

Structure Evolution of Melt-Spun Poly(vinyl alcohol) Fibers During Hot-Drawing

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ABSTRACT: The drawability of melt-spun poly(vinyl alcohol) (PVA) fibers and its structure evolution during hot-drawing process were studied by differential scanning calorimetry (DSC), two dimensional X-ray diffraction (2-D WAXD) and dynamic mechanical analysis (DMA). The results showed that the water content of PVA fibers should be controlled before hot-drawing and the proper drying condition was drying at 200°C for 3 min. PVA fibers with excellent mechanical properties could be obtained by drawing at 200°C and 100 mm/min. The melt point and crystallinity of PVA fibers increased with the

draw ratio increasing. The 2-D WAXD patterns of PVA fibers changed from circular scattering pattern to sharp diffraction point, confirming the change of PVA fibers from random orientation to high degree orientation. Accordingly, the tensile strength of PVA fibers enhanced by hot-drawing, reaching 1.85 GPa when the draw ratio was 16. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 421–428, 2012

Key words: poly(vinyl alcohol) fibers; melt spinning; drawability; structure evolution

INTRODUCTION

High strength and high modulus poly(vinyl alcohol) (PVA) fibers are widely used in high-tech fields because of their excellent comprehensive properties.¹ However, due to the multi-hydroxyl structure, the melting point of PVA and its decomposition temperature are so close that the melt spinning of PVA is very difficult. So far, the preparation of PVA fibers are usually based on and limited to solution spinning.^{2–4} Based on intermolecular complexation and plasticization, water and an amido group containing compound (Ac) were selected as the compound plasticizer of PVA. A novel and environmental friendly technique has been developed by our group to control the supermolecular structure of PVA, decrease its melting point and realize its thermal processing,^{5–8} and obtain PVA fibers with circular cross section and uniform structure by melt spinning.⁹

To further enhance the mechanical properties of PVA fibers, drawing is a necessary and important method. For our melt-spun PVA fibers, there are

three important factors that significantly affect the drawability of PVA fibers: water content, drawing temperature, and drawing speed. Water is the key modifier for melt spinning of PVA. By the newly formed strong hydrogen bonds between water and the hydroxyl groups of PVA, the intra- and intermolecular hydrogen bonds of PVA are disrupted. Accordingly, the melt point of PVA decreases and the thermal processing temperature range of PVA is obtained. During drawing process, the water in PVA fibers also plays an important role and needs to be further carefully studied. Meanwhile, the aggregation structure of PVA fibers is controlled by the drawing temperature and drawing speed. So it is important to study the three factors to obtain PVA fibers with excellent mechanical properties. Furthermore, during drawing process, molecular chains of polymer fibers orient along fiber axis, and the structure changes with the crystal orientation, lateral periodicity in amorphous region and crystallization, which makes the performance of fibers different from the as-spun fibers.

There are many research works on the structure evolution of PVA fibers and films. But the PVA fibers used in these studies were mostly obtained by solution process. Miyazaki¹⁰ proposed a structure model of PVA film stretched uniaxially in water. The result showed that the strain induced crystallization took place in the interfibrillar extended amorphous regions, which produced the increasing stress with increasing strain, and the lamellar stacked in

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the film contribute to the system hardening, which was attributed to the extension of the interfibrillar amorphous regions. Hong¹¹ studied the structure of the amorphous phase in highly drawn PVA fibers and pointed out that the amorphous chains must be highly oriented in the highly drawn fibers. Lyoo¹² studied the crystal and microstructures of PVA fibers with different syndiotactic diad contents, and suggested that the crystallinity, the apparent lateral and longitudinal crystal sizes, and the crystal to amorphous length in long period of drawn PVA fibrils were larger in PVA fibers with higher syndiotacticity. It turned out that PVA fibril drawn at 230°C had a well oriented lamellar structure.

However, no studies on both crystalline and amorphous phase changes of melt-spun PVA fibers during drawing process have been reported. Mechanical performances of PVA fibers are controlled by the crystalline and amorphous phase, where crystalline region is the main component of PVA fibers and the amorphous region is the mechanical weak point of PVA fibers. Thus, it is very important to investigate the structure evolution of PVA fibers during drawing process. In this article, the drawability of melt-spun PVA fibers as well as the crystalline and amorphous phase changes of melt-spun PVA fibers during hot drawing was studied.

EXPERIMENTAL

Materials

Melt-spun PVA fibers were prepared according to the Ref.¹³ Drawing of PVA fibers was conducted with a laboratory made hot pipe drawing equipment.

Differential scanning calorimeter

Differential scanning calorimeter (DSC) curves were recorded on TA Q20 DSC differential scanning calorimetry. Approximately 6 mg sample was used and the measurements of the samples were performed by heating from 100 to 260°C at a heating rate of 10°C/min under nitrogen atmosphere. The crystallinity of PVA fibers was calculated by the following equation:

$$X (\%) = \Delta H_f / \Delta H_f^0 \times 100\% \quad (1)$$

where ΔH_f is the melting enthalpy of PVA fibers and ΔH_f^0 is the melting enthalpy of the 100% crystalline PVA with the value of 168 J/g.¹⁴

Two dimensional wide angle X-ray diffraction

Two dimensional wide angle X-ray diffraction (2-D WAXD) data were recorded on Rigaku R-Axis Spider

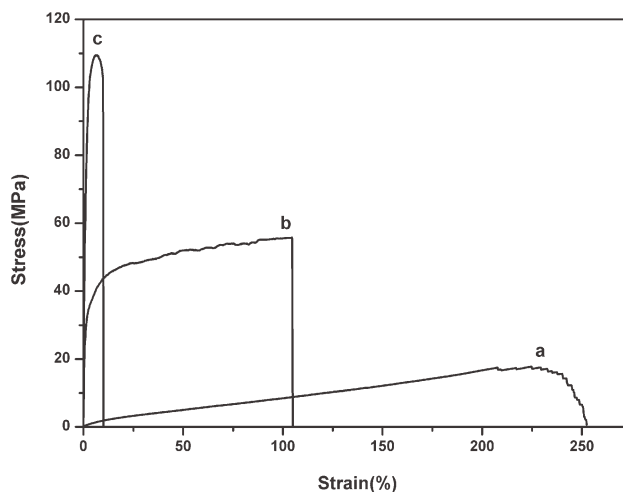


Figure 1 Stress–strain curves of PVA fibers with different water content (a) 35 wt %, (b) 10 wt %, and (c) 2 wt %.

detector with a power of 18 kW and Ni-filtered Cu K α radiation. The accelerating voltage was 40 kV, the electric current was 200 mA, the area detector was 460 \times 256 mm², and the exposure time was 30 s.

Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) of PVA fibers were performed with TA Q800 dynamic mechanical analysis apparatus. Adopting forced-non-resonant stretching mode to obtain the temperature spectrum, the frequency was 1 Hz, the amplitude was 50 μ m and the force track was 135.0%. The storage modulus (G') temperature curves, the loss modulus (G'') temperature curves and the internal friction value ($\tan \delta$)-temperature curves were recorded and the full-width at half-maximum ($T_{H/2}$) of the $\tan \delta$ peak was calculated from the $\tan \delta$ -temperature curve. The measurements of the samples were performed by heating from -100 to 100°C at a heating rate of $3^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

Mechanical properties test

The tensile strength and elongation of PVA fibers were obtained using a RG-10 computer controlled tensile testing machine manufactured by Shenzhen Reger Instrument. Clamp distance was 50 mm and the drawing rate was 50 mm/min.

RESULTS AND DISCUSSION

Effects of water content on the drawability of PVA fibers

Figure 1 shows the stress–strain curves of PVA fibers with different water content drawing at room temperature. When the water content decreased from 35 to 2 wt %, the yield stress of PVA fibers increased

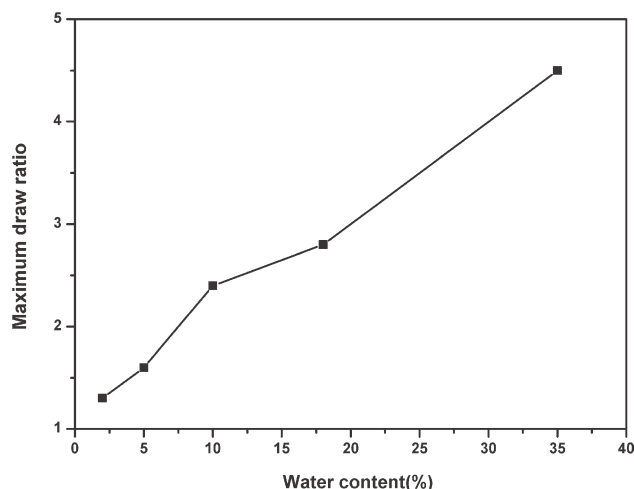


Figure 2 Effects of water content on the maximum draw ratio of PVA fibers drawing at room temperature.

from 17 to 109 MPa. This was the result of plastic effect of water on PVA fibers. When the water content was high, strong hydrogen bonds were formed between water and PVA, and the intra- and intermolecular hydrogen bonds of PVA were weakened. As a result, PVA molecular chains were easy to move and PVA fibers were easy to be drawn. With the water content of PVA fibers decreasing, enhanced hydrogen bonds of PVA made the molecular slip-page difficult, so the plastic deformation of PVA fibers became harder and the yield stress increased rapidly with the elongation decreased.

The effects of water content on PVA fibers drawn at room temperature are also reflected in the maximum draw ratio of PVA fibers. Figure 2 shows the relationship between the maximum draw ratio of PVA fibers and the water content. When the water content decreased from 35 to 2 wt %, the maximum draw ratio of PVA fibers decreased from 4.5 to 1.3.

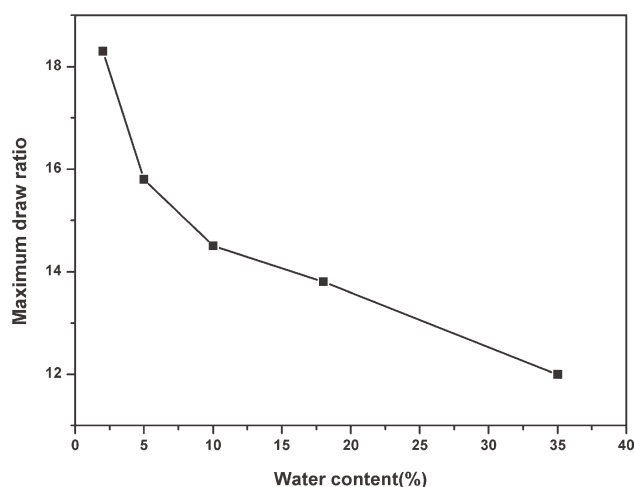


Figure 3 Effects of water content on the maximum draw ratio of PVA fibers drawing at 200°C.

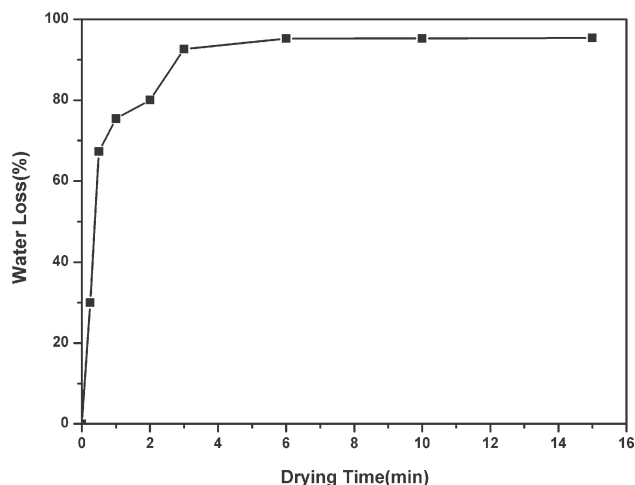


Figure 4 Effects of drying time on the water loss of PVA fibers.

It is shown that water is good plasticizer of PVA fibers drawing at room temperature.

To improve the draw ratio of fibers, hot drawing is usually adopted. The effects of water content on the maximum draw ratio of PVA fibers drawn at 200°C are shown in Figure 3. It is observed that the maximum draw ratio of PVA fibers decreased with water content increasing. When the water content of PVA fibers was too high during hot drawing, it was easy to form internal defects in fibers because of the evaporation of excessive water. As a result, the drawability of PVA fibers was reduced and the maximum draw ratio decreased. Therefore, the drying is necessary for the as-spun PVA fibers before hot drawing.

Figure 4 presents the relationship between the water loss of PVA fibers and drying time. As shown in Figure 4, PVA fibers lose water quickly when dried at 200°C with the increasing time. The water loss rate increased during hot drawing, which was unfavorable to drawing. So, to obtain PVA fibers with excellent drawability during hot drawing, the water content should be controlled.

The effects of drying time on the tensile strength of drawn PVA fibers are shown in Figure 5. It can be seen from Figure 5 that the tensile strength of PVA fibers increased first with the drying time increasing. However, it was unfavorable for as-spun PVA fibers dried too long time. The tensile strength of PVA fibers decreased sharply when PVA fibers dried at 200°C over 3 min. This was because that the negative impact of serious degradation of PVA fibers after too long time drying far beyond the positive impact of water decreasing. When as-spun PVA fibers dried at 200°C for 3 min, PVA fibers with excellent drawability were obtained. Therefore, this drying process was carried out for all PVA fibers in the later part of this article.

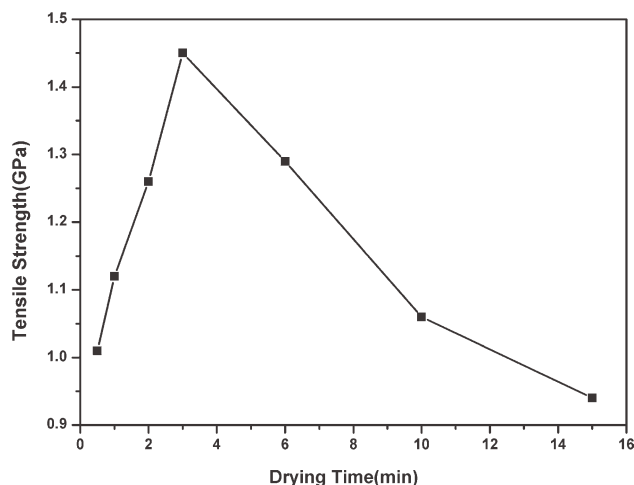


Figure 5 Effects of drying time on the tensile strength of PVA fibers with draw ratio of 10.

Effects of drawing parameters on the drawability of PVA fibers

The effects of drawing temperature on the maximum draw ratio of PVA fibers are shown in Figure 6. With the drawing temperature increasing, the maximum draw ratio of PVA fibers increased. When the drawing temperature was 90°C, PVA molecular chains were hardly move and the internal stress was high, PVA fibers were easy to break and the maximum draw ratio was only 5. With the drawing temperature increasing, PVA chains were more easily to stretch along the direction of tensile stress because of the enhanced molecular mobility.¹⁵ As a result, the maximum draw ratio of PVA fibers increased. When the drawing temperature was 200°C, the maximum draw ratio of PVA fibers was 18.5. While with the drawing temperature increased to 210°C, the maximum draw ratio of PVA fibers decreased instead. This was because that when the drawing temperature was too high, some PVA fibers became

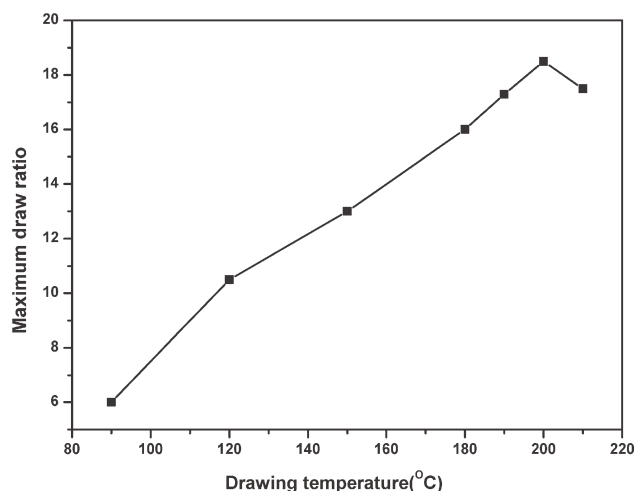


Figure 6 Effects of drawing temperature on the maximum draw ratio of PVA fibers.

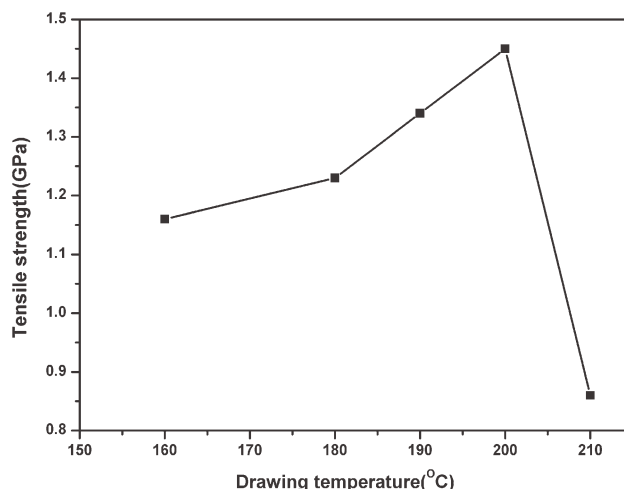


Figure 7 Effects of drawing temperature on the tensile strength of PVA fibers.

fused at the effect of tensile stress and thus affecting the smooth drawing of PVA fibers.

The effects of drawing temperature on the tensile strength of PVA fibers drawn at 100 mm/min are shown in Figure 7. With the drawing temperature increased to 200°C, the tensile strength of PVA fiber increased. When the drawing temperature was over 210°C, the tensile strength of PVA fibers decreased instead. As we known, two opposite phenomena existed during the drawing process, i.e., orientation and disorientation.¹⁶ When the drawing temperature was too high, the effect of disorientation surpassed the effect of orientation, and the increased chain slippage reduced the efficiency of the orientation. Moreover, the thermal degradation of PVA fibers caused the internal defects of fibers. Therefore, the tensile strength of PVA fibers decreased when drawn at 210°C. The proper drawing temperature for melt spun PVA fibers was 200°C.

Figure 8 reflects the relationship between the maximum draw ratio of PVA fibers and drawing speed.

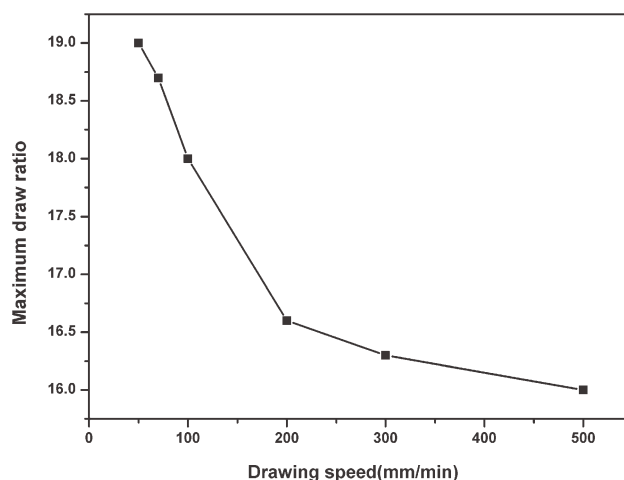


Figure 8 Effects of drawing speed on the maximum draw ratio of PVA fibers drawn at 200°C.

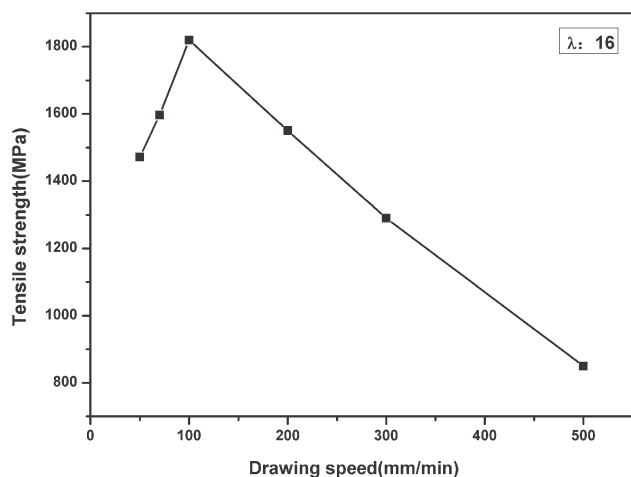


Figure 9 Effects of drawing speed on the tensile strength of PVA fibers drawing at 200°C.

The lower drawing speed, the higher maximum draw ratio of PVA fibers was obtained. With the drawing speed decreasing, the available relaxation time for PVA molecular chains increased so that there was more time for the rearrangement of PVA chains. As a result, the internal stress of PVA fibers was reduced and the maximum draw ratio increased.

The mechanical properties of PVA fibers drawn at different drawing speeds with the draw ratio of 16 are shown in Figure 9. With the drawing speed increasing, the tensile strength of PVA fibers increased first and then decreased. When the drawing speed was too low, the thermal degradation of PVA fibers was aggravated in accordance, resulting in the decrease of the tensile strength of PVA fibers. When the drawing speed was too high, the available relaxation time for PVA molecular chains was not long enough that PVA chains could not respond to external force timely under the effect of tensile

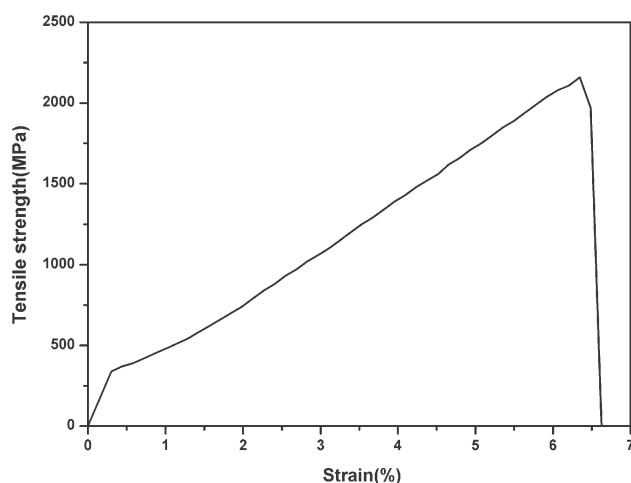


Figure 10 Stress-strain curve of PVA fibers with the draw ratio of 16.

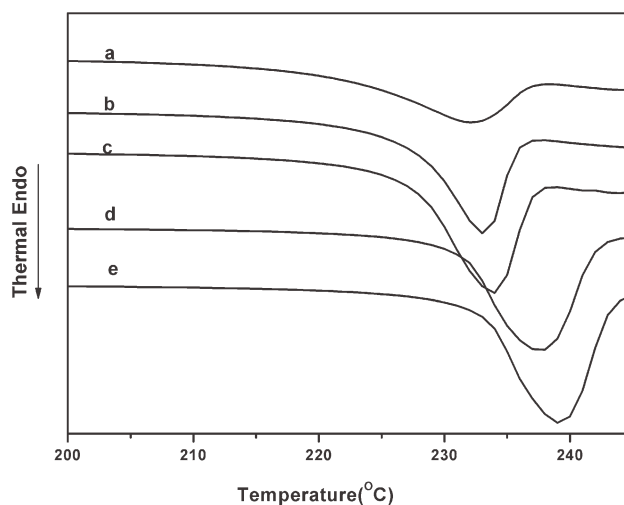


Figure 11 DSC curves of PVA fibers with different draw ratio (a) $\lambda = 1$, (b) $\lambda = 2$, (c) $\lambda = 4$, (d) $\lambda = 10$, and (e) $\lambda = 13$.

stress. Therefore, the internal stress of PVA fibers increased and the tensile strength of PVA fibers decreased. At the proper drawing speed of 100 mm/min, the mechanical properties of PVA fibers were the best.

The typical stress-strain curve of drawn PVA fibers with the draw ratio of 16 is shown in Figure 10. Under the drawing condition of 200°C and 100 mm/min, the average diameter, average tensile strength and the highest tensile strength of PVA fibers were 40 μm , 1.85 and 2.06 GPa, respectively.

The crystalline structure changes of PVA fibers during drawing

The DSC curves of PVA fibers drawn at 200°C with different draw ratios are shown in Figure 11, and the related thermal properties data are accordingly listed in Table I. As shown in Figure 11 and Table I, the crystallinity of PVA fibers increased rapidly with the draw ratio increasing. When the draw ratio was 13, the crystallinity of PVA fibers increased from 33.1 to 66.8%. This was due to the combined effect of stress induced crystallization and thermal induced crystallization.¹⁷ The melting point of PVA fibers increased from 232.2 to 239.3°C with the increase of draw ratio, suggesting that the disarrangement crystalline region of PVA fibers decreased, the lamellar

TABLE I
DSC Analyze Results of PVA Fibers with Different Draw Ratio

Draw ratio	Melt temperature (°C)	Crystallinity (%)
1	232.2	33.1
2	233.0	47.1
4	233.7	55.0
10	237.4	61.8
13	239.3	66.8

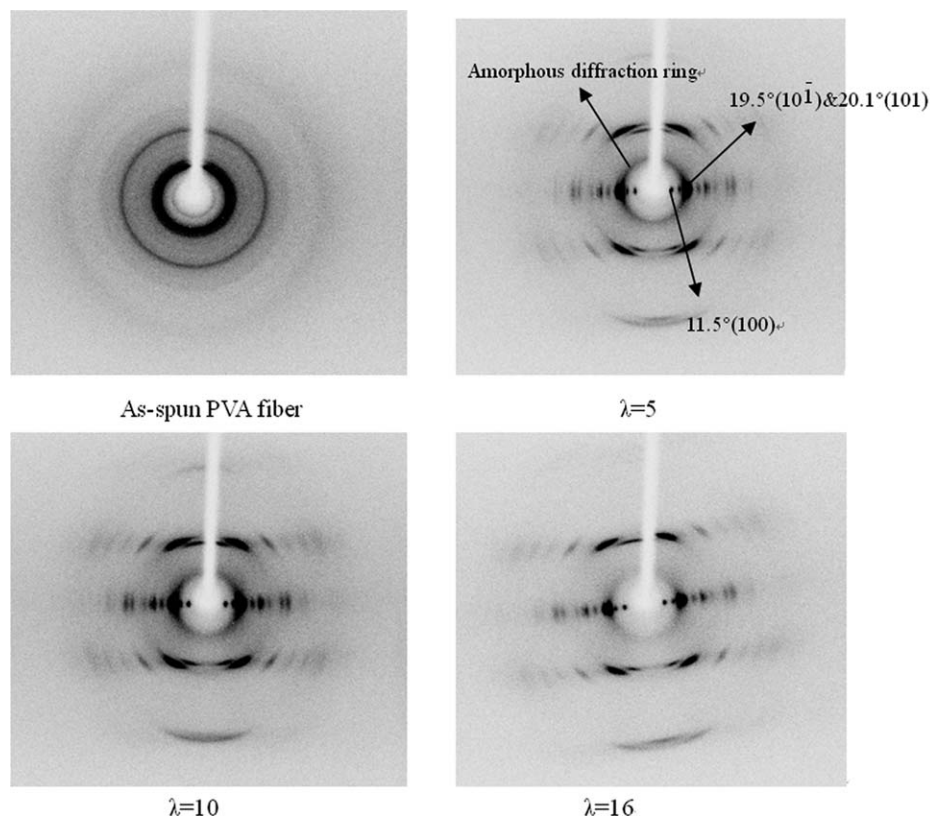


Figure 12 2-D WAXD profiles of PVA fibers with different draw ratio.

thickness of PVA fibers increased, and the crystalline structure was improved.

The 2-D WAXD scattering patterns of PVA fibers drawn at 200°C with different draw ratios are shown in Figure 12. According to the changes of 2-D scattering pattern of PVA fibers, the changes of planes of PVA fibers during hot drawing could be qualitatively analyzed.

In the 2-D scattering pattern of PVA fibers without drawing, a circular scattering pattern with a homogeneous intensity distribution along the circle was observed, indicating that PVA fibers were random oriented.¹⁸ With the draw ratio increasing, the circular diffraction concentrates on the transversal direction at some specific angles, indicating that axial ordered structure existed in the drawn PVA fibers,¹⁹ which was attributed to the molecular orientation of different motion unit during drawing, on the other hand, the polarity group of —OH was beneficial to keep the ordered arrangement and orientation of PVA chains.

When the draw ratio of PVA fibers was 5, the diffraction arcs of planes of PVA fibers could be clearly picked out in the 2-D WAXD scattering pattern, which were the diffraction arc of (100) plane at $2\theta = 11.5^\circ$, (10 $\bar{1}$) plane at $2\theta = 19.5^\circ$, (101) plane at $2\theta = 20.1^\circ$.^{20,21} In particular, (10 $\bar{1}$) plane and (101) plane were overlap and formed one diffraction arc in the

$2\theta = 20^\circ$. Different length of diffraction arcs on the transversal direction reflected the preferred orientation of different planes of PVA fibers. The diffraction arc of (100) plane was concentrated on the transversal direction, indicating that the (100) plane of PVA fibers was oriented along the drawing direction. The diffraction arc of (10 $\bar{1}$) and (101) plane was relative longer, indicating that the orientation of (10 $\bar{1}$) and (101) plane was weaker than (100) plane. This is because that (101) plane is closely related with molecular chain interface along the inter hydrogen bond. During hot drawing, molecular mobility in the plane was lower because of inter hydrogen bond interaction. It was more difficult for the molecular chains to move along the tensile stress, thus the orientation of (10 $\bar{1}$) and (101) plane was smaller along the drawing direction. There was circular background in the 2θ of 20° , which was amorphous dispersion ring.

With the draw ratio increased further, diffraction arcs on the transversal direction became shorter. When the draw ratio was 16, the 2-D WAXD scattering pattern of planes showed the diffraction spots, suggesting that high degree orientation of PVA fibers was formed. Besides, the amorphous dispersion ring in the 2θ of 20° became weaker, suggesting that the amorphous content of PVA fibers decreased with draw ratio increasing.

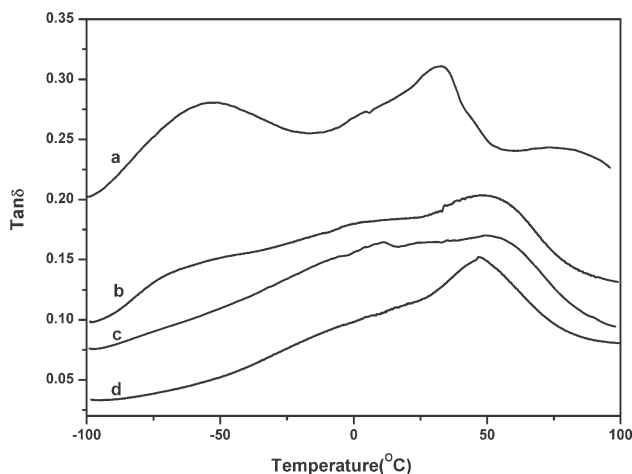


Figure 13 DMA curves of PVA fibers with different draw ratio (a) $\lambda = 1$, (b) $\lambda = 5$, (c) $\lambda = 10$, and (d) $\lambda = 16$.

The amorphous region change of PVA fibers during drawing

The dynamic mechanical analysis curves of PVA fibers with different draw ratio are shown in Figure 13, in which the high temperature peak is correspond to the glass transition temperature T_{α} , and the low temperature peak is correspond to secondary transition peak T_{β} . β relaxation is attributed to the movement of side groups, heteroatom or local relaxation mode of short chain segments.

Tan δ is closely related to the amorphous content and molecular mobility. Under the periodic effect, more activity amounts cause more energy loss, leading to higher tan δ value. As shown in Figure 13, tan δ value of PVA fibers decreased with draw ratio increasing, indicating that the amorphous molecular mobility weakened with draw ratio increasing. The amorphous molecular mobility was restricted by gradually compact arranged amorphous and the increased crystalline region.^{22–24} As a result, tan δ of PVA fibers decreased under the periodic effect. In addition, the low temperature peak of PVA fibers became weaker after drawing. When the draw ratio was 16, the low temperature peak almost disappeared, indicating that the amorphous region of PVA fibers was ordered arrangement, and the interaction of side group -OH of PVA fibers was strong.

TABLE II
 T_g and T_g Peak Widths at Half Maximum ($T_{H/2}$)
Obtained from Tan δ vs. Temperature Curves of PVA
Fibers with Different Draw Ratio

Draw ratio	T_g (°C)	$T_{H/2}$ (°C)
1	33.6	101.4
5	48.3	91.1
10	50.3	76.9
16	47.8	68.2

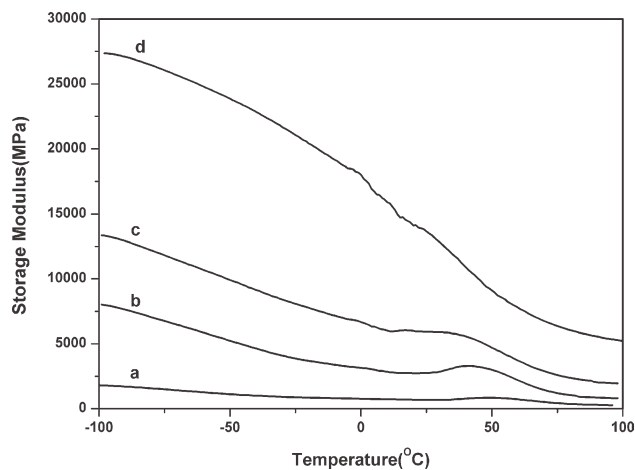


Figure 14 Storage modulus curves of PVA fibers with different draw ratio (a) $\lambda = 1$, (b) $\lambda = 5$, (c) $\lambda = 10$, and (d) $\lambda = 16$.

In consequence, it was hard to observe the low temperature peak because of weak β relaxation.

Table II lists the T_g and the full-width at half-maximum ($T_{H/2}$) of the tan δ peak, obtained from tan δ versus temperature curves for each sample. The full-width at half-maximum of the tan δ peak refers to the homogeneity of the amorphous phase, so that a bigger $T_{H/2}$ value implies a higher inhomogeneity of the amorphous phase. Clearly the $T_{H/2}$ of PVA fibers without drawing was the widest, while the span of tan δ of PVA fibers with draw ratio of 16 was narrower, indicating that the amorphous structure in PVA fibers without drawing was complex and there were multiple structures with different molecular mobility. With draw ratio increasing, the amorphous arrangement became regularer, the defective reduced and the molecular mobility was relatively uniform.

Storage modulus G reflects the elastic component in material viscoelasticity, characterizing the deformation resistance of materials. The higher the storage

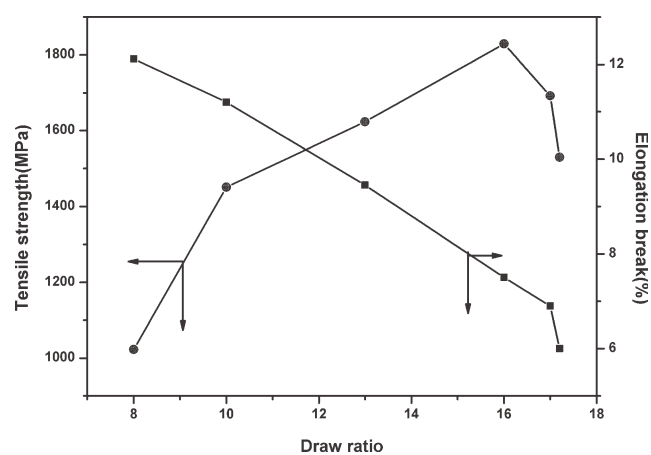


Figure 15 Effect of draw ratio on the tensile strength and elongation of PVA fibers.

modulus, the harder the deformation of materials, that is, the greater the stiffness. As shown in Figure 14, the storage modulus of PVA fibers increased with draw ratio increasing, suggesting the increased resistance of PVA fibers deformation.

The change of tensile strength of PVA fibers during drawing

Figure 15 shows the effect of draw ratio on the tensile strength and elongation of PVA fibers drawn at 200°C. With draw ratio increasing, the tensile strength of PVA fibers increased and the elongation decreased. According to the above discussion, the crystallinity, orientation, ordered degree of amorphous arrangement, and storage modulus were increased with draw ratio increasing within the draw ratio of 16. Hence, the tensile strength of PVA fibers increased correspondingly. However, when the draw ratio was over 16, excessive drawing happened and part of PVA fibers was broken. Axial internal stress of PVA fibers concentrated to form microporous, which gathered into cracks. The tensile strength and elongation of PVA fiber decreased rapidly and high performance PVA fibers could not be obtained. When the draw ratio was 16, the tensile strength of PVA fibers was 1.85 GPa in average and up to 2.06 GPa, which was two to three times that of the fiber obtained by wet spinning¹ and was higher than that obtained from other spinning methods with the same polymerization degree.^{25–27} Hence it was shown that PVA fibers with good mechanical properties can be prepared through melt spinning and hot drawing.

CONCLUSION

The drawability of melt spun PVA fibers, the crystalline and amorphous phase changes of PVA fibers during hot drawing process were studied. The results showed that water was good plasticizer of PVA fibers drawn at room temperature, whereas the water content should be controlled before hot drawing. When as-spun PVA fibers dried 200°C for 3 min, the PVA fibers with excellent drawability can be obtained. The proper drawing condition for PVA fibers was 200°C and 100 mm/min. The crystallinity and melt point of PVA fibers increased with the

draw ratio increasing, and the crystalline structure was improved. The 2-D WAXD scattering pattern of PVA fibers changed from a circular and homogeneous scattering pattern to diffraction point, indicating that the crystal orientation gradually increased. With draw ratio increasing, the amorphous gradually arranged ordered and the molecular mobility in PVA fibers amorphous region decreased. When PVA fibers were drawn at 200°C with the draw ratio of 16, the tensile strength of PVA fibers reached at 1.85 GPa.

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