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Fiber-Forming Properties of Poly(vinyl alcohol) Derived from Poly(vinyl pivalate)

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Abstract: Fiber-forming properties of poly(vinyl alcohol)s (PVAs) with high syndiotacticities (diad syndiotacticity = 61–65%) derived from poly(vinyl pivalate) (PVP) were studied. PVA with moderate molecular weight (ca. 7×10^4), which was derived from PVP, showed a high fiber-formability and provided fibers having a high degree of crystallinity and a high mechanical strength. On the other hand, PVAs having fairly high molecular weights ($> 4 \times 10^5$) and having high syndiotacticities were less drawable owing to the strong intermolecular forces caused by the stereoregularity.

1. Introduction

The crystal modulus of poly(vinyl alcohol) (PVA) in the direction parallel to the chain axis is very high, estimated to be from 250 to 300 GPa, because the molecular chains in the crystal take a planar zigzag conformation [1]. In addition, having a high modulus in the direction perpendicular to the chain axis and a high crystal melting point, PVA can be expected to provide a prominent fiber with high strength and modulus.

Many methods, such as gel-spinning [2, 3], solid state-extrusion of single crystal mat [4], zone drawing [5], and use of PVA with high molecular weight, have been applied to obtain PVA fibers with ultra-high strength and modulus. Most PVAs used for these methods were derived from poly(vinyl acetate) (PVAc) and their stereoregularities were low.

We developed a new preparation method of PVA with high syndiotacticity. The process consists of the photo-emulsion polymerization of vinyl pivalate (VP) and the exhaustive saponification of obtained poly(vinyl pivalate) (PVP) [6, 7]. The PVA prepared using this process exhibited a higher crystal melting point and a higher modulus in the temperature range above the glass transition than a commercial PVA derived from PVAc [8]. These

different characteristics are attributed to an intense intermolecular force caused by hydroxyl groups with high syndiotactic configurations. Regulation of the intermolecular force is an important factor in order to obtain good fiber-formability by allowing the molecular chains to build up advanced molecular orientation.

At the present stage of the study on stereoregularity of PVA, little is known about the physical properties other than results obtained by Yamaura *et al.* [9–11] which deals with poly(vinyl trifluoroacetate) (PVTFAc). Stereoregularity of PVA derived from PVP is higher than that derived from PVTFAc. In addition, when using VP as a monomer, PVA with high molecular weight is easily obtained by photo-emulsion polymerization at low temperatures [7]. Thus, PVP makes it possible to provide highly stereoregulated PVA, and the adaptation of the obtained PVA to a fiber manufacturing process is of important significance to the textile industry. Reports on the fiber preparation of PVA having syndiotacticity over 60% and ultra-high molecular weight have not been published to date. The present investigation was undertaken to observe the fiber-formability of PVA with high syndiotacticity ($> 61\%$ (diad)) derived from PVP and to evaluate the fiber properties.

Table 1 PVA Samples Used for Fiber Preparation

Sample No.	Degree of polymerization ^{a)}	Diad syndiotacticity (%)	Degree of saponification (%)
s-PVA(VH)	12,900	62.8	>99.9
s-PVA(H)	9,000	62.8	>99.9
s-PVA(M)	4,400	64.7	>99.9
s-PVA(L)	1,690	61.2	>99.9
s-PVA(VL)	730	64.9	>99.9
a-PVA(L)	1,750	53.9	>99.9

^{a)} Estimated from intrinsic viscosity of acetylated PVA.

2. Experimental

2.1 Preparation of PVA

PVP was obtained by photo-emulsion and solution polymerization of VP according to the process previously reported by us [7]. Desired PVAs with high syndiotacticities (s-PVAs) were prepared by exhaustive saponification of PVP. Degrees of polymerization (P_n), syndiotacticities and degrees of saponification of several PVA samples for the fiber forming process are summarized in Table 1. s-PVA(VH) and s-PVA(H) shown in Table 1 were derived from PVPs which were prepared by the photo-emulsion polymerization of VP at 0 °C. s-PVA(L) was derived from PVP which was prepared by solution polymerization of VP at 60 °C with MeOH as a solvent. s-PVA(M) and s-PVA(VL) were also derived from PVPs prepared by solution polymerization of VP at 0 °C with MeOH. a-PVA(L) was a commercially available PVA(Kuraray Co., Ltd.), which was derived from PVAc.

2.2 Characteristics of PVA Samples

The P_n of PVA was estimated from the intrinsic viscosity of the acetylated polymers. The degree of syndiotacticity and saponification were determined from the ¹H NMR spectrum of PVA. ¹H NMR spectroscopy was carried out with a JEOL JNM EX-270 using 1% DMSO-*d*₆ solution of PVA.

2.3 Spinning of PVA Solution

A DMSO solution of PVA of given concentration was prepared for spinning. The solution was extruded into a MeOH bath held at 0 °C through a single nozzle having an internal diameter of 0.3 mm with an air gap of 2 mm. The gel-fiber was rolled up and then kept in an excess amount of MeOH to extract the solvent.

2.4 Drawing and Annealing

A two-step drawing process was employed in the present work. At the first stage of drawing, fibers were drawn at the rate of 130% or 670% of original length per minute at 150 °C in an oven filled with nitrogen gas. A second drawing of the above drawn fibers was carried out at the same drawing rates and at various temperatures. The drawn fibers were gradually cooled to 100 °C in the oven while continuing the tension.

2.5 Birefringence of Fibers

The birefringence (Δn) was determined using Eq. 1 with a polarizing microscope Olympus BH-2 with a Berek compensator [12].

$$(c/1000) \times 10000 f(i) / d = \Delta n \times 10^3 \quad (1)$$

where $i = (a + b)/2$, c is the constant of the compensator (nm), a is the graduation of the compensator when corresponding the top of zero-order stripe to the cross-point of the polarizing microscope, b is the graduation in the reverse direction, $f(i)$ is a constant determined by the i value and d is the diameter of the fiber (μ m). A mixture of dibutyl phthalate and tricresyl phosphate (1:1) was used for soaking the samples.

2.6 Crystallinities of Fibers

Crystallinities of fibers were estimated from their densities using the assumption that the densities of a fully amorphous sample and a fully crystalline sample of PVA are 1.269 and 1.345 g/cm³, respectively [13]. The density was measured at 25 °C by the floating method in light liquid paraffin-carbon tetrachloride mixture.

2.7 X-ray Diffraction Analysis

The wide-angle X-ray diffraction patterns were recorded on a flat film camera with a Rigaku X-ray Dif-

fractometer, using nickel-filtered $\text{CuK}\alpha$ radiation (30 kV, 20 mA). Film were exposed at a distance of 9.5 mm for 5h.

2.8 Tensile Test

The tensile tests were carried out at 20 °C and 65% RH on the fibers of 20 mm gauge length and at a cross-head speed of 20 mm/min, using a tensile tester, Autograph AG-1000 (Shimadzu Co., Ltd.). The tensile strength and modulus were evaluated from the stress-strain curves.

2.9 Dynamic Viscoelasticity

The dynamic storage modulus E' and the loss tangent δ were measured at 110 Hz and at a heating rate of 3 °C/min from -130 °C using a dynamic viscoelastic DVE-V4 (Rheology Engineering Co., Ltd.).

Fig. 1 Changes in birefringence with total draw ratios for s-PVA (L) fibers: ●, 1st drawing at 150 °C; ○, 2nd drawing at 230 °C after 1st drawing; △, 2nd drawing at 240 °C; □, 2nd drawing at 250 °C.

2.10 Crystal Melting Points of Fibers

Determination of crystal melting points of fibers was carried out by using a differential scanning calorimeter DSC 8230 (Rigaku Denki Co., Ltd.). The heating rate was 10 °C/min.

3. Results and Discussion

3.1 s-PVA(L) Fibers

3.1.1 Fiber Forming

Four percent of DMSO solution of s-PVA(L) was prepared to spin as dilute solution as possible in our spinning apparatus. In the first drawing at 150 °C, the gel-fibers stretched maximally to 8 times the original length to exhibit a birefringence value of 44×10^{-3} . Fibers were then drawn again in the oven at elevated temperatures, i.e., 230 °C, 240 °C, and 250 °C, respectively.

Fig. 1 shows the changes in birefringence with the total draw ratios in the two-step drawing of fibers. The draw ratio increases with the rise in drawing temperature, and the birefringence of the fiber increases as the draw ratio increases. The efficiency of drawing decreases as the fiber is stretched to more than 10 times of its original length. In the case of drawing at 250 °C, close to the melting point of s-PVA(L), the fiber can be maximally drawn to 27 times its original length, and the value of the birefringence reaches 60×10^{-3} . It has been reported [14] that the value of the birefringence of the crystal region of a commercially available PVA derived from PVAc is 51.8×10^{-3} . The value of the birefringence of PVA, which was derived from PVP in the present work, is higher than that derived from PVAc.

Table 2 Mechanical Properties of s-PVA (L) and a-PVA (L) Fibers^{a)}

PVA sample	Drawing ^{b)}		Total draw ratio	Birefringence ($\Delta n \times 10^3$)	Crystallinity (%)	Tensile strength (GPa)	Young's modulus (GPa)
	1st (°C)	2st (°C)					
s-PVA(L)	150	—	8	44	45	0.7	35
	150	230	23	51	77	1.9	53
	150	240	24	57	79	2.2	61
	150	250	27	59	81	2.3	70
a-PVA(L)	150	—	7	38	36	0.9	32
	150	230	15	45	47	1.5	39

^{a)}Concentration of PVA in spinning solution: s-PVA (L), 4%; a-PVA (L), 7%.

^{b)}Drawing rate: 130% of original length/min.

Fig. 2 Temperature dependences of dynamic storage modulus E' and $\tan \delta$ for PVA fibers: $\circ$, α -PVA (L) fiber; $\square$, s-PVA (L) fiber.

3.1.2 Fiber Properties

Table 2 shows the properties of s-PVA(L) fibers drawn maximally at each drawing temperature. After the second drawing, crystallinity of the fiber fairly increased comparing with that of the fiber treated with first drawing only. The higher the temperature in the second drawing, the higher the crystallinity of the fiber becomes. Specifically, it is noticeable that s-PVA(L) fibers drawn at 250 °C shows crystallinity of 81%. In this case, the tensile strength of the fiber is 2.3 GPa and Young's modulus is 70 GPa, respectively.

For comparison, the fibers prepared from commercially available PVA, α -PVA(L) were examined, which had approximately the same molecular weight as that of the s-PVA(L). Gel-spinning was done using 7% DMSO-PVA solution, and fiber-drawing was carried out at 150 °C followed by the drawing at an elevated temperature of 230 °C. s-PVA(L) fibers showed higher crystallinity and more desirable mechanical properties than the α -PVA(L) fibers (Table 2). Fig. 2 shows the temperature dependence of dynamic viscoelasticities of α -PVA(L) and s-PVA(L) fibers. At all temperatures measured, the storage modulus values for s-PVA(L) were higher than those for α -PVA(L), and the degree of decrease in modulus value of s-PVA(L) with the rise in temperature was smaller than

Fig. 3 Changes in birefringence with total draw ratios for s-PVA (VH) fibers: $\bullet$, 1st drawing at 150 °C; $\circ$, 2nd drawing at 230 °C after 1st drawing; $\triangle$, 2nd drawing at 240 °C; $\square$, 2nd drawing at 250 °C.

that of α -PVA(L) in the temperature region over the glass transition temperature.

3.2 s-PVA(VH) Fibers

3.2.1 Fiber Forming

Enhancing of molecular weight causes the fewer terminal points in the molecular chains and allows the tie molecules to increase, resulting in an enhancement of the fibrous structure [2, 3]. s-PVA(L) formed a fiber having a higher Young's modulus than that of α -PVA(L) as described above. Therefore, s-PVA(VH) with high syndiotacticity and high molecular weight is considered to form a fiber with more desirable mechanical properties.

s-PVA(VH)-DMSO solution (2.5 wt%) was used for spinning. The first drawing was carried out at 150 °C, and the second drawings were at various temperatures. As shown in Fig. 3, though s-PVA(VH) fiber is maximally drawn to as the same degree as that of s-PVA(L) in the first drawing, the birefringence of the drawn fiber remains low in comparison with the case of s-PVA(L).

In the second drawing, the drawing is effective to increase birefringence value at every testing temperature at a low drawing ratio. However, the maximum draw ratio is 12 at 230 °C and the draw ratio and the birefringences value are lower at 240 °C and 250 °C than those in the cases of s-PVA(L) fibers. It is very hard to draw s-PVA(VH) fiber effectively, even though the temperature is close to its crystal melting point.

Fig. 4 shows wide angle X-ray diffraction patterns of

Fig. 4 Wide angle X-ray diffraction patterns for PVA fibers: (a) *s*-PVA (VH) fiber drawn at 150 °C; (b) *s*-PVA (VH) fiber drawn at 150 °C (1st drawing) and 250 °C (2nd drawing); (c) *s*-PVA (L) fiber drawn at 150 °C (1st drawing) and 250 °C (2nd drawing).

Table 3 Mechanical Properties of *s*-PVA (VH) Fibers^{a)}

Drawing ^{b)}		Total draw ratio	Birefringence ($\Delta n \times 10^3$)	Crystallinity (%)	Tensile strength (GPa)	Young's modulus (GPa)
1st	2st					
slow	—	9	36	37	0.7	29
fast	—	9	35	32	0.7	25
slow	slow	16	52	62	1.7	49
slow	fast	15	45	60	1.4	46
fast	slow	15	47	58	1.1	41

^{a)}Concentration of PVA in spinning solution, 2.5%. ^{b)}Drawing: in an oven at 150 °C (1st) and 250 °C (2nd). Drawing rate: slow, 130% of original length/min; fast, 670% of original length/min.

s-PVA(VH) fibers. By adding the second drawing, the lattice spots of (100) and (001) planes are located near the equatorial axial line as the crystal can align along the drawing direction. However, the degree of orientation of *s*-PVA(VH) fiber is not so high as that of *s*-PVA(L) fiber under the drawing condition shown in Fig. 4.

3.2.2 Fiber Properties

Fiber properties of *s*-PVA(VH) are listed in Table 3. The birefringence values and degree of crystallinities are low. Also, the tensile strength is 1.7 GPa and Young's modulus is 49 GPa when heat-treatment is done at 150 °C and 250 °C. Though *s*-PVA(VH) was expected to have advanced mechanical properties, its tensile strength and Young's modulus were somewhat lower than those of *s*-PVA(L). Drawings at various speeds were tried but no

clear effects were observed.

3.3 Effect of Molecular Weight on Fiber Forming of *s*-PVA

s-PVA fibers having various molecular weights were prepared and examined in order to discuss the effect of molecular weight on fiber forming. These properties are listed in Table 4. *s*-PVA(H) fibers, which have smaller molecular weight compared to that of *s*-PVA(VH), show properties similar to those of *s*-PVA(VH) fibers. The drawing of *s*-PVA(VH) seemed to be insufficient for aligning its molecular chains, due to entanglement by long molecular chains with strong intermolecular forces enhanced by high syndiotacticity. *s*-PVA(M) fibers, which have twice or larger molecular weight compared to that of *s*-PVA(L), showed inferior mechanical properties. As

Table 4 Mechanical Properties of *s*-PVA Fibers^{a)}

PVA sample	Degree of polymerization	Conc. in spinning solution (%)	Total draw ratio	Birefringence ($\Delta n \times 10^3$)	Crystallinity (%)	Tensile strength (GPa)	Young's modulus (GPa)
<i>s</i> -PVA(VH)	12,900	2.5	16	52	62	1.7	49
<i>s</i> -PVA(H)	9,000	2.5	16	54	63	1.8	50
<i>s</i> -PVA(M)	4,400	2.5	22	51	54	1.4	47
<i>s</i> -PVA(L)	1,690	4.0	27	59	81	2.3	70
<i>s</i> -PVA (VL)	730	5.7	14	46	57	1.1	47

^{a)}Drawing: in an oven at 150 °C and 250 °C; Drawing rates; 130% of original length/min.

Fig. 5 Crystal melting points of PVA fibers with various tacticities: ○, *a*-PVA (L) [crystallinity (X_c) = 47%]; ▽, *s*-PVA (L) (X_c = 81%); △, *s*-PVA (VH) (X_c = 62%); □, *s*-PVA (M) (X_c = 54%); ◇, *s*-PVA (VL) (X_c = 57%).

for the fiber forming of PVA with over 60% syndiotacticity, it was found that PVA having a degree of polymerization of ca. 1,700 shows good fiber formability to provide considerable tensile strength properties.

Also, the fiber forming of *s*-PVA(VL) with a comparatively low molecular weight was attempted. In spite of a fairly low degree of polymerization, it showed a good fiber-forming capability, and yielded a fiber with high crystallinity. *s*-PVA(VL) exhibited nearly the same fiber strength as that of commercial PVA fibers.

3.4 Crystal Melting Points of *s*-PVA Fibers

Fig. 5 shows the crystal melting points of fibers prepared from *s*-PVAs. Crystal melting points of *s*-PVAs are 10 °C higher than that of *a*-PVA(L). The tendency for an increase of crystal melting points with an increase in syndiotacticity was observed. Especially, *s*-PVA(M)

showed a fairly high crystal melting point (256 °C). This suggests the usefulness of *s*-PVA fibers for heat-resistant applications.

4. Conclusion

PVA derived from PVP provides a fiber with a high tensile strength and a high Young's modulus. Even when the molecular weight of *s*-PVA derived from PVP was rather low, it was sufficient to provide a good tensile property. The degree of crystallinity of PVA fiber having a degree of polymerization of 1,700 goes up to 81%, and the fiber shows a tensile strength of 2.3 GPa and a Young's modulus of 70 GPa. On the contrary, *s*-PVA with a fairly high degree of polymerization (12,900) showed a lower fiber formability owing to an entanglement of a long chain and a tight intermolecular force caused by the high syndiotacticity.

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