고강도 폴리비닐알코올 섬유 개발

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High-Strength Poly (Vinyl Alcohol) Fibers

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1. Introduction

The theoretical modulus and strength for the PVA fiber was calculated to be 2251 g/d and 236 g/d, respectively. To enhance mechanical properties, organic solvent has been introduced such as, glycerin(GC), ethylene glycol(EG), ethyleneurea for dry spinning[1] and dimethyl sulfoxide(DMSO) with non-solvent coagulating bath for wet spinning[2]. By using these methods, 20g/d of tensile strength and 500g/d of initial modulus could be achieved.[3]

To get excellent mechanical properties, some conditions should be satisfied. (I) spinning dope solution has no phase separation, (II) the crystallite for the junctions in gel should not grow that big, (III) appropriate concentration is needed to control entanglement density. In summary, size and spatial distribution of crystallites should distributed evenly and crystallite size must be small to be drawn easily. These conditions can be satisfied by gel-spinning of PVA solutions from water/DMSO mixed solvent.

2. Experimental

2.1 Spinning dopes

The at-PVA powder is supplied by Unitika Co.,LTD, Osaka, Japan and it's viscosity-average degree of polymerization is 5000 with degree of saponification of 99.5 mol%. Extra pure DMSO(Oriental chemical industry) and deionized water is used as solvent. Solutions are made at 105℃ for 1 hours and then stored at 85℃ overnight to homogenize and remove bubbles.

A at-PVA was produced from the PVAc by a photoinduced emulsion polymerization, which has DP of 5000 and degree of branch of 0.3.

The PVA concentration for the gel-spinning/drawing was 6wt%, which gave the maximum draw ratios for the gel-spun fibers.

2.2 Gel spinning

Solutions kept at 70 ℃ extruded into open air through nozzle having hole size of 0.2 mm by a metering pump, then immediately coagulated in methanol coagulation bath(-20±1℃).

2.3 Drawing of fibers

Hot drawing of fibers are performed in silicone oil bath at 140℃ and 200℃ using hand-driven drawing apparatus. Tensile tests of the PVA fibers conducted with 3 cm gauge length and crosshead speed of 30 mm/min. The tensile test machine was product of ORIENTEC Corp.(RTM-500).

2.4 XRD and birefringence

Equitorial diffractogram the drawn PVA fiber was obtained by thin film X-ray diffractometer(Philips X'pert MPD). The incident angle was 1.5° and 2 theta range was from 5° to 50° . Birefringence of the drawn PVA was measured by a Nikon polarizing microscope with the compensators.

3. Results and discussion

Many inventors have reported aqueous PVA solutions have spinodal phase separation and this causes unevenly distributed crystallites. Takeshita et al., reported that solvent mixtures ranging from 73.9~81.5 wt% DMSO has no phase separation at room temperature.[6] So we tested 60, 70 and 80 wt% DMSO solutions. We can predict that 60 and 70 wt% DMSO mixtures has phase

separation and fibers or films of that composition has low mechanical properties because they has uneven crystallites distribution. But 60, 70 wt% DMSO solvent mixtures may different behavior at low temperature(-20℃). Under -20℃, rate of phase separation is slower than that of gellation, and transparent and homogeneous gel can be obtained at any compostion of solvent.[7] We set the temperature of coagulation bath to -20±1℃. Spinning dope kept at 70℃ are extruded into methanol coagulation bath through air gap of 5 cm.

The quenched gel-fibers were always transparent. The DMSO80/water20 solvent mixture does not show any phase separation. Thus the gels must be transparent at initial stage of gelation.

Both of water and DMSO molecules are polar solvents, thus they can form complexes between them. This phenomenon causes different solubility for PVA. Different solubility means different PVA chain conformation in each solvent. In terms of the entanglement density, 80wt% DMSO solvent mixture is best one for obtaining high strength and high modulus PVA fibers.

Residual DMSO was removed overnight at room temperature.

Two different fibers from, Unitika and Our PVA sample was drawn in hot silicone oil bath.

The tensile properties of these fibers are shown in Table 1.

Table 1. The tensile properties of the gel-spun and drawn PVA fibers.

Fibers	Strength	Tensile modulus	Strain at break
Unitika(DP=5000)	19.0 g/d (2.18GPa)	472g/d (54.3 GPa)	5.5%
Inha(DP=5000)	18.3 g/d (2.10GPa)	291 g/d (33.5GPa)	16.5%

Fig. 2. is the equatorial diffractogram for the drawn PVA in hot silicone oil. The completely dried gel fiber was drawn 20 times and 3 times in 140℃ and 200℃, respectively. And then the drawn fibers was cooled to room temperature under tension. Birefringence of the drawn PVA fiber was 0.0485.

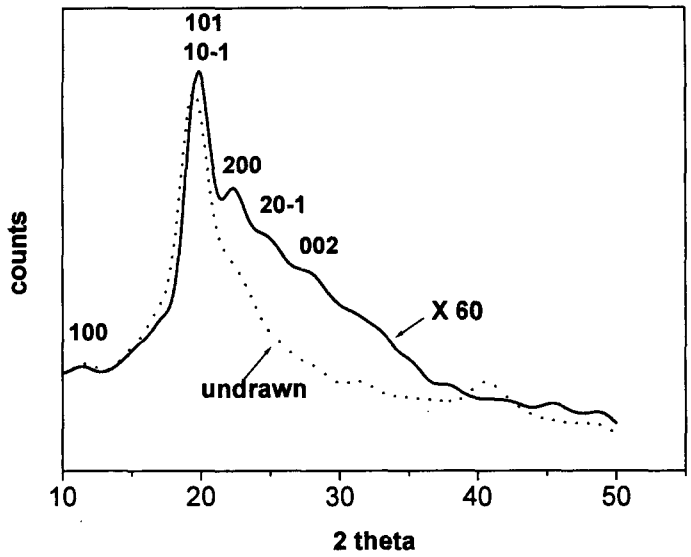

Fig 23. XRD diffraction profile of undrawn and drawn PVA fibers

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