

Water Stability of High-Molecular-Weight (HMW) Syndiotacticity-rich Poly(vinyl alcohol) (PVA)/HMW Atactic PVA/Iodine Complex Blend Films

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ABSTRACT: To precisely identify the effect of blend ratios of syndiotacticity-rich poly(vinyl alcohol) (s-PVA)/atactic PVA (a-PVA) on the water stability of s-PVA/a-PVA/iodine complex blend films, we prepared two PVAs with similar number-averaged degrees of polymerization of 4000 and degrees of saponification of 99.9% and with different syndiotactic diad contents of 58.5 and 53.5%, respectively. The desorption behavior of iodine in s-PVA/a-PVA/iodine complex films in water was investigated in terms of the solubility of s-PVA/a-PVA blend films in water. The degree of solubility of s-PVA/a-PVA blend films with s-PVA content over 50% in water at 70°C was limited to about 10–20%, whereas that of s-PVA/a-PVA blend films with s-PVA con-

tent of 10% was 85% under the same conditions. The degree of iodine desorption of complex blend films decreased with increasing s-PVA content. The degree of iodine desorption of s-PVA/a-PVA drawn film with s-PVA content of 90% was limited to 7%, regardless of the soaking temperature from 30 to 70°C. The desorption of iodine in water was strongly affected by the dissolution of blends. Moreover, the stability of iodine in the drawn s-PVA/a-PVA/iodine blend films in hot water was far superior to that of the undrawn film. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1435–1439, 2004

Key words: s-PVA/a-PVA; water stability; complex film; iodine desorption

INTRODUCTION

Recently, high-molecular-weight (HMW) syndiotactic poly(vinyl alcohol) (s-PVA) has attracted much attention because of its potential in applications such as fibers for the replacement of carcinogenic asbestos, films for polarizer, food, and drug packaging, gels for drug delivery system, and barrier membranes.^{1–3}

PVA forms a complex with iodine in its amorphous region when PVA films are soaked in comparatively lower concentrated iodine/potassium iodide solutions. S-PVA is especially favorable for complex formation.^{4–7} PVA molecules associate with one another more easily because of increasing intermolecular hydrogen bonds with increasing content of long syndiotactic sequences, and iodine molecules enter into the aggregates formed to yield polyiodine. Recently, we reported that PVA with high syndiotacticity was hardly soluble in hot water.⁸ Also, according to Choi et al.,⁴ the complex formed in the s-PVA has higher thermal stability in the soaking solution than that formed in the atactic PVA (a-PVA).

PVA/iodine complex film is the best polarizing material for a liquid crystal display. But commercial polarizing films made from a-PVA have serious problems, such as poor water stability and easy iodine desorption under warm and humid atmosphere, because water as well as iodine has a high affinity to PVA molecules. To resolve these problems, efforts to produce PVA with higher syndiotacticity and increased molecular weight have centered on the preparation of polarizing film.

Generally, in the crystalline and amorphous phases of the polarizing film, PVA molecules form a complex with oligo iodide ions, which orient parallel to the drawing direction to give a polarizing effect.^{4,5,9} However, the drawability of PVA is very poor due to the presence of intermolecular hydrogen bonding between adjacent hydroxyl groups in both crystalline and amorphous regions. It may be reasonable to suppose that the poor drawability of PVA is due more to the drawability of the crystal than that of the amorphous region. It is difficult to prepare s-PVA polarizing film with good drawability due to the presence of more intermolecular hydrogen bonding between adjacent hydroxyl groups and higher crystallinity. Tanigami et al.^{10,11} studied miscibility in the crystal phase of s-PVA/a-PVA blend films. Recently, Matsuo et al.¹²

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studied the relationship between the drawability of PVA films, prepared semidilute solutions, and phase separation of the solutions in terms of stereoregularity and molecular weight of PVA. According to their work, the crystallinity of the a-PVA films shows a gradual increase with draw ratio and attains a value of 40% beyond a draw ratio of 12. The change in crystallinity of the s-PVA film shows almost the same tendency, but the value reaches about 50% beyond a draw ratio of 12, indicating that the alignment of s-PVA chains with high stereoregularity promotes an increase in crystallinity. Crystallinities for s-PVA films at each draw ratio are higher than those for the a-PVA films.

In this study, to enhance the drawability of s-PVA film, blending, which is expected to be a useful technique for enhancing water stability from the cheaper a-PVA, was used. To prepare HMW s-PVA/HMW a-PVA/iodine complex blend films with high resistance to water and iodine desorption, we synthesized two PVAs with similar number-averaged degrees of polymerization (P_n)s of 4000 and degrees of saponification (DS)s of 99.9% and with different syndiotactic diad (s-diad) contents of 58.5 and 53.5%, respectively. We compared the desorption of iodine, under hot and humid atmospheres, from HMW s-PVA/HMW a-PVA/iodine blend films with different blend ratios. The drawing conditions, such as drawing temperature and draw ratio, affecting the iodine desorption of s-PVA/a-PVA/iodine blend films were also investigated.

EXPERIMENTAL

Materials

To prepare a water-soluble HMW s-PVA,^{13,14} copolymerization of vinyl pivalate (VPi) and vinyl acetate (VAc) with feed ratio of $\text{mol}_{\text{VPi}}/\text{mol}_{\text{VAc}}$ (4/6), using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) as initiator with conversions of 25 to 35%, was performed, followed by saponification of copoly(VPi/VAc). Water-soluble s-PVA was prepared by saponification with NaOH aqueous solution at 30°C. Also, to prepare HMW a-PVA,¹⁵ solution polymerization of VAc in dimethyl sulfoxide (DMSO), using ADMVN as initiator, with conversions of 25 to 35%, was performed, followed saponification of poly(vinyl acetate).

Determination of S-diad content and DS¹³

The syndiotactic triad and s-diad contents of PVAs were determined using a Varian Sun Unity 300-MHz proton-nuclear magnetic resonance (¹H-NMR) spectrometer, using DMSO-d₆ as the solvent, based on the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm. DS was determined by the ratio of

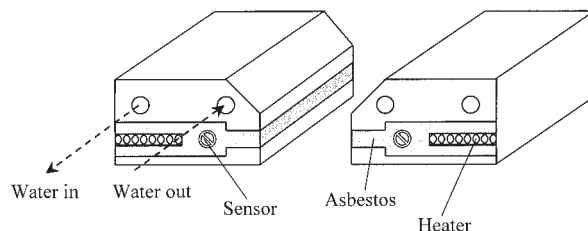


Figure 1 Schematic representation of band heater assembly.

tert-butyl and acetyl and methylene proton peaks in the ¹H-NMR spectrum.

Preparations of s-PVA/a-PVA and s-PVA/a-PVA/iodine films

s-PVA/a-PVA blend films, with a similar thickness of about 70 μm , were prepared by casting HMW s-PVA/HMW a-PVA/water in a solution of 2.5 g dl⁻¹. 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 iodine concentration of 0.1 mol l⁻¹. s-PVA/a-PVA blend films were soaked in the soaking solution at 20°C for 60 s. The films removed from the solutions were rinsed with cold water to remove the solution adhered to the film surfaces and dried in a vacuum for 24 h.

Zone drawing of films

The films were one-step zone drawn before blend films/iodine complexation. Zone drawing was carried out between a pair of narrow-band heaters with dimensions of 7 cm length, 2.5 cm width, and 1 mm thickness and moving at a speed of 10 mm min⁻¹ (Fig. 1). The film, with 70 μm thickness, 10 mm width, and 4 cm length, was drawn under tension on an Instron Model 4201 (Fig. 2).^{16–20}

Determination of degree of solubility

The degree of solubility of s-PVA/a-PVA blend films in hot water after 2 h was calculated using the equation^{7,21}

$$\text{Degree of solubility (wt. \%)} = (w_0 - w'_0)/w_0 \times 100 \quad (1)$$

where w_0 and w'_0 are the weights of s-PVA/a-PVA blend films before and after treatment in water for 2 h at treatment temperature.

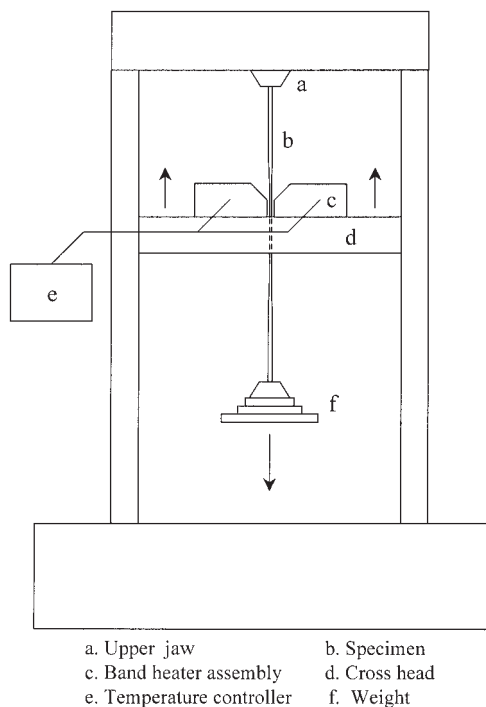


Figure 2 Schematic representation of zone-drawing apparatus.

Determination of iodine desorption

Films were soaked in hot water at 30–70°C for 2 h to calculate the ratio of iodine desorption in s-PVA/a-PVA/iodine films. The ratio of iodine desorption was calculated from the equation²¹

$$\text{Iodine desorption (wt. \%)} = (w_i - w'_i - w_0 f_{PVA}) / w_i \times 100 \quad (2)$$

where w_i and w'_i are the weights of s-PVA/a-PVA/iodine films before and after treatment in water for 2 h at treatment temperature.

$$f_{PVA} = (w_0 - w'_0) / w_0 \quad (3)$$

The f_{PVA} is coincident with the solubility of film at the desired temperature.

RESULTS AND DISCUSSION

Solubility of s-PVA/a-PVA blend films

The solubility of PVA in water is a very important factor governing the desorption behavior of iodine in PVA.^{7,21} If PVA molecules dissolve in water, iodine is less likely to remain in the complex film. Table I shows characteristic features of HMW s-PVA and HMW a-PVA. The two PVAs show similar DSs of 99.9% and P_n s of 4000. The difference in the syndiotacticity be-

tween the two PVAs was only 5% in diad content. Nevertheless, outstanding differences between s-PVA and a-PVA will still be expected to appear in degree of solubility and iodine desorption. The degree of solubility of undrawn s-PVA/a-PVA blend films, with different blend ratios in water for 2 h, with temperature, is shown in Figure 3. Despite of the s-PVA content of 50%, the degree of solubility in water at 70°C did not exceed about 20%. Furthermore, in the case of s-PVA/a-PVA blend films with s-PVA content of 90%, the degree of solubility in water at 70°C is limited, at below 15%. Although water is a good solvent for a-PVA, it is almost a nonsolvent for s-PVA.

The iodine desorption of the film, drawn or undrawn, before HMW s-PVA/HMW a-PVA/iodine complexation was calculated by considering the solubility of the drawn or undrawn s-PVA/a-PVA blend films. Figure 4 shows the degree of solubility of s-PVA/a-PVA blend films, with different blend ratios, drawn at 200°C. Compared with the case of undrawn s-PVA/a-PVA blend films, s-PVA/a-PVA blend films, drawn by 3 and 5 times, showed a lower degree of solubility due to increases in crystallinity and crystal and amorphous orientations of the film by drawing. This is because water molecules have difficulty penetrating in drawn blend films compared to the undrawn film, indicating that both crystallinity and orientations were increased. With increasing s-PVA content in s-PVA/a-PVA blends, the degree of solubility in water decreased to a very low level of 7%. The effect of drawing temperature on the solubility of s-PVA/a-PVA blend films drawn by 5 times is shown in Figure 5. As the s-PVA content in blend films was increased, so was the drawing temperature effect decreased. From the solubility data of s-PVA/a-PVA blend films, it is obvious that the mutual affinity of s-PVA mole-

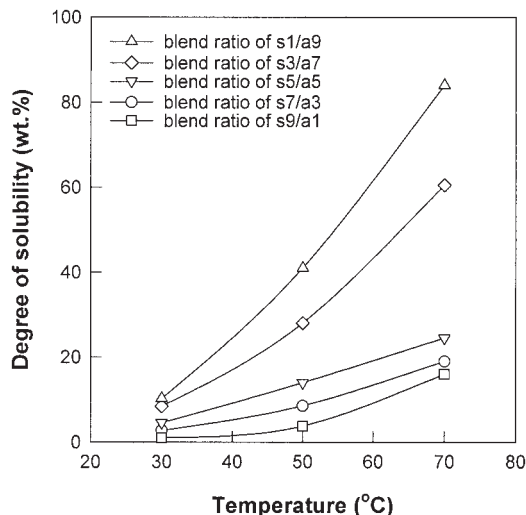


Figure 3 Degree of solubility of s-PVA/a-PVA blend films with different blend ratios in water for 2 h with temperature.

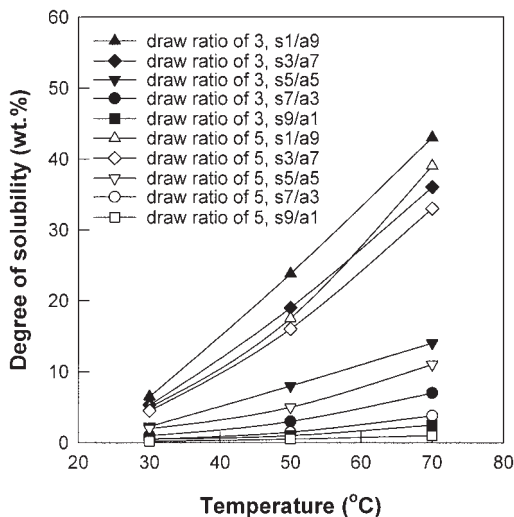


Figure 4 Effects of the draw ratio and solubility test temperature on the water solubility of s-PVA/a-PVA blend films with different blend ratios drawn at 200°C.

cules is higher than that to water, resulting in a much lower degree of solubility than that of blend films with higher a-PVA content. It is clearly shown that syndiotacticity is an essential molecular parameter for suppressing the water solubility of PVA films.

Influence of blend compositions in s-PVA/a-PVA blend films on iodine desorption

Figure 6 shows the desorption of iodine in s-PVA/a-PVA/iodine undrawn film, after treatment in water for 2 h, at treatment temperature. Due to the poor water resistance of a-PVA, iodine desorption of commercial PVA polarizing film in hot water was not measurable. In this study, iodine desorption is considered the percent-

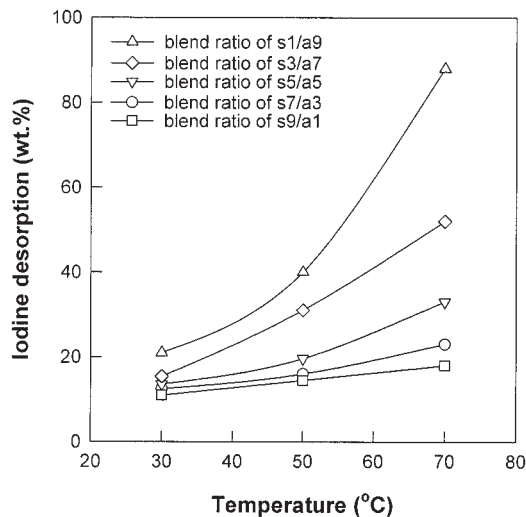


Figure 6 Desorption of iodine in s-PVA/a-PVA/iodine blend films after treatment in water for 2 h with treatment temperature. The s-PVA/a-PVA/iodine blend films were prepared by soaking in aqueous iodine solution (0.1 mol L⁻¹).

age of weight loss of iodine to weight of s-PVA/ a-PVA/ iodine blend films before the desorption experiment. PVA molecules are dissolved in water to some extent as well as iodine. The weight loss caused by dissolution of PVA molecules should be eliminated from the total weight loss of s-PVA/a-PVA/iodine blend films to calculate the weight loss of iodine. The iodine desorption (wt %) was calculated from Eq. (2). The s-PVA/a-PVA/iodine blend films, with higher s-PVA content, showed little difference in iodine desorption with increasing treatment temperature. This means that the desorption of iodine in water was strongly affected by the dissolution of PVA. The desorption of iodine in predrawn s-PVA/a-PVA/iodine blend films in water with treatment temperature is shown in Figure 7. Predrawn s-PVA/a-PVA/iodine blend films were prepared by zone drawing of s-PVA/a-PVA blend films and by subsequent soaking in aqueous iodine solution (0.1 mol l⁻¹) for 60 s. HMW s-PVA/HMW a-PVA/iodine blend films drawn at 200°C showed similar iodine desorption regardless of draw ratio. The desorption also decreased with increased s-PVA content of s-PVA/a-PVA blends. s-PVA/a-PVA/iodine blend films, with s-PVA content over 70%, in particular showed much lower iodine desorption, about 10%.

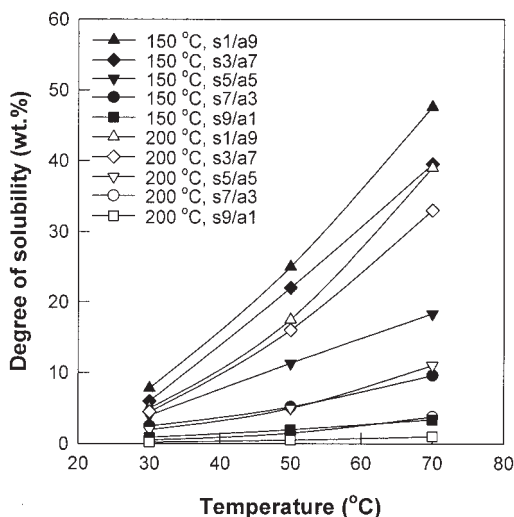


Figure 5 Effects of the drawing temperature and solubility test temperature on the water solubility of s-PVA/a-PVA blend films with different blend ratios drawn five times.

Figure 8 shows a more significant effect on iodine desorption with drawing temperature. At constant draw ratio of 5, the higher the drawing temperature the lower the desorption of iodine. Compared with the results shown in Figure 7, when the film is drawn at constant draw ratio, the desorption of iodine in s-PVA/a-PVA/iodine blend films in hot water preferentially depends on drawing temperature rather than draw ratio. This is in line with the results from Figure 5 and it is supposed that the amount of iodine desorption in water decreases

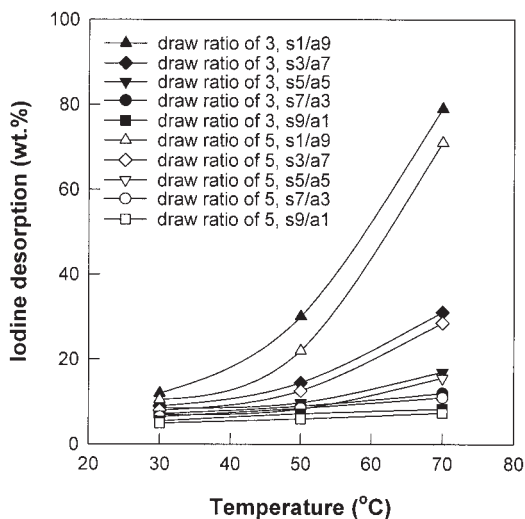


Figure 7 Effects of the draw ratio and blend ratios of s-PVA/a-PVA and water treatment temperature on the desorption of iodine in s-PVA/a-PVA/iodine blend films prepared by drawing at 200°C and subsequent soaking in aqueous iodine solution (0.1 mol L^{-1}) for 60 s.

by decreasing the solubility of s-PVA/a-PVA blends in water, which increases with drawing temperature. From the results described above, therefore, it is identified that polarizing film prepared from HMW s-PVA/HMW a-PVA blends has a high water-resistant quality and longer retention of iodine.

CONCLUSION

To prepare s-PVA/a-PVA/iodine complex blend films with high resistance to water and iodine desorption,

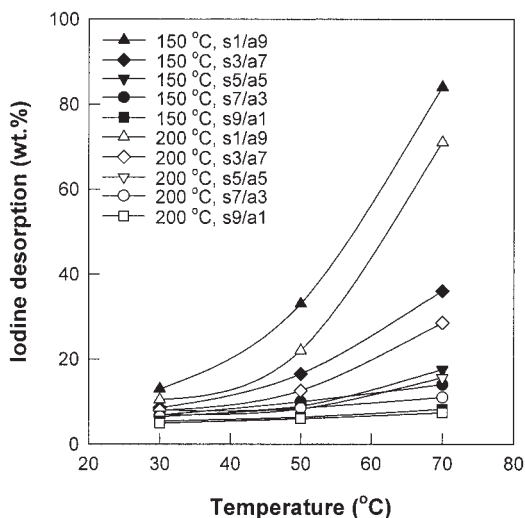


Figure 8 Effects of the drawing temperature and blend ratios of s-PVA/a-PVA and water treatment temperature on the desorption of iodine in s-PVA/a-PVA/iodine blend films prepared by drawing five times and subsequent soaking in aqueous iodine solution (0.1 mol L^{-1}) for 60 s.

we synthesized two PVAs with similar P_n s of 4000 and DSs of 99.9%, but with different s-diad contents of 58.5 and 53.5%, respectively. The blend ratios of s-PVA/a-PVA strongly influenced not only the degree of solubility but also the desorption of iodine in water. The water-resistant quality of the s-PVA/a-PVA blend films with larger s-PVA content at a high temperature was superior to that of s-PVA/a-PVA blend films with lower s-PVA content. The desorption of iodine in s-PVA/a-PVA/iodine blend films, as well as the degree of solubility in s-PVA/a-PVA blend films, decreased outstandingly with an increase of s-PVA content. The degree of iodine desorption of s-PVA/a-PVA drawn film, with s-PVA content of 90%, drawn 5 times at 200°C was only about 7% at 70°C. It was concluded that HMW s-PVA/HMW a-PVA/iodine blend films are the best candidates for replacement material of a-PVA polarizer. In the near future, we will report on the preparation of s-PVA/a-PVA/dye blend films.

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