# Effect of degree of saponification on properties of films obtained from PVA/NaCl/$H_2O$ system

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Properties of the film obtained from the solution of *atactic*-polyvinyl alcohol (PVA)/NaCl/$H_2O$ system were investigated through changing the degree of saponification (DS) and NaCl concentration. The films had a higher crystallinity as well as a higher draw ratio than pure PVA film. Maximum values of degree of crystallinity and draw ratio of the films were 38.5% and 17.8, respectively. The highest tensile modulus of the films was at DS 99.05 mol% and NaCl concentration 2 wt.%. These results indicated that the NaCl concentration control has a beneficial effect on properties upgrade of PVA film, but the DS control was effective in control of degree of crystallinity. 

## 1. Introduction

Nowadays, all sorts of materials need to have high added-value, such as low damage for global environment and living body [1, 2]. The poly(vinyl alcohol)(PVA) is applied to various products as the biocompatible and the degradable materials [3–5]. Additionally, the PVA with a planar zigzag structure like polyethylene has the potential to induce the modulus and the strength to close to ideal values which are 250–300 GPa and ∼30 GPa [6–8].

Various investigations have been carried out for upgrade of mechanical properties of PVA products such as gel, film, and fiber [9–17]. In one of them, the PVA hydrogels with the sugars and the salts have been known to get the thermal and mechanical stabilities [18–20]. In our previous studies, the film obtained by casting and the fiber obtained by spinning from the *atactic*-PVA/NaCl/$H_2O$ system at room temperature had got the high crystallinity as well as the high draw ratio after removal of NaCl from the film and the fiber [21, 22]. Moreover, this system excels at low cost and non-toxicity.

Degree of saponification (DS) (degree of hydrolysis) is one of the important factors that determine properties of PVA products [23–26]. In this paper, the change in properties of films obtained from PVA/NaCl/$H_2O$ system was investigated by using different DS PVA samples.

## 2. Experimental

### 2.1. Sample

The *atactic* PVA (*a*-PVA) offered from JAPAN VAM & POVAL Co., Ltd. (former Unitika Chemical Co., Ltd.) was used. The degree of polymerization and the degree of saponification of used samples were shown in Table I. The sodium chloride (NaCl) was purchased from Wako Pure Chemical Industries, Ltd.

### 2.2. Preparation of films

The *a*-PVA was washed by methyl alcohol and then was dried, because sodium acetate remained in the offered PVA powder. Each concentration of NaCl aqueous solutions was controlled at 1, 2, 3, 4 wt.%, and 5 wt.%. The aqueous solution containing PVA and NaCl was maintained a constant weight of PVA (0.5 g). The PVA concentration of each solution was controlled at 5 g/dL.

The PVA/NaCl/$H_2O$ solution was cast on petri dishes (inside diameter was 89 mm) at room temperature after the solution was dissolved at 120°C. The PVA films containing NaCl were obtained by casting at room temperature. These films were soaked in distilled water of 1 L at 30°C until NaCl was removed, exchanging water

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TABLE I PVA samples used

| DS (mol%) | 99.95 | 99.5 | 99.05 | 97.89 | 95.32 | 89.05 |
|---|---|---|---|---|---|---|
| DP | 1730 | 1730 | 1780 | 1780 | 1790 | 1830 |

TABLE II Removal time (h) of NaCl and appearance of dissolution

| Degree of saporufication (mol%) | NaCl concentration (wt.%) | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| 89.05 | × | × | × | × | × |
| 95.32 | × | 48 | 48 | × | 72 |
| 97.89 | 48 | 48 | 48 | 48 | 48 |
| 99.05 | 48 | 48 | 48 | 48 | 48 |
| 99.50 | 48 | 48 | 48 | 48 | 48 |
| 99.95 | 48 | 48 | 48 | 48 | 48 |

×: Films dissolved during removing.

every 24 h. In this time, residual NaCl in the soaked water was checked by silver nitrate aqueous solution. The soaked time of films was shown in Table II. Finally, the removal NaCl films were dried at room temperature. By the way, the films removed NaCl were used for following experiments. The film thickness was ca. 30–50 $\mu$m.

### 2.3. Degree of crystallinity (DC)

The density of films obtained from PVA/NaCl/water system was measured by sink-float method to estimate their degree of crystallinity (DC). In sink-float method, carbon tetrachloride and benzene were used. $X$, the DC of films, was determined by following equation:

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

where, $d$ is density of films.

### 2.4. Draw ratio (DR)

The film was cut into 30 × 2 mm and each of both ends was clamped 10 mm by sandpaper. The films were drawn in an oven at 200°C after annealing at the same temperature for 10 min. The draw rate was 0.5 mm/s.

### 2.5. DSC

DSC studies were conducted using a RIGAKU DSC 8230. The measurement of DSC for the films was carried out at a constant heating rate of 20°C/min.

### 2.6. Mechanical properties

The sample was prepared in the same shape as described in par. 2.4. These samples were annealed at 200°C for 10 min, and then they were drawn until 0.9 times their breaking length. Each of both ends of the drawn samples were clamped 10 mm by sandpaper after being cut into 30 mm. The tensile modulus and the strength at break of these samples were measured by TCM-50G.

### 2.7. X-ray diffraction

The photograph of wide angle X-ray diffraction was taken by a SIMAZU XD-610 with a flat camera using Ni filtered CuK$\alpha$ radiation generated at 30 kV and 30 mA.

## 3. Results and discussion

### 3.1. Appearance of the films

For all the films before NaCl was removed, precipitates of NaCl were found, but the films became transparent after removing NaCl. All the films of DS 89.05 mol% and a part of the films of DS 95.32 mol% dissolved in water (Table II). It was indicated that the film had a water-stable structure at the particular NaCl concentration, because the insoluble film existed discontinuously against NaCl concentration in DS 95.32 mol%. In the following sections, the properties of the films with DS above 97.89 mol% were measured.

### 3.2. Properties of the films

The results of degree of crystallinity (DC) that were calculated by densimetry, are shown in Fig. 1. The PVA

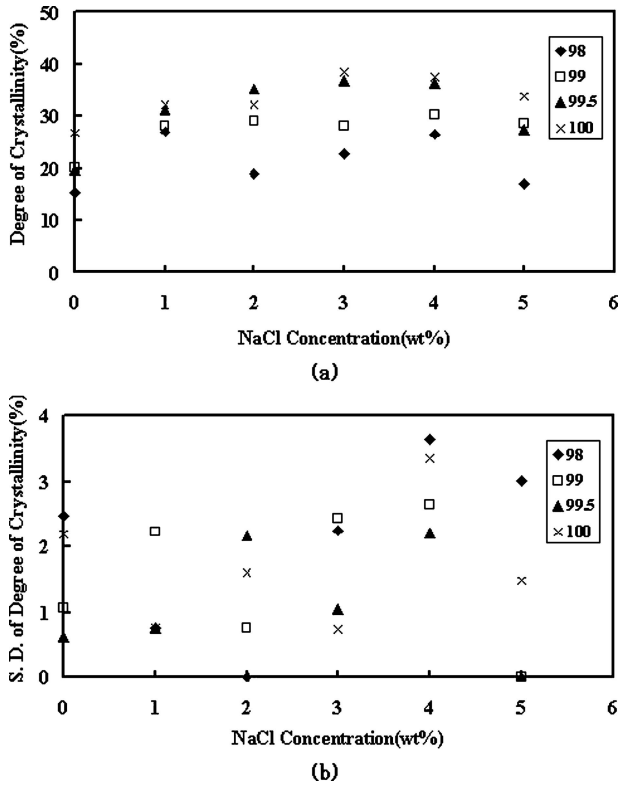


*Figure 1* Relationships between NaCl concentration and degree of crystallinity for the films of PVA with different DS.

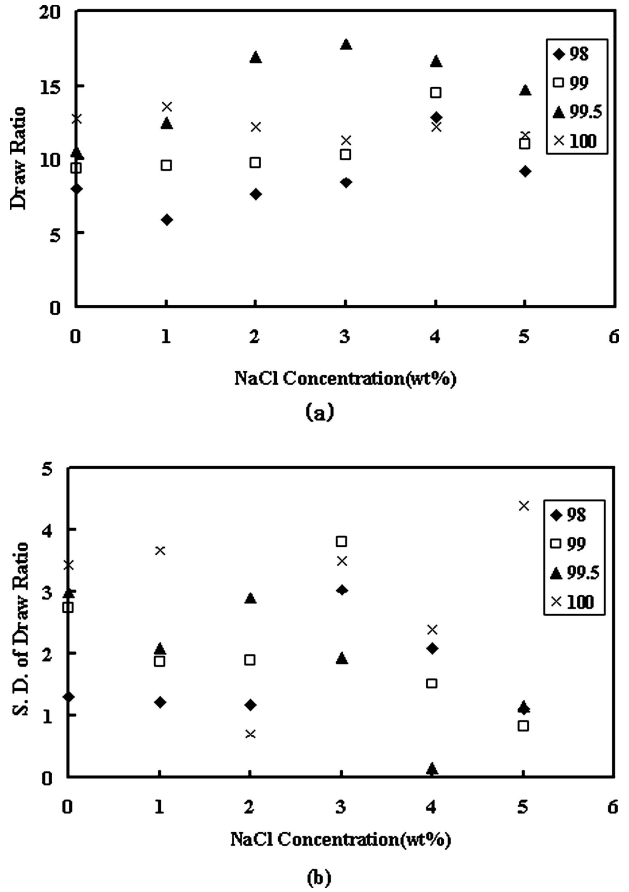


*Figure 2* Relationships between NaCl concentration and draw ratio for the films of PVA with different DS. (a) Draw ratio, (b) S.D. of the draw ratio.

products have got higher DC if PVA of higher DS is used. However, one film of DS 99.5 mol% had higher DC than films of 99.95 mol%. DR for some films of DS 99.5 mol% was higher than that of others. In addition, one of the DS 99.05 mol% films had the best performance in the mechanical properties (Figs 2 and 3). These films were prepared with NaCl concentration ranging from 2 to 4 wt.%. In this range of concentrations, DR and DC of the films were enhanced regardless of DS, especially at the same time. Strength at break of all films was below 1 GPa. The value was less than that mentioned in our previous study [21].

The relation between NaCl concentration and the melting temperature obtained from DSC thermogram is shown in Fig. 4. The melting temperature of the films except DS 99.95 mol.% dropped slightly than that of pure-PVA film, and then became approximately constant regardless of NaCl concentration. The heightening of melting temperature attributes to an increase of the scale of the microcrystals. In this case, hence, the size of microcrystals in crystal region reduced although DC increased. It means that the number of small-size microcrystals increased and the microcrystals distributed more homogeneously than film of PVA only.

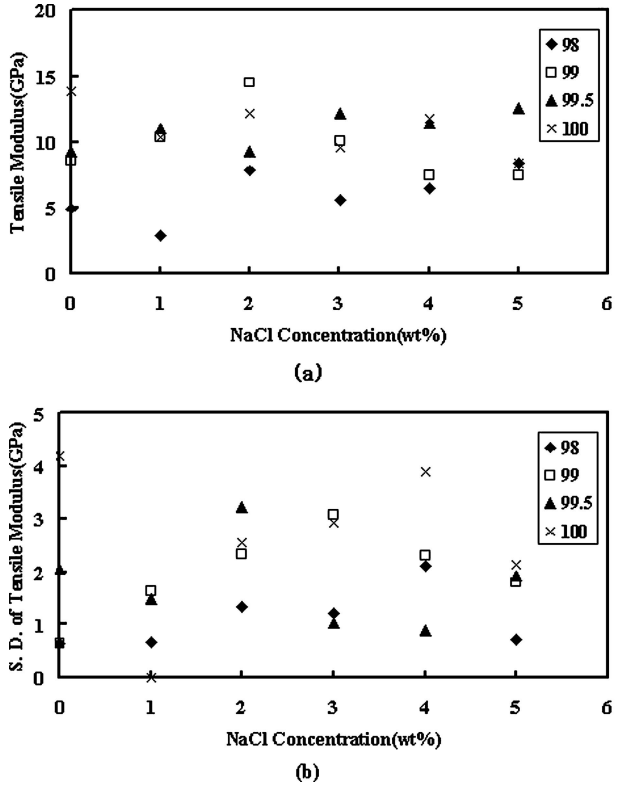


*Figure 3* Relationships between NaCl concentration and tensile modulus for the films of PVA with different DS. (a) Tensile modulus, (b) S.D. of the tensile modulus.

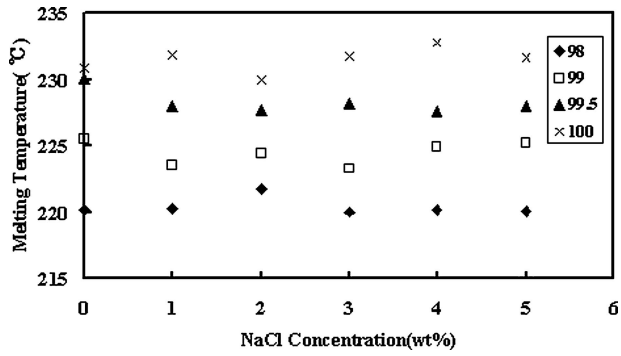


*Figure 4* Relationships between NaCl concentration and melting temperature for the films of PVA with different DS.

The films which DS was 99.95 mol% had low-DR tendency. It was considered that few PVA molecules in the films moved more easily than those in the films of 99.5 mol% and 99.05 mol% films, because the heat treatment temperature (at 200°C) was set up low against melting temperature of 99.95 mol% films. Conversely, the applied heat was excessive against melting temperature of 97.89 mol% films, that was speculated one of the causes of lower DR of 97.89 mol% films. X-ray diffraction pattern was shown in Fig. 5. The diffraction pattern of film changed scale of broad along DR.

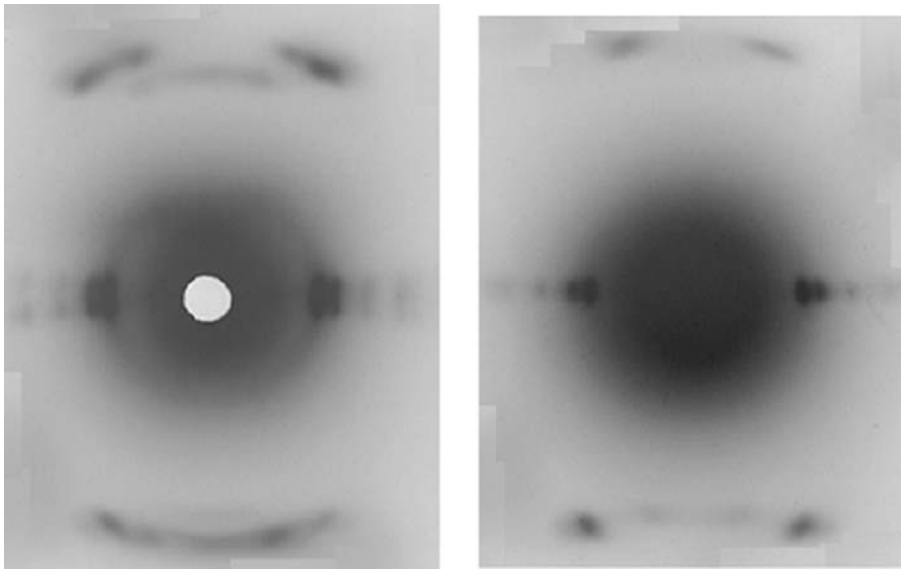

*Figure 5* Wide angle X-ray photographs for the drawn films. (a) DS = 99.5 mol%, NaCl Conc. = 0 wt.% film, λ = 10.7; (b) DS = 99.5 mol%, NaCl Conc. = 3 wt.% film, λ = 17.8.

## 4. Conclusion

The change of DS affected mainly the scale of microcrystals in PVA/NaCl/$H_2O$ system. However, influence of NaCl was more distinct than that of DS. The slight difference of DS in the category of fully hydrolyzed PVA, less than 1 mol%, could cause a change of properties.

Tensile modulus was best improved when a combination of DS 99.05 mol% and NaCl concentration 2 wt.% was formed. Moreover, it was confirmed influence of NaCl on the properties of PVA films.


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