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Spinning of the solutions of poly(vinyl alcohol)/ NaCl/H_2O systems and their fiber properties

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The NaCl/water solutions of commercial poly(vinyl alcohol) (*a*-PVA) with the degrees of polymerization and saponification of 1730 and 99.39%, respectively were gel-spun into methanol (−30°C) and then the removed NaCl dry-filaments were drawn at 200°C. The draw ratio showed the maximum at NaCl concentration $C_N = 3$ wt% (polymer concentration $C_P = 150$ kg/m^3). The Young's modulus and strength at break were 95 and 6 GPa ($\lambda = 19$). In the case of DMSO system ($C_P = 170$ kg/m^3), the Young's modulus was 52 GPa ($\lambda = 25$) and the strength at break was 3.3 GPa. Under a polarized microscope, the fine lateral structure was observed for the DMSO system, but not for the NaCl system, that is, the smooth structure was recognized. The smooth structure, like a Netlon packing net for oranges, might be considered to result in heightening of mechanical properties.

1. Introduction

The preparation of ultrahigh modulus polyethylene (PE) fibers and films from the ultra drawing of dried gels, produced by gelation from semi dilute solution, has been extensively studied in recent years [1–5]. Matsuo and Sawatari produced ultrahigh drawn PE with a Young's modulus at 20°C of 216 GPa [5]. Poly(vinyl alcohol) (PVA) with a planar zigzag structure, such as PE, has the potential to induce high modulus and high strength. The crystal modulus of PVA and the strength of perfectly oriented PVA fiber are high; they are estimated to be 250–300 GPa and ∼30 GPa, respectively [6, 7]. To this day, despite various attempts the limiting values have not been obtained experimentally for PVA [8]. Recently, numerous studies have been reported [9–15]. A Young's modulus of 115 GPa is the highest value reached so far [16]. It does not reach the theoretical values. This is considered to be caused by intermolecular hydrogen bonding, which interferes with drawing.

Authors have found that *atactic* PVA (*a*-PVA) hydrogels with NaCl have got higher melting points (90–100°C) [17, 18] and the film obtained from *a*-PVA/NaCl/H_2O systems had high degree of crystallization [19]. In this paper, we carried out the spinning of the solutions of *a*-PVA/NaCl/H_2O systems and the drawing of filaments obtained, and examined the effect of NaCl on the drawing.

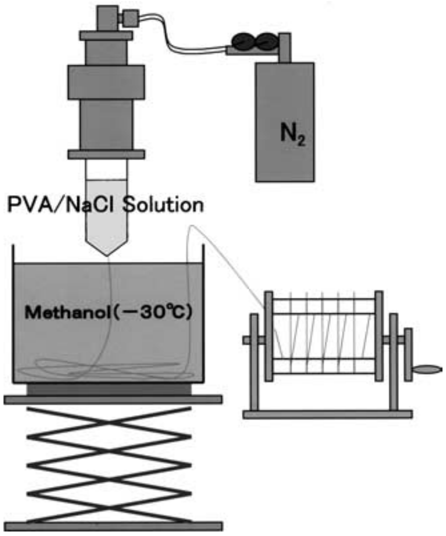

Figure 1 Diagram of spinning process.

2. Experimental

2.1. Samples

A PVA (*atactic* PVA, *a*-PVA) derived from vinyl acetate, supplied from Unichica Chemical Co. Ltd. was used. The degrees of polymerization and saponification were 1730 and 99.39 mol%, respectively.

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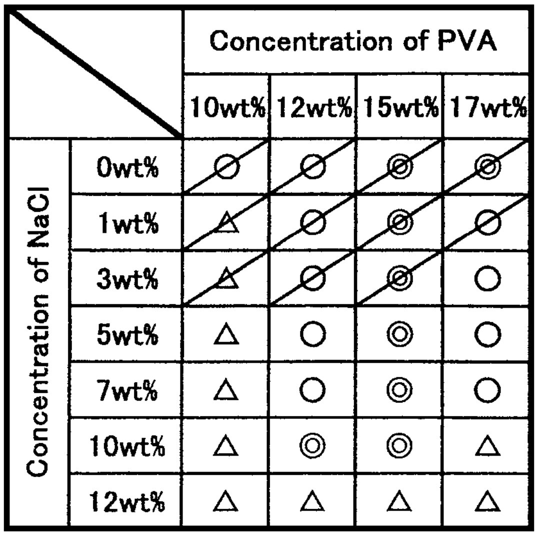
2.2. Solutions and spinning

The PVA Solutions were prepared in a sealed tube at 120°C. Mixed solutions of NaCl and water were used as solvent. The spinning apparatus shown in Fig. 1 was used for the spinning. The solutions (at about 30°C) were extruded into a methanol bath at −30°C, the filaments were kept there for 2–3 h, then wound around on a reel in air and dried. The dry filament with NaCl was washed in water and then dried. The dry filaments

TABLE I Results of spinning



Concentration of NaCl		Concentration of PVA			
		10wt%	12wt%	15wt%	17wt%
	0wt%	○	○	◎	◎
	1wt%	△	○	◎	○
	3wt%	△	○	◎	○
	5wt%	△	○	◎	○
	7wt%	△	○	◎	○
	10wt%	△	◎	◎	△
	12wt%	△	△	△	△

The shaded portion: as-spun filaments are opaque.
△: fiber-like, but heterogeneous.
○: fiber-like.
◎: homogeneous fiber and continuous formation.

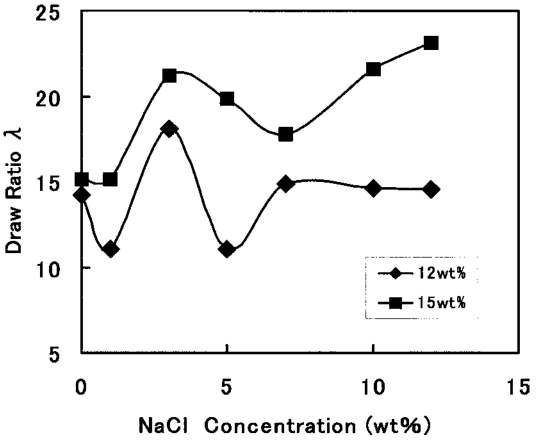


Figure 2 Relationship between draw ratio and concentration of NaCl for filaments drawn at 200°C (C_P = 12 and 15 wt%).

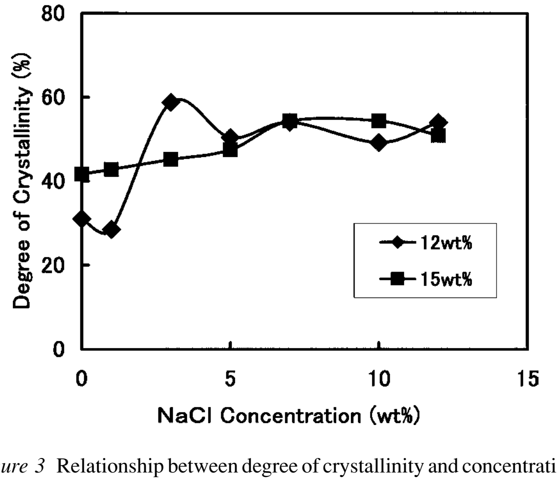


Figure 3 Relationship between degree of crystallinity and concentration of NaCl for filaments drawn at 200°C (C_P = 12 and 15 wt%).

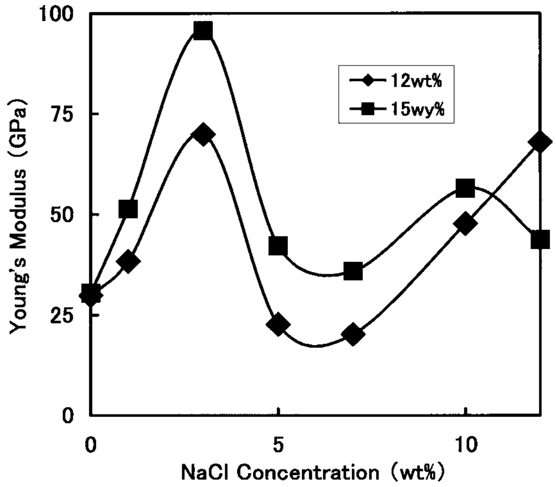


Figure 4 Relationship between Young's modulus and concentration of NaCl for filaments drawn 90% of length at break at 200°C (C_P = 12 and 15 wt%).

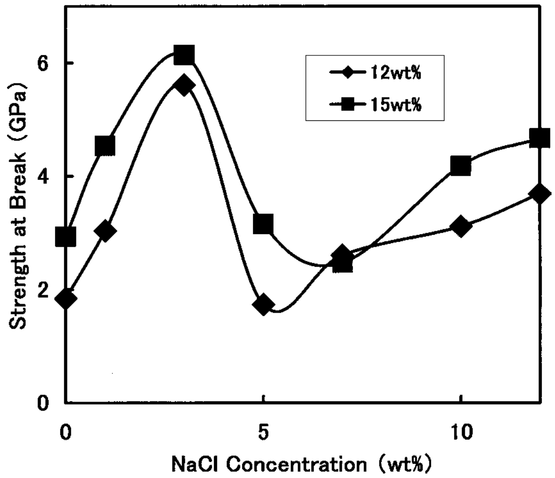


Figure 5 Relationship between strength at break and concentration of NaCl for filaments drawn 90% of length at break at 200°C (C_P = 12 and 15 wt%).

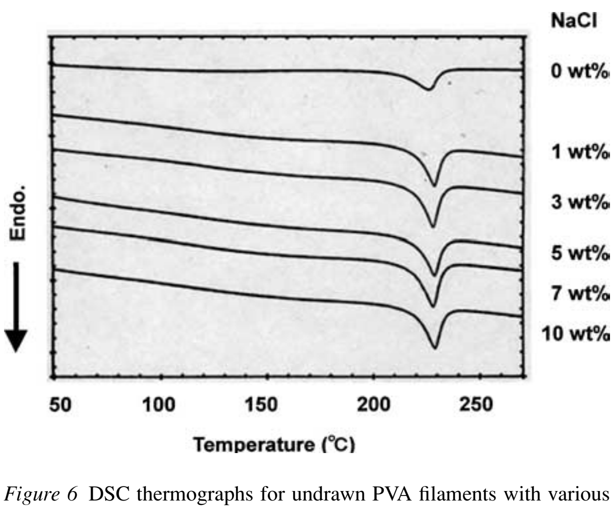


Figure 6 DSC thermographs for undrawn PVA filaments with various different concentration of NaCl (C_P = 12 wt%).

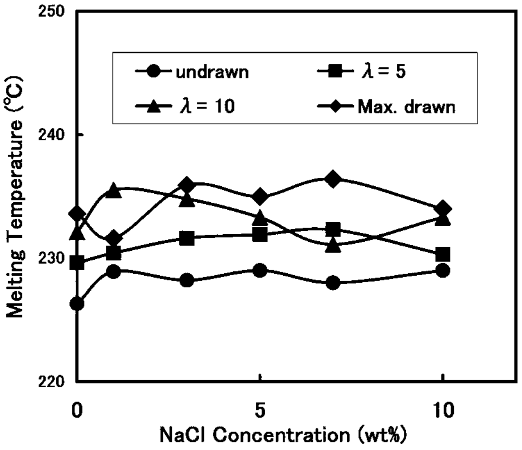


Figure 7 Relationship between melting temperature and concentration of NaCl for filaments with various draw ratio ($C_P = 12$ wt%).

were drawn in an oven. For comparison, the solutions of PVA/DMSO/H_2O system (about 30°C) were also extruded into a methanol bath at −30°C to form filaments. The PVA was dissolved in the 80 vol% DMSO and 20 vol% water mixture in a sealed test tubes at about 120°C.

2.3. Measurements of properties of filaments

Tensile properties of filaments were measured using a tensile tester of a TOM/5 type of Shinko Tsushin Kogyo (Japan) at 200°C and relative humidity about 50%. The microscope observation was performed using an Olympus BHSM (Olympus, Lake Success, NY, USA). The thermal properties of the filaments were tested at a heating rate of 20°C/min using a differential scanning calorimeter (DSC3200) made by Mac Science Co. Japan. The melting points of the filaments were taken as the maximum of the melting curves. The density of filaments was determined by floatation in a benzene-carbon tetrachloride mixture. X-ray diffraction pattern was recorded with a flat camera in a Shimadzu X-ray reflection apparatus XD-610 (Cu-K_α X-ray, 30 kV, 30 mA; Shimazu, Kyoto, Japan).

3. Results and discussion

3.1. Spinning

Table I shows the spinning results for the solutions of *a*-PVA/NaCl/H_2O systems. The solutions with polymer concentration C_P = 120–150 kg/m^3 were spun stably,

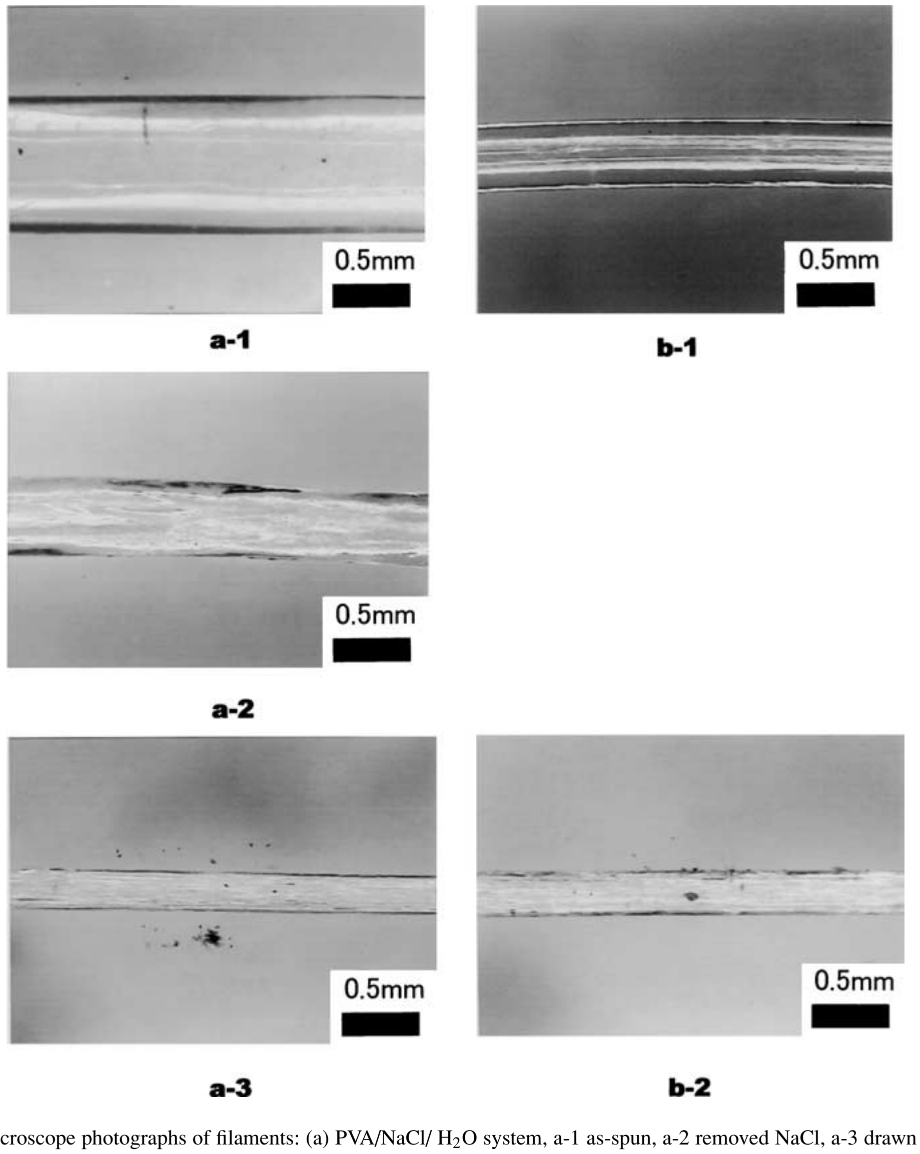


Figure 8 Optical microscope photographs of filaments: (a) PVA/NaCl/ H_2O system, a-1 as-spun, a-2 removed NaCl, a-3 drawn filament of a-2, (b) PVA/DMSO/H_2O system, b-1 as-spun, b-2 drawn filament of b-2.

especially at $C_P = 150\,\text{kg/m}^3$. The drawn filaments that were extended to 90% of the draw ratio at break were used for mechanical measurement. At NaCl concentration $C_N = 3$ wt% or less, the filaments were opaque and at $C_N = 5$ wt% or over, they were transparent. In the case of PVA/DMSO/H_2O systems, the spinning was carried out stably in the range of polymer concentration $C_P = 100$–$170\,\text{kg/m}^3$.

3.2. Drawing of filaments and the crystallinity

Fig. 2 shows the relationship between the draw ratio and NaCl content after extracting salt. The draw ratio showed a maximum at $C_N = 3$ wt% ($C_P = 150\,\text{kg/m}^3$, draw ratio $\lambda = 23$). The tendency was similar to that of casting film for *a*-PVA/NaCl/H_2O systems [19]. Comparing with casting film, in the case of the spun filament, an increment in draw ratio at $C_N = 3$ wt% was smaller than that when no-addition was made. It is thought that the structure formation in the latter film causes very slowly compared with that of the former filament. The draw ratio of the DMSO system ($C_P = 100\,\text{kg/m}^3$; $\lambda = 18$, $C_P = 170\,\text{kg/m}^3$; $\lambda = 28$) was higher than that for the NaCl system on the basis of polymer concentration.

Fig. 3 shows the relationship between the degree of crystallinity and NaCl content after drawing 90% of

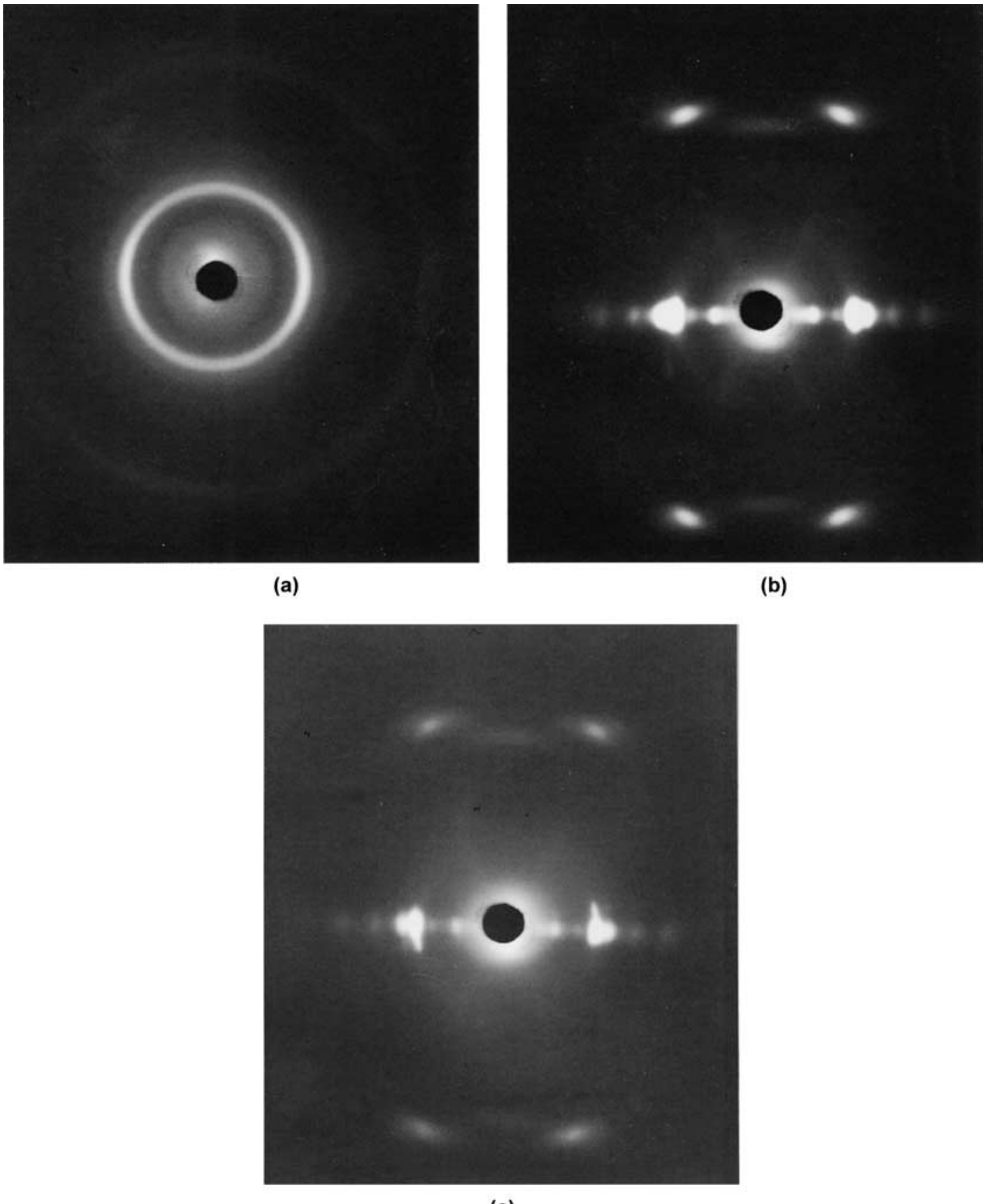

(a)
(b)
(c)

Figure 9 Wide angle X-ray photographs: (a) PVA/NaCl/H_2O system, as-spun, $C_N = 3$ wt%, $C_P = 15$ wt%, (b) drawn filament of a-1 ($\lambda = 19.1$), and (c) PVA/DMSO/H_2O system, $C_P = 17$ wt%, $\lambda = 24.8$.

breaking length. The result was similar to that of draw ratio shown in Fig. 2 for $C_P = 120$ kg/m^3, but for $C_P = 150$ kg/m^3 the similarity was low. The maximum degree of crystallinity was 60% at $C_N = 3$ wt% for $C_P = 120$ kg/m^3. For the DMSO system, the degree of crystallinity decreased with an increase of PVA concentration ($C_P = 100$–170 kg/m^3) and the maximum was 54% at $C_P = 100$ kg/m^3.

3.3. Mechanical properties of filaments

Figs 4 and 5 show the relations between the Young's modulus or the strength at break and the draw ratio for the filaments of *a*-PVA/NaCl/H_2O systems ($C_P = 120$ and 150 kg/m^3).

Both the Young's modulus and the strength at break showed the maximum at $C_N = 3$ wt%. The Young's modulus of $C_P = 120$ and 150 kg/m^3 ($\lambda = 16$ and 19) was 70 and 95 GPa and the strength at break of $C_P = 120$ and 150 kg/m^3 were 5.5 and 6 GPa, respectively. In the case of DMSO system ($C_P = 150$ and 170 kg/m^3), the Young's modulus were 27 and 52 GPa ($\lambda = 20$ and 25) and the strength at break were 2.5 and 3.3 GPa, respectively. Although the draw ratio of the former is lower than that of the latter, the mechanical properties of the former were higher than that of the latter one. Moreover, in order to raise the mechanical properties, neither the formation of polymers with high stereoregularity nor ultra-high molecular weight is needed.

3.4. Thermal properties of filaments

Fig. 6 is the DSC curves of the undrawn PVA filaments ($C_P = 120$ kg/m^3) with various different concentrations of NaCl. The temperature at the peak (the melting point) was constant and independent on C_N, namely about 228°C. The heat of fusion increased slightly with increase in NaCl concentration until $C_N = 3$ wt% and then it was constant.

Fig. 7 shows the relation between the melting point and the NaCl concentration for the samples with various draw ratios. The melting point increased with an increase of draw ratio and it was about 235°C at the draw ratio just before fracture. These results were similar to that of the casting films [19].

3.5. Morphology of filaments

Fig. 8 shows the optical microscopic photographs of filaments. In the case of undrawn filaments (a-1 and b-1), the difference in both filaments can be recognized slightly. In the case of filament of DMSO system (b-1), three-phase structure can also be recognized. But in the case of drawn filaments (a-3 and b-2), the difference in both filaments is not clear.

Fig. 9 shows the wide angle X-ray diffraction patterns of both filaments. For drawn filaments, though the draw ratio is recognized to be different for the both filaments, the X-ray diffraction patterns are fairly similar.

Fig. 10 shows polarized microscopic photographs of drawn filaments. The fine lateral structure, that is, the band structure can be observed for the DMSO system (b), but not for the NaCl system (a). The band structure found in the previous paper has been considered to be formed as a results of the breakdown of microfibrils aligned along with the fiber axis because of the

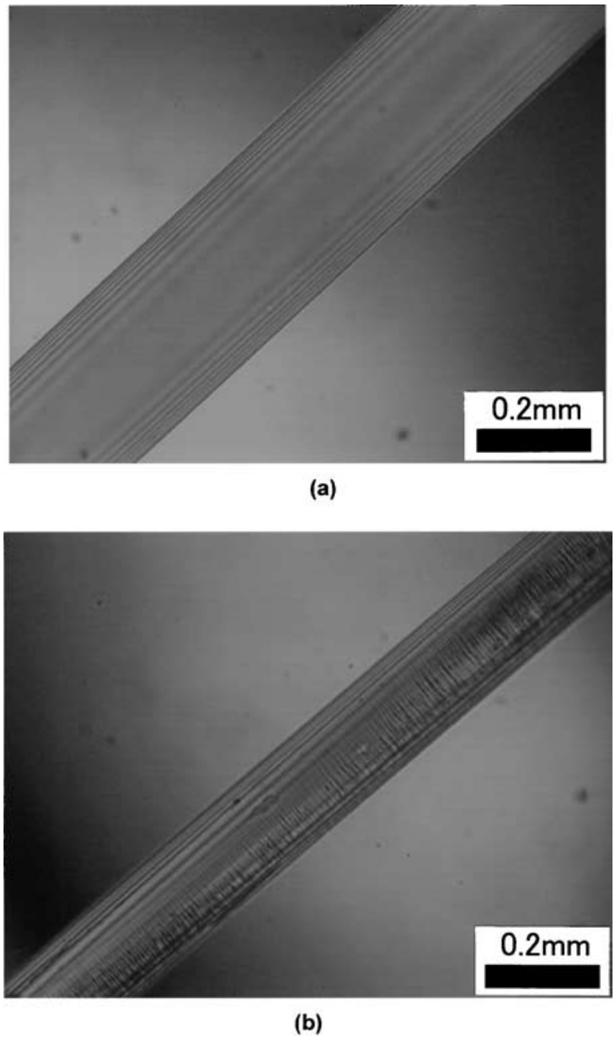


Figure 10 Polarized microscope photographs of drawn filaments: (a) PVA/NaCl/H_2O system, as-spun, $C_N = 3$ wt%, $C_P = 15$ wt%, $\lambda = 19.1$ and (b) PVA/DMSO/H_2O system, $C_P = 17$ wt%, $\lambda = 24.8$.

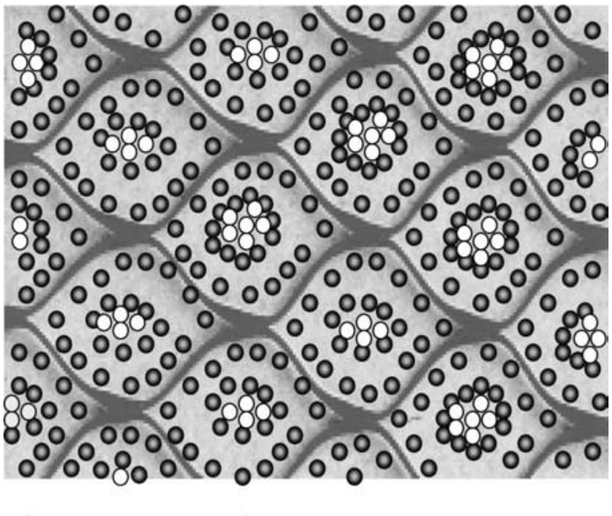


Figure 11 Ideal two-dimensional structure model in filament of PVA/NaCl/H_2O system.

drawing at high temperature [15]. The band structure is considered here to result in lowering of mechanical properties.

3.6. An ideal structure model in filaments of PVA/NaCl/H_2O system

Fig. 11 shows the two-dimensional structure model in the filament of the PVA/NaCl/H_2O system. In the optimum PVA/NaCl/H_2O system, if it is considered that homogenous phase separation occurs and the length of the amorphous chains between crystallites is equal, it seems to resemble the "Netlon" type of packing net for oranges. If the net is pulled, the networks close only, but the strands between the bonding points do not break easily. However, if gels, films and fibers are considered, it is finally necessary to replace the two-dimensional structure model with the three-dimensional structure model.

4. Conclusions

NaCl/water solutions of *a*-PVA with the degrees of polymerization and saponification of 1730 and 99.39% were gel-spun into methanol (−30°C), and the removed NaCl dry-filaments obtained were drawn at 200°C. The draw ratio showed the maximum at NaCl concentration $C_N = 3$ wt% (polymer concentration $C_P = 150\,\mathrm{kg/m^3}$). The Young's modulus and strength at break were 95 and 6 GPa ($\lambda = 19$), respectively. In the case of DMSO system ($C_P = 170\,\mathrm{kg/m^3}$), the Young's modulus was 52 GPa ($\lambda = 25$) and the strength at break was 3.3 GPa. Under a polarized microscope, the fine lateral structure can be recognized for the DMSO system, but not for the NaCl system, that is, the smooth structure was observed. The smooth structure might be considered to result in heightening of mechanical properties. As a result, it was not necessary of ultra high molecular weight or high stereoregularity to obtain higher mechanical properties.

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