Studies on Fibers Spun from Poly(vinyl alcohol-*b*-acrylonitrile) Emulsions Prepared by Ultrasonic Technique. II. Properties of the Fibers

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ABSTRACT: The moisture content of poly(vinyl alcohol-*b*-acrylonitrile) fibers decreases with an increasing hydrophobic AN content and crystallinity of the fibers; however, the copolymer fiber with 26.94% AN, drawn × 5, and heat-treated at 200°C has a moisture content value slightly lower than that of commercial PVA fiber, but much higher than that of commercial PAN fiber. The block copolymer fibers have a water-retention value higher than that of commercial PVA fiber, owing to the presence of voids in these fibers, and have a stronger wicking ability than that of commercial PVA, PAN fibers, and wool and cotton mainly due to the grooved surface and bulk porous morphology of the fibers. The tensile strength of the copolymer fibers with an appropriate AN content are lower than that of commercial PVA fiber, but higher than that of commercial PAN fiber and much higher than that of wool and cotton. The melting temperatures of the copolymer fibers increase with increasing heat-treatment temperature. The copolymer fibers possess a lower peak cyclizing temperature than that of the PAN fiber and have a higher thermal stability than that of both PVA and PAN fibers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 989–994, 2001

INTRODUCTION

In two previous articles, we reported the spinnability of aqueous emulsions of poly(vinyl alcohol-*b*-acrylonitrile) prepared by an ultrasonic technique[1] and the structure of the block copolymer fibers fabricated by a wet-spinning process from the above emulsions.[2] In that work, emphasis was placed on the relationship between the spinnability and the composition of the block copolymer and the supermolecular structure and surface and internal morphology for the fibers. We now report studies on the hydrophilicity, mechanical, and thermal properties of the copolymer fibers, compared with that of the homopolymer PVA and PAN fibers and some natural fibers.

EXPERIMENTAL

Samples

The block copolymer fiber samples investigated in this work were drawn, heat-treated, and acetal-

Table I   Characteristics of Fiber Samples

Fiber Designation	AN Content (wt %)	Relative Viscosity	Draw Ratio	Heat Treatment	
				Temperature (°C)	Time (min)
B1-4-160	10.80	1.204	4	160	5
B1-4-200	10.80	1.204	4	200	5
B2-3-160	18.66	1.360	3	160	5
B2-3-200	18.66	1.360	3	200	5
B2-4-160	18.66	1.360	4	160	5
B2-4-200	18.66	1.360	4	200	5
B2-5-160	18.66	1.360	5	160	5
B2-5-200	18.66	1.360	5	200	5
B3-3-160	26.94	1.330	3	160	5
B3-3-200	26.94	1.330	3	200	5
B3-4-160	26.94	1.330	4	160	5
B3-4-200	26.94	1.330	4	200	5
B3-5-160	26.94	1.330	5	160	5
B3-5-200	26.94	1.330	5	200	5
B4-0-160	38.90	1.231	Undrawn	160	5
PVA (commercial)					
PAN (commercial)					
PVA-4-160			4	160	5
PVA-4-160UA[a]			4	160	5
PVA-4-180UA[a]			4	180	5
PVA-4-200UA[a]			4	200	5

[a] Unacetalized.

ized with formaldehyde as described in a previous article.[2] Commercial PVA and PAN fibers and natural fibers were purified with alcohol and hot water, dried, and air-conditioned before measurement. Table I shows the characteristics of the samples. The relative viscosity determined in a dimethyl sulfone (DMSO) solution (0.549/L), of the block copolymers was used for estimation of their molecule size: (0.54 g/L).

Hydrophilicity

Measurement of Moisture Content

The gravimetric method was employed. The sample to be tested was dried to a constant weight w_1, in an oven kept at 105°C, then placed in an environment with a given humidity and constant temperature for 48 h and weighed again, obtaining a weight w_2. The moisture content M of the samples was calculated as follows:

$$M = \frac{w_2 - w_1}{w_1} \times 100\% \tag{1}$$

Determination of Water Retention

A centrifugal method was used. The dried fiber sample was immersed in water at 20°C for 1 h, then put in a centrifuge with a centrifugal acceleration of 1000 G (g = 9.8 m/S$_2$) for 1 h and weighed. The water retention, WR, was calculated as follows:

$$WR = \frac{W_2 - W_1}{W_1} \times 100\% \tag{2}$$

where W_1 is the weight of the dried sample, and W_2, the weight of the wet sample after centrifugation.

Wicking Height

A bundle of fibers, to one end of which was applied a load for it to undergo a tension of 0.2cN/dtex, was vertically immersed into colored water. The water rises up along the fibers. The height the water attained and the corresponding time consumed were recorded.

Mechanical Properties

A stress–strain diagram of the samples, on which tensile strength and elongation at break was determined, was plotted with a YG-001 Model fiber tenacity tester, according to conventional procedures.

Table II   Moisture Content and Water Retention of Fibers

| Fibers | Moisture Content (%) | | | Water Retention (%) |
	70% RH 15°C	60% RH 22°C	40% RH 25°C	
B1-4-160	9.04	7.4		30.7
B2-4-160	8.03	6.80	5.73	
B3-3-160	6.75	5.96	4.56	44.94
B3-3-200	5.88	4.67	4.17	24.32
B3-4-160	6.56	5.73	4.63	38.55
B3-4-200	5.78	4.98	4.48	23.94
B3-5-160	6.28	5.54	4.56	34.22
B3-5-200	5.12	4.65	4.34	22.85
PVA (commercial)	6.41	5.23	3.31	22.44
PAN (commercial)	1.37	1.23		7.0
PVA-4-160[a]	9.75	8.97		74.44
PVA-180[b]	9.02	7.99		50.05
PVA-4-200[a]	8.04	7.32		32.09
Wool	17.49	14.54		37.88
Cotton	8.13	6.67		35.54

[a] Unacetalized.
[b] Undrawn and unacetalized.

Thermal Behavior

Differential Scanning Calorimetry Analysis

Thermal measurement of the fibers was performed using a Perkin–Elmer differential scanning calorimeter (DSC) Model 2. The sample in a form of powder was cut from the fibers to be tested. About 5 mg of the sample was encapsulated in an aluminum pan. Nitrogen was used as the purge gas. The heating rate was 20°C/min.

Thermal Gravimetric Analysis

Thermal stability was measured using a Shimadron thermal gravimetry analyzer in a nitrogen atmosphere at a heating rate of 20°C/min. Also, 5 mg of the sample was used.

RESULTS AND DISCUSSION

Moisture Content and Water Retention

Table II shows that the moisture content, M, is dependent on the chemical composition (number of hydrophilic hydroxyl groups in the macromolecular chain) and microstructural features (crys-

tallization, orientation, and morphology) of the fibers. The unacetalized PVA fibers have the highest M values. The acetalized B1-4-160 and B2-4-160 samples with a lower AN content have fairly high M (higher than that of commercial PVA fiber and cotton) due to a lower crystallinity and a somewhat microphase separation of PVA and PAN blocks in these fibers, as can be seen in a previous article.[2] With increase of the AN content, the draw ratio and heat-treatment temperature, and, hence, increasing orientation and crystallinity, the M value has a tendency to decrease, but is still relatively high due to the incompatibility and existing phase separation of PVA and PAN blocks in the copolymer fibers. For example, sample B3-5-200 has an M of 5.12%, which is much higher than that of the PAN fiber. It is worth noting that under low humidity conditions all the copolymer fibers possess higher M values than that of commercial PVA fiber. The cause may be that the block copolymer fibers have a rough surface and an inner porous structure and thus provide more surface area for water absorption.

The data in Table II show that the degree of crystallization is a major factor determining the water retention (MR) of the fibers. The copolymer fibers, heat-treated at 160°C and acetalized, have a comparative WR value with that of wool and cotton. Nevertheless, the fiber morphology has an important effect on the WR. The copolymer fibers, heat-treated at 200°C (high crystallinity) and acetalized, possess a higher WR than that of commercial PVA fiber owing to the presence of voids in these fibers, as shown in the previous article.[2]
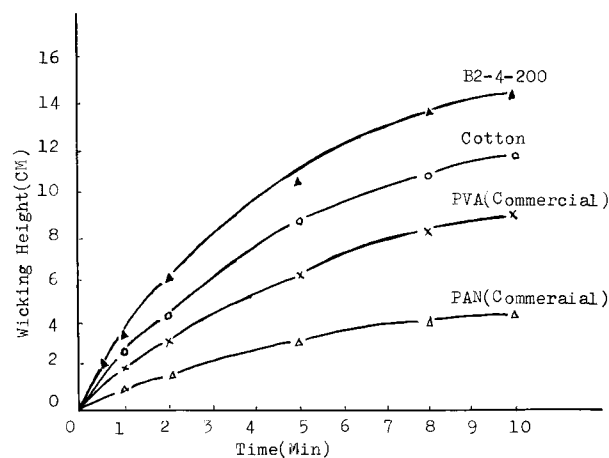

Figure 1   Kinetic curves of water-transporting for selected fibers.

Table III Mechanical Properties of PVA, PAN, and Block PVA/PAN Copolymer Fibers and Natural Fibers

Fibers	Tensile Strength (MPa)	Elongation at Break (%)
B1-5-160	220.5	55.64
B1-5-200	276.9	49.29
B2-4-160	304.8	64.83
B2-4-200	328.1	52.50
B2-5-160	397.0	45.15
B2-5-200	512.2	42.57
B3-5-160	274.0	67.60
B3-5-200	330.2	62.90
PVA (commercial)	664.1	28.31
PAN (commercial)	420.2	26.70
Wool	188.1	33.42
Cotton	273.6	6.80
Silk	420.7	22.53
Viscose staple	299.6	26.21

Wicking Height

This quantity stands for the ability of a fiber material to transport water. It is fairly important to address the quality. When a bundle of fibers is immersed in water, the water will rise up the fiber surface due to the capillary effect; at the same time, the water will penetrate into the inner part of the fiber if there exist pores in it. Figure 1 shows that the wicking height of the block copolymer fiber B2-4-200 is higher than that of cotton, PVA, as well as PAN fibers. This type of copolymer fiber not only contains more hydrophilic hydroxyl groups, but also has a grooved surface and inner porous morphology as described in a previous article.[2] All these structure features are favorable for enhancing the wicking ability of the fibers.

Mechanical Properties

The mechanical properties of the fibers are dependent on the composition, molecular weight, crystallinity, orientation of molecular chains, and morphological structure of the fibers. In the case of the poly(vinyl alcohol-b-acrylonitrile) fibers studied here, as shown in Table III, sample B1-5-200, mainly due to its lower molecular weight (MW), has a lower tensile strength and lower elongation to break. Sample B2-5-200 possesses higher strength and lower elongation because of its higher MW, moderate AN content, higher degree of crystallization and orientation, and

Table IV DSC Analysis for PVA, PAN, and PVA/PAN Block Copolymer Fibers

| Fiber Samples	Endothermic Melting		Exothermic Cyclization	
	Fusion Enthalpy ΔH_m (J/g)	Peak Temperature T_m (°C)	Cyclization Enthalpy ΔH_c (J/g)	Peak Temperature (°C)
PVA (commercial)	67.1	231		
PAN (commercial)			575.0	333
PVA-4-160	60.0	229		
PVA-4-200	68.8	231		
B1-4-160	55.8	227		
B1-4-200	61.6	231		
B2-3-160	20.5	220		
B2-3-200	51.6	224		
B2-4-160	28.4	221		
B2-4-200	47.0	225		
B2-5-160	24.3	225		
B2-5-200	62.5	229	21.2	315
B3-3-160	36.7	220	35.7	304
B3-3-200	52.5	230	42.1	306
B3-4-160	39.9	229	37.8	303
B3-4-200	51.2	232	49.6	307
B3-5-160	32.7	220	44.1	303
B3-5-200	48.0	229	50.4	309
B4-0-160	34.0	229	65.1	314
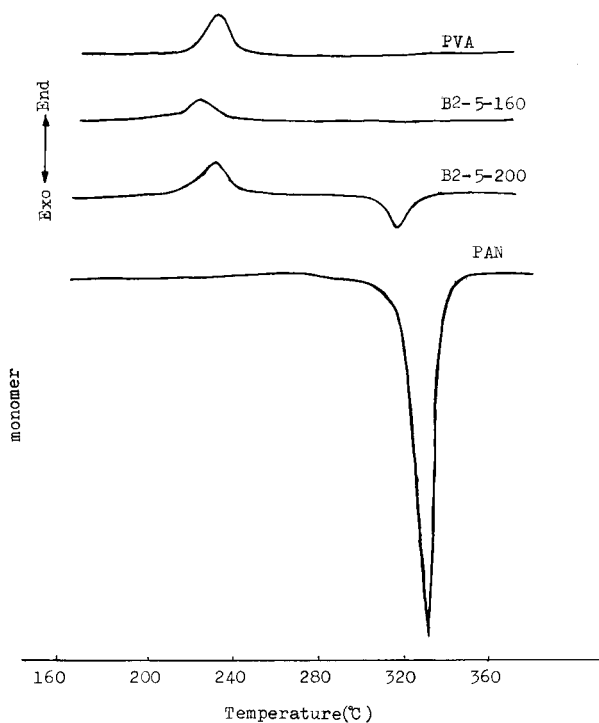
Figure 2 DSC thermograms of fibers.

smoother surface and tighter inner structure. Sample B3-5-200 has a higher MW, but also has a higher AN content, which leads to an irregularity of its molecular structure and therefore lower crystallization, orientation, and a rougher surface and more porous inner morphology. As a result, it

has lower strength and higher elongation. The data presented in Table III show that the tensile strengths of copolymer fibers with an appropriate AN content are lower than that of commercial PVA fiber but similar to that of commercial PAN fiber and much higher than that of wool and cotton.

Thermal Behavior

Table IV indicates that the melting temperatures of the block copolymer fibers heat-treated at 200°C are higher than are those of the fibers heat-treated at 160°C. Figure 2 shows that the peak temperature of the exothermic cyclization peak of commercial PAN fiber is high to 333°C. Since no the peaks due to cyclization are found, as shown in Table IV, B1 exhibits a short PAN sequence length, which is consistent with the crystalline behaviors exhibited by X-ray diffraction as can be seen in ref. 2. It appears that the sequence length required for crystallization and for cyclization of PAN blocks within the block copolymer fibers is approximately identical. Sample B2-5-200 starts cyclization as shown by Figure 2. Table IV indicates that the exothermic cyclization peak temperatures of the block copolymer fibers are all lower than that of conventional PAN fiber and that the samples with higher crystallinity possess a higher exothermic cyclization peak temperature than that of the counterparts with lower crystallinity. With a highly ordered state, more energy is
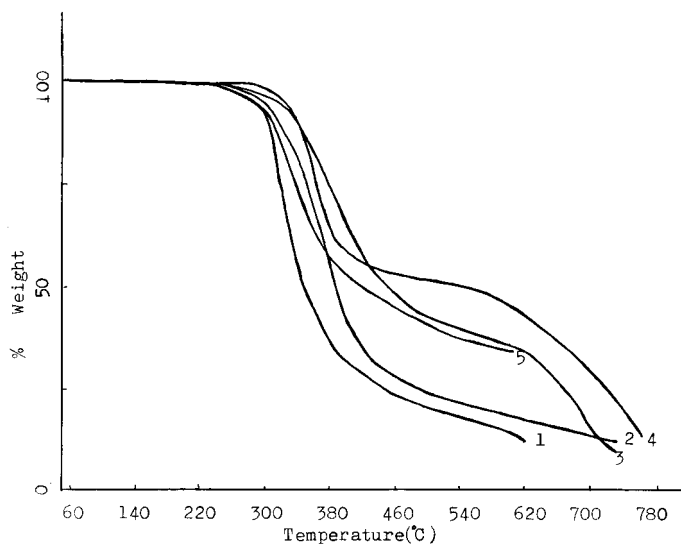

Figure 3 TG thermograms of PVA fiber, PAN fiber, and representative PVA/PAN block copolymer fibers containing different AN content. (1) commercial PAN fiber; (2) commercial PVA fiber; (3) B2-5-200; (4) B3-4-200; (5) B4-0-160.

Table V   TGA Data of PVA/PAN Block Copolymer Fibers Compared to PVA and PAN Fibers

Fiber Samples	Temperature Range (°C)	Weight Loss (%)	Temperature Range (°C)	Weight Loss (%)
PAN	264–489	79		
PVA	269–474	73		
B2-5-200	267–472	54	472–716	31
B3-3-160	276–426	40	426–760	51
B3-3-200	297–432	46		
B3-4-160	220–475	50	500–706	38
B3-4-200	281–470	48	524–779	35
B3-5-160	252–456	48	554–753	36
B3-5-200	269–448	45		
B4-0-160	270–480	60		

required for the molecular conformation transition necessary for cyclization.

Figure 3 and Table V exhibit that, unlike PVA and PAN fibers, the copolymer fibers are slowly decomposed relative to the two homopolymer fibers and include two degradation stages. Over a temperature range from 260 to 480°C, PVA and PAN fibers lose 70–80% of their weight. It might be considered that PAN blocks dispersed in copolymer fibers cannot cyclize so intensely and sharply as can homopolymeric PAN fibers and, consequently, slow down and retard the degradation of the whole copolymer fibers, improving their thermal stability.

REFERENCES

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2. Xiao, W.; Xu, X.; Chen, K. to be published.