

# Design of Spinning and Subsequent Drawing Parameters to Improve the Mechanical Properties of PVA Fibers

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**Abstract** In this study, efforts were made to enhance the mechanical properties of the poly(vinyl alcohol) (PVA) fibers of medium molecular weight(number-average degree of polymerization=1735) varying the ratio in DMSO/H<sub>2</sub>O mixed solvent and spinning/drawing conditions. The gel fibers prepared from pure DMSO were opaquely frozen in the coagulating bath of -20°C. However, transparent gel fibers were formed without freezing for the mixture to contain water less than 80wt%. As the amount of water in the mixture increased the residual solvent in the coagulated gel fibers decreased ranging from 85 to 42wt%. The complex viscosity increased with increasing PVA concentration in 80/20 DMSO/H<sub>2</sub>O exhibiting remarkable shear thinning at 18wt%. In the Cole-Cole plot, the 18wt% PVA solutions gave a deviated curve from 12 and 15wt% ones. Thus the optimum PVA concentration for the spinning processing of medium MW PVA solutions in 80/20 DMSO/H<sub>2</sub>O was determined to 18wt% with rheological concept. Low degree of drawing during hot drawing process in the dry state was available for high bath draft in the coagulation bath. The most improved mechanical properties were observed by applying the highest possible draw ratio attained by reducing bath draft over multi-step drawing process. In the given bath draft, linear relationship was observed between both tensile strength and modulus and draw ratio showing the inflection points at the draw ratio of 19.5 and 18.0 for tensile strength and modulus, respectively.

**Keywords** poly(vinyl alcohol) fibers, spinning, drawing, rheology, mechanical properties

## 1. Introduction

During the past decade, much attention has been paid to the gel processing of ultra-high molecular weight(UHMW) polymer to produce high strength and modulus materials. It was motivated from gel formation of UHMW polyethylene, reported by Smith and Lemstra<sup>1,2</sup>. Even though poly(vinyl alcohol)(PVA), another candidate for gel processing, has relatively low molecular weight, it is expected to be processed into high strength and modulus materials because

the elastic modulus along the chain axis of PVA has been evaluated theoretically<sup>3</sup>) and experimentally<sup>4</sup>) to be almost the same as that of polyethylene. The hydroxyl groups in PVA enable gel formation in combination with proper organic solvents or crosslinking agents<sup>5-7</sup>). This gel formability of PVA makes it a potential candidate for various applications such as high-performance industrial materials, medical substitutes, and adhesives<sup>8-10</sup>). Thus, many studies have been performed on the characterization of PVA gels caused by the interaction between PVA and solvent<sup>11-15</sup>).

Several spinning techniques such as gel spinning<sup>16-18)</sup> and crosslinking spinning<sup>19)</sup>, of great importance in commercial aspect, have been developed to enhance the mechanical properties of PVA fiber. Additional attempts to obtain high performance fibers following fiber spinning include ultrahigh drawing of gel-spun fiber<sup>17)</sup>, zone drawing<sup>20)</sup>, multi-step drawing<sup>21)</sup>, hot drawing<sup>22)</sup>, and annealing<sup>23)</sup>. However, up to now the reported mechanical properties of PVA fibers fall far short of theoretically predicted values, which is attributed to the presence of hydroxyl groups. Hydrogen bonds have a significant effect on the crystallization of polymers and therein their physical properties. On one hand, hydrogen bonding is of great help to enhance the mechanical properties in that it gives rise to a strong physical association of polymer molecules.

On the other hand, hydrogen bonding has a negative effect on the mechanical properties in that it might impede orientation and crystallization by interrupting the slippage and alignment of polymer molecules during drawing and annealing<sup>20)</sup>.

Hence it is accepted that the formation of rigid crystals by hydrogen bonding should be limited for the effective drawing to obtain high-performance PVA fibers<sup>16,20)</sup>. The extent of drawing which is applied in the preparation of gel fiber and then ultimate fiber has a critical effect on mechanical properties. In order to control strong hydrogen bonding between PVA chains, it is essential to understand the variation of physical properties of PVA fibers with spinning and drawing conditions. Nevertheless, there is little report on the control of hydrogen bonding in association with the properties of spinning dope, gel fiber, and ultimate fiber.

In this work, the spinning dopes of medium molecular weight PVA and resultant gel fibers were prepared in various ratios of DMSO/H<sub>2</sub>O mixtures. In addition, the gel fibers prepared by dry-jet wet spinning were further processed to obtain high performance PVA fibers by multi-step drawing at elevated

temperature near melting temperature. The physical properties of gel fiber and ultimate PVA fiber were investigated varying the compositions of solvent mixtures, bath draft, and drawing conditions.

## 2. Experimental

### 2.1 Sample preparation

PVA resin was prepared by bulk polymerization of vinyl acetate using azobisisobutyronitrile(AIBN) as an initiator. Its number-average degree of polymerization( $P_n$ ) was 1735 and degree of saponification was 99.5mol%. DMSO, H<sub>2</sub>O, and DMSO/H<sub>2</sub>O mixtures were used to prepare PVA spinning dopes. DMSO/H<sub>2</sub>O mixture in a weight ratio of 80/20~20/80 were prepared by being homogenized at 120°C in nitrogen atmosphere to prevent oxidative degradation.

Dry-jet spinning was performed at an air gap of 5 mm using a multihole nozzle( $\phi=0.1$ mm, 12holes, L/D=3). Coagulation was performed at -20°C with 80/20(by weight) methyl alcohol(MeOH)/DMSO mixtures. Bath drafts, defined as a ratio of take-up speed to extrusion rate, ranged from 1.1 to 4.0. The obtained gel fibers were wet drawn in methanol bath at 45°C to 3.5 times, immersed in methanol for 24h to completely extract residual solvents, and dried at 90°C. Hot drawing was followed at 210°C to the highest possible drawing ratio and then at 230°C by 1.2 times to prepare high performance PVA fiber. The linear density of the fiber ranged from 2.5 to 4.3 denier over the bath draft of 4.0 to 1.1, respectively.

### 2.2 Measurement of physical properties

The dynamic rheological properties of PVA solutions in 80/20 DMSO/H<sub>2</sub>O mixtures were measured at 30°C varying polymer concentration using Rheometric Mechanical Spectrometer(RMS, Rheometric Scientific Rhios). The cone and plate geometry was used, whose diameter and angle were 50mm and 0.1°, respectively. The gap of the cone was 30 $\mu$ m and strain

level was 10%.

The cross section and surface morphology of the PVA fiber were investigated using a Scanning Electron Microscope (SEM; Hitachi S-510, Japan). The surface was sputter-coated with a thin gold layer to avoid charging.

Tensile properties of PVA fibers were measured using Instron Tensile Tester 4201. The crosshead speed and gauge length were 10mm/min and 25mm, respectively. Average values of ten measurements were taken as data.

### 3. Result and Discussion

#### 3.1 Effects of DMSO/H<sub>2</sub>O ratio on the coagulating properties of PVA gel fibers

The mixtures of DMSO and H<sub>2</sub>O exhibit quite different viscoelastic properties from a single solvent of DMSO or H<sub>2</sub>O depending on their compositions. There is strong association between the two liquids which may be attributed to hydrogen bonding in the binary liquid system resulting in DMSO-H<sub>2</sub>O association complex in liquid mixtures<sup>24</sup>. This suggests that the mixture of DMSO and H<sub>2</sub>O can be applied as a new solvent with commercial importance. Table 1 summarizes the coagulating properties of PVA gel fibers prepared by dry-jet wet spinning at a given condition. All of spinning dopes are prepared at the PVA

concentration of 15wt% because the extremely high viscosity of PVA solutions in 60/40 mixture (>15wt%) makes it unfeasible to spin fibers. MeOH/DMSO(80/20 by weight) mixture is used as a coagulant and bath draft is 1.1. Optimum spinning temperatures for each solvent system are determined from 55 to 85 °C in giving proper spinning viscosity. The highest spinning temperature of 85 °C is applied to PVA spinning dopes in 60/40 DMSO/H<sub>2</sub>O which give the highest viscosity. Regardless of temperature and coagulant the coagulation does not occur when pure water is singly used. The gel fibers prepared from the spinning dope in pure DMSO are opaquely frozen in the coagulating bath of -20 °C. However, transparent gel fibers are formed without freezing in the coagulating bath for mixed solvents to contain water less than 80wt%. Coagulation rate decreases with increasing water content in the mixed solvent, giving the fastest gelation at 80/20 DMSO/H<sub>2</sub>O mixture. Because of high miscibility of MeOH with water the spinning dope with a proper amount of water shows the fast gelation. However, coagulation ability is greatly reduced for the coagulating bath to contain more than a critical level of extracted water, showing slow and weak gelation. As the amount of water in the mixture increases the residual solvent in the coagulated gel fibers decreases ranging from 85 to 42wt%. When DMSO (freezing temperature = 17 °C) is singly used, its abrupt freezing

**Table 1.** Effects of DMSO/H<sub>2</sub>O ratio in the mixed solvent on the spinning temperature and coagulation properties of PVA gel fibers spun at the bath draft of 1.1.

DMSO/H <sub>2</sub> O (wt%)	Spinning Temperature (°C)	Coagulated Gel Fiber		
		Color	Coagulating State	Residual Solvent (wt%)
100/0	55	Turbid	fast freezing	85
80/20	75	Clear	very fast gelation	75
60/40	85	Clear	fast gelation	72
40/60	78	Clear	slow and weak gelation	53
20/80	70	Turbid	very slow and weak gelation	42
0/100	–	–	not coagulated	–

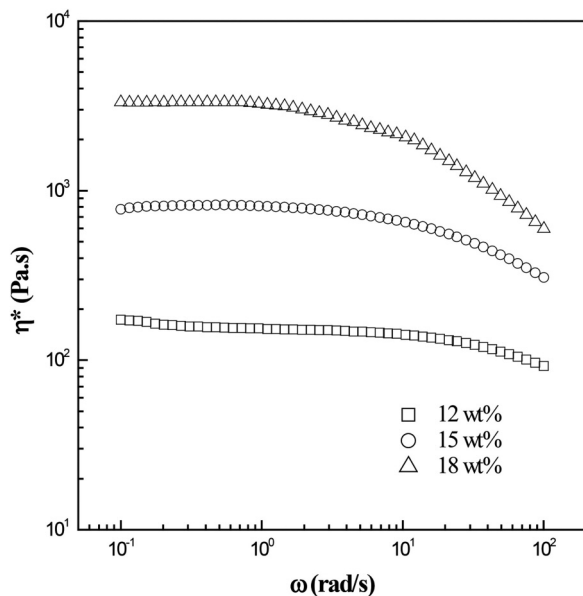
occurs at the surface of gel fiber and it is then caged in the fiber, resulting in the opaque and high residual solvent. On the contrary, at the water content of 20 and 40wt%, the gel fibers exhibit relatively little difference in the amount of residual solvent and a stable transparency without freezing in the coagulating bath of  $-20^{\circ}\text{C}$ . It is known that removal of solvent from gel fiber does not change the intermolecular topology<sup>16</sup>. Thus, the networked gel structure present in the gel fiber allows the as-spun fiber to be drawn to a high ratio.

### 3.2 Variation of rheological properties of PVA solutions with polymer concentration

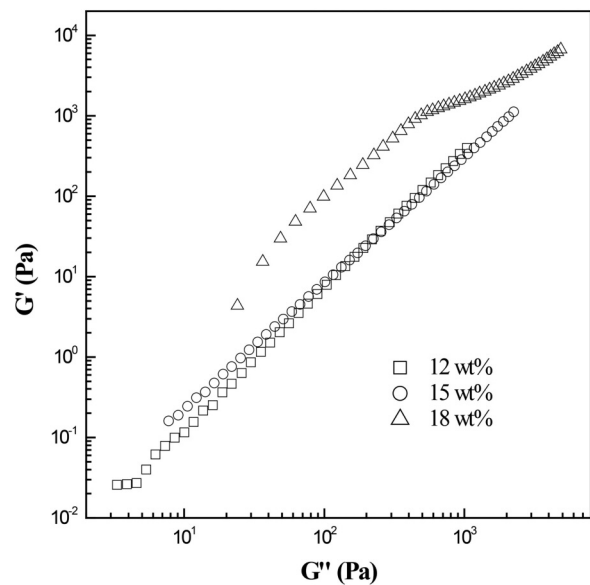
Rheological properties of spinning dopes give a crucial clue to determine optimum spinning conditions such as spinning solvent and polymer concentration. Generally, the polymer concentration in spinning dope depends on type of solvents and molecular weight of polymer used. Figure 1 shows the variation of complex viscosity ( $\eta^*$ ) of PVA solutions in 80/20 DMSO/H<sub>2</sub>O with frequency at several PVA concentrations. The complex viscosity increases with in-

creasing PVA concentration exhibiting lower Newtonian flow region followed by shear thinning. As the PVA concentration increases, lower Newtonian flow region is reduced and more notable shear thinning behavior is observed at the high frequency range. In particular, the degree of shear thinning increases abruptly at the PVA concentration of 18wt%. This reveals that the entanglements between polymer chains or network structures in PVA solutions increases remarkably at the concentration more than 15wt% and this formed structure is favorably oriented under shear force. In other words, the morphological state in highly concentrated PVA solutions might be greatly changed during high shear flow resulting in relatively small difference of  $\eta^*$  at high frequency.

To assess the conformations of PVA molecules in the mixed solvent of 80/20 DMSO/H<sub>2</sub>O, the log-log plot of storage modulus ( $G'$ ) vs loss modulus ( $G''$ ) is shown in Figure 2. On the so-called Cole-Cole plot, two groups of slopes are distinctively observed exhibiting definitely deviated plot at 18wt% PVA concentration. Theoretically, isotropic and homogeneous solution where there is not any specific interactions

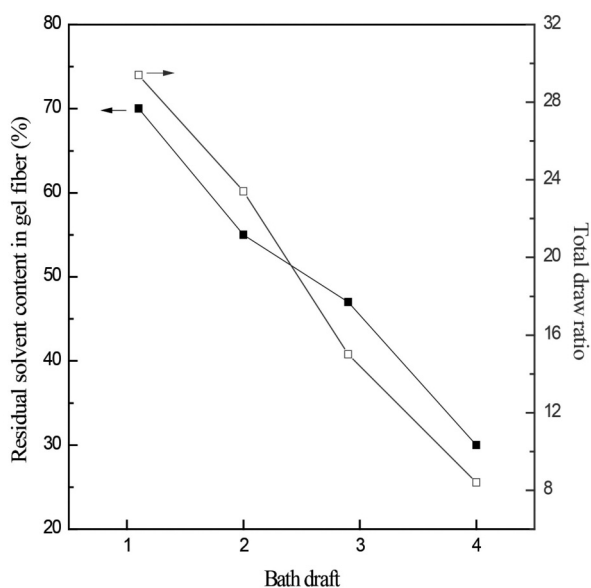


**Figure 1.** Complex viscosity ( $\eta^*$ ) curve of PVA solutions in 80/20 DMSO/H<sub>2</sub>O at  $30^{\circ}\text{C}$ .

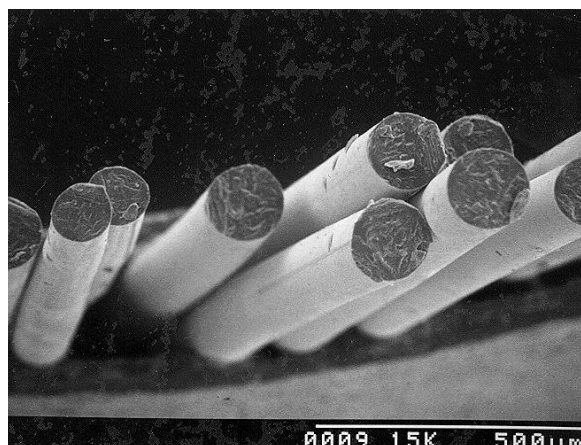


**Figure 2.** Cole-Cole plot of PVA solutions in 80/20 DMSO/H<sub>2</sub>O at  $30^{\circ}\text{C}$ .

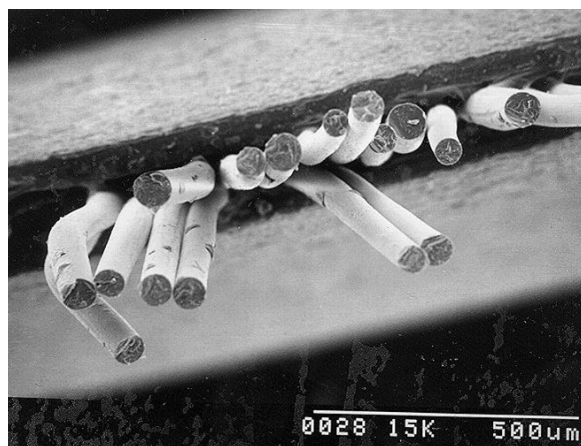
gives the slope of 2 while inorganic filler system or rigid liquid crystal system gives the slope close to 1<sup>25</sup>. Therefore, this plot is very useful to evaluate the degree of heterogeneity, that is, microstructure change in entangled viscoelastic polymeric system. The increase in PVA concentration decreases the slope, indicative of increased heterogeneity. 18wt% PVA solutions exhibit notable shift of the plot compared with the other lower concentrations. This notable deviation of the plot indicates that notable structural difference of PVA chain in the solutions is made between 15 and 18wt%<sup>26</sup>. PVA is prepared from saponification of polyvinylacetate which has high linearity without branching. Therefore, the slope change for 18wt% PVA solutions seems to be caused by the formation of hydrogel or network structure resulting from the strong interaction between hydroxyl groups in the ternary system of PVA/DMSO/H<sub>2</sub>O. In other words, for medium MW PVA (Pn=1735), the entanglement of polymer chains increases greatly at the concentration of 18wt% resulting from the interaction between hydroxyl groups. Thus 18wt% is regarded as the optimum concentration for the spinning processing of



**Figure 3.** Effects of bath draft on the residual solvent content in gel fiber and total draw ratio.



(a)



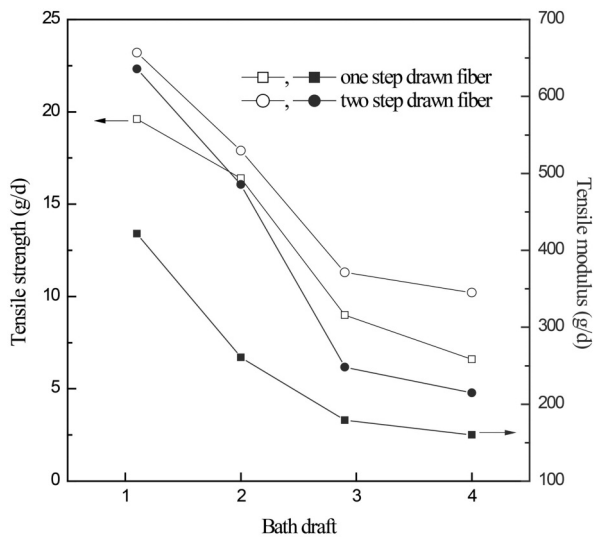
(b)

**Figure 4.** SEM photograph of as-spun PVA fibers prepared by gel spinning at the bath draft of (a) 2.0 and (b) 4.0.

medium MW PVA solutions in 80/20 DMSO/H<sub>2</sub>O due to favorably induced entanglement and orientation of polymer chains.

### 3.3 Effects of bath draft and draw ratio on the properties of PVA gel fibers and resulting PVA fibers

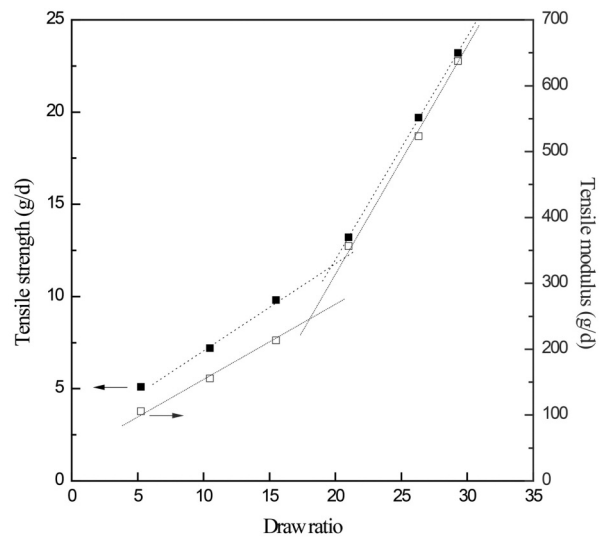
The gel fibers are prepared at 75 °C from 18wt% PVA spinning dope in 80/20 DMSO/H<sub>2</sub>O mixture varying the bath draft. The physical properties of gel fiber and resultant fiber are expected to depend greatly on extrusion speed, coagulants, and take-up speed. Figure 3 shows the effects of bath draft on the residual sol-



**Figure 5.** Variation of tensile strength and modulus of PVA fibers with bath draft at two different drawing steps. One step drawn fibers were drawn at 210°C, and two step drawn fibers were first drawn at 210°C and subsequently drawn at 230°C.

vent content in the gel fiber and total draw ratio applied to the ultimate PVA fibers. The amount of residual solvent in gel fiber and total draw ratio decrease in a similar manner with increasing the bath draft. Increase in the bath draft gives rise to the orientation of polymer molecules when solvent is extracted in the gel state where relatively low entanglement between polymer chains exists. Due to already highly oriented structure, low degree of drawing is available during further hot drawing process in the dry state resulting in reduced total draw ratio for high bath draft.

Figure 4 shows the SEM images of cross section of as-spun PVA fibers obtained at two different bath drafts. The PVA fibers have uniform circular cross section, whose diameter is ca. 120 and 60 μm at 2.0 and 4.0 bath draft, respectively. The solution spinning such as wet, dry, and dry-jet wet spinning, generally produces dog-bone or ellipse shaped cross section because of abrupt extraction of solvent during solidification. However, the spinning conditions applied in this study do not cause an abrupt extraction of solvents in the coagulating bath by inducing a fast gela-



**Figure 6.** Variation of tensile strength and modulus with draw ratio in the PVA fibers prepared by dry-jet wet spinning at the bath draft of 1.1.

tion at a low temperature (-20°C), leading to a circular cross section of uniform diameter.

PVA fibers are generally prepared from hot or zone drawing at high temperature (ca. 190-220°C) to increase drawability and mechanical properties<sup>21,22</sup>. PVA fibers were prepared by two step drawing at two different temperatures. The first drawing was carried out at 210°C, followed by the second drawing at an elevated temperature of 230°C near melting point. The fibers are easily drawn at a high temperature under relatively low tension because hydrogen bonds and rigid crystallites can be simultaneously loosened or destroyed near melting point. Figure 5 shows the dependence of tensile properties of PVA fibers on bath draft at two different drawing steps. Two step drawn fibers exhibit the higher tensile strength and modulus than one step drawn fibers all over the bath draft indicating that additional drawing at elevated temperature of 230°C is quite effective in improving mechanical properties. In particular, decreasing pattern in both tensile properties with bath draft is quite similar exhibiting relatively low dependence on the bath draft between 2.9 and 4. In addition, the tensile

strength and modulus of PVA fibers decrease with increasing bath draft. Both bath draft in the gel state and drawing process in the solid fiber state have a significant combined effect on tensile properties. It is worth noting that increasing the degree of drawing in the solid fiber state by reducing the extent of draft in the coagulation process is more effective to improve mechanical properties rather than vice versa.

Figure 6 shows the variation of tensile strength with draw ratio for the PVA fiber prepared by dry-jet wet spinning at a given bath draft of 1.1. Tensile strength and modulus increase with draw ratio at a similar manner<sup>27</sup>. There is linear relationship observed between both tensile properties and draw ratio showing the inflection points at the draw ratio of 19.5 and 18.0 for tensile strength and modulus, respectively. In addition, the slope at the inflection points increases sharply from 0.46 to 1.21 for tensile strength and from 10.5 to 33.5 for tensile modulus. This reveals that the draw ratio far greater than the critical level is required to be applied in the hot drawing process to obtain superior mechanical properties.

#### 4. Conclusions

We raised the possibility of preparing high performance PVA fiber by using medium MW PVA resin. This result has a practical importance because the ultrahigh molecular weight PVA is too expensive. When 80/20 DMSO/H<sub>2</sub>O mixture was used as solvent for medium MW PVA resin, transparent gel fibers were formed in the coagulating bath of MeOH/DMSO (80/20) mixture exhibiting the fastest gelation behavior. The optimum PVA concentration was determined from the dynamic rheological properties of PVA spinning dope. At the PVA concentration of 18wt% remarkably deviated plot was exhibited on the Cole-Cole plot, indicative of the change in the microstructure of PVA chain in the solutions. Possible draw ratio in the multi-step drawing process was di-

rectly associated with amount of residual solvents in the gel fibers which decreased with increasing bath draft. The highest possible draw ratio increased with lowering the bath draft, suggesting the relatively low degree of orientation in the gel fiber makes more drawing feasible in a dry state. Increasing the degree of drawing in dry state at the expense of that in gel state was quite effective in improving mechanical properties. In addition, at a given bath draft, there was a linear relationship between draw ratio and tensile strength/modulus exhibiting the inflection point. The highly enhanced mechanical properties of PVA fibers were attained with a medium molecular weight atactic PVA resin (DP=1735) by controlling the spinning and subsequent drawing parameters such as spinning solvents, polymer concentration, bath draft during coagulation process, and draw ratio during multi-step drawing process.

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