

Water Stability of Syndiotactic Poly(vinyl alcohol)/Iodine Complex Film

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ABSTRACT: The desorption behavior of iodine in syndiotactic poly(vinyl alcohol) (*s*-PVA) with a syndiotactic diad content of 63.1% iodine film in water was investigated in relation to the solubility of *s*-PVA in water. Despite a low number-average degree of polymerization of 900, the degree of solubility of *s*-PVA film in water at 80°C was limited to about 10%, whereas atactic poly(vinyl alcohol) (*a*-PVA) film was completely soluble at a lower temperature, 50°C. The degree of iodine desorption of *s*-PVA/iodine film at a high temperature decreased remarkably compared with that of *a*-PVA/iodine film. The fastness of iodine of the drawn *s*-PVA/iodine film was far superior to that of the undrawn film. Over a draw ratio of 5, the iodine desorption was suppressed significantly with increasing drawing temperature rather than the draw ratio. In addition, the iodine desorption of postdrawn *s*-PVA/iodine film was lower than that of predrawn *s*-PVA/iodine film. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 108–113, 2001

Key words: desorption; iodine; syndiotactic poly(vinyl alcohol) (*s*-PVA); solubility; drawing

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer with hydroxyl groups that give rise to intermolecular and intramolecular hydrogen bondings. PVA is classified into three types, isotactic, atactic, and syndiotactic, according to the stereoregularity of its hydroxyl groups. The phys-

ical properties of PVA are highly dependent on the degree of syndiotacticity, which is determined primarily by the choice of vinyl ester monomer. Efforts to enhance of syndiotacticity of PVA, as well as its molecular weight, have been centered on the polymerization of vinyl trifluoroacetate,¹ vinyl trichloroacetate,² and vinyl pivalate (VPi).^{3–9} The best results were obtained with VPi because of the strong steric effects of the *tert*-butyl group.

It is well known that PVA forms iodine complexes by changing color from brown to blue.^{10,11} Iodine/PVA complexation occurs both in an aqueous solution and in a swollen gel state of PVA. For example, in solution, the amount of complex in-

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creases with increasing concentrations of PVA, iodine, and boric acid.¹² Investigations of PVA/iodine complex formation have revealed the influence of the molecular parameters of PVA, such as stereoregularity,^{13–17} 1,2-glycol bonds,¹⁸ short branches,¹⁹ the degree of hydrolysis, and the degree of polymerization.¹³ Among them, the stereoregularity effect is obvious. It was reported that the amount of iodine complex formed in syndiotactic poly(vinyl alcohol) (*s*-PVA) was much larger than that formed in atactic poly(vinyl alcohol) (*a*-PVA).^{20–22} Yamaura et al.¹⁴ found that PVA/iodine complex formation was increased with increasing syndiotactic diad (*s*-diad) content of PVA, using *s*-PVA with *s*-diad content of 56–58% derived from poly(vinyl trifluoroacetate).

Commercial polarizing films produced from *a*-PVA have the serious problem of iodine desorption under humid and warm atmospheres, which results mainly from the higher affinity of *a*-PVA molecules to water than to iodines. In this study, to make *s*-PVA/iodine film with a high resistance to iodine desorption, we prepared *s*-PVA with an *s*-diad content of 63% by solution polymerization of VPi, and the desorption behavior of iodines from *s*-PVA/iodine film was investigated. In particular, molecular weight of *s*-PVA was limited to a low level to disclose the syndiotacticity effect on the desorption. The films were one-step zone-drawn before and after *s*-PVA/iodine complexation, and the effects of the draw ratio and drawing temperature on the desorption of iodine were examined.

EXPERIMENTAL

Materials

s-PVA was synthesized from poly(vinyl pivalate), which was solution polymerized in tetrahydrofuran as a solvent. To determine the molecular weight of PVA, a sample was reacylated into poly(vinyl acetate) (PVAc), and the number-average degree of polymerization (P_n) of PVAc was calculated from the intrinsic viscosity in benzene at 30°C. The *s*-diad content and degree of saponification (DS) were determined from the spectrum obtained by ¹H-NMR spectroscopy. The P_n , *s*-diad content, and DS of PVA used in this study were 900, 63%, and 99%, respectively.

Preparation of *s*-PVA and *s*-PVA/Iodine Films

s-PVA film was prepared by casting *s*-PVA/dimethyl sulfoxide in a solution of 2.5 g/dL. The

homogenized solution was poured into a stainless steel dish and dried under vacuum at 40°C for about 3 days. Iodine/potassium iodide aqueous solutions with a molar ratio of 1:2 were prepared at an iodine concentration of 1×10^{-1} mol/L. *s*-PVA films were soaked in the soaking solution at 20°C for 5, 20, 40, and 60 s. The *s*-PVA/iodine films taken out of the solutions were rinsed with water to remove the iodine/potassium iodide aqueous solution adhering on the film surfaces and dried in a vacuum for 24 h.

Zone Drawing of Films

The films were one-step zone-drawn before and after *s*-PVA/iodine complexation. Zone drawing was carried out between a pair of narrow-band heaters 7 cm long, 2.5 cm wide, and 1 mm thick and moving at a speed of 10 mm/min. The film, 70 μm thick, 10 mm wide, and 4 cm long, was drawn under a tension on an Instron model 4201.^{23–25}

Determination of Iodine Desorption

Films were soaked in hot water at 40–80°C for 2 h to determine the ratio of iodine desorption in *s*-PVA/iodine films. The ratio of iodine desorption was calculated from the following equation:

Iodine desorption (wt.%)

$$= (w_i - w_i' - w_o \cdot f_{\text{PVA}}/w_i) \times 100 \quad (1)$$

where w_i and w_i' are the weights of the *s*-PVA/iodine film before and after treatment in water for 2 h, respectively, w_o is the weight of the *s*-PVA film, $f_{\text{PVA}} = (w_o - w_o')/w_o$, and w_o' is the weight of the *s*-PVA film after treatment in water for 2 h.

RESULTS AND DISCUSSION

Solubility of *s*-PVA Film

PVA molecules dissolve out in water to some extent as well as iodines. So, the solubility of PVA in water is a significant factor governing the desorption behavior of iodine in PVA. If PVA molecules dissolve out in water, iodines are hard to maintain in the complex film. Figure 1 shows the degree of solubility of undrawn *s*-PVA film in water for 2 h with temperature. Despite a low P_n of 900 for PVA, the degree of solubility in water at 80°C did not exceed 10%. In contrast, the film of *a*-PVA with an *s*-diad content of 51% and P_n of 900,

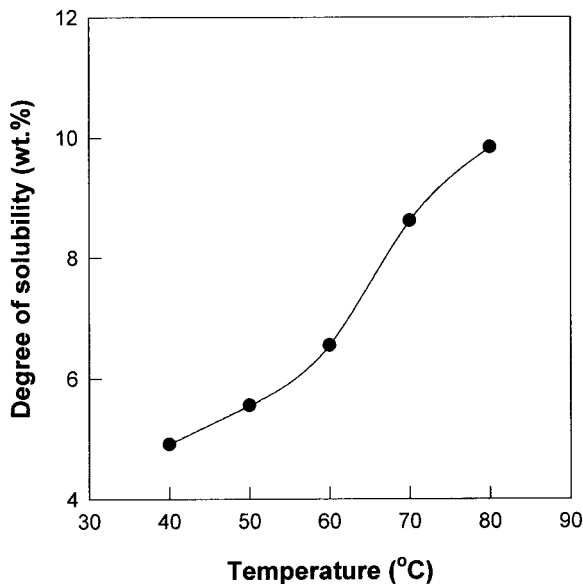


Figure 1 Degree of solubility of *s*-PVA film in water for 2 h with temperature.

which were identical to that of *s*-PVA, was perfectly dissolved at 50°C. Although water was a good solvent for *a*-PVA, it was almost a nonsolvent for *s*-PVA.

Figure 2 shows the degree of solubility of the *s*-PVA film drawn at 200°C. As compared with the undrawn *s*-PVA film, *s*-PVA film drawn three times showed a lower degree of solubility. This was related to the increase in crystallinity and to the crystal and amorphous orientations of the drawn film. However, a further drawing of *s*-PVA films over a draw ratio of 3 did not make a difference in the water resistance. The effect of drawing temperature on the solubility of the *s*-PVA film drawn five times is shown in Figure 3. The solubility of the *s*-PVA film depended on the drawing temperature rather than on the draw ratio over a draw ratio of 3. This can be explained by the fact that the penetration of water molecules into PVA molecules, when the polymer chain has a certain degree of orientation, is impeded by the increase in interchain density and the loss of defect induced by temperature rather than by further drawing. From the solubility test of the *s*-PVA film, it was clear that the affinity of *s*-PVA molecules between themselves was higher than that to water, resulting in a much lower degree of solubility than that of *a*-PVA.

Iodine Desorption in *s*-PVA/Iodine Film

Figure 4 shows the desorption of iodine in the *s*-PVA/iodine film calculated from eq. (1) after

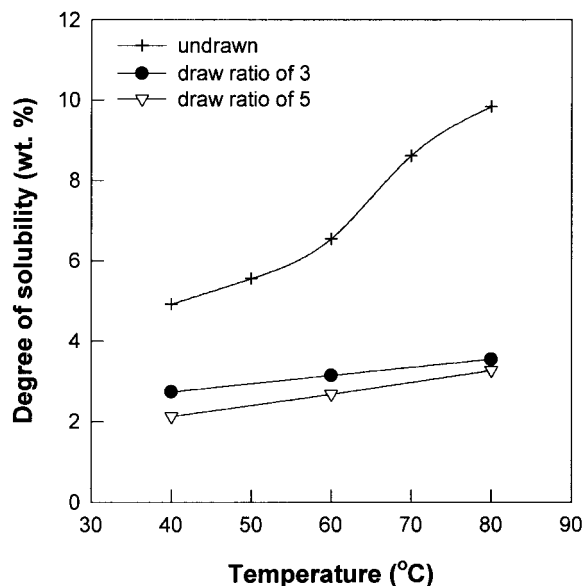


Figure 2 Effects of the draw ratio and solubility test temperature on the water solubility of *s*-PVA film drawn at 200°C.

treatment in water for 2 h with treatment temperature. The weight loss caused by the dissolution of PVA molecules was eliminated from the total weight loss of *s*-PVA/iodine film when the weight loss of iodine was calculated. Irrespective of soaking time, the desorption of iodine showed a similar tendency to the temperature–solubility

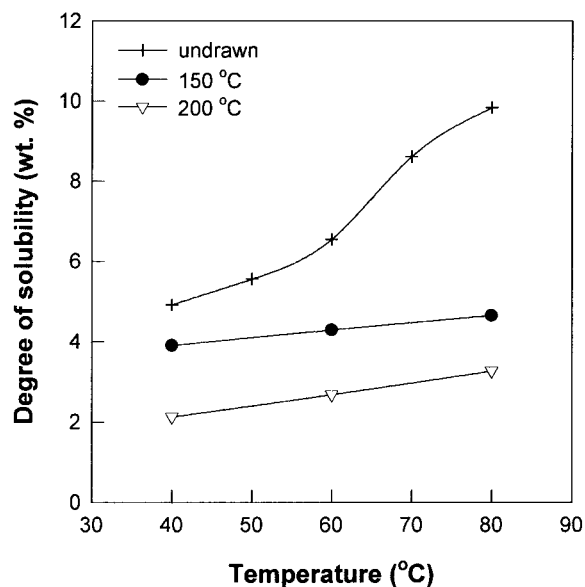


Figure 3 Effects of the drawing temperature and solubility test temperature on the water solubility of *s*-PVA film drawn five times.

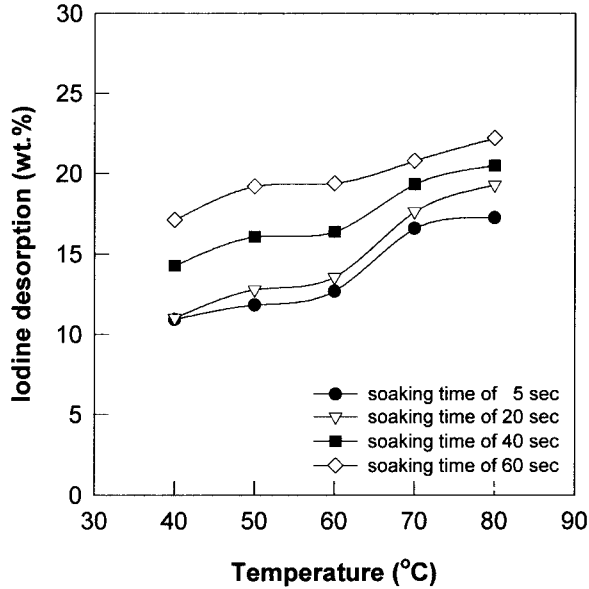


Figure 4 Desorption of iodine in *s*-PVA/iodine film after treatment in water for 2 h with treatment temperature. The *s*-PVA/iodine film was prepared by soaking in aqueous iodine solution (0.1 mol/L).

relationship shown in Figure 1, supporting the conclusion that the desorption of iodines in water was strongly affected by the dissolution of PVA. On the other hand, the longer the soaking time was, the larger the desorption of iodine was, regardless of treatment temperature. This means that although the total amount of adsorption increased with soaking time, the adsorption of iodine beyond a certain degree did not contribute markedly to the stable complex formation with the *s*-PVA molecules.

Figure 5 shows the desorption of iodine in the predrawn *s*-PVA/iodine film in water with treatment temperature. Predrawn *s*-PVA/iodine films were prepared by zone drawing of *s*-PVA films and subsequent soaking in aqueous iodine solution (0.1 mol/L) for 60 s. *s*-PVA/iodine films drawn at 200°C showed a similar iodine desorption of about 7–8% regardless of draw ratio. In contrast, the undrawn *s*-PVA/iodine film prepared with the same conditions showed a higher iodine desorption of 17–22% and a steeper increase of the iodine desorption with an increase of temperature. The drawing temperature had a more significant effect on the iodine desorption, as shown in Figure 6. At constant draw ratio of 5, the higher the drawing temperature was, the lower the desorption of iodine was. Compared with the result shown in Figure 5, when the film was drawn at

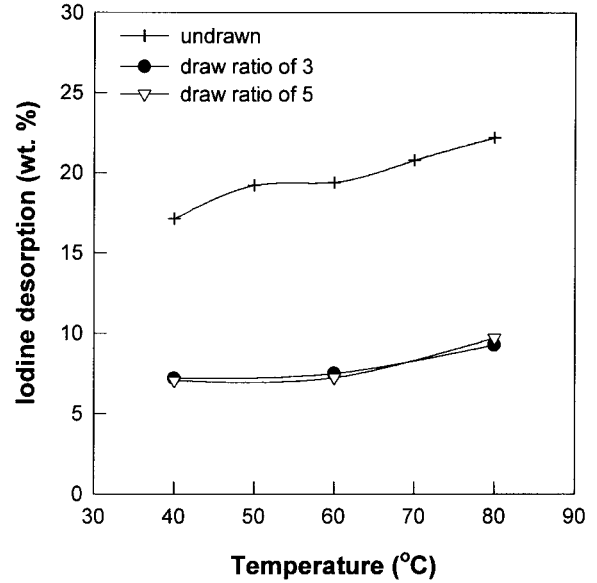


Figure 5 Effects of the draw ratio and water treatment temperature on the desorption of iodine in *s*-PVA/iodine film prepared by drawing at 200°C and subsequent soaking in aqueous iodine solution (0.1 mol/L) for 60 s.

constant draw ratio, the desorption of iodine in the *s*-PVA/iodine film in hot water preferentially depended on the drawing temperature rather

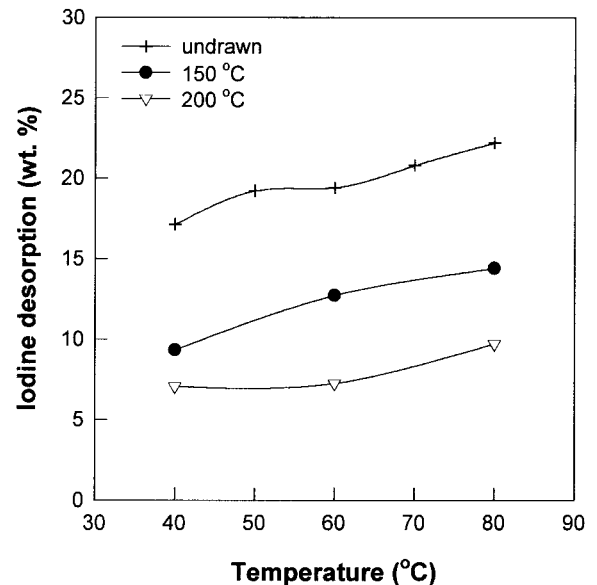


Figure 6 Effects of the drawing temperature and water treatment temperature on the desorption of iodine in *s*-PVA/iodine film prepared by drawing five times and subsequent soaking in aqueous iodine solution (0.1 mol/L) for 60 s.

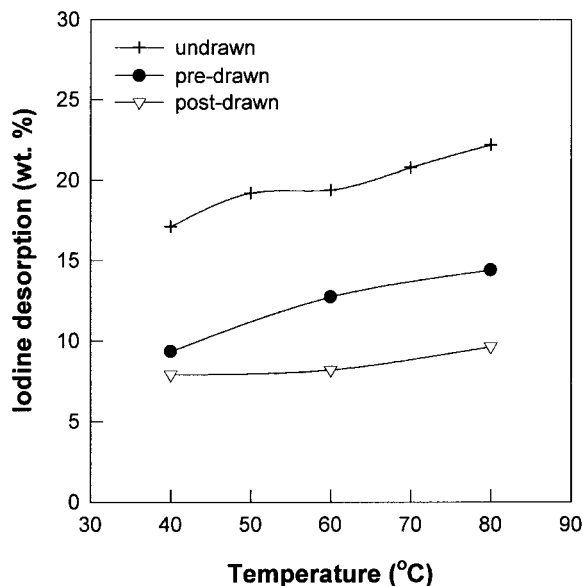


Figure 7 Desorption of iodine in predrawing and postdrawing to iodination of the *s*-PVA/iodine films after treatment in water for 2 h with temperature. The *s*-PVA/iodine film was prepared by soaking in aqueous iodine solution (0.1 mol/L) for 60 s.

than on the draw ratio. This fact agreed with the result shown in Figure 3, and so, it was determined that the amount of iodine desorption in water decreased by the decrease in the solubility of the *s*-PVA in water, which increased with drawing temperature.

Figure 7 shows the iodine desorption of pre-drawn and postdrawn *s*-PVA/iodine films in water with temperature. The drawing temperature and draw ratio were 150°C and 5, respectively. Compared with the predrawn film, the film postdrawn after iodination had a lower degree of iodine desorption even though the two films might have had the same solubility in water because of the same draw ratio and drawing temperature. When the iodinated film was drawn at 150°C, absorbed iodines sublimed partially, the total amount of absorbed iodine in the drawn film decreased, but the desorption of unsublimed iodines was highly suppressed because of the adherence of iodines with the PVA molecules, which was simultaneously strengthened by drawing. The difference in the two processes rose from the fact that in the case of predrawing, the iodines penetrated partially into the well-oriented *s*-PVA molecules, whereas they mainly remained between well-oriented *s*-PVA molecules in the postdrawing procedure. Therefore, the desorption of iodine in the predrawing procedure was higher because the

number of iodines present out of well-oriented *s*-PVA molecules was relatively large. So, we suppose that the postdrawing technique has a merit for increasing the fastness of iodine under hot water.

CONCLUSIONS

The degree of solubility of *s*-PVA film prepared by casting *s*-PVA/dimethyl sulfoxide solution at a concentration of 2.5 g/dL was only about 10% at 80°C, and the water-resistant quality of *s*-PVA film at a high temperature was superior to that of α -PVA film. Also, the iodine desorption of *s*-PVA/iodine film by hot water treatment was estimated to be at a very low level. The desorption of iodine adsorbed in *s*-PVA/iodine film decreased with drawing. Over a draw ratio of 5, the suppression of iodine desorption was achieved more effectively through the increase of drawing temperature than through the increase of the draw ratio. The iodine desorption of postdrawn *s*-PVA/iodine film was lower than that of predrawn *s*-PVA/iodine film.

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