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Preparation of high performance films from poly(vinyl alcohol)/NaCl/H_2O systems

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The atactic poly(vinyl alcohol) (a-PVA) aqueous solutions with NaCl were cast to prepare films and then the NaCl in the films was removed. The films prepared by removing NaCl in water had a water-resistance property. The degree of crystallization of the films increased with an increase of the content of NaCl in the solutions up to 3 wt%. However, the melting temperature (222–225°C) was independent of the content of NaCl in the solutions. The draw ratio and Young's modulus of the films prepared from the solutions with 3 wt% NaCl were about 2.5 and 3 times than that of the films obtained from an aqueous solution. Namely, in case of the films obtained from a-PVA/H_2O/NaCl systems, both the drawability and mechanical properties as well as the degree of crystallization was 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 Young's modulus and strength at break for PVA did not reach the theoretical limited values [3–13]. This is considered due to intermolecular hydrogen bondings which interfere with drawing.

Here we have evaluated the effects of the addition of sodium chloride (NaCl) on the drawability and physical properties of the films prepared by casting of *a*-PVA/water/NaCl hydrogel systems.

2. Experimental

2.1. Sample

An atactic PVA (*a*-PVA) offered from Unitika chemical Co. Ltd. was used. The degree of polymerization and the degree of saponification of this polymer were 1720 and 98.89 mol%, respectively.

2.2. Film preparation

The *a*-PVA (5 wt%) was dissolved in the aqueous solution with various NaCl concentration (0–10 wt%) at 120°C. Blend films were obtained by casting the *a*-PVA solutions in a Petri dish and dried at the room temperature. NaCl in the films was removed later on by steeping the films in water at 30°C followed by drying.

2.3. Degree of swelling

The removed NaCl films were held in water for 48 h at 30°C. The degree of swelling of the removed NaCl films was estimated from the following equation.

$$\text{Degree of Swelling} = \text{Weight of Swelled Films}/\text{Weight of Dried Films}$$

2.4. Drawing

The dry films were drawn in an oven at 200°C or 220°C and the drawn films were annealed at the same temperatures for 10 min in the same oven by fixing the both ends.

2.5. 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 [14]:

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

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.

2.6. Differential scanning calorimetry (DSC)

The measurement of DSC for the films was carried out using a MAC SCIENCE DSC 3200 at a heating rate of 20°C/min.

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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 cross-head speed was 10 min min^{-1}. From those results, Young's modulus of the dried films was estimated.

2.8. X-ray diffraction

X-ray diffraction photographs were taken using a Shimazu XD-610 with a flat camera using Ni filtered Cu K α radiation generated at 30 kV and 30 mA.

3. Results and discussion

The cast PVA films with NaCl had many fine crystals of NaCl on the surface. 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. Though the films with NaCl were white and opaque, the NaCl removed films were transparent.

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

Fig. 2 shows the relationship between the degree of crystallization estimated from the density and the concentration of NaCl in the NaCl aqueous solution. The degree of crystallization increased with an increase of NaCl content up to 3 wt% and then remained constant. Fig. 3 shows the relationships between the heat of fusion obtained from DSC measurement and the concentration of NaCl. The heat of fusion increased up to 3 wt% of NaCl and then remained constant. The heat of fusion corresponds to the degree of crystallization shown in Fig. 2. Fig. 4 shows the relationships between the melting temperature obtained from DSC and the concentration of NaCl. The melting temperature was

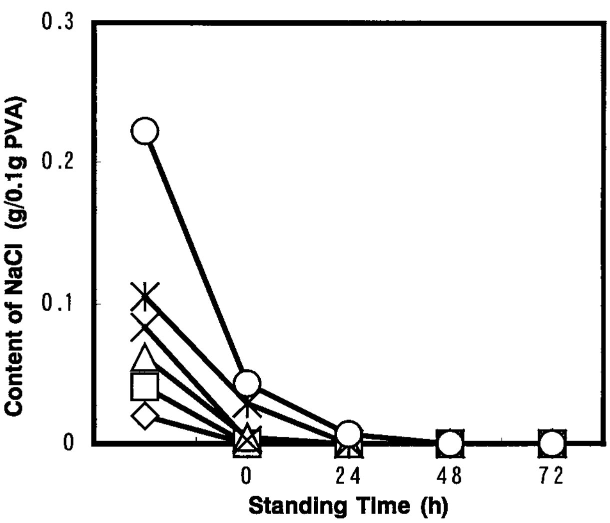

Figure 1 Relationship between standing time and content of NaCl. The concentration of NaCl in the aqueous solution: ○10 wt%, ∗ 5 wt%, × 4 wt%, △ 3 wt%, □ 2 wt%, ◇ 1 wt%.

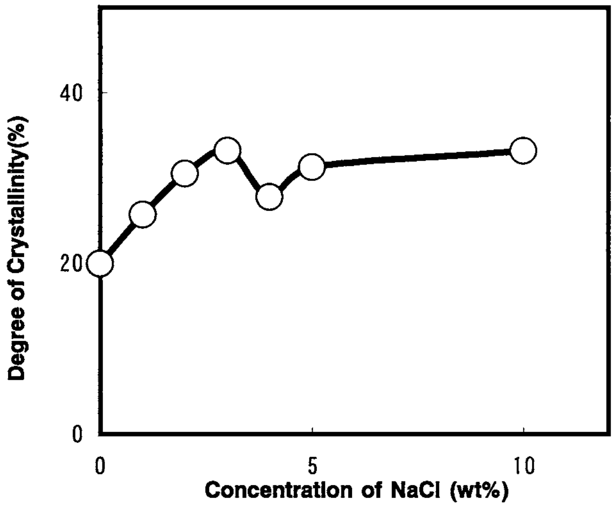

Figure 2 Relationship between degree of crystallinity and concentration of NaCl.

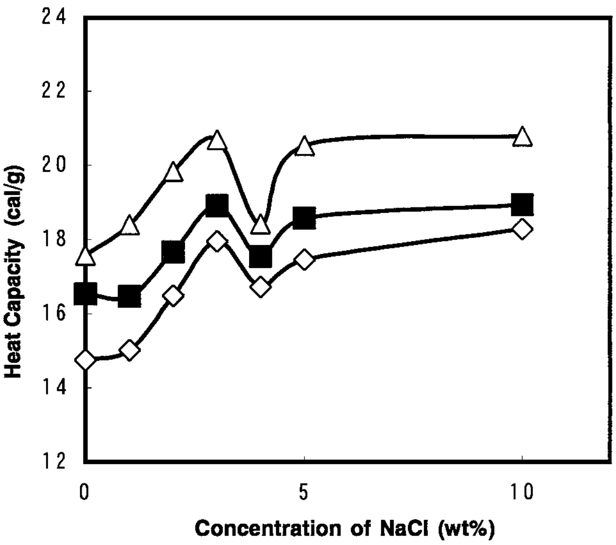

Figure 3 Relationship between heat capacity and concentration of NaCl. ◇ untreated films, ■ heat-treated films under free, △ heat-treated films under fix.

nearly constant (222–225°C). The results of these thermal analyses show that the size of crystals does not change but the number of crystal changes.

Fig. 5 shows the relationships between the swelling ratio of films in water and the concentration of NaCl. The film obtained from an aqueous solution without NaCl swelled considerably accompanying the dissolution of a part. Therefore the swelling rate could not be measured. The degree of crystallization increased with an increase of the NaCl content, but the swelling rate also increased. This result is abnormal. Namely, the water resistance of the removed NaCl film was higher than that of the cast films obtained from aqueous solution. The untreated films prepared by removing NaCl swelled but was insoluble even at 50°C in water. The relationships between the draw ratio of the removed NaCl films and the NaCl concentration are shown in Fig. 6. The draw ratio increased up to 3 wt% NaCl, then decreased a little and held to be constant values. The draw ratio of the films cast from the solution containing 3 wt% NaCl was three times than that of the

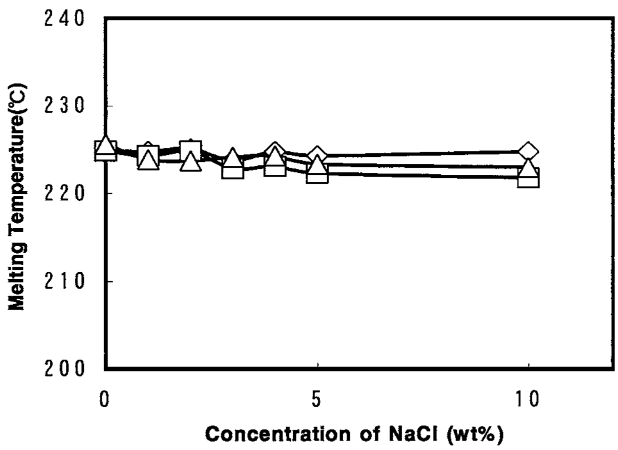

Figure 4 Relationship between melting temperature and concentration of NaCl. ◇ untreated films, □ heat-treated films under free, △ heat-treated films under fix.

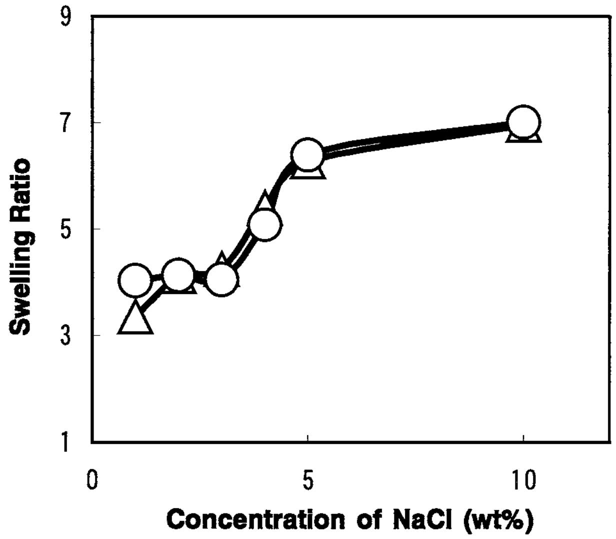

Figure 5 Relationship between swelling ratio and concentration of NaCl. △ 30°C, ○ 38°C.

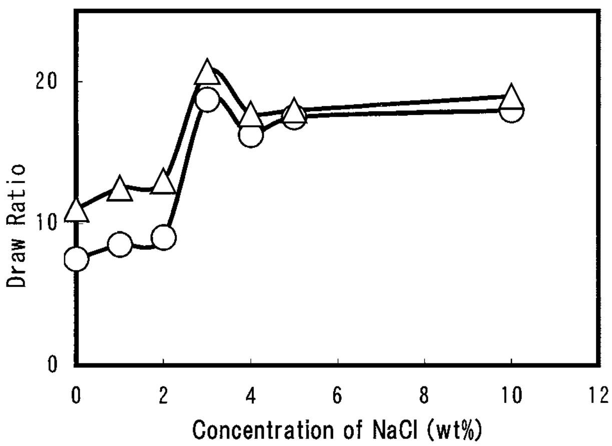

Figure 6 Relationship between draw ratio and concentration of NaCl. ○ 200°C, △ 220°C.

films cast from aqueous solution without NaCl. 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 NaCl films drawn at 200°C 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].

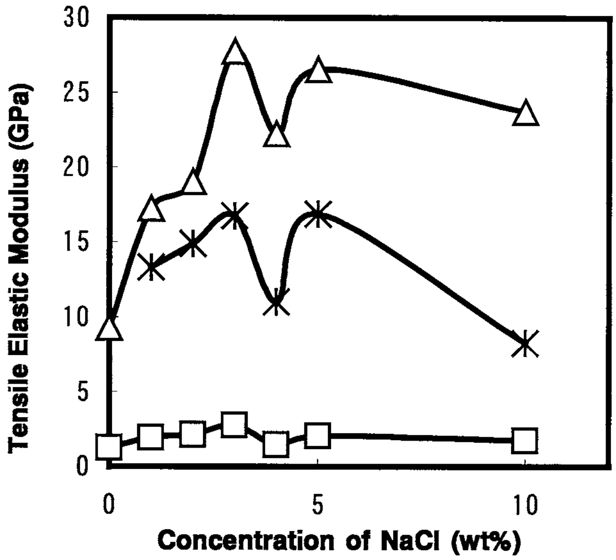

Figure 7 Relationship between modulus and concentration of NaCl. □ undrawn films annealed at 200°C, △ films drawn at 200°C, ∗ films drawn at 200°C after drawing in water.

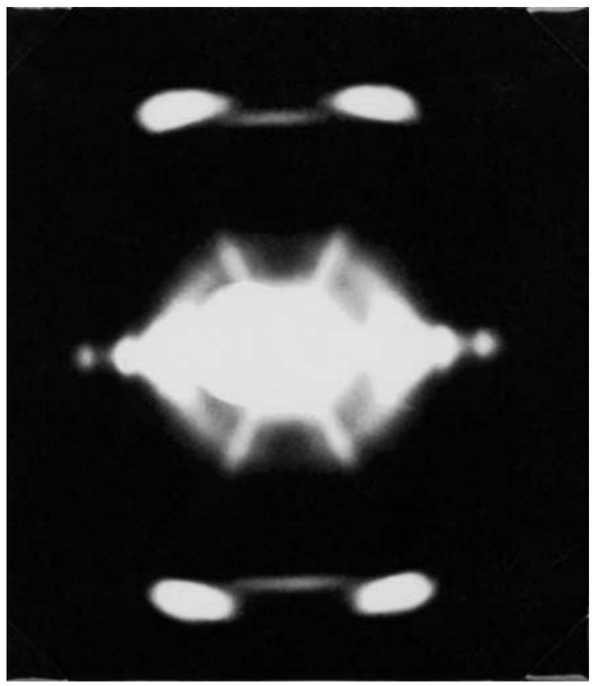

Figure 8 Wide Angle X-ray photograph for the drawn films (NaCl content = 3 wt%, Draw temperature = 200°C, $\lambda = 19$).

In Fig. 6, the draw ratio also at 220°C is shown and was higher than that of drawn at 200°C. Moreover, the latter colored to brown. The draw ratio for the films with 3 wt% NaCl was noticed to be 3 times higher than that of the films without NaCl. So far, it is known that such effect has not been found for PVA blends.

The relationship between the Young's modulus of the removed NaCl films drawn until just before breaking, and the NaCl concentration is shown in Fig. 7. The Young's modulus of the films containing 3 wt% NaCl was three times (30 GPa) than that of the films without NaCl. Fig. 8 shows wide angle X-ray diffraction photograph for the drawn film with the modulus of 30 GPa. The X-ray pattern of the former was more clear than the latter, but was broader than that of gel-spinning PVA fibers.

4. Conclusion

Generally, in crystalline high polymers higher the degree of crystallization, lower the draw ratio. In this study, the results obtained were reverse. These results can be understood by considering that certain polymer aggregates which have the drawability to a higher extent are made after separation of NaCl. The incomplete crystallites which increase with an increase in NaCl concentration (until 3 wt%) of the aqueous solutions are considered to be made during drying process due to hydration ability of sodium and chlorine ions. This leads the increase in density i.e. crystallites with increasing sodium chloride 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.

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