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High performance films obtained from PVA/Na_2SO_4/H_2O and PVA/CH_3COONa/H_2O systems

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The *atactic* poly(vinyl alcohol) (*a*-PVA) aqueous solutions with Na_2SO_4 or CH_3COONa were cast to prepare films and then the Na_2SO_4 or CH_3COONa in the films was removed. Both films prepared by removing Na_2SO_4 or CH_3COONa in water had a water-resistance property. The degree of crystallization of the films increased with an increase of the contents of Na_2SO_4 and CH_3COONa in the solutions up to 0.05 and 0.1 wt%, respectively. However, the melting temperature (226–228°C) was independent of the content of Na_2SO_4 and CH_3COONa in the solutions. The draw ratio and tensile modulus of the films prepared from the solutions with 0.01 wt% Na_2SO_4 and 0.1 wt% CH_3COONa were 1.3–1.6 times more than that of the films obtained from an aqueous solution. Namely, in case of the films obtained from *a*-PVA/H_2O/Na_2SO_4 and *a*-PVA/H_2O/CH_3COONa systems, both the drawability and mechanical properties as well as the degree of crystallization were higher than those for the film obtained from an aqueous *a*-PVA solution.

1. Introduction

Poly(vinyl alcohol) (PVA) is a non-toxic water-soluble synthetic polymer and is widely used as an engineering material and recently in biochemical and medical fields. PVA with a planar zigzag structure like polyethylene (PE) has the potential to induce high modulus and high strength [1, 2]. The recent investigations have shown that the experimental values of tensile modulus and strength at break for PVA did not reach the theoretical limited values [3–13]. This is considered due to intermolecular hydrogen bond which interfere with drawing.

Authors have found that *atactic* PVA (*a*-PVA) hydrogels with NaCl have got higher melting points (90–100°C) [14, 15] and the film and fiber obtained from *a*-PVA/NaCl/H_2O systems had high degree of crystallization [16, 17]. In this paper, we have evaluated the effects of the addition of sodium sulfate (Na_2SO_4) and sodium acetate (CH_3COONa) on the drawability and physical properties of the films prepared by casting of *a*-PVA/water/Na_2SO_4 or CH_3COONa hydrogel systems. Poly(vinyl alcohol) fiber has been manufactured via wet spinning. Generally, as an effective coagulant, saturated aqueous Na_2SO_4 is used when PVA fiber is manufactured via wet spinning [18], while CH_3COONa is residual in PVA powder after saponification during production.

2. Experimental

2.1. Sample

An atactic PVA (*a*-PVA) offered from Japan Vam & Poval Co., Ltd. was used. The degree of polymerization and the degree of saponification of this polymer were 1730 and 99.5 mol%, respectively.

2.2. Film preparation

The *a*-PVA solutions (5 wt%) were prepared dissolving the *a*-PVA in the aqueous solution with various Na_2SO_4

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and CH_3COONa concentration (0–1 wt%) at 120°C. The films with salts films were obtained by casting the *a*-PVA solutions in a Petri dish (inner diameter is 89 mm) and dried at the room temperature. Na_2SO_4 and CH_3COONa in the films were removed later on by steeping the films in water at 30°C followed by drying. The thickness of the dry films was 31–56 μm.

2.3. Surface and cross-section morphology by scanning electron microscopy (SEM)

Surface and cross-section of morphology of the films were studied using a SEM, S-2830N HITACHI.

2.4. Density and crystallinity of films

The density of films was determined by a floating method in a benzene-carbon tetrachloride mixture. The crystallinity X of films was determined by the following equation [19]:

$$\frac{1}{d} = \frac{X}{1.345} + \frac{1 - X}{1.269}$$

where d is the density (g/cm^3) of the films, 1.345 is the density of crystal region, and 1.269 is the density of the amorphous region.

2.5. Differential scanning calorimetry (DSC)

The measurement of DSC for the films was carried out using a RIGAKU DSC8230 at a heating rate of 20°C/min.

2.6. Drawing

The dry films were drawn until 90% their breaking length in an oven at 200°C and the drawn films were annealed at the same temperature for 10 min in the same oven by fixing the both ends.

2.7. Mechanical properties

The tensile strength and modulus were measured using an NMB TOM-5 tensile tester. The gauge length was set at 10 mm and the crosshead speed was 10 mm/min. From those results, tensile modulus of the dried films was estimated.

3. Results and discussion

The cast PVA films with NaCl had many fine crystals of NaCl on the surface [16]. The extent of phase separation became large when the content of NaCl in the solutions exceeds 5 wt% and many holes were made in the films [16]. However, even the films with 1 wt% Na_2SO_4 and CH_3COONa were transparent or faintly opaque, the Na_2SO_4 and CH_3COONa removed films were transparent. The cast films with 1 wt% NaCl were opaque completely due to NaCl precipitation [16].

Fig. 1 shows the relationships between the content of Na_2SO_4 in the casting films and the standing time in water. Na_2SO_4 in the films was nearly removed when the films were preserved in water for 2 days. Thus in the following part, the films prepared by removing Na_2SO_4 through steeping for 48 h in water were used. For CH_3COONa, the same results were obtained. In all the figures, the content of Na_2SO_4 and CH_3COONa means the values before Na_2SO_4 and CH_3COONa were removed.

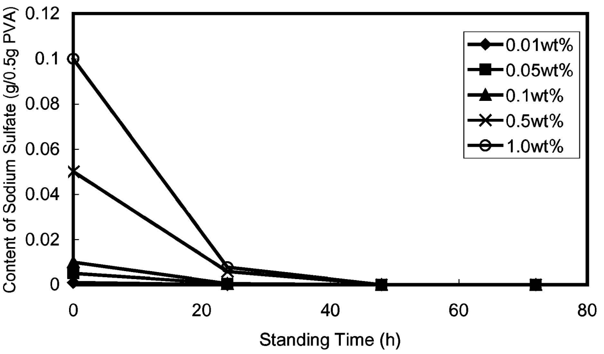
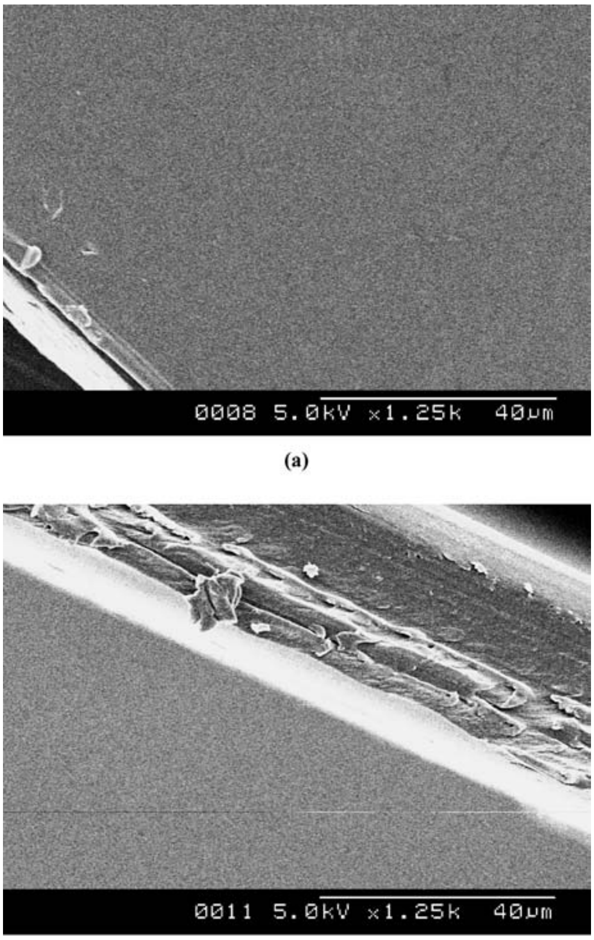


Figure 1 Relationships between the content of Na_2SO_4 in the soaking films and the standing time in water.

Fig. 2 shows the surface (a) and cross-section (b) morphology of the film removed salts (0.05 wt% Na_2SO_4 film). Though the surface is smooth, it can recognize the several thin layers which is piled up to the cross-section even repeatedly. The layers were not



(a)

(b)

Figure 2 SEM photograph for the PVA/Na_2SO_4 0.05 wt% Film. (a) Surface and (b) Cross-section.

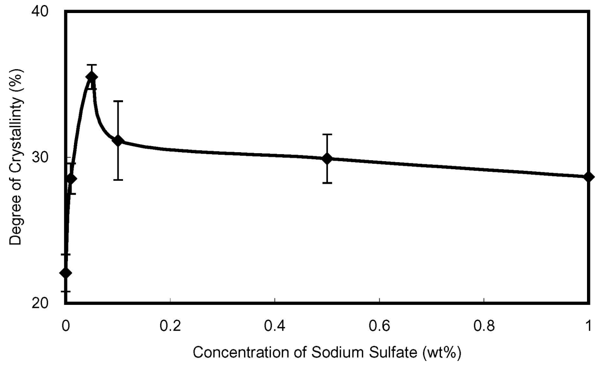


Figure 3 Relation between degree of crystallinity and concentration of sodium sulfate.

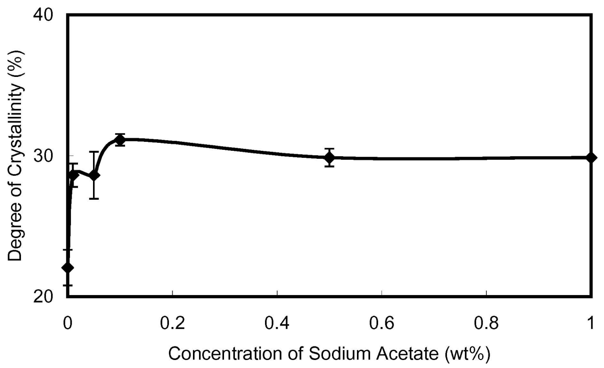


Figure 4 Relation between degree of crystallinity and concentration of sodium acetate.

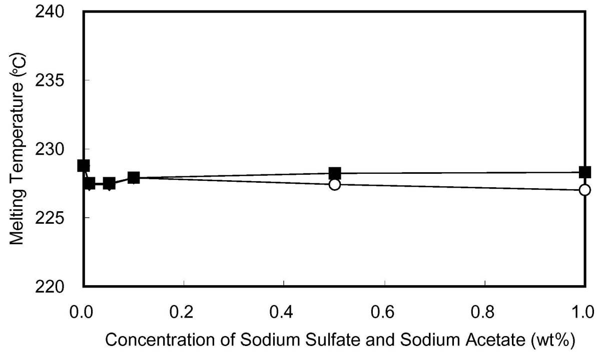


Figure 6 Relation between melting temperature and concentration of sodium Sulfate (○) and sodium acetate (■).

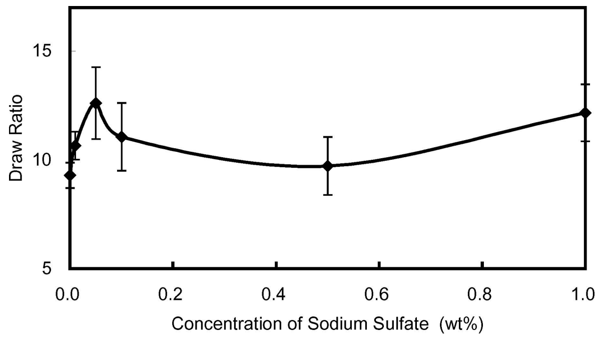


Figure 7 Relation between draw ratio and concentration sodium sulfate.

recognized for the film obtained from the aqueous solution without salts.

Figs 3 and 4 show the relationship between the degree of crystallization estimated from the density and the concentration of Na_2SO_4 and CH_3COONa in the aqueous solution. The degree of crystallization increased with an increase of Na_2SO_4 content up to 0.05 wt% and then it decreased, but it became almost constant when exceeded 0.1 wt%. The peak positions are lower than that (3 wt%) obtained for PVA/NaCl/H_2O system [16, 17]. The degree of crystallization increased with an increase of CH_3COONa content up to 0.1 wt% and then remained constant. Fig. 5 shows the relationships between the heat of fusion obtained from DSC measurement and the concentration of Na_2SO_4. The heat of fusion increased up to 0.05 wt% of Na_2SO_4 content and then decreased. The heat of fusion corresponds to the degree of crystallization shown in Fig. 3. Fig. 6 shows the relationships between the melting temperature obtained from DSC and the concentration of Na_2SO_4 and CH_3COONa. The melting temperature was nearly constant (226–228°C) and was lower than that of film obtained from aqueous solution without salts (ca. 229°C). The results of these thermal analyses show that the size of crystals does not change but the number of crystal changes.

The water resistance of the removed Na_2SO_4 and CH_3COONa films was higher than that of the cast films obtained from aqueous solution. The relationships between the draw ratio of the removed Na_2SO_4 and CH_3COONa films and the Na_2SO_4 and CH_3COONa concentration are shown in Figs 7 and 8, respectively. The draw ratio increased up to 0.05 wt% for Na_2SO_4 concentration and 0.1 wt% for CH_3COONa concentration, then decreased a little and held constant values. The draw ratios of the films cast from the solution containing Na_2SO_4 0.05 wt% and CH_3COONa 0.1 wt%

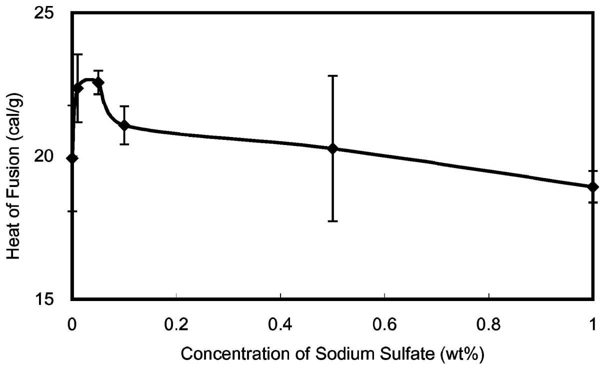


Figure 5 Relation between heat of fusion and concentration of sodium sulfate.

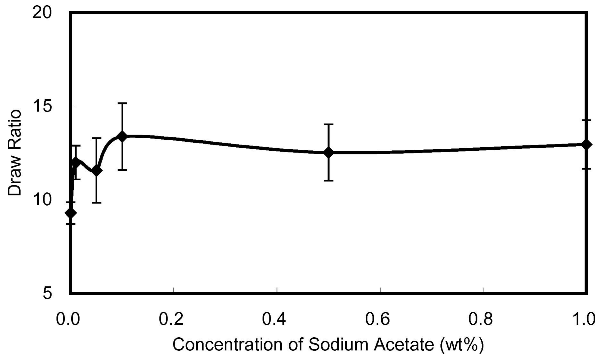


Figure 8 Relation between draw ratio and concentration sodium acetate.

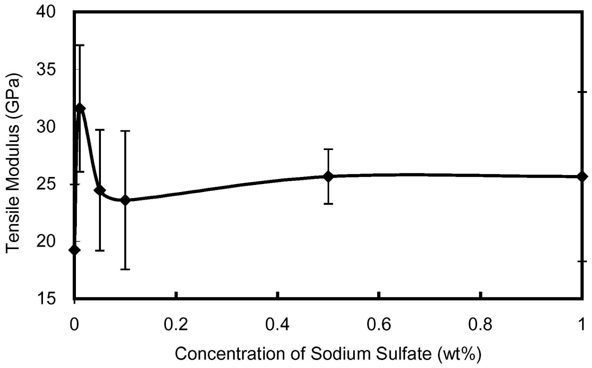


Figure 9 Relation between Young's modulus and concentration of sodium sulfate.

were 1.34 and 1.44 times than that of the films cast from aqueous solution without Na_2SO_4 and CH_3COONa. The films of removed 0.05 wt% Na_2SO_4 and 0.1 wt% CH_3COONa were improved for drawability. In this paper, the drawing of the films with 0.05 wt% Na_2SO_4 and 0.1 wt% CH_3COONa was not done. If it is needed to enhanced the draw ratio of the films in the PVA products plant, the perfect ion washing of PVA powder during preparation of PVA is shown to be unnecessary in the case of drawing.

It is well known that the raw PVA colors to yellow by annealing at 160°C and the color changes to brown with an increment of annealing temperature. The removed Na_2SO_4 and CH_3COONa films drawn at 200°C, however, did not color to light brown. The coloring of films owing to annealing has been described to be suppressed by the addition of alkali [6].

The relationship between the tensile modulus of the removed Na_2SO_4 films drawn until 90% before breaking and the Na_2SO_4 concentration is shown in Fig. 9. The tensile modulus of the films containing 0.01 wt% Na_2SO_4 was 1.6 times (32 GPa) more than that of the films without Na_2SO_4.

4. Conclusion

Generally, the higher the degree of crystallization, the lower the draw ratio for crystalline polymers. In this study, the results obtained were reverse. These results can be understood by considering that suitable networks, which have the drawability to a higher extent, are made after separation of Na_2SO_4 and CH_3COONa [16, 17]. The crystallites which increase with an increase in Na_2SO_4 and CH_3COONa concentration (until 0.05 and 0.1 wt%) of the aqueous solutions are considered to be made during drying process due to hydration ability of sodium, sulfate and acetate ions. This leads the increase in density i.e., crystallites with increasing Na_2SO_4 and CH_3COONa concentration. If the draw ratio can be increased with an increase of the degree of crystallization even for other systems, the innovation of new conception for the dried gel structure is necessary. The method shown in this paper is given attention as a new method for making polymer materials and so we named the salt ions-induced crystallization or the high drawing of polymer materials with ion holes [17].

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