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ORIGINAL PAPER

Crystallization behavior of melt-spun poly(vinyl alcohol) fibers during drawing process

Qian Wu · Ning Chen · Qi Wang

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Abstract The crystallization behavior of melt-spun poly (vinyl alcohol) (PVA) fibers during hot drawing process was studied by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and computer controlled electronic universal testing machine. The effects of drawing temperature and drawing speed on the crystallinity and the stress induced crystallization of PVA fibers were discussed. The results showed that the crystallization process of PVA fibers during hot drawing presented three stages: initial stage, stress induced crystallization stage and slowly increasing stage. And PVA fibers with high crystallinity can be obtained by properly increasing the drawing temperature and drawing speed, especially when the drawing temperature and speed were 453 K and 100 mm/min respectively. The stress induced crystallinity of PVA fibers during drawing process was the difference between the crystallinity of PVA fibers after drawing and after only heat treatment. At the low drawing speed, i.e. 50 mm/min, due to the strong molecular movement and orientation relaxation under high temperature, the effect of stress induced crystallization weakens with the increase of drawing temperature, the ratio between stress induced crystallinity and thermal induced crystallinity changed from 8.7%:0% (393 K) to 1.7%:5% (453 K). While at the high drawing speeds, i.e. 100 mm/min and 500 mm/min, with the decrease of available orientation relaxation time, the stress induced crystallization plays an important role during the drawing process, the ratio between stress induced crystallinity and thermal induced crystallinity were 8%:2.9% and 10.2%:0.5% at 453 K respectively.

Keywords Poly(vinyl alcohol) · Melt-spun fiber · Drawing · Stress induced crystallization

Introduction

Poly(vinyl alcohol) (PVA) is a flexible chain polymer, with plane zigzag conformation similar to that of polyethylene (PE) and high theoretical strength and crystal lattice modulus, i.e 30 GPa and 250 GPa, respectively [1], so PVA is expected to produce high strength and high modulus fibers by high drawing. Furthermore, PVA fibers have superior qualities of impact strength, weather durability, antialkaline resistance, abrasion resistance, etc [2]. More importantly, the crystal relaxation and melting point of PVA is higher than that of PE, which endows PVA fibers with better creep resistance and wider application than PE fibers [3]. Therefore, the preparation of high strength and high modulus PVA fibers has absorbed the interests of more and more researchers in recent decades.

Melt spinning is the simplest process among all the spinning methods, highly efficient and environmental friendly. However, the multi-hydroxyl structure of PVA makes its melting point so close to its decomposition temperature that the melt spinning of PVA is very difficult. So far, high strength PVA fibers are usually prepared by gel spinning [4], crosslinking wet spinning [5], alcoholysis spinning from polyvinyl acetate [6] and so on. All above methods use high molecular weight PVA and are based on and limited to wet spinning process, which contains the complex procedures of dissolution, coagulation bath or spinning bath and desolventization, etc.

Q. Wu · N. Chen · Q. Wang (✉)
State Key Laboratory of Polymer Materials Engineering,
Polymer Research Institute of Sichuan University,
Chengdu 610065, China
e-mail: qiwang@scu.edu.cn

Numerous studies have been devoted to realize the melt spinning of PVA by blending [7, 8], copolymerization [9–11] and plasticization [12–14]. Nevertheless, the industrialization of these methods was limited by the complicated treatment of PVA. Based on intermolecular complexation and plasticization, we have developed a novel and environmental friendly technique to control the supermolecular structure of PVA, and decrease its melting point and realize its thermal processing [15–18], thus obtaining PVA fibers with circular cross, uniform structure and excellent drawing ability by melt spinning [19].

To obtain high strength and high modulus fibers, drawing is an important process. During drawing process, stress induced crystallization is an important phenomenon, which increases the crystallization rate and the crystallinity of polymer, thus improves the mechanical properties of polymer products. Many studies were conducted to investigate the stress induced crystallization of synthetic polymer fibers such as polyethylene terephthalate (PET). Salem suggested that deformation of PET presents two stages: (i) smooth increase of stress with rapid increase in the crystallinity of the material; (ii) rapid increase of stress at almost constant crystallinity [20]. Kawakami evidenced the formation of the mesophase as a precursor of strain hardening in PET [21].

However, few studies on stress induced crystallization of PVA fibers during drawing process have been reported. Mechanical properties of PVA fibers are greatly affected by the degree of orientation and crystallinity imparted during drawing process, in which stress induced crystallization plays an important role. Thus, it is of prime interest to observe and to understand the development of the crystallization behavior of PVA fibers during drawing.

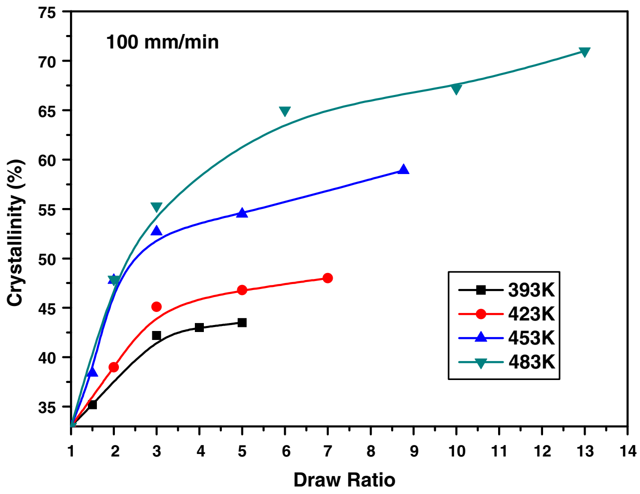

Fig. 1 Effects of temperature on the crystallinity of PVA fibers drawing at 100 mm/min

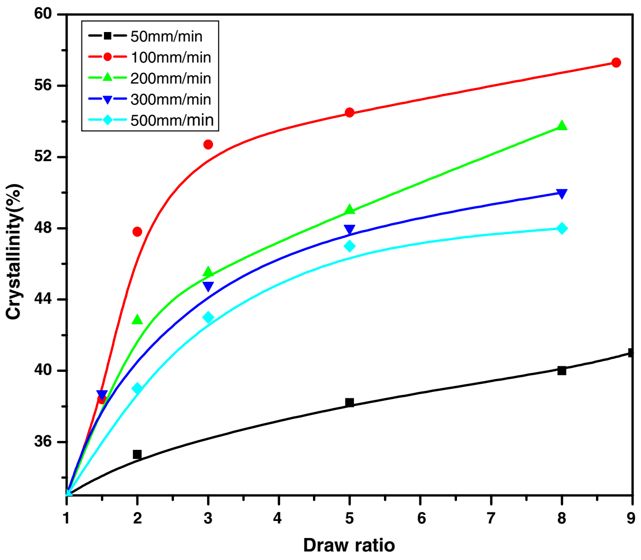

Fig. 2 Effects of drawing speed on the crystallinity of PVA fibers drawing at 453 K

According to the difference between the crystallinity of PVA fibers after drawing and the crystallinity of PVA fibers after only heat treatment, the stress induced crystallinity could be obtained and the role of stress induced crystallization during different drawing conditions could be better understood.

In this paper, hot drawing was employed and the change of the crystallinity, the stress induced crystallization behavior of melt spun PVA fibers during hot drawing were studied.

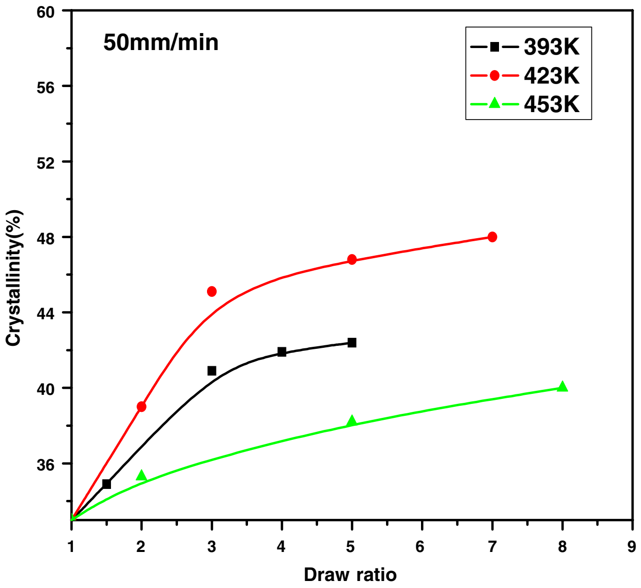

Fig. 3 Effects of temperature on the crystallinity of PVA fibers drawing at 50 mm/min

Experimental

Materials

Melt spun PVA fibers were prepared according to Ref. [22]. Drawing of PVA fibers was conducted with a laboratory made hot pipe drawing equipment. Drawing rates were 50 mm/min, 100 mm/min, 200 mm/min, 300 mm/min and 500 mm/min respectively. Drawing temperature were 393 K, 423 K and 453 K respectively.

Characterization

Differential scanning calorimeter (DSC) curves were recorded on a Netsch 204 DSC differential scanning calorimetry. Approximately 6 mg of sample was used and the measurements of the samples were performed by heating from 373 K to 533 K at a heating rate of 10 K/min under a nitrogen atmosphere. The crystallinity of PVA fibers was calculated by the following equation:

$$X(\%) = \Delta H_f \Big/ \Delta H_f^o \times 100\% \qquad (1)$$

where ΔH_f is the melting enthalpy of PVA fibers and ΔH_f^o is the melting enthalpy of the 100% crystalline PVA with the value of 168 J/g [23].

The crystalline structure of PVA fibers were characterized by Dmax-1000 X-ray diffractometer manufactured by Philips Company. The samples were continuously scanned from 5° to 40° at a rate of 0.06 °/s. The accelerating voltage was 40 kV and the electric current was 25 mA.

The stress-strain curves of PVA fibers during hot drawing were obtained by the laboratory made hot pipe drawing equipment simultaneously using with RG-10 computer controlled tensile testing machine manufactured by Shenzhen Reger Instrument Corporation. Drawing rates were 50 mm/min, 100 mm/min, 200 mm/min, 300 mm/min and 500 mm/min, respectively. And drawing temperatures were 393 K, 423 K and 453 K, respectively.

Measurements of stress induced crystallinity and thermal induced crystallinity

Stress induced crystallinity, the crystallinity induced by tensile stress (X_s) during drawing is defined as: $X_s = X_c - X_t$, where X_c is the crystallinity of PVA fibers drawn t minute at T temperature, X_t is the crystalinity of PVA fibers without drawing but heat treated for t minute at T. Thermal induced crystallinity part is the increased crystallinity value of PVA fibers after heat treated for t minute at T.

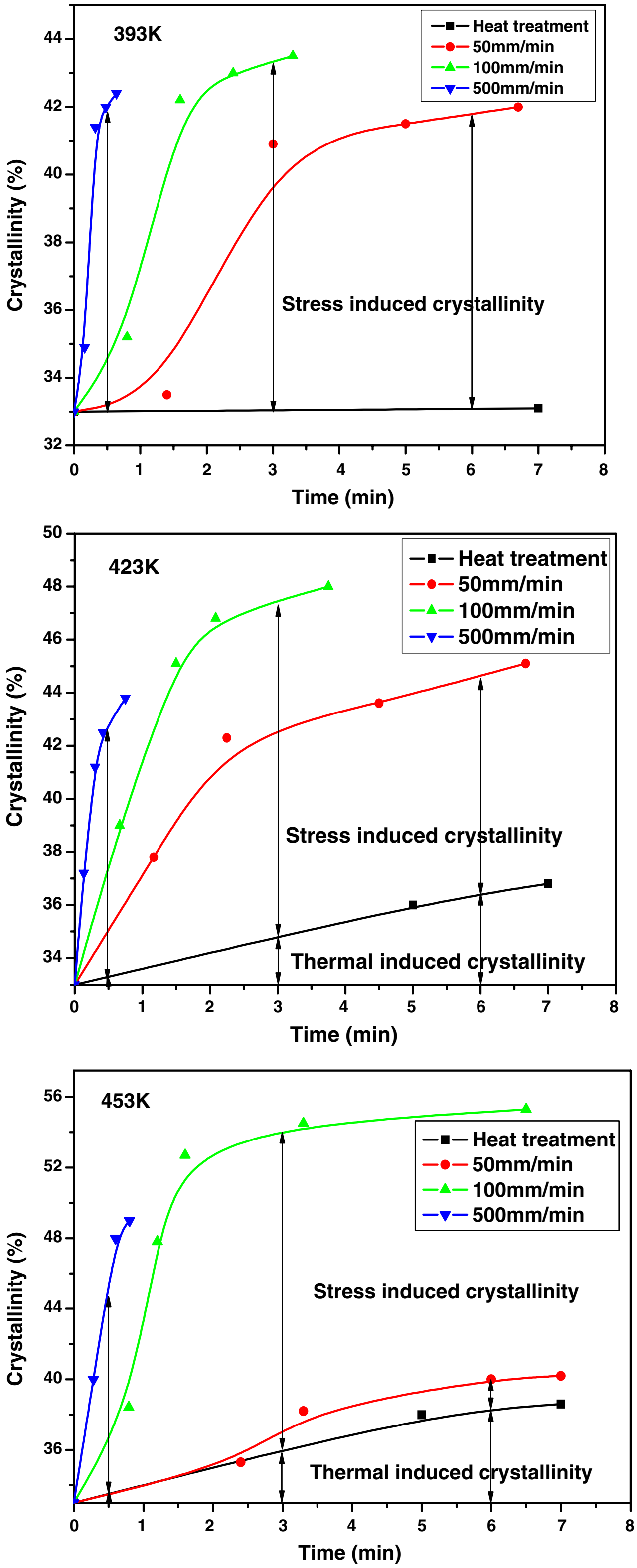

Fig. 4 Thermal induced crystallinity and stress induced crystallinity of PVA fibers at various temperatures and drawing speeds

Results and discussion

The change of crystallinity of PVA fibers during drawing

The effects of drawing temperature on the crystallinity of PVA fibers drawn at 100 mm/min are shown in Fig. 1. With the increase of drawing temperature, the crystallinity of PVA fibers increased at the same draw ratio, especially when the drawing temperature increased to 483 K, the crystallinity increased even more remarkably. This is because PVA chains are more easily to stretch along the direction of tensile stress when the drawing temperature increases ascribed to the enhanced molecular mobility [24], resulting in the increase of crystallization rate and the crystallinity of PVA fibers.

Figure 2 shows the effects of drawing speed on crystallinity of PVA fibers drawing at 393 K. At the same draw ratio, the crystallinity of PVA fibers increased first and then decreased with the increase of the drawing speed. The highest crystallinity of PVA fibers was reached at 100 mm/min drawing speed. As known, two opposite phenomena exist during the drawing process, i.e. orientation and disorientation. Melt spun PVA fibers have more chain entanglement, so the adequate energy supplied by high temperature and the time are needed for the tie molecules between the adjacent lamellar to disentanglement and orient under the tensile stress. When PVA fibers were drawn under the condition of 453 K and the low speed of 50 mm/min, the drawing was similar to "flow drawing" [25]. The available relaxation time for PVA molecular chains was so long that the orientation degree, the crystallization rate and the crystallinity were low. While at the high drawing speed (above 100 mm/min), there was no enough time for the orientation and rearrangement of PVA chains, resulting in the decrease of the crystallization rate and crystallinity of PVA fibers. Only at the proper drawing speed (100 mm/min), the orientation could surpass the disorientation and induced the crystallization, the crystallization rate of PVA fibers was fast and the crystallinity was high.

Figure 3 shows the effects of drawing temperature on the crystallinity of PVA fibers at low drawing speed of 50 mm/min. At the same draw ratio, the crystallinity of PVA fibers first increased and then decreased with the increase of drawing temperature. This is due to the balance between two opposing effects, i.e. the relaxation rate of amorphous chains and the crystallization rate at given amorphous orientation [25, 26]. When PVA fibers were drawn at relative low temperature (393 K and 423 K), the thermal mobility enhanced and the orientation relaxation accelerated as the temperature increasing, whereas the crystallization rate at given degree of amorphous orientation also increased rapidly and played a dominate role, leading the increase of the crystallinity of PVA fibers. However, PVA fibers drawn at 453 K with low drawing speed were tended to "flow drawing". The relaxation effect played a dominate role during the drawing process, resulting in the decrease of crystallization rate and crystallinity of PVA fibers.

Stress induced crystallinity and thermal induced crystallinity

During the hot drawing, the increased crystallinity of PVA fibers included stress induced crystallinity and thermal induced crystallinity. Figure 4 presents the comparison between the crystallinity of PVA fibers drawn at the given speed and undrawn fibers but heated for the same time at the same temperature. Obviously, the crystallinity of PVA fibers increased significantly after drawing, indicating that the tensile stress had remarkable inducing effects on crystallization of PVA fibers. To further illustrate the contribution of stress induced crystallinity and the thermal induced crystallinity to PVA fibers, the ratios between stress induced crystallinity and thermal induced crystallinity is shown in Table 1, where the draw ratios of PVA fibers were 5 under drawing speeds of 50 mm/min 100 mm/min and 500 mm/min.

A problem worth to be pointed out in Table 1 is that thermal induced crystallinity of PVA fibers within only heat treatment for 6 min at 393 K was 0%. This is due to the changed crystallinity of PVA fibers was not large enough to be detected out through DSC. It can be seen from Fig. 4 and Table 1 that when the drawing speed was low (50 mm/min), the ratio between stress induced crystallinity and thermal induced crystallinity decreased with the drawing temperature increasing, from 8.7%:0% at 393 K to 1.7%:5% at 453 K, meaning that the stress induced crystallization effect decrease. This is because that at the relative low drawing temperature, the thermal mobility of

Table 1 The ratio between stress induced crystallinity and thermal induced crystallinity of PVA fibers at different drawing conditions

PVA fibers	Stress induced crystallinity: Thermal induced crystallinity		
	393K	423K	453K
50 mm/min (6 min)	8.7%:0%	8.3%:3.3%	1.7%:5%
100 mm/min (3 min)	10.3%:0%	12.5%:1.7%	8%:2.9%
500 mm/min (0.5 min)	9%:0%	9.2%:0.3%	10.2%:0.5%

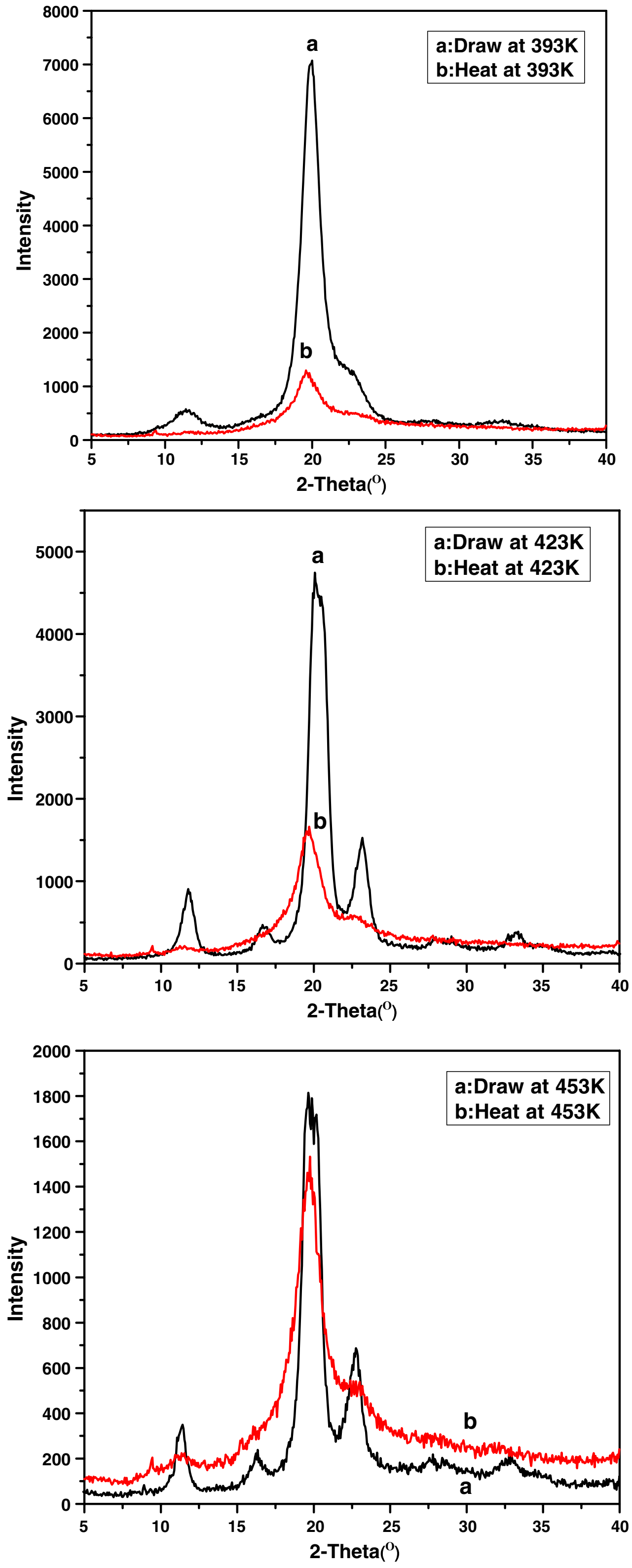

Fig. 5 WXRD profiles of PVA fibers without drawing and drawn at various temperatures with draw ratio of 5

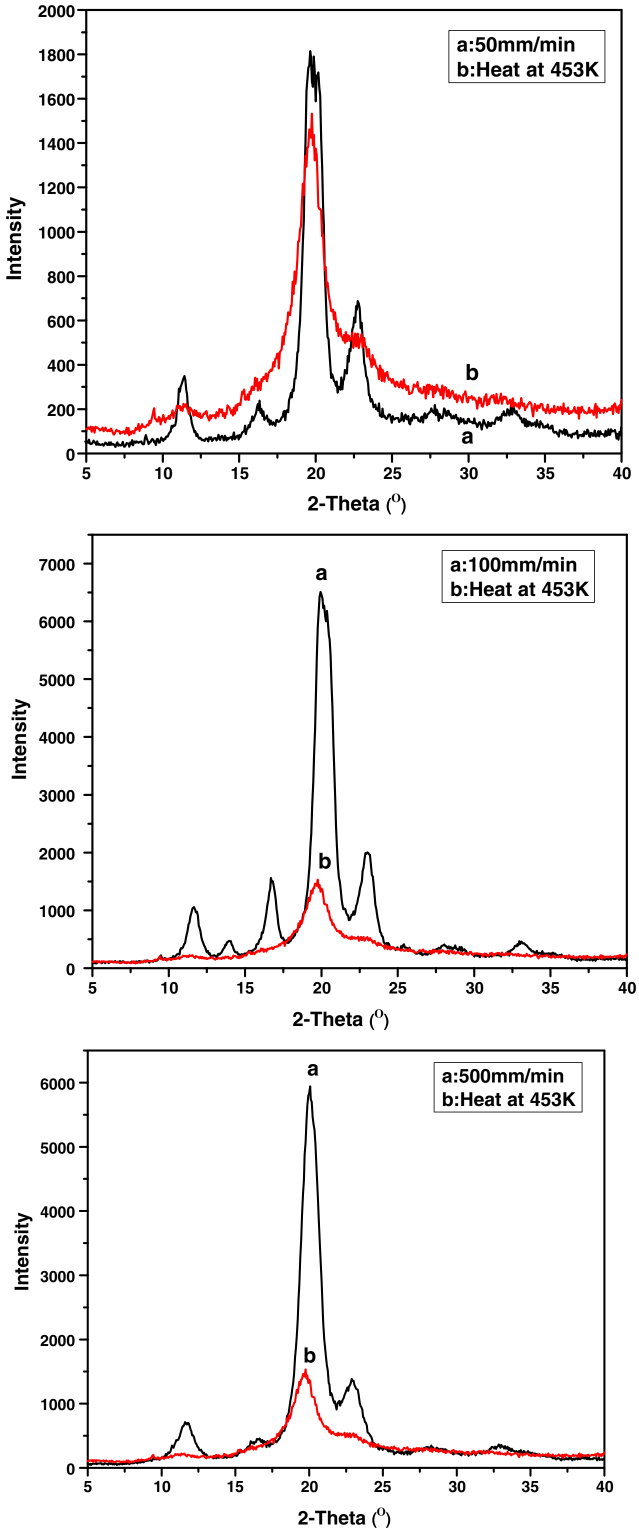

Fig. 6 WXRD profiles of PVA fibers without drawing and drawn at various draw speeds with draw ratio of 5

Table 2 XRD analytic results of PVA fibers drawing at 50 mm/min with draw ratio of 5

Drawing temperature (K)	I_{101}		I_{101}/I'_{101}
	Drawing	Heat treatment	
393	2,436	322	7.57
423	2,304	736	3.13
453	630	419	1.50

PVA chains was so weak that the disorientation was low although the relaxation time was long. As the temperature increased to 453 K, the molecular mobility of PVA was enhanced, the PVA chains were easy to disorientate, thus resulting in the decrease of orientation and the weakening of the stress induced crystallization. When the drawing speed increased to 100 mm/min, the relaxation time for the orientation of PVA chains reduced, therefore leading to the high orientation degree and the increased stress induced crystallization. The stress induced crystallization played a dominant role here. As the drawing speed furtherly increased to 500 mm/min, it was the stress induced crystallization that made the crystallinity increased in PVA fibers because of the short drawing time.

The above results can also be confirmed by the XRD analysis. Figures 5 and 6 are melting spun PVA fibers drawn under various conditions with the draw ratio of 5. Obviously, the intensity of crystallization diffraction peaks increased remarkably after drawing. The crystallization diffraction peak of (101) plane at $2\theta=20.1°$, relating to the interface of the PVA molecular chains along the intermolecular hydrogen bond, can reflect the regularity of PVA fibers [27, 28]. Hence, the intensity ratio of (101) plane diffraction peak between I_{101}/I'_{101}, where I_{101} is the intensity of PVA fibers drawn under certain temperature and I'_{101} is the intensity of PVA fibers only heat treated for the same time at the same temperature, can exclude the contribution of heat treatment to the regularity of PVA fibers and reflect the orientation degree of PVA fibers contributed by drawing.

The XRD profiles of PVA fibers were peak fitted by MDI Jade 5.0, and the ratios of I_{101}/I'_{101} were calculated, as shown in Table 2 and Table 3. When the drawing speed was 50 mm/min, I_{101}/I'_{101} decreased from 7.57 at 393 K to 1.5 at 453 K, meaning that the orientation degree of the PVA fiber decreased and the thermal induced crystallization

Table 3 XRD analytic results of PVA fibers drawing at 453 K with draw ratio of 5

Drawing speed (mm/min)	I_{101}		I_{101}/I'_{101}
	Drawing	Heat treatment	
50	630	419	1.50
100	3,106	419	7.41
500	1,886	419	4.50

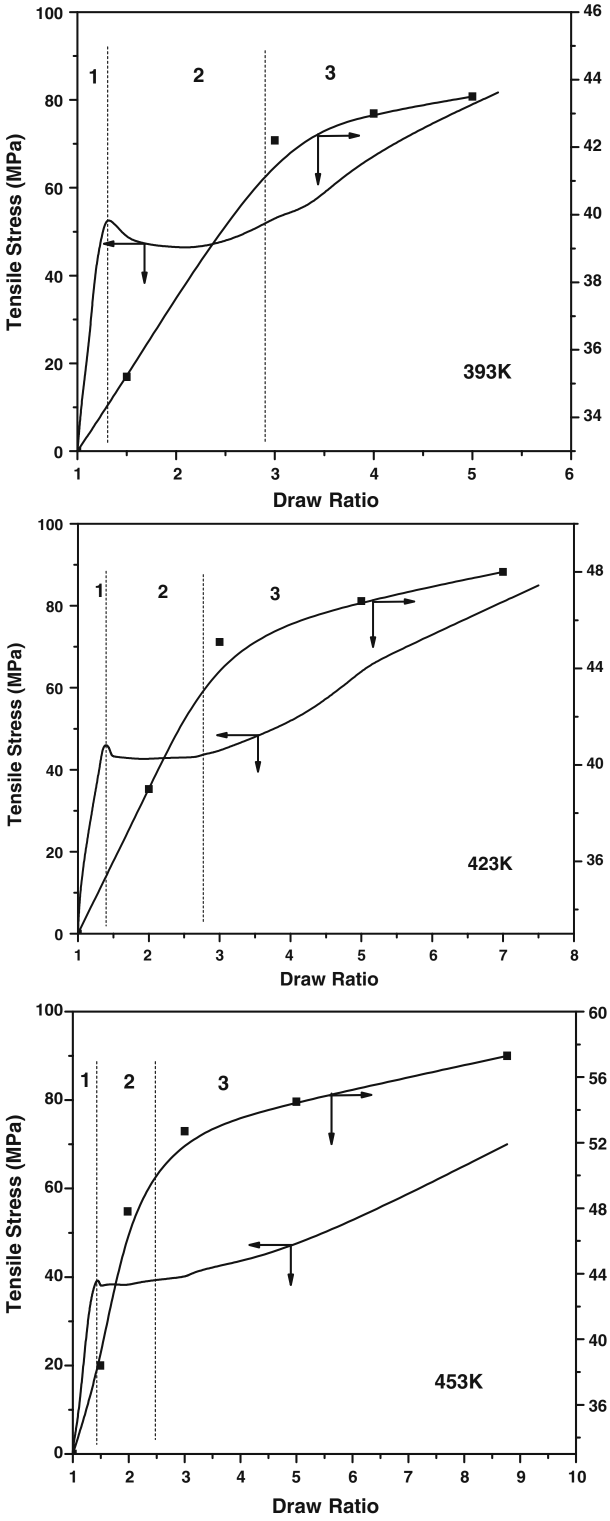

Fig. 7 Plot of the tensile stress and crystallinity of PVA fibers versus draw ratio

played an important role with the increase of drawing temperature. While fixed the drawing temperature at 453 K, I_{101}/I'_{101} increased to 7.41 at 100 mm/min and 4.5 at 500 mm/min respectively, indicating that properly increasing the drawing speed was beneficial to the orientation of PVA chains and can enhance the effect of the stress induced crystallization.

The crystallization process of PVA fibers during drawing

It can be seen from the above analyses that when drawn at 100 mm/min, the stress induced crystallization of PVA fibers was strong and the crystallinity was high. In order to clarify the crystallization process during drawing, the stress-strain curves of PVA fibers during hot drawing and the curves of crystallinity versus draw ratio of PVA fibers drawn at 100 mm/min are shown in Fig. 7. It is clear that the crystallization process presents three stages during the drawing process.

At the first stage, PVA chains need more energy to overcome the macromolecular internal stress and begin to move, so the tensile stress of the fibers increases rapidly, while the crystallinity of the fibers slightly increase with the draw ratio. After reaching the necking point, the crystallization process of PVA fibers enter into the second stage. At this stage, the tensile stress is almost invariant, the loose entanglement chains in amorphous are gradually stretch, and the chains tied between lamellas are partly straightened. Under the double effects of tensile stress and drawing temperature, the folded-chain lamellas joined these straightened chains gradually unfold and convert into the anisotropic mocrofibril structure [29]. The microfibril structure can induce the crystallization, thus the crystallinity of PVA fibers increases rapidly at this stage. This stage generally takes place at the draw ratio ranging from 1.5 to 3, and corresponds to the cold drawing process in the stress-strain curve. At the third stage, the folded chains keep on obtaining energy to unfold and gradually participate in the arrangement of tie chains. Possibly, parts of the folded chains form new extended crystalline area together with the adjacent tensioned tie chains. Ascribed to the gradually compact structure, the stress hardening happens with the increase of tensile stress, and the crystallinity increased more slowly compared to the previous two stages.

Conclusions

The crystallization behavior of as-spun PVA fibers prepared by melt spinning during hot drawing was studied. The results show that the crystallization of PVA fibers during drawing presented three stages: initial stage, the stress induced crystallization stage, and increasing slowly stage. The crystallinity of PVA fibers increased with the drawing temperature increasing, but with the drawing speed increasing, the cytstallinity of PVA fibers increased first and then decreased. When the drawing speed was 50 mm/min, the stress induced crystallization strongly depended on the temperature. With the increase of drawing temperature, the thermal mobility of PVA chains enhanced and the relaxation of orientation increased, resulting in the weakening of stress induced crystallization. While increasing the drawing speed to 100 mm/min and 500 mm/min, the available relaxation time of PVA chains decreased, resulting in the large orientation degree of PVA fibers. The stress induced crystallization played an important role during this drawing process.

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