A Novel Method to Prepare Poly(vinyl alcohol) Water-Soluble Fiber with Narrowly Dissolving Temperature Range

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ABSTRACT: Poly(vinyl alcohol) (PVA) is an important water-soluble polymer. In this study, a novel method has been developed for preparing water-soluble PVA fiber with narrowly dissolving temperature range via wet spinning of partly acetalized PVA. The structures and properties of the fiber were characterized by IR, ^{1}H-NMR, DSC, WAXD, tensile strength tester, etc. IR and NMR spectra showed that acetal groups were successfully generated on the lateral chains of PVA with the catalysis of acid. As a small quantity of CH_2O was added, the introduction of the acetal group could reduce both the hydrophilicity of amorphous region and the crystallinity of PVA water-soluble fiber, and hence narrowed the dissolving temperature range of fiber. However, the dissolving temperature range was broadened with a further increase of CH_2O amount, because of the large decrease of crystallinity and crystallite perfection. When the CH_2O added amount reached up to 20%, the acetalized PVA was completely insoluble, so that the spinning process could not be carried out. The breaking strengths of most acetalized fibers were beyond 4 cN/dtex, which satisfied the ordinary use of industrial and domestic field. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2956–2962, 2012

Key words: acetalization; dissolving temperature range; poly(vinyl alcohol); water-soluble fiber

INTRODUCTION

Poly(vinyl alcohol) (PVA) is an important water-soluble polymer for its polyhydroxyl groups and strong hydrogen bonds. It has been used in many applications, such as coatings, adhesives, paper and textile sizing, dispersant agents, fibers, and films.[1–3] As a kind of functional fiber, water-soluble fiber plays an important role in traditional textiles, nonwovens, medical, and hygiene fields. Compared with many other polymers,[4–6] for instances, alginic acid, hydroxymethyl cellulose, and polyoxyethylene, PVA is less expensive and possesses excellent tensile strength, good weather resistance, and alkali resistance.[7–9] After dissolving in water, the solution is colorless, odorless, and truly biodegradable, which attracts renowned interest for the production of environmentally friendly water-soluble fibers.[10,11]

However, there is a relatively wide dissolving temperature range when the PVA water-soluble fiber is dissolved in water, that is, the fiber begins to dissolve in a relatively low temperature, but dissolves completely in higher temperature. The dissolving temperature range for conventional PVA water-soluble fibers made from wet spinning process is about 40°C.[12] The wide dissolving temperature range is unfavorable in the production of high quality wool fabrics and papers. In previous studies, we mostly concern the dissolving temperature at which fibers are totally dissolved, but neglect the dissolving temperature range, which has very important influence on fiber uses. For example, when used as fibrous adhesive in papermaking, it demands PVA fiber not to dissolve in cold water but rapidly dissolve in hot water. However, this concept of dissolving temperature range is rarely mentioned in literatures.

The solubility of water-soluble fibers depends on its molecular and aggregation structure. Therefore, fine control of PVA molecular structure,[13–16] degree of crystallinity and orientation should be required in order to narrow the dissolving temperature range of PVA fiber. PVA can participate in chemical reactions in a manner similar to other secondary polyhydric alcohols.[17–19] Of greatest commercial importance are reactions with aldehydes to form acetals. After reacting PVA with formaldehyde (CH_2O), the hydroxyl of PVA is converted to acetal group, which improves its hydrophobicity. Besides, since some hydroxyl groups are replaced by acetal groups, the

TABLE I
Compositions and Actual Degree of Acetalization of Acetalized PVA Solutions

Sample code	Corresponding fiber code	PVA (g)	Distilled water (g)	CH_2O solution (37 wt %) (g)	Actual degree of acetalization (mol %)
Solution-0	fiber-0	144	656	–	–
Solution-1	fiber-1	144	653.35	2.65	1.6
Solution-2	fiber-2	144	642.73	13.27	4.5
Solution-3	fiber-3	144	629.46	26.54	8.7
Solution-4	–	144	602.92	53.08	17.5

aggregation structure of acetalized PVA fiber such as crystallinity is also changed compared with pure PVA. As a result, the dissolving temperature range of acetalized fiber is expected to be distinctly different from that of pure PVA fiber.

In this study, acetalized PVA with different degrees of acetalization is synthesized in aqueous solution under acid catalysis. The water-soluble fiber is subsequently prepared via conventional wet spinning process. The molecular structures of both acetalized PVA and pure PVA fibers are characterized. The dissolving temperature range of the two kinds of fibers under different draw ratios is also investigated.

EXPERIMENTAL

Materials

PVA of polymerization degree = 1700 ± 50 and alcoholysis degree > 99% were provided by Sichuan Vinylon Works, SINOPEC (Chongqing, China). Sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) and CH_2O solution (37–40 wt %) were purchased from Kelong Chemical Reagent Company (Chengdu, China). Industrial grade sodium sulfate (Na_2SO_4) was from Sichuan Glauber's Salt Factory. All materials were used without any further purification.

Preparation of acetalized PVA solution

PVA was dissolved in water at 95°C for 6 h to form a uniform solution. Then the pH value of solution was adjusted to 1 with H_2SO_4. A prescribed amount of CH_2O solution was added to the mixture at 80°C and the reaction continued for 3 h. After that, the pH value of solution was readjusted to 7 with NaOH. The amount of H_2SO_4 and NaOH was relatively small compared with that of PVA and water, so that the overall concentration of acetalized PVA solution was not much changed, which was about 18 wt %. The compositions of acetalized PVA solutions and corresponding fibers are listed in Table I.

Preparation of acetalized PVA water-soluble fiber

After filtration and deaeration, the spinning solutions mentioned above were ejected from spinneret into a coagulating bath consisting of saturated Na_2SO_4 solution at 40–45°C to complete fiber forming. Then the fiber left the coagulating bath and passed through two sets of rollers at certain speeds. The fiber was drawn between the two sets of rollers. Finally, the fiber was taken up in a bobbin as the as-spun fiber. The fiber was then subjected to a two-stage dry hot stretching and heat setting as the conventional PVA fibers. The resultant fibers had a linear density of 3 dtex with 17 μm diameter.

Testing and characterization

Solution viscosity was measured using a Brookfield DV-II+ Pro Digital Viscometer (Brookfield Engineering Laboratories, INC) using a small sample adapter and spindle 28. The sample cell was enclosed in a jacket connected to a water bath with temperature 80°C.

The FTIR analysis was carried out on a Nicolet MAGNAIR560 spectrometer in the transmission mode with KBr disks at room temperature.
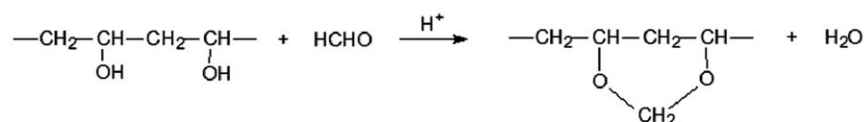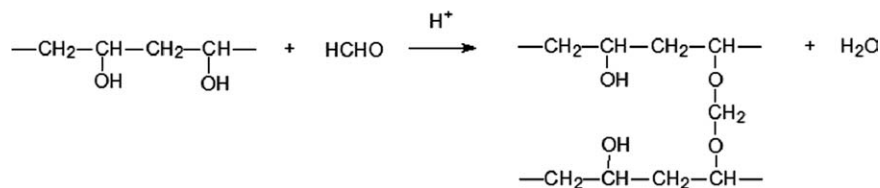
^{1}H-NMR spectra were recorded on a Bruker 600 MHz Ultra Shield NMR spectrometer using DMSO-d_6 as the solvent and tetramethylsilane (TMS) as an internal standard.

DSC measurements were conducted on a Netzsch DSC 204 thermal analyzer at a heating rate of 10°C/min from 80 to 280°C under a nitrogen flow with sample weight of approximately 6–10 mg. The melting behaviors of the acetalized PVA fiber samples were recorded. The data analysis was performed by Netzsch Proteus Thermal analysis software. Peak values were taken as melting temperatures. The crystallinity (X) of PVA and acetalized PVA was calculated according to eq. (1):

$$X(\%) = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \tag{1}$$

where ΔH_f is the fusion enthalpy of the sample, obtained from DSC. The fusion enthalpy of the 100% crystalline PVA (ΔH_f^0) is 152J/g.[20]

The chain orientation factor of sonic velocity was determined by measuring the transmitting time of a sound between two transducers coupled to the
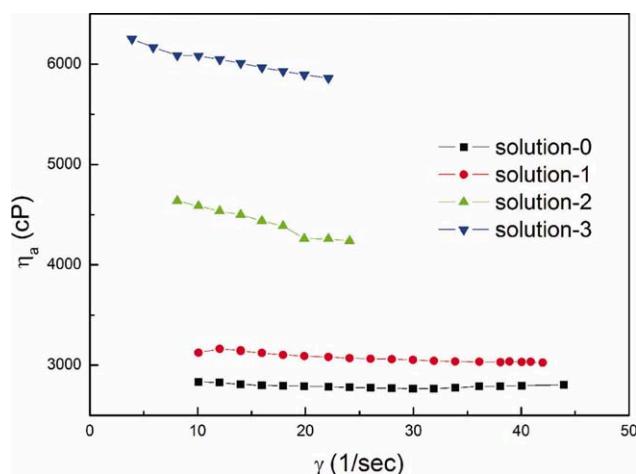
Figure 1 Solution viscosity as a function of shear rate with different CH_2O added amount. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of acetalized PVA fiber

To identify the formation of the special interactions between PVA and CH_2O, the FTIR spectra of PVA and acetalized PVA were tested, as shown in Figure 2. As can be seen from the figure, there is little difference among PVA and acetalized PVAs with different CH_2O added amount. As is well known, the C—O absorption peak of newly generated ether will appear at 1150–1160 cm^{-1}. But any molecule that contains C—O (such as alcohol, phenol, and ester) will cause interference to characteristic absorption peak of ether. Therefore, it is difficult to identify ether only by FTIR spectra.

In Figure 3, the ^{1}H-NMR spectrum of the pure PVA is compared with those of the acetalized PVAs The resonance peaks of the methine protons in the

Figure 3 ^{1}H-NMR spectra of PVA and acetalized PVA. (a) fiber-0; (b) fiber-1; (c) fiber-2; (d) fiber-3; (e) solution-4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

main chain of both PVA and acetalized PVA appear at 3.89, 3.83, and 3.80 ppm, respectively, and those of the methylene protons in the 1.1–1.6 ppm spectral region.

The three resonance signals of the hydroxyl protons of the PVA fiber appear at 4.67, 4.47, and 4.22 ppm which are attributed to the syndiotactic, heterotactic, and isotactic triads, respectively.[18] It is clear that the resonance at 4.94 ppm in the spectra of the acetalized PVAs corresponds to the O—CH—O

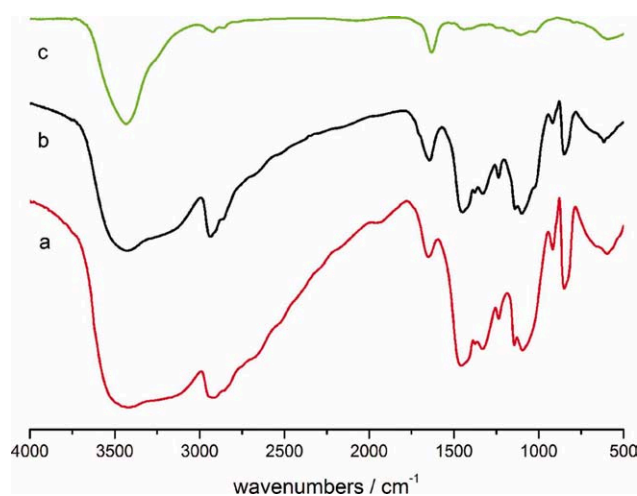**Figure 2** FTIR spectra of PVA and acetalized PVA. (a) fiber-0; (b) fiber-1; (c) solution-4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
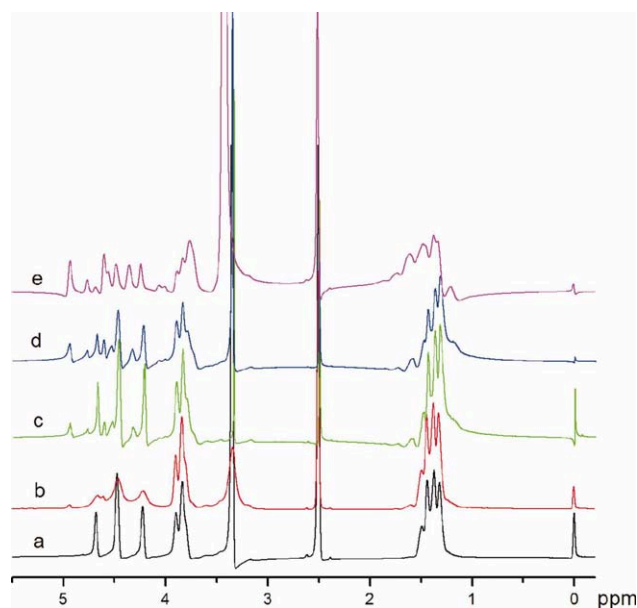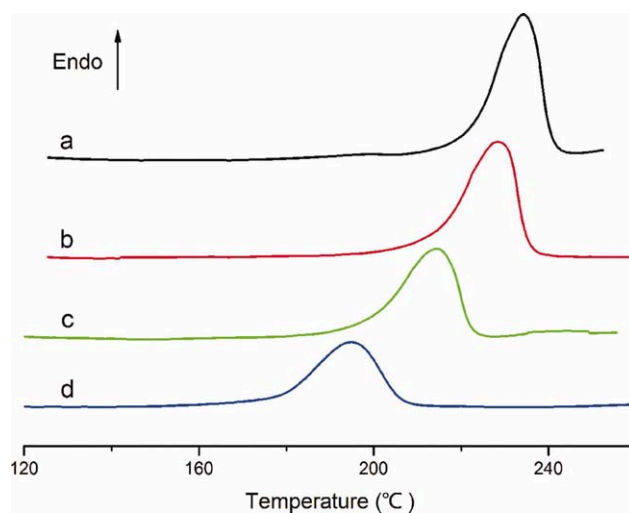

Figure 4 DSC curves of PVA and acetalized PVA fibers. (a) fiber-0; (b) fiber-1; (c) fiber-2; (d) fiber-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Thermal Parameters of PVA and Acetalized PVA Fibers Obtained from DSC

Sample code	Before dissolution			After dissolution		
	Crystallinity (%)	Melting peak width (°C)	Melting temperature (°C)	Crystallinity (%)	Melting peak width (°C)	Melting temperature (°C)
fiber-0	54.4	17.6	234.1	54.1	16.5	235.1
fiber-1	53.8	19.8	228.4	52.9	18.8	228.2
fiber-2	43.8	21.8	214.6	41.7	16.6	214.9
fiber-3	35.9	26.4	195.1	28.0	18.4	210.7

protons of the acetal ring, whereas the signals of the residual —OH group are split to multiplet. The actual degrees of acetalization are calculated from the integral ratio of the signals assigned to the acetal O—CH—O protons to the signals of the methine groups in the main chain.[18] The result is listed in Table I.

The DSC heating curves of PVA and acetalized PVA are shown in Figure 4, and the corresponding thermal parameters are listed in Table II. Obviously, both the melting point and crystallinity of PVA decrease after acetalization. The decreasing trend becomes more apparent with an increase in the CH_2O added amount.

As mentioned previously, the acetal group, which has a bigger spatial volume than the hydroxyl, is formed in the side groups of PVA during acetalization. Therefore, the chain regularity of PVA decreases. As a result, the crystallinity of fiber is decreased. It can also be seen that with increasing CH_2O added amount, the breadth of the corresponding melting peak increases and the melting temperature decreases, indicating that the acetalization could decrease the perfection degree of the PVA crystallite.

The thermal properties of residual fiber after dissolution in 40°C were also measured by DSC at the same testing conditions, which are shown in Figure 5. The corresponding thermal parameters are also listed in Table II. After dissolution in 40°C, the crystallinity and melting temperature of fiber-0 and fiber-1 do not change much, compared with the original fibers. However, for fiber-2 and fiber-3, both the crystallinity and melting temperature increase while the melting peak becomes narrower after dissolution. These reveal that the imperfect crystallite is dissolved in water and original crystalline region has potential of recrystallization for PVA fibers with higher degree of acetalization.

According to DSC analysis, added amount of CH_2O has a great influence on the crystallinity. What's more, the WAXD patterns (Fig. 6) show that addition of CH_2O also affects the crystallization of PVA fiber. PVA shows a typical monoclinic crystal structure where crystalline peaks appeared at $2\theta =$ 11.3° (100), 16.1° (001), 19.7° (101) (10$\bar{1}$) and 22.7° (200).[23,24] The intensities decrease and peaks broaden with increasing CH_2O added amount as is shown in Figure 6. The 101 and 200 diffraction peaks of fiber-3 merge into one wide peak. The corresponding crystallite parameters after peak fit are listed in Table III.
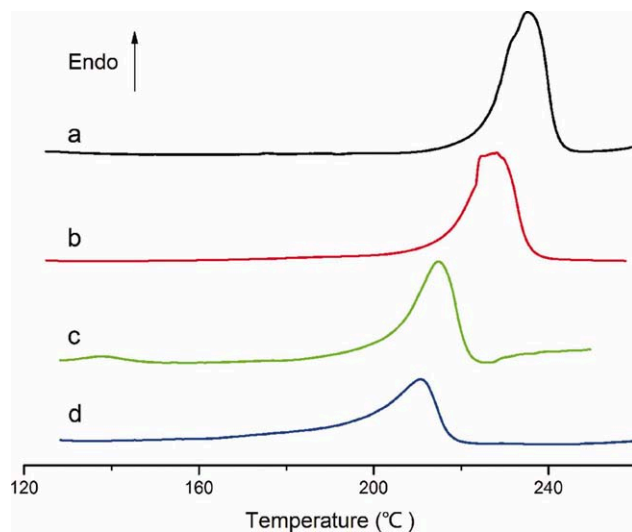
Figure 5 DSC curves of PVA fiber and acetalized PVA fiber after dissolution at 40°C. (a) fiber-0; (b) fiber-1; (c) fiber-2; (d) fiber-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 WAXD patterns of PVA and acetalized PVA fibers. (a) fiber-0; (b) fiber-1; (c) fiber-2; (d) fiber-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
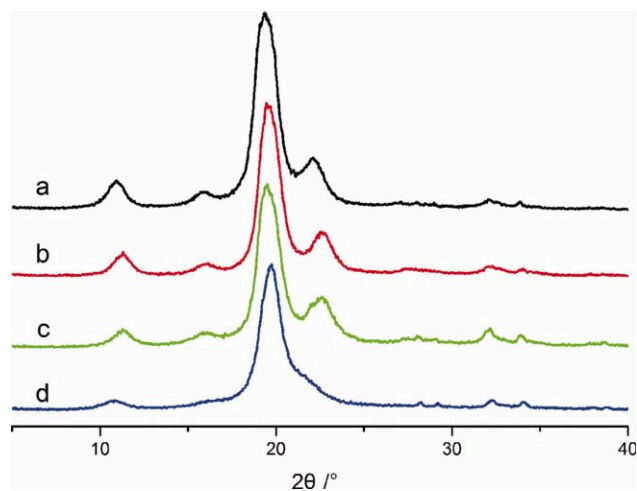
TABLE III
Crystallite Size of PVA and Acetalized PVA Fibers

Sample code	$2\theta(^\circ)$	Full width at half maxima (FWHM) (radian)	Crystallite size (Å)
fiber-0	19.539	1.304	62
fiber-1	19.451	1.410	57
fiber-2	19.320	1.407	57
fiber-3	19.556	1.522	52

The 101 diffraction peak of PVA is due to the intermolecular interface between PVA molecular chains in the direction of intermolecular hydrogen bonding.[25] The decrease in the intensity of 101 diffraction peak after acetalization corresponds to the decrease in the number of PVA chains packing together and hence results in a smaller crystallite size in the acetalized PVA.

Figure 7 demonstrates that the orientation factors of PVA and acetalized PVA fibers all increase with increasing draw ratio. This is due to the stretching of tie molecules under high temperature. When the draw ratio is lower than 3, the orientation factor drops with increasing CH_2O added amount at each draw ratio. The introduction of acetal group will increase the spatial volume of side group, and therefore increase the intermolecular distance. The acetal group prevents the molecules from getting close enough to form ordered structure during hot-drawing process.[26] The maximum draw ratio also decreases with the increase of CH_2O added amount. It is possibly due to the decrease of intermolecular hydrogen bonding and crystallinity.

Solubility of acetalized PVA fibers

The dissolving temperature ranges of PVA and acetalized PVA fiber are shown in Figure 8. The corre-
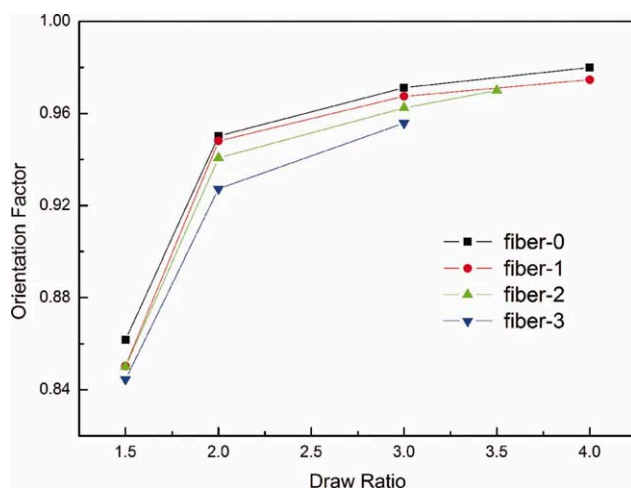
Figure 7 Sound orientation factors of PVA and acetalized PVA fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
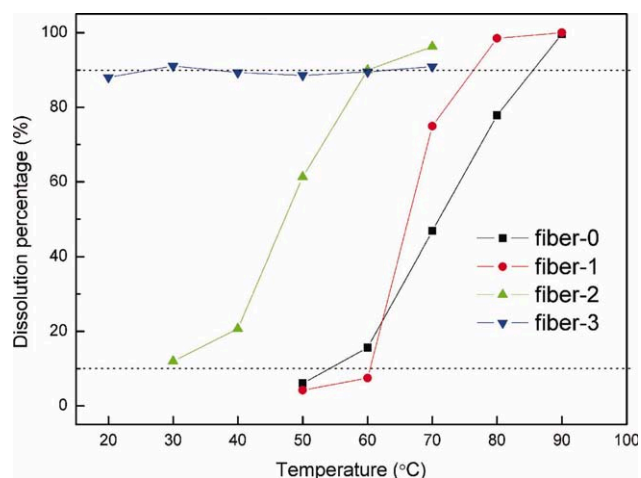
Figure 8 Dissolving temperature ranges of PVA and acetalized PVA fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sponding dissolving temperatures obtained from the figure are listed in Table IV. Compared with the dissolution behavior of pure PVA fiber (fiber-0) to that of fiber-1, it can be seen that fiber-1 has the higher initial dissolving temperature and the lower final dissolving temperature, i.e., fiber-1 has a narrower dissolving temperature range. The reasons may be due to that fiber-1 has the more hydrophobic amorphous region which results in less weight loss in low temperature, and the lower crystallinity which leads to the lower final dissolving temperature. When CH_2O added amount is increased to 5% (fiber-2), both the initial and final dissolving temperatures largely decrease and the dissolving temperature range becomes wide again because of the lower crystallinity and the imperfect crystallite. With a further increasing of CH_2O added amount to 10% (fiber-3), more than 80% of the acetalized fiber has been dissolved at 20°C since the crystallinity is very low. No more fiber tends to be dissolved with the rise of temperature. This is possibly due to some crosslink of polymer generated by intermolecular acetalization.

Mechanical properties of acetalized PVA fibers

Figure 9 shows the mechanical properties of acetalized PVA fiber with different degree of acetalization.

TABLE IV
Dissolving Temperature Ranges of Acetalized PVA Fibers

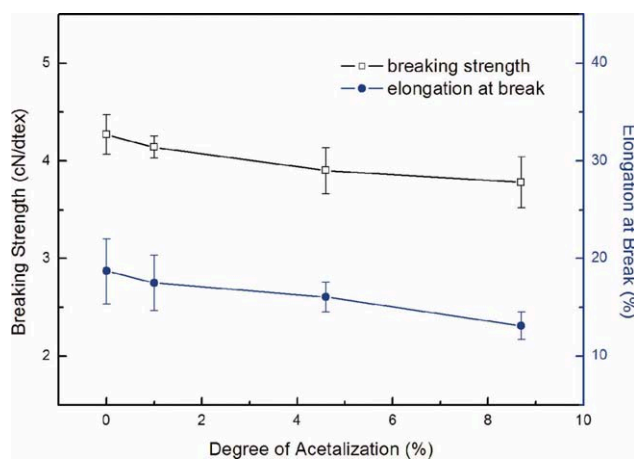| Sample code	Initial dissolving temperature (°C)	Final dissolving temperature (°C)	Dissolving temperature range (°C)
fiber-0	54.1	85.6	31.5
fiber-1	60.3	76.4	16.1
fiber-2	27.0	60.0	33.0
fiber-3	–	–	–

Figure 9 Plot of mechanical properties of PVA and acetalized PVA fibers with different degrees of acetalization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

All the fibers in the mechanical properties test are drawn two times. The tensile strength and elongation at break decreases with the increase of CH_2O added amount, as a result of the decrease of the orientation degree. The breaking strengths of fiber-1 and fiber-2 are over 4 cN/dtex, which are still higher than that of conventional textile fibers (2–3.5 cN/dtex), so they can find many potential uses in textiles and papermaking.

CONCLUSION

The CH_2O acetalized PVA spinning solution is successfully prepared under acid catalysis. The spinnability is good until CH_2O added amount reaches 20%. Both crystallinity and orientation factor of fiber decline with increase of CH_2O added amount. As small quantity of CH_2O is added, the hydrophobicity of amorphous region is increased and crystallinity is decreased, resulting in narrowing of dissolving temperature range. With a further increasing of CH_2O added amount, the dissolving temperature is much lowered and the range is widened because of a significant reduction in crystallinity. When the CH_2O added amount is up to 10%, most fiber is dissolved in cold water and the dissolved percentage

does not change much with the rise in temperature, which suggests the intermolecular crosslink of acetalized fiber has been created. The mechanical properties of the acetalized fibers decline with an increase in the degree of acetalization. All the acetalized fibers are strong enough for domestic and industrial use.

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