABSTRACT: The drawability of iodinated at solution before casting (IBC) polyvinyl alcohol films prepared by casting aqueous solutions of 10 wt % PVA containing 15.2, 39.8, 83.2, 117.0, and 140.1% was examined with a tensile tester at 20–60°C. The tensile behavior of IBC films showed that the yield and breaking loads were much lower, and the breaking elongation was even higher than those of the unoriented iodinated after casting (IAC) films as well as the untreated PVA films. The maximum draw ratios of the films with the weight gain of 15.2, 39.8, 83.2, 117, and 140.1% were 4.5, 5.5, 8.5, 8.0, and 7.5, respectively, which were achieved at 20°C in all. The crystallinity of all films increased by the maximum draw, regardless of crystallinity before drawing. The crystalline structure was recovered to the original PVA crystalline lattice by deiodination. Amorphous orientation and initial moduli increased with the maximum draw ratio, while the orientation of crystals was constant. The orientation and moduli increased up to the weight gain of 83.2%, whose highest draw ratio and initial modulus were 8.5 and of 7.1 GPa, respectively, and then decreased. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 34–38, 2008

Key words: poly(vinyl alcohol); film; drawing; crystal structure

INTRODUCTION

Although polyvinyl alcohol (PVA) is a kind of thermoplastic polymer, it has a limitation for processability such as drawability due to relatively low degradation temperature for side chain (—OH). But iodine, as polar plasticization aid, can intrude and rupture intermolecular hydrogen bonds in the crystalline and amorphous regions of PVA to improve softness and processability.[1–6]

Especially, we prepared IBC (iodinated at solution before casting) films by casting aqueous solutions and investigated their structure as in a previous article.[7] The crystallinity of the IBC films decreased with the weight gain of I_2/KI in the films, and the films with the weight gain of 140.1% were almost in an amorphous state. This result showed the decrease of intermolecular force. Namely, it was possible to prepare the amorphous film of the polymer by iodination due to the ability of iodine to plasticize the crystalline state of the films and the difficulty to crystallize the films, which were prepared by casting PVA aqueous solutions containing the selected quantities of I_2/KI.

This unique property of the IBC films is expected to have an effect on postprocessability of PVA.

Therefore, in this study, we investigated the drawability of the IBC films at various temperatures, and the structure of the films drawn to the maximum draw ratio (MDR) and deiodinated was determined through X-ray diffractometry, differential scanning calorimetry (DSC), birefringence, and so on.

EXPERIMENTAL

IBC film preparation

PVA powder from Kuraray Company in Japan was used to prepare films. The PVA films iodinated at solution before casting (IBC films) were prepared by casting 10 wt % PVA solution containing I_2/KI of 15.2, 39.8, 83.2, 117.0, and 140.1 wt % to the PVA, which were poured on a glass plate at 60°C and were put in air at 30°C for 24 h. Three kinds of weight gain of I_2/KI (15.2, 39.8, and 83.2 wt %) were controlled with the same as described in the first part of this study,[8] while two kinds (117.0 and 140.1wt %) were added because more weight gain of I_2/KI was possible in the IBC method.

Drawing

A drawing test was performed with a tensile tester (Autograph AGS-500D, Shimadzu) with a hot chamber at 20–60°C. The starting temperature of the drawing

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test was adopted by the results of DMTA in the previous article.[7] The glass transition temperature (T_g) of IBC was observed at 20°C, and the sublimation temperature of iodine was 70°C. So, we examined the tensile test of the films up to 60°C. The width and length of the sample were 5 and 10 mm, respectively, and the test speed was 2 mm/min.

Deiodination

The iodinated films were deiodinated by dipping in an aqueous solution of 7 wt % sodium thiosulfate and 5 wt % ethylene glycol at 20°C for 3 h, which is enough time for the complete removal of iodine.

Measurements

The X-ray diffractometry was performed by using Rigaku D/max->III-A with Cu-K$_\alpha$ radiation.

The crystalline orientation factor (f_c) was evaluated from the azimuthal intensity distribution of well-resolved equatorial reflection line from the (101) plane, and its quantity was calculated by the following eq. (1):

$$f_c = 180° - \beta/180° \tag{1}$$

where β is the half-width of the intensity distribution of the (101) plane on the equator.

The amorphous orientation factor (f_a) was evaluated by combining X-ray and optical birefringence data. Birefringence was measured by using a Leica polarizing microscope and the tilting compensator K. Amorphous orientation factors were then calculated by the following eq. (2):

$$\Delta n = x_c \Delta n_c^o f_c + (1 - x_c)\Delta n_a^o f_a + \Delta n_f, \tag{2}$$

where Δn is the measured birefringence, Δn_c^o and Δn_a^o are the intrinsic birefringence of crystalline and amorphous phases, x_c is the degree of crystallinity of fibers, and f_c and f_a are crystalline and amorphous orientation factors of fibers, respectively. The values of $\Delta n_c^o = 51.8 \times 10^{-3}$ and $\Delta n_a^o = 43.8 \times 10^{-3}$ were used.

Differential scanning calorimetry (DSC) was performed by a TA DSC 2910 at the heating rate of 20°C/min in the atmosphere of N_2. Stainless steel open pans were used to allow the evaporation of iodine.

RESULTS AND DISCUSSION

Drawability

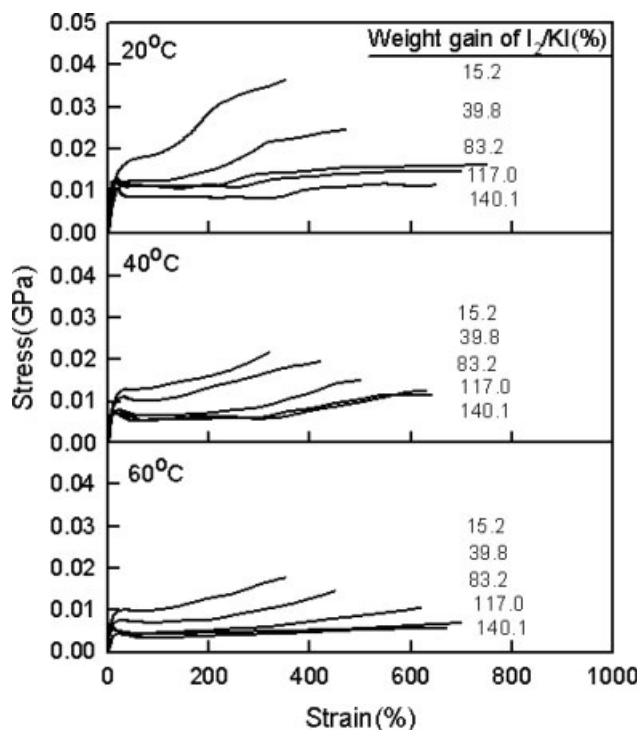Figure 1 shows the stress–strain curves of the IBC films at 30–60°C. Generally, the breaking stress was

Figure 1 The stress–strain curves of IBC films at 20, 40, and 60°C.

much lower than that of the untreated PVA films as in the previous article,[9] whose yield stress and breaking strain at 30°C were 0.16 GPa and 130%, respectively. The maximum draw ratio increased with the weight gain of I_2/KI up to 83.2% and then decreased.

At 20°C, the best yield stress and breaking strain were 0.01 GPa and 750% ($\lambda = 8.5$), respectively, and then decreased. This is due to a low degree of crystallinity of the IBC films. That is, the films contained much weight gain of I_2/KI to create a flow between molecules, which contained I_2/KI fairly and had low molecular entanglement and degree of crystallinity, instead of molecular chain extension. The maximum draw ratios (MDR) of the films with the weight gain of 15.2, 39.8, 83.2, 117, and 140.1% were 4.5, 5.5, 8.5, 8.0, and 7.5, respectively.

At 40 and 60°C, the increase of strain did not exist anymore. It was estimated to be related to the T_g of the IBC films (20°C),[7] over which a molecule's flow merely increased not to contribute to chain extension. Therefore, in this text, we investigated the properties of the films drawn at 20°C only.

Structure of the drawn films

Figure 2 shows the X-ray diffraction scans of the drawn IBC films to the MDR. Generally, the X-ray
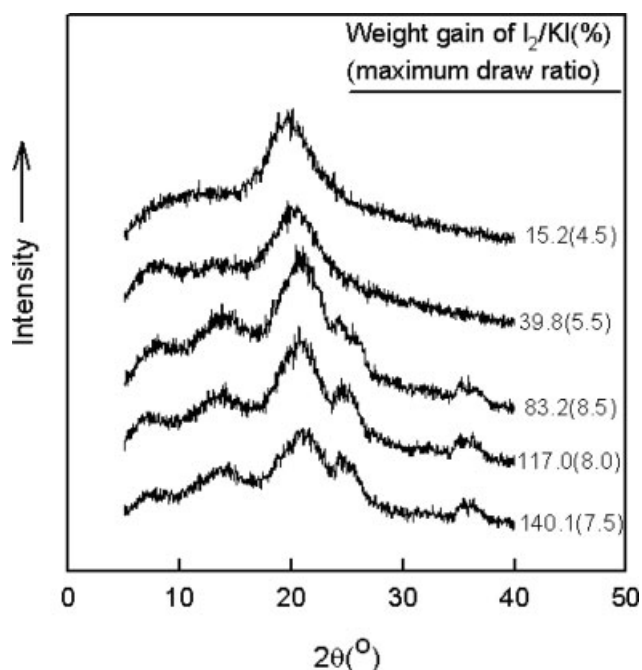
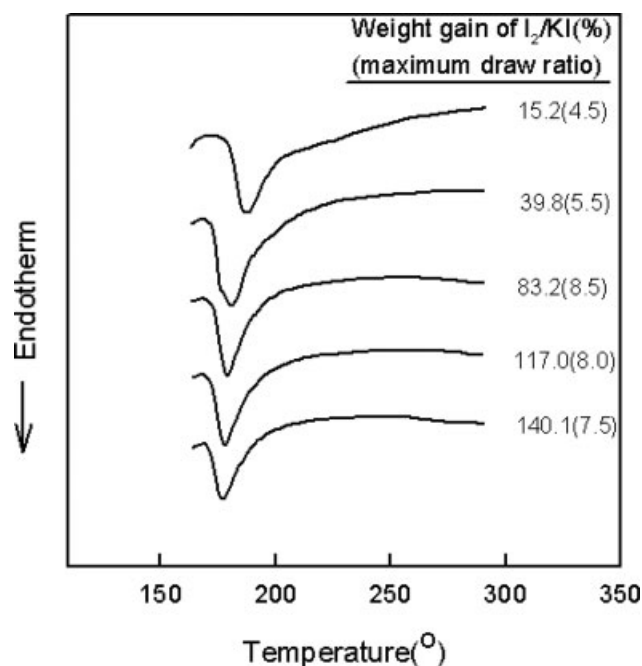**Figure 2** The X-ray diffraction scans of drawn IBC films.

Figure 3 The DSC thermograms of drawn IBC films.

diffraction peaks were similar to the undrawn films though the peaks became clearer. Also, their intensity was higher than that of the undrawn films according to the draw. That is, crystallinity of all films increased by drawing, regardless of crystallinity before drawing. Especially, the films contained 117.0 wt % I_2/KI and, in an almost amorphous state, crystallinity was advanced. The study of the X-ray peaks was discussed as in the previous article.[7–9]

Figure 3 shows the DSC thermograms of the drawn IBC films to the MDR. To compare with the undrawn IBC films, the tendency of 15.2 and 38.9% I_2/KI was similar to that of the drawn IBC films. But in the cases of 83.2, 117.0, and 140.1% I_2/KI, the exothermic peaks appeared in the undrawn IBC films and disappeared by drawing. Because of that, fair crystals of the drawn IBC films were made, referring to the X-ray results. The temperature of the degradation peaks decreased according to the increase of I_2/KI by the action of I_2 molecules, precedent-generated, as an oxidizer.

Structure of the drawn films after deiodination

Crystallinity

Figures 4 and 5 show the X-ray diffraction scans and DSC thermograms of the films drawn to the MDR and deiodinated. All the films indicated the diffraction peaks as being characteristic of the original crystalline lattice of the PVA. $2\theta = 19.5°$ in X-ray and $T_m = 230°C$ in DSC were restored through

deiodination, irrespective of the crystalline structure in the iodinated state. Generally, the original PVA crystal peak was clearer than that of the undrawn films, especially in the case of 83.2 wt % of I_2/KI. From this fact, we can know that the increasing orientation by drawing helps restore PVA through deiodination.
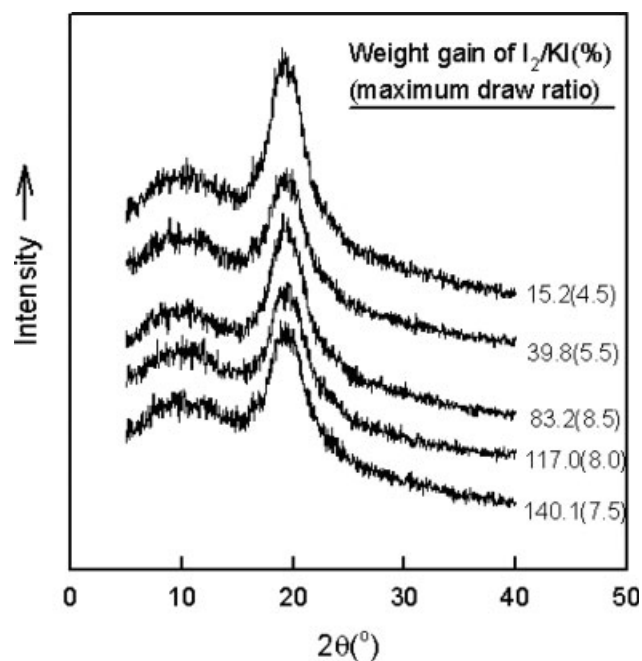

Figure 4 The X-ray diffraction scans of PVA films obtained by deiodination of drawn IBC films.
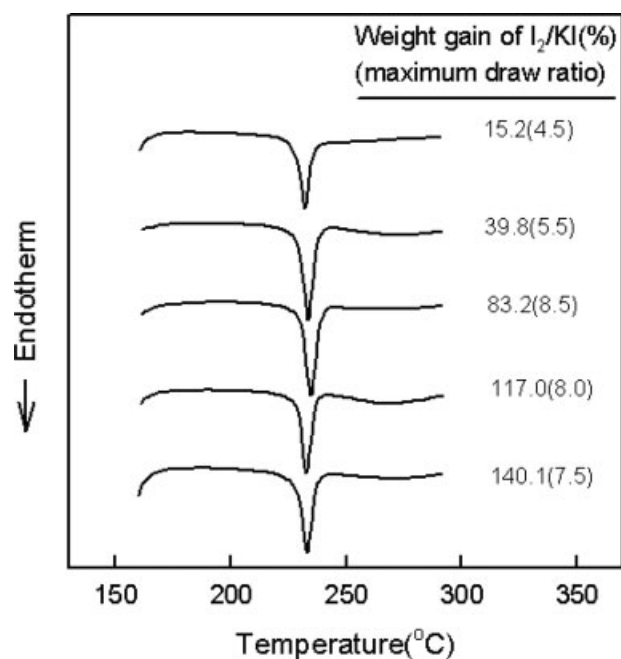
Figure 5 The DSC thermograms of PVA films obtained by deiodination of drawn IBC films.

Orientation

Table I shows the birefringence (Δn) as well as the orientation functions of crystalline (f_c) and amorphous (f_a) regions of the PVA films obtained by the deiodination of the maximum drawn IBC films. Birefringence and f_a increased with the weight gain of I_2/KI to 83.2% and decreased, though f_c was constant. Such results showed a similar tendency to the trend of the draw ratio. However, the decrease of the draw ratio for the weight gain of 117.0% and over was lower than that of birefringence and f_a. This must be caused by the molecular flow during the draw, which may be the state of the lack of crystallinity or entanglement between molecules. That is, in the case of large weight gain of I_2/KI, f_c was made up by the extended chain during the draw; so, it had no difference between samples. But the mole-

TABLE I
The Birefringence and Orientation Functions of Crystalline (f_c) and Amorphous (f_a) Regions of the PVA Films Obtained by Deiodination IBC Films

Weight gain (%)	Maximum draw ratio	Birefringence ($\times 10^{-3}$)	f_c	f_a
15.2	4.5	24.00	0.872	0.343
39.8	5.5	24.93	0.861	0.386
83.2	8.5	27.02	0.839	0.505
117.0	8.0	22.04	0.844	0.299
140.1	7.5	22.00	0.861	0.259

TABLE II
The Initial Moduli and Draw Ratios of the PVA Films Obtained by Deiodination IBC Films

Weight gain (%)	Maximum draw ratio	Initial modulus (GPa)
15.2	4.5	6.0
39.8	5.5	6.5
83.2	8.5	7.1
117.0	8.0	5.6
140.1	7.5	5.0

cules in a flow with no extension remained amorphous and decreased orientation.

Initial moduli

Table II shows the initial moduli and draw ratios of the PVA films obtained by deiodination IBC films. Initial moduli increased with the maximum draw ratios of I_2/KI to 83.2% and then decreased. The highest draw ratio of 8.5 and the initial modulus of 7.1 GPa were achieved from the film with the weight gain of 83.2%. The initial moduli of the weight gain of I_2/KI 117.0 and 140.1% decreased greatly, while the draw ratios of those decreased a little. From this fact, we can see that initial moduli mainly depend on f_a.

CONCLUSIONS

To investigate the drawability of IBC films, the films were prepared by casting aqueous solutions of 10 wt % PVA containing 15.2, 39.8, 83.2, 117.0, and 140.1%, and were drawn at 20–60°C. The structure of the films drawn to the MDR and deiodinated was determined.

The tensile behavior of the iodinated at solution before casting (IBC) films showed that the yield and breaking loads were much lower and the breaking elongation was even higher than those of the unoriented iodinated after casting (IAC) films as well as the untreated PVA films. The maximum draw ratio increased with the weight gain of I_2/KI up to 83.2% and then decreased. The maximum draw ratios of the films with the weight gain of 15.2, 39.8, 83.2, 117, and 140.1% were 4.5, 5.5, 8.5, 8.0, and 7.5, respectively, which were achieved at 20°C in all. The crystallinity of all films increased by the maximum draw, regardless of crystallinity before drawing. The crystalline structure was recovered to the original PVA crystalline lattice by deiodination. Amorphous orientation and initial moduli increased with the maximum draw ratio, while the orientation of crystals was constant. The orientation and moduli increased up to the weight gain of 83.2%, whose highest draw ratio and initial modulus were 8.5 and

of 7.1 GPa, respectively, and then decreased. Especially, the amorphous orientation and initial modulus of the almost amorphous-state film were fairly low against the draw ratio.

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