

## 고강도 및 고탄성률 폴리비닐알코올 섬유의 제조에 관한 연구 ( II ) -존연신된 고분자량 폴리비닐알코올 섬유의 구조 및 물성-

이성준, 김준호, 윤원식, 전한용\*, 류원석  
영남대학교 섬유패션학부, \*전남대학교 응용화학공학부

## Studies on the Preparation of High Strength and High Modulus Poly(vinyl alcohol) Fiber ( II ) -Structure and Properties of Zone Drawn High Molecular Weight Poly(vinyl alcohol) Fiber-

Sung Jun Lee, Joon Ho Kim, Won Sik Yoon, Han Yong Jeon\*, and Won Seok Lyoo

*School of Textiles, Yeungnam University, Kyongsan, Korea*

*\*Faculty of Applied Chemical Engineering, Chonnam National University, Gwangju, Korea*

### 1. Introduction

Recently, many attempts have been made to develop high strength and high modulus fibers from conventional polymers such as poly(vinyl alcohol) (PVA)[1-4] and polyethylene (PE). PVA has potentiality to yield high strength and high modulus fiber, since they have high theoretically attainable moduli because of their planar zig-zag structure. As PVA has a melting temperature as high as 230 °C in contrast to PE with a low melting temperature such as 130 °C, it seems possible that high strength and high modulus fibers comparable to Aramid can be fabricated from PVA.

PVA fibers produced by wet spinning from aqueous solution have been widely used in industry, but are quite low in both strength and modulus in comparison with Aramid fibers. Therefore, to enhance the strength and modulus, organic solutions have been selected as spinning dope instead of aqueous solutions. They include: 1, glycerin (GC), ethylene glycol (EG), or ethyleneurea solutions, from which dry spinning was carried out; 2, dimethyl sulfoxide (DMSO) solution, which was used for wet spinning into organic non-solvents such as methanol, ethanol, benzene, and chloroform; 3, DMSO solution, from which dry-wet spinning was performed, followed by 20 times drawing of the undrawn fibers; and 4, GC, EG or GC/EG/water solutions, which dry-wet spinning was performed. However, the fibers obtained from these dopes exhibit in all cases strength lower than 20 g/d and modulus lower than 500 g/d, which are far inferior to those of Aramid fibers.

Cha and coworkers[5] found that high water content and high strength transparent PVA hydrogel with approximately 2 times higher strength and 1.5 times higher elongation than those of conventional PVA hydrogel could be obtained from PVA solution prepared by mixed solvents consisting of water and water-miscible organic solvent such as DMSO. Also, they reported that DMSO/water (8/2 v/v) mixture probably meet the demand to produce highly drawable PVA fibers. Actually, to prepare high strength and high modulus fibers, properties of gel formed by spinning and the other process are critical factor. However, it is more important to investigate dissolving properties of polymer by various organic solvent and viscoelastic behavior of polymer solution.

Thus in this paper, we will study rheological properties of solutions of high molecular weight (HMW) atactic PVA (a-PVA) in DMSO/water mixture with diverse polymer concentrations under different temperatures and then carry out gel spinning of PVA to prepare high-performance a-PVA fiber.

## 2. Experimental

### 2.1. Preparation of A-PVA

HMW a-PVA with number-average degree of polymerization ( $P_n$ ) of 4,000 and degree of saponification of 99.9% was prepared by suspension polymerization of vinyl acetate at low temperature and subsequent saponification in our laboratory.

### 2.2. Solution Preparation and Measurement of Rheological Properties of PVA Solution

HMW a-PVA was dissolved in a mixture of DMSO and water (8/2, v/v) at 80 °C for 2 h and was maintained for 30 min to ensure homogenization. For more precise rheological measurement, physical USD 200 Rheometer, with a couette geometry having an outer and an inner diameters of 23.50 mm and 22.75 mm respectively, at maximum strain amplitude of 10% was used. The strain level was determined in the strain sweep test so that all measurements were carried out within the linear viscoelastic regime. The shear and dynamic rheological properties of solutions of PVA in DMSO/water were measured at 90 °C, 70 °C, 50 °C, and 30 °C.

### 2.3. Gel Spinning

Dry-wet spinning was performed by extruding the dope from a nozzle having a hole size of 0.6 mm. The dope was first extruded into open air at 30 °C, and then immediately coagulated in methanol at 0 °C to obtain undrawn PVA fibers. Unless otherwise specified, the PVA concentration of spinning dope was 13 g/dl and the lengths of air gap were 50 and 100 mm respectively. The dried fibers were hot- and zone-drawn at 150 °C.

### 2.3. Wide-angle X-ray Diffraction[6,7]

The degree of orientation of the crystallite regions was determined using the Herman's equation, based on the azimuthal halfwidth of the meridional reflection on the second layer line measured using an optical densitometer.  $\theta/2\theta$  diffractometer scans were recorded using a Rigaku D/MAX-2200H diffractometer with scintillation counter in the transmission mode. CuK radiation was used in all measurements. The apparent crystallite size  $D_{(hkl)}$  was estimated using Scherrers eq. (1):

$$D_{(hkl)} = \lambda / \beta \cos\theta \quad (1)$$

where  $\lambda$  is an X-ray wavelength,  $\theta$  is the Bragg angle of the reflection and  $\beta$  is the pure integral width of the reflection.

### 2.4 Crystal Melting Temperature

The crystal melting temperature of PVA fiber was measured on a differential scanning calorimeter (Perkin-Elmer, DSC 7).

### 2.5 Surface Structure Observation

Scanning electron microscopes were used to observe surface structure of PVA fiber.

### 2.6 Tensile property

Load-elongation curves were recorded on an Instron 4201. The reported tensile strength and modulus of PVA fiber were the average value of 10 samples.

## 3. Results and Discussion

### 3.1 Rheological Properties of PVA Solutions

Figure 1 shows complex viscosity ( $\eta^*$ ) of a-PVA solutions with  $P_n$  of 4,000 at different solution temperatures. As expected solution temperature has a profound influence on the viscoelastic properties of PVA solution. Over the frequency range examined, as the polymer concentration is increased and solution temperature is decreased,  $\eta^*$  of PVA solutions is increased. In Figures 1a and 1b, the solutions of PVA exhibit almost Newtonian flow behavior in the low frequency ranges, and exhibit slight shear thinning behavior in the high frequency ranges. However, in Figures 1c and 1d, except PVA solution of 10 g/dl, all the PVA solutions show shear thinning behavior. Also, as the polymer concentration is increased, the extent of shear thinning is increased. As results of above, this may imply that solutions of a-PVA with HMW, high polymer concentration, and low solution temperature develop molecular orientation more easily by shear.

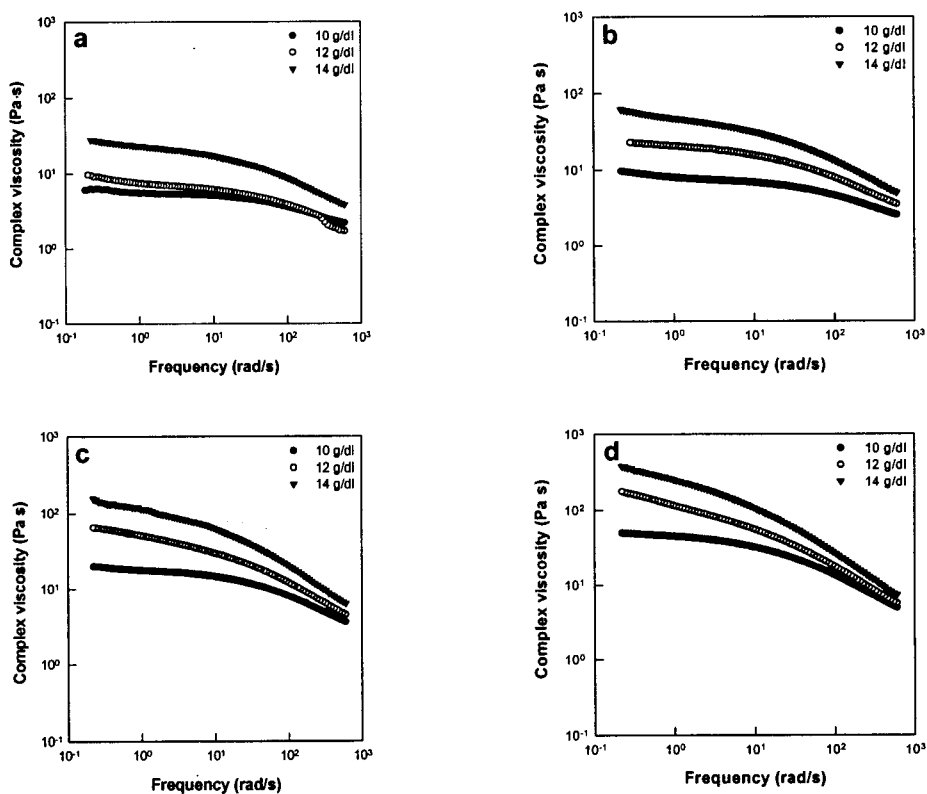


Figure 1. Complex viscosity of a-PVA solution with  $P_n$  4,000 of in DMSO/water (8/2, v/v) at different solution temperature: Solution temperatures: a, 90 °C; b, 70 °C; c, 50 °C; d, 30 °C.

### 3.2 Properties of PVA Fiber

Figure 2 represents the effect of draw ratio on the tensile strength and Young's modulus of PVA fiber spun at different air gap lengths. As seen, the PVA fiber prepared at air gap of 100 mm has the greater tensile strength and modulus than PVA fiber prepared at air gap of 50 mm and the tensile strength and Young's modulus for the 4 times hot- and zone drawn PVA fiber are

16.5 and 180 g/d, respectively.

Estimated crystallinity and crystallite size of PVA fiber are shown in Figure 3. Both the crystallinity and crystallite size of PVA fibers increase with the increasing draw ratio. However those of the PVA fiber spun at air gap of 50 mm don't show apparent increase.

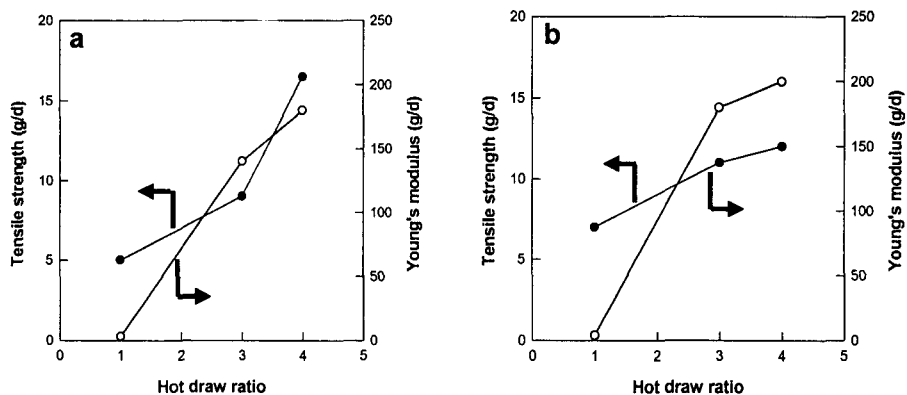


Figure 2. The tensile strength and Young's modulus of PVA fibers spun at different air gap lengths: Air gap length: a, 100 mm; b, 50 mm.

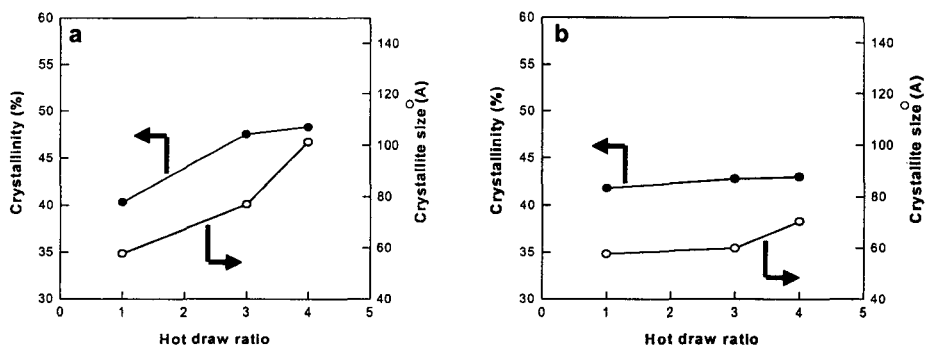


Figure 3. The crystallinity and crystallite size of PVA fibers spun at different air gap lengths: Air gap length: a, 100 mm; b, 50 mm.

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