

# Water-Absorptive Blend Fibers of Copoly(acrylic acid–acrylamide) and Poly(vinyl alcohol)

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**ABSTRACT:** Through the addition of *N*-hydroxymethyl acrylamide as a potential crosslinker, water-absorptive blend fibers of copoly(acrylic acid–acrylamide) and poly(vinyl alcohol) with three-dimensional network structures were prepared with heat-crosslinking technology after fiber formation. Fourier transform infrared, scanning electron microscopy, dynamic mechanical analysis, and thermogravimetry were used to analyze the structures and properties of the fibers. The tensile behavior and absorbent capacities of

the fibers were also studied. The results showed that there were lots of chemical crosslinking points in the fibers, the compatibility of copoly(acrylic acid–acrylamide) and poly(vinyl alcohol) was perfect, and the tensile properties of the fibers could be improved effectively through stretching in a vapor bath. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3353–3357, 2006

**Key words:** fibers; blends; crosslinking; swelling

## INTRODUCTION

Superabsorbent fibers absorb moisture up to several thousand times their original weight, undergoing significant expansion and eventually becoming gels.<sup>1</sup> For this ability to be converted into a wide range of textile structures, superabsorbent fibers are far more suitable for special applications than superabsorbent polymers. Fiber production processes are flexible, so it is probable that the range of product types will be extended.<sup>2</sup> Recently, there have been some reports about the preparation of superabsorbent fibers, such as alginate superabsorbent fibers crosslinked with glutaraldehyde,<sup>3</sup> cellulose fibers modified by graft copolymerization or blending with superabsorbent polymer powder,<sup>4–6</sup> and crosslinked poly(carboxylic acid) fibers.<sup>7,8</sup>

In this work, we used acrylic acid (AA) and acrylamide (AM) as monomers because of their affinity to water. *N*-Hydroxymethyl acrylamide (NHMA) was introduced into the polymerization system as a potential crosslinker. Poly(vinyl alcohol) (PVA) was used as a blend component to improve the fiber flexibility and tensile strength. A spinning solution was prepared by copolymerization of AA, AM and NHMA in the PVA aqueous solution. After fiber formation, a kind of superabsorbent fiber based on a blend of copoly(acrylic acid–acrylamide) and PVA with a three-dimensional network structure was prepared by a heat treatment at

a certain temperature for a certain time. Fourier transform infrared (FTIR), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), and thermogravimetry (TG) were used to analyze the fiber structure. The water-absorption capacity and tensile behavior were also studied.

## EXPERIMENTAL

### Materials

AA was distilled under reduced pressure before use. AM was purified by recrystallization from chloroform. Potassium persulfate (KPS) and NHMA were recrystallized from distilled water. PVA was rinsed by distilled water at least three times and dried before use. Sodium hydroxide (NaOH) and acetone were used as purchased.

### Preparation of the spinning solution

Typically, in a 1000-mL beaker, cooled in a 10°C recycled water bath, a stirred 53 wt % AA aqueous solution was neutralized into 70 mol % of the degree of neutralization by the dropwise addition of a 20 wt % NaOH aqueous solution, and its concentration was about 35 wt %. A monomer solution was prepared by the dissolution of AM (25 wt % AA) and NHMA (0.6 wt % AA) in the neutralized AA solution. The monomer solution was added to an 11% PVA aqueous solution at the ambient temperature with full stirring to get a mixture. After that, N<sub>2</sub> was slowly purged into the mixture to drive off the remaining oxygen. A given quantity of the initiator KPS aqueous solution was

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added dropwise when the mixture was heated to 60°C. The temperature was raised slowly to 70°C with effective stirring. After 2 h of reaction and 24 h of staying for the removal of the bubbles, the copoly-(acrylic acid-acrylamide)/PVA blend solution was formed.

### Preparation of the blend fibers

The blend solution was extruded into an acetone coagulation bath to form continuous HAMP fibers, which did not have any crosslinking structure, via a wet-spinning method. The CAMP fibers with a three-dimensional network structure were prepared by a heat treatment in a heating oven at different temperatures for different times. The stretching of CAMP fibers four times in a vapor bath made the LCAMP fibers.

### Test and analysis of the CAMP fibers

The water/saline absorbencies of the fibers were measured by a suction-filtration method. A sample from the CAMP fibers was immersed in distilled water (or a 0.9 wt % sodium chloride aqueous solution) at room temperature until equilibrium was reached. The absorbability was determined by the weighing of the swollen fibers after draining for 10 min. The water/saline absorbency ( $Q$ ) was calculated with the following equation:<sup>9</sup>

$$Q(\text{g/g}) = (W_2 - W_1) / W_1$$

where  $W_1$  and  $W_2$  was the weights of the fibers before and after water/saline absorption, respectively. The absorbency was expressed as the ratio of the retained water in the fibers to the weight of the dried fibers.

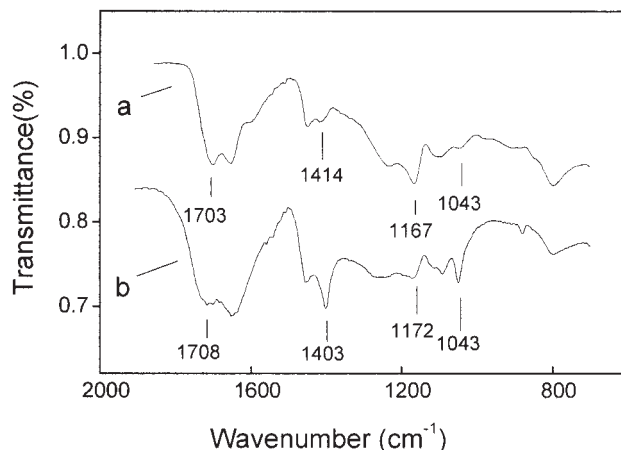
A Bruker Co., Germany FTIR spectrometer (Vector-22) was used for IR analysis of the chemical structure of the CAMP fibers (KBr pellets).

The cross-section (breaking in liquid nitrogen) and surface morphologies of CAMP fibers were observed on a scanning electron microscope (Quanta-200; FEI Co., Brno, Czech Republic).

The glass-transition temperature ( $T_g$ ) was determined with a DMA Instrument (DMA 242C, Selb, Germany). The temperature range covered in this analysis was 25–340°C at a heating rate of 5°C/min, and the stress frequency was 10 Hz.

TG spectra of CAMP fibers were obtained with a TG-DTA instrument (STA409PC, Selb, Germany). The temperature range covered in this analysis was 25–600°C at a heating rate of 10°C/min, and the reference compound was  $\text{Al}_2\text{O}_3$ .

The tensile data and stress-strain curves of the fibers were gained with an electron single-fiber strength



**Figure 1** FTIR spectra of (a) HAMP fibers and (b) CAMP fibers.

instrument (LLY-061, Laizhou electron instrument Ltd., Shandong, Republic of China).

## RESULTS AND DISCUSSION

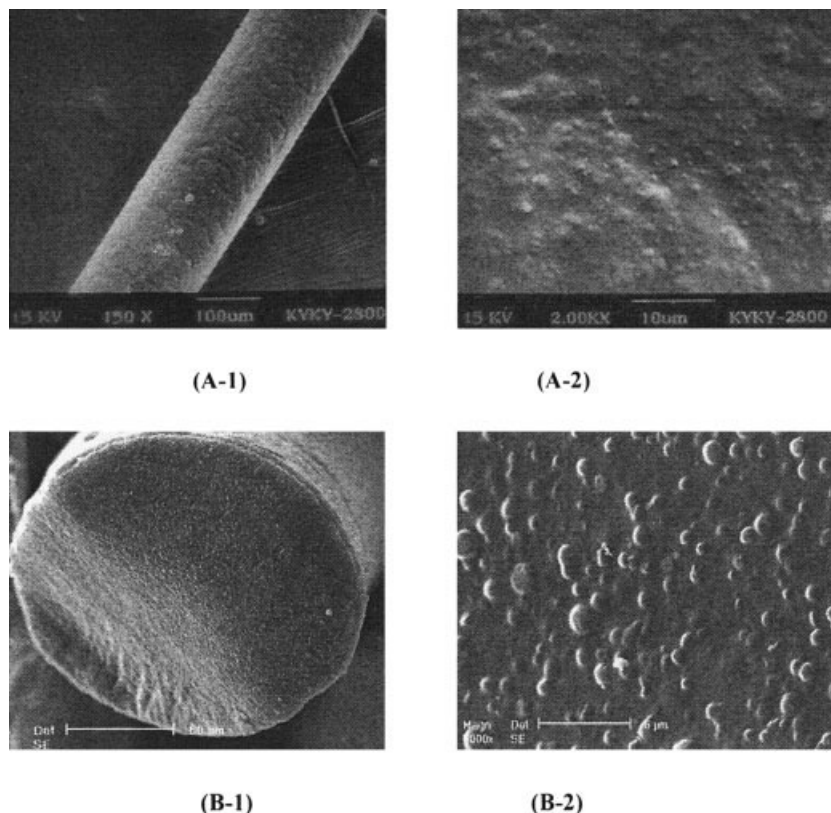
### IR spectra

The characteristics of the HAMP fiber and CAMP fiber (heat-treated for 30 min at 160°C) were indicated by FTIR transmission spectroscopy, as shown in Figure 1.

The very strong peaks at 1703 and 1708  $\text{cm}^{-1}$  were attributed to the C=O stretching in AA,<sup>10</sup> the peaks at 1170 and 1250  $\text{cm}^{-1}$  were due to C—O stretching in AA, the peaks at 1650 and 1600  $\text{cm}^{-1}$  were due to C=O stretching in AM,<sup>11</sup> the peaks at 1102 and 1090  $\text{cm}^{-1}$  were due to C—O stretching in PVA, the peak at 1410  $\text{cm}^{-1}$  was the characteristic peak of sodium acrylate, and the less intense peak at 1043  $\text{cm}^{-1}$  was assigned to C—O—C stretching in acrylate. The C—O—C stretching peak at 1043  $\text{cm}^{-1}$  became stronger in the crosslinked fiber in comparison with that in the uncrosslinked fiber. This may be due to the dehydration reaction between the —CH<sub>2</sub>OH group in NHMA and the —COOH group in AA or two —CH<sub>2</sub>OH groups in NHMA during the crosslinking process, which increased the C—O—C links.

### Morphologies observed by SEM

SEM was used to observe the cross-section and surface morphologies of CAMP fibers, as shown in Figure 2. The graphs show that the cross-section and surface structures had tight morphologies and lots of PVA particulates like islands diffused in the matrix of copoly(acrylic acid-acrylamide). The diameter of the PVA particulates measured from Figure 2(B-2) was 0.54–1.54  $\mu\text{m}$ . A blend aqueous solution of copoly(acrylic acid-acrylamide) and PVA was not delami-



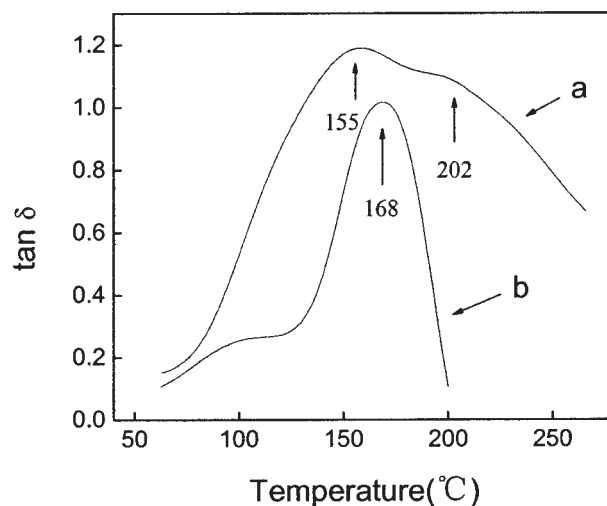
**Figure 2** SEM photographs of CAMP fibers: (A) surface [(1) 150 $\times$  and (2) 2000 $\times$ ] and (B) cross section [(1) 500 $\times$  and (2) 5000 $\times$ ].

nated for a long time. The phenomenon of double diffusion appeared between the even solution and acetone in the coagulation bath after injection, and the PVA macromolecules were gathered together to become islands during the solidification process of the fibers. The size of these islands might depend on the concentration of the spinning solution, the content of PVA, the blending conditions (stirring speed, etc.), and the shearing effect of the spinning solution in the spinneret.

#### DMA of the fibers

Crosslinking often brings about drastic changes in the mechanical and physical properties of polymers. The most important physical property to be affected is  $T_g$ . The loss tangent ( $\tan \delta$ ) of CAMP fibers (heat-treated for 30 min at 160 $^{\circ}\text{C}$ ) and HAMP fibers was determined with DMA. The results are shown in Figure 3. Two peaks of  $\tan \delta$  appeared for the HAMP fiber at 156 and 202 $^{\circ}\text{C}$ , which indicated the  $T_g$  values of PVA and poly(acrylic acid), respectively, whereas only one peak of  $\tan \delta$  in the CAMP fiber appeared at 170 $^{\circ}\text{C}$ . The two  $\tan \delta$  peaks in the HAMP fiber showed that there were two kinds of molecules in this fiber, and there was no bond between them. However, some  $-\text{OH}$  groups on the PVA molecule could be dehydrated with the

$-\text{COOH}$  and  $-\text{CONH}_2$  groups during the heat-treatment process. A tighter three-dimensional network structure was formed in the fiber molecule after heat treatment. Therefore, the two  $T_g$ 's tended to be closer. Two closer peaks may form one dispersive  $\tan \delta$  peak of the CAMP fiber.



**Figure 3** DMA spectra ( $\tan \delta$ ) of (a) HAMP fibers and (b) CAMP fibers.

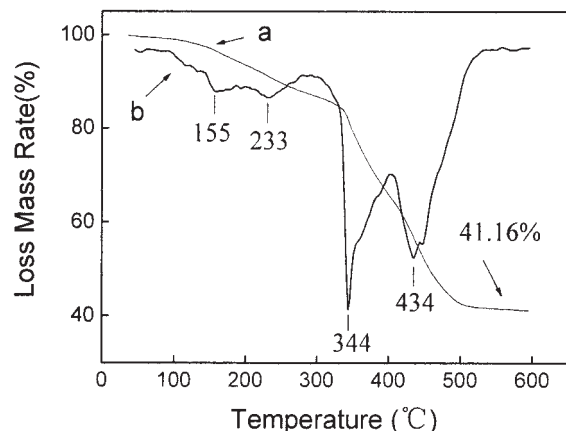


Figure 4 (a) TG and (b) DTA spectra of HAMP fibers.

### TG analysis of the fibers

The thermal stability of a binary copolymer is intermediate between its two homopolymers and varies according to their proportions. The thermal behavior of fibers can also be useful for analyzing the fiber components. TG and differential thermal analysis (DTA) spectra of the HAMP fiber are shown in Figure 4. There are five mass-loss regions in this figure: first, free water escaped from the fibers at 100°C; anhydride was formed by the dehydration of internal —COOH groups of poly(acrylic acid) molecules at 155°C; thermal decomposition of the PVA molecule appeared at 233°C; degradation of poly(acrylic acid) happened at 344°C; and last, degradation of polyacrylamide took place at 434°C. TG spectra can conveniently tell us whether a polymer is random (only one degradation) or block (two degradations).<sup>12</sup> From this figure, we could easily conclude that AA and AM in the fibers were arranged to form block copolymer molecules.

### Tensile properties of the fibers

The tensile properties of unstretched CAMP fiber and LCAMP fiber stretched four times are listed in Table I, and stress-strain curves of those fibers are shown in Figure 5.

In comparison with CAMP fiber, the breaking tenacity, tensile breaking specific work, yielding elongation,

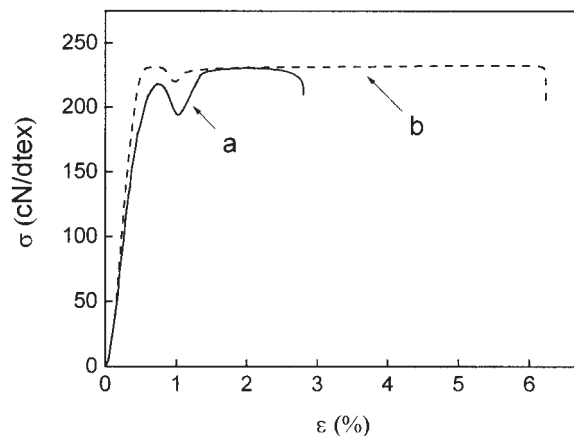


Figure 5 Stress ( $\sigma$ ) versus the strain ( $\epsilon$ ) for (a) CAMP fibers and (b) LCAMP fibers.

and original modulus of the LCAMP fiber are higher, but the linear density and elongation at break are lower. This may be due to molecular orientation along the fiber axis during the stretching process, and the flexibility of the fiber is also improved.

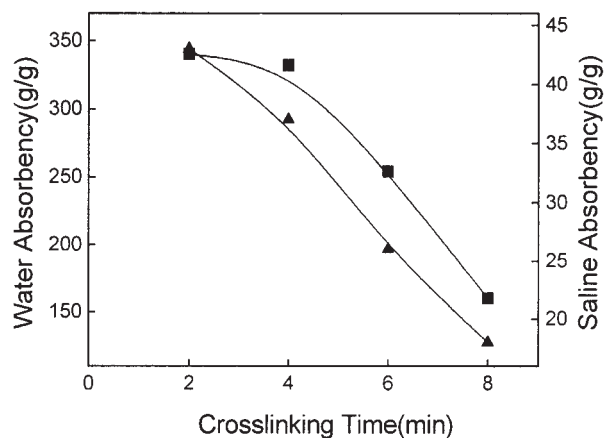
The first maximum of the stress-strain curves of the fiber is due to the physical disintegration of the molecular entanglement network, and this cannot be recuperated until the outside force is removed. The valley after the first peak can be attributed to the low modulus of the uncoiling molecular chains in the amorphous regions. Because of the high modulus of taut-tie molecules, the deformation increases dramatically, whereas the tensile stress stands still until the fiber is broken.

### Water/saline absorption of the fibers

The diameter and length of the CAMP fiber could be increased to 5–8 times and 3–4 times the original size, respectively, after it was immersed in distilled water until equilibrium was reached. This phenomenon showed the water-absorptive anisotropy on the radial orientation and the axial orientation of the fiber during the absorption process. The molecules in the fiber, which were oriented along the fiber axis after spinning and stretching, were distributed parallel to the fiber

TABLE I  
Tensile Test Data of CAMP Fiber and LCAMP Fiber

Sample	Tensile property				
	Breaking tenacity (cN/dtex)	Elongation at break (%)	Tensile breaking specific work (mJ/dtex)	Yielding elongation (%)	Original modulus (N/dtex)
CAMP fiber	0.478	62.30	0.025	5.4	6.348
LCAMP fiber	1.061	27.99	0.028	6.5	9.605



**Figure 6** Effect of the crosslinking time on the CAMP fiber absorbency: (■) water absorbency and (▲) saline absorbency.

axis. A majority of the hydrophilic groups were dispersed beside the molecules, and the distance between the molecules increased dramatically when the fibers were immersed in distilled water; that is, the diameter of the fiber increased obviously. However, the relative slippage of the molecules of the fiber was limited by the network structure, and the length of the fiber increased less.

The crosslinking time directly affected the crosslinking degree and had an important influence on the water/saline absorbency of the fibers. The results in Figure 6 show that all the tested fibers were heat-treated at 120°C. As shown in Figure 6, although the crosslinking time was more prolonged, the crosslinking points were multiplied and led to tighter interactions among the molecules, and the free volume in the polymer molecule was reduced, so the water/saline absorbency was reduced relatively. The CAMP fiber,

which was heat-treated at a lower temperature (120°C) for 2–6 min, could absorb 250 g of distilled water or 30 g of a 0.9% NaCl aqueous solution per gram of fiber at least.

## CONCLUSIONS

The CAMP fibers were prepared with AA, AM, NHMA, and PVA. The structures of the fibers were analyzed, and the water/saline absorbency properties were tested. The results showed that, with heat treatment after spinning, a water-absorptive fiber was prepared with blends of copoly(acrylic acid–acrylamide) and PVA; chemical crosslinking points were formed after heat treatment, and the compatibility of copoly(acrylic acid–acrylamide) and PVA was perfect. Stretched in a vapor bath, CAMP fibers were improved obviously with respect to their tensile properties; the highest absorbency of CAMP fibers to various solutions was 340 g of distilled water/g of fiber and 43 g of a 0.9% NaCl aqueous solution/g of fiber after heat treatment at 120°C for 2 min.

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