

# Modified Polyacrylonitrile Blends with Cellulose Acetate: Fibers' Properties

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**ABSTRACT:** Fiber forming polyacrylonitriles (PAN) were modified by copolymerizing acrylonitrile monomer with methyl acrylate (MA) and 2-acrylamido-2-methyl propane sulfonic acid (AP), respectively, and blended with cellulose acetate (CA). Fibers of MA-PAN, AP-PAN, and their blends with CA were wet-spun in dimethylformamide in a broad range of coagulation bath concentrations (CBC). The effects of hydrophilic and hydrophobic modification of PAN and the CBC, as well as the coagulation behavior, were studied in terms of morphology, mechanical properties, and water regain property of the fibers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1937–1946, 1997

**Key words:** polyacrylonitrile; cellulose acetate; blend fibers

## INTRODUCTION

Blend fibers are filaments obtained from polymer–polymer blends and have been rapidly developed as an approach for new fiber products as well as a method to modify the property of existing fiber. Blend fibers can be manufactured by spinning homogeneous blends of miscible polymers to produce a single phase, or heterogeneous blends of immiscible polymers segregated into spatial regions. Typical phase arrangements in heterogeneous blend fibers are side by side, sheath-core, and matrix-fibril.<sup>1</sup>

The first blend fibers were prepared through dry-spinning of the matrix-fibril blends of polyacrylonitrile (PAN)/cellulose acetate (CA) and PAN/regenerated cellulose by Cates and White.<sup>2,3</sup> Later, Duiser and Copper prepared similar blend

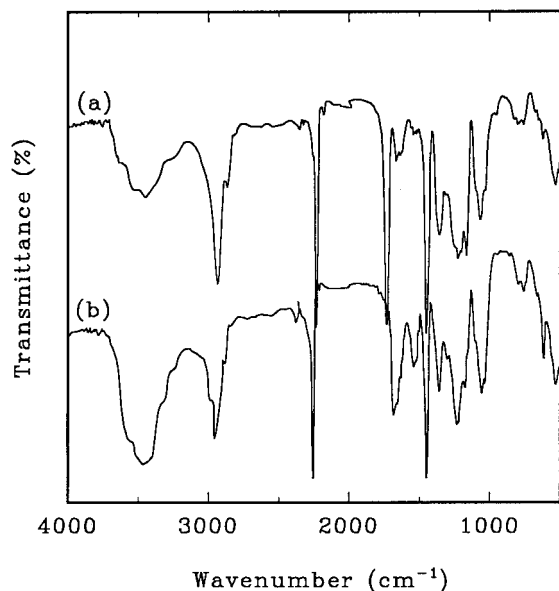
fibers of PAN/CA by phase separation spinning and fine fibrils by extracting the matrix with a solvent to investigate their graphitization.<sup>4</sup> Hagemeyer et al. augmented the miscibility of PAN and CA blend using CA-graft-PAN as a compatibilizer.<sup>5–8</sup>

However, no work has appeared in the open literature concerning the coagulation behavior of PAN/CA or modified PAN/CA blend fibers, as well as the characteristics of such fibers obtained at various coagulation bath conditions.

In the wet spinning of PAN in organic solvent, the cross-sectional shape, the size and shape of voids, and the homogeneity of internal fibrils generally vary with the rate of coagulation of the fine dope stream, which can be governed by the coagulation bath concentration (CBC) and temperature (CBT), dope concentration, and additives.<sup>9–13</sup> Specifically, the coagulation process of the fine dope stream is a counter-diffusion process between solvent outflux from the inside of the coagu-

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**Figure 1** IR spectra of (a) MA-PAN and (b) AP-PAN.

lating fiber and nonsolvent influx into the coagulating fiber, which is closely related with the skin rigidity and consequent macrovoid formation.<sup>14,15</sup> Moisture regain is known to depend on the presence of polar groups as well as on the amorphous content of the fibers.

Hence, we prepared two types of PAN copolymers, namely, the hydrophobic MA-PAN and the hydrophilic AP-PAN by polymerizing acrylonitrile (AN) with methyl acrylate (MA) as a hydrophobic source and 2-acrylamido-2-methyl propane sulfonic acid (AP) as a hydrophilic source and investigated the hydrophilicity effect on moisture re-

gain and water content of fibers; and we have attempted to elucidate the coagulation behavior during the fiber formation of both copolymers as well as their blends with CA at various CBCs. Morphology, mechanical properties, and the water regain characteristics of the experimental fibers (hereafter called fiber) have also been studied.

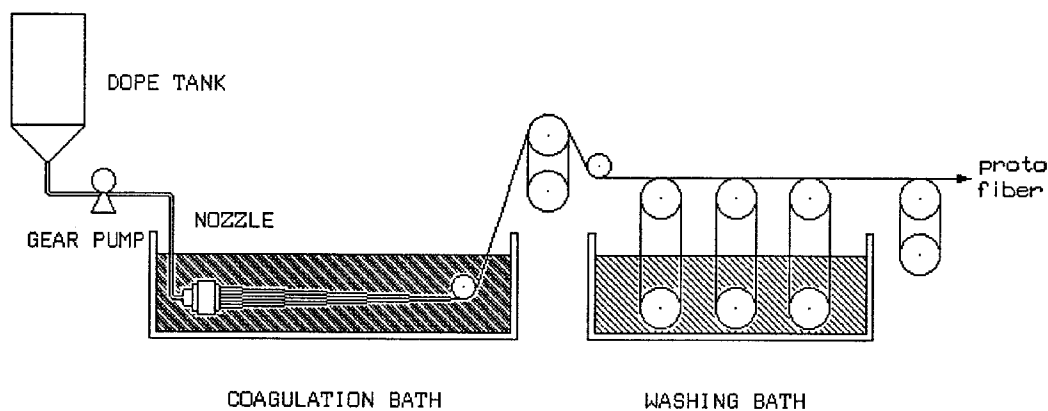
## EXPERIMENTAL

### Materials

Extra pure grades of MA, AP, and AN (Tokyo Kasei Co.) were used as received. CA (Sigma Chemical Co), having the degrees of polymerization and substitution of 160 and 2.4 (54–56% of acetyl content), respectively, was used.

### Preparation of PAN Copolymers

Both MA-PAN and AP-PAN copolymers were prepared by copolymerization of AN and comonomers in dimethylformamide (DMF) at 55°C with an azobisisobutyronitrile (AIBN) initiator. The weight-average molecular weights obtained from gel permeation chromatography (GPC) (Waters Associates 150C) were 145,000 and 138,000 g/mol for MA-PAN and AP-PAN, respectively. The MA content of MA-PAN copolymer (7.7 wt %) and AP content of AP-PAN (6.1 wt %) were estimated with infrared (IR) spectroscopy (Digilab FTS-65). The formation of copolymers was confirmed through IR spectra (Fig. 1). MA-PAN showed the C≡N and ester C=O stretching absorption bands at 2242 and 1735 cm<sup>-1</sup>, respectively, and



**Figure 2** Schematic sketch of wet-spinning apparatus.

AP-PAN showed the  $C\equiv N$ , amide  $C=O$ , and  $S=O$  stretching bands at 2242, 1672, and  $1042\text{ cm}^{-1}$ , respectively.

### Preparation of Fibers

To prepare the spinning dopes of MA-PAN and AP-PAN copolymers, the copolymers were first dissolved in DMF (20 wt %) and filtered. Continuous spinning of dopes to make fibers was carried out from a 300-hole (0.060 mm diameter) jet, as shown in Figure 2. CBC was varied over a broad range ( $H_2O/DMF = 100/0$  (w/w) (D0), 75/25 (D25), 50/50 (D50), and 25/75 (D75)) in a 1M coagulation bath at  $20^\circ\text{C}$  (CBT) with 8M/min spinning rate.

### Morphology

Morphologies of cross-sectional and lateral faces of the vacuum-dried fibers were studied from the

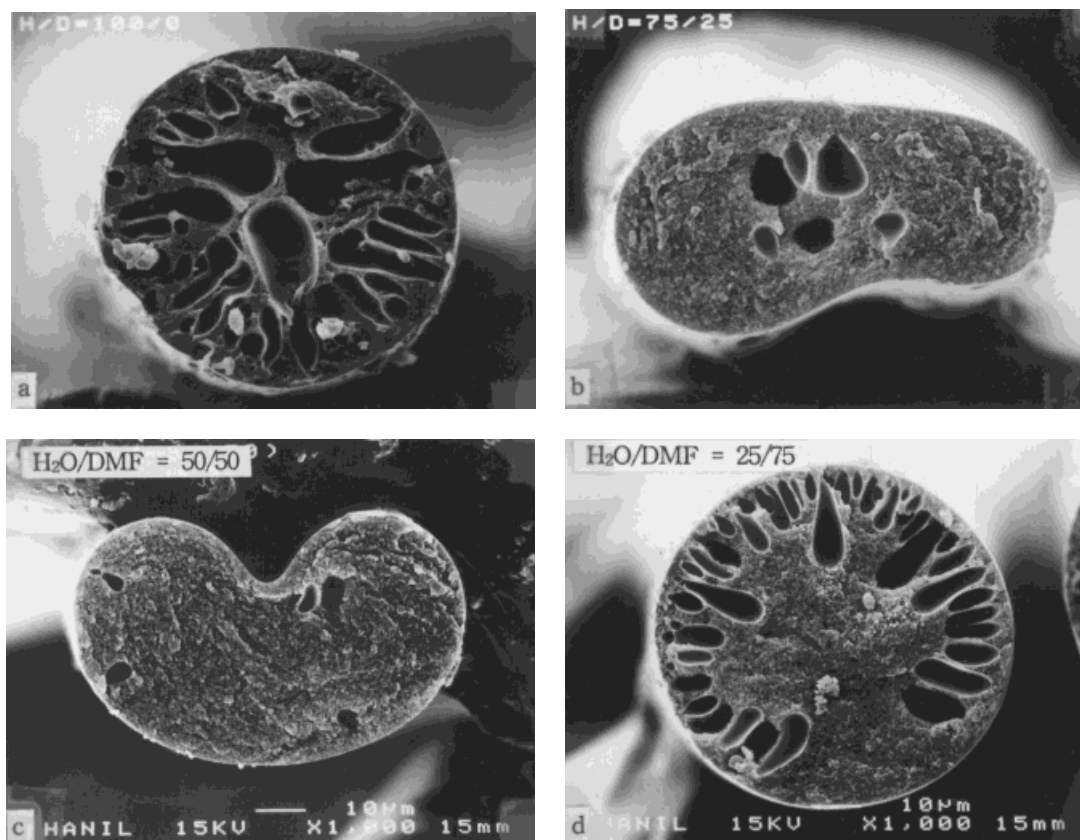
cryogenically fractured samples, sputtered with gold before viewing under a scanning electron microscope (SEM; JSM 6400).

### Moisture Regain and Water Retention

Moisture regain was measured at 65% relative humidity (RH), and the water retention value (WRV) was obtained by weighing the fiber after centrifuging the water-saturated fibers for 5 min at 3000 rpm, followed by drying in a vacuum oven at  $100^\circ\text{C}$ . The WRV was calculated according to

$$WRV = \frac{\omega_1 - \omega_2}{\omega_2} \times 100$$

where  $\omega_1$  is the moistured fiber (after centrifuging), and  $\omega_2$  is the dried fiber (after vacuum drying).



**Figure 3** SEM micrographs of a cross-section of MA-PAN fibers obtained at various CBC: (a) D0, (b) D25, (c) D50, and (d) D75.

### Tensile Properties of Fibers

Tensile properties of fibers were measured by using Fafegraph FPE/H at 65% RH and 20 cm/min of crosshead speed, with a gauge length of 20 mm.

## RESULTS AND DISCUSSION

### Cross-sectional Shape Change of MA-PAN Fibers

Cross-sectional shapes of MA-PAN fibers obtained at various CBC are shown in Figure 3. Circular cross-sections are obtained from D0 and D75, but noncircular cross-sections are obtained from D25 and D50. The cross-sectional shape of acylic fibers formed by wet spinning is more or less round or symmetrical. When the rate of coagulation is mild (in the cases of D25 and D50), the cause of such a distorted profile is easily understood. The skin formed under a mild condition is rather thin and pliable. As the coagulation proceeds, the diffusion of solvent out of the fiber becomes faster than the diffusion of nonsolvent into the fiber; consequently, a low pressure is created inside the fiber to induce an unsymmetrical cross-section.<sup>16</sup> When the rate of coagulation is high (in the case of D0), a thick and rigid skin will be formed; hence, indentations become impossible under such conditions. If there are weak spots on the skin, bath liquor will puncture through these spots to form finger-shaped voids at the peripheral region of the cross section.<sup>17</sup> On the contrary, fiber obtained from D75 showed a perfect circular shape with more voids.

### Cross-sectional Shape Change of MA-PAN/CA Blend Fibers Obtained at Various CBC

SEM micrographs of cross-sections of MA-PAN/CA blend fibers obtained from D50 with different amounts of CA are shown in Figure 4(a) and (b). With an increase in CA contents in the blend, the shape of cross-sections changes from unsymmetrical to circular, and the number of voids, especially macrovoids, increases due to the acceleration of coagulation rate by CA. This acceleration by CA in our immiscible blends is presumably due to the low dope viscosity and low intermolecular cohesive force between MA-PAN and CA. The solubility parameter of CA ( $11.0 \text{ (cal/cm}^3)^{1/2}$ ) is very close to that of DMF (10.5). Thus, the dope viscos-

**Table I** Water Retention and Moisture Regain of Fibers Obtained at Various CBC

Fibers		Moisture Regain (%) at 65% RH	Water Retention (%)
MA-PAN	D0	2.3	3.26
	D25	2.2	2.79
	D50	2.3	2.30
	D75	2.1	2.47
MA-PAN/CA	D0	2.8	3.52
	D25	2.7	3.33
	D50	2.9	2.95
	D75	2.8	2.72
AP-PAN D	0	7.3	2.80
	D25	7.2	2.71
	D50	7.4	2.60
	D75	7.5	2.55
AP-PAN/CA	D0	5.1	3.72
	D25	5.3	3.40
	D50	5.2	3.10
	D75	5.2	2.78

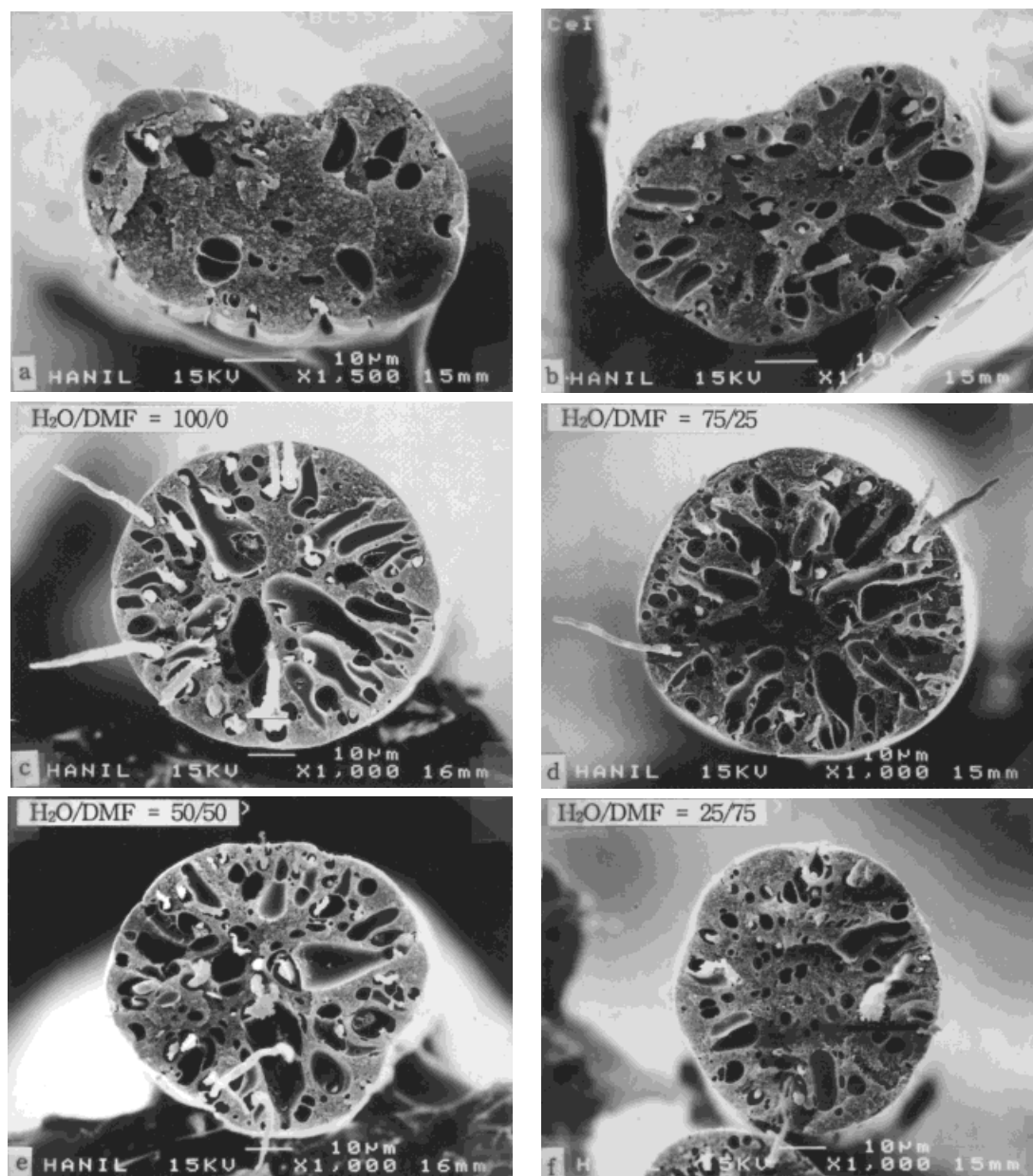
ity seems to be low in blends where CA acts as a diluent.<sup>10</sup>

MA-PAN/CA (9 : 1 by weight) blend fibers have circular cross-sections regardless of CBC, as shown in Figure 4(c)–(f), due to the acceleration of coagulation by CA. However, the number of tear-shaped voids increases with the decrease of CBC.

The lateral view of the micrographs (Fig. 5) shows that MA-PAN/CA blend fiber contains a hollow surface due to the differences in deswelling and shrinkage between MA-PAN and CA.<sup>18</sup> At the hole entrance, a rapid coagulation begins, which produces an elongational flow that deforms dispersed CA particles into fibrils; then, CA shrinks more than PAN during solidification in the coagulation bath. The circular voids are preliminarily formed, and those around fiber surfaces are transformed into a hollow surface due to elongational stress.

### Cross-sectional Shape Change of AP-PAN or AP-PAN/CA Blend Fibers Obtained at Various CBC

The coagulation phenomena of PAN copolymer can generally vary with the addition of ionic com-



**Figure 4** SEM micrographs of a cross-section of MA-PAN/CA blend fibers obtained at various CBC: (a) D50 with 3 wt % CA, (b) D50 with 5 wt % CA, (c) D0 with 10 wt % CA, (d) D25 with 10 wt % CA, (e) D50 with 10 wt % CA, and (f) D75 with 10 wt % CA.

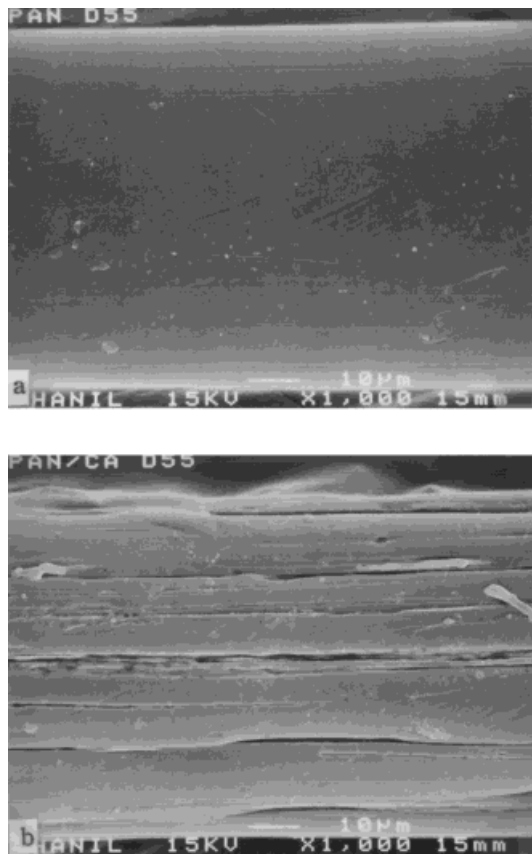
nomer.<sup>19</sup> In such a case, since the coagulation rate is retarded, the size and the number of voids are significantly decreased. As shown in Figure 6, our AP-PAN fibers obtained at all CBC show dense and circular cross-sections without voids, unlike the ones from MA-PAN fibers. This result is also caused by the retardation of coagulation due to the introduction of 6.1 wt % AP, a hydrophilic

comonomer built in PAN copolymer. Moreover, AP-PAN fiber obtained with D75 had an irregular fiber diameter and showed the partial elution of polymer on the surface owing to the incomplete coagulation in the bath.

As shown in Figure 7, AP-PAN/CA (9 : 1 by weight) blend fibers obtained at all CBC also show dense and circular cross-sections without voids

**Table II** Tensile Properties of Fibers Obtained at Various CBC

	Fibers	Denier (De)	Tenacity (g/De)	Elongation (%)	Modulus (g/De)
MA-PAN	D0	24.5	0.31	46.6	7.20
	D25	25.9	0.30	44.0	5.61
	D50	16.8	0.52	66.6	10.9
	D75	22.4	0.40	61.3	7.21
MA-PAN/CA	D0	26.3	0.26	33.2	6.45
	D25	28.1	0.24	29.8	4.67
	D50	22.2	0.33	31.8	8.48
	D75	21.9	0.36	46.5	8.98
AP-PAN	D0	15.6	0.57	112	12.6
	D25	13.9	0.57	89.9	15.7
	D50	16.6	0.47	59.1	8.48
	D75	—	—	—	—
AP-PAN/CA	D0	28.9	0.16	21.9	2.66
	D25	21.5	0.30	32.2	6.10
	D50	16.7	0.38	35.8	8.40
	D75	15.9	0.49	40.5	11.4

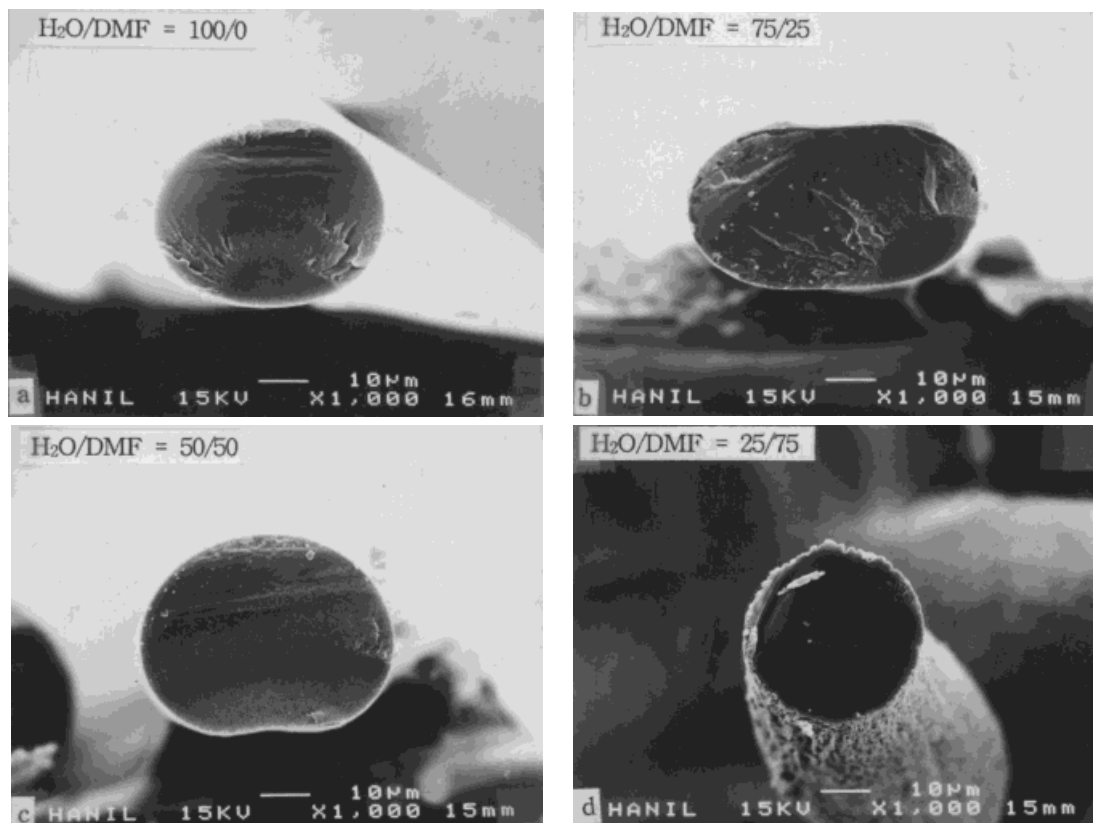
**Figure 5** SEM micrographs of lateral face: (a) MA-PAN and (b) MA-PAN/CA blend fibers.

like AP-PAN fibers, even though the shrinkage rates of CA and AP-PAN are completely different. These results come from the relatively good interfacial adhesion in AP-PAN/CA blends.

#### Moisture Regain and Water Retention of Fibers

As shown in Table I, moisture regains of fibers obtained under different CBC are nearly similar, regardless of the types of PAN. However, MA-PAN/CA blend fibers (2.8%) show slightly higher moisture regain than MA-PAN fibers (2.2%) due to the hydrophilic groups in CA. However, AP-PAN fibers show about 7% of moisture regain due to the hydrophilicity of AP. The moisture regain in AP-PAN/CA blend fibers is reduced to 5%, compared to the parent fiber. This probably comes from the introduction of CA having lower moisture regain (about 4%) than that of AP-PAN.

Since water retention generally depends on density, porosity, and hydrophilicity of fiber, water retentions of blend fibers are higher than those of unblended PAN fibers and decrease with increasing CBC. These higher WRV of blend fibers are caused by the hydrophilicity of AP-PAN and the generation of more pore sites



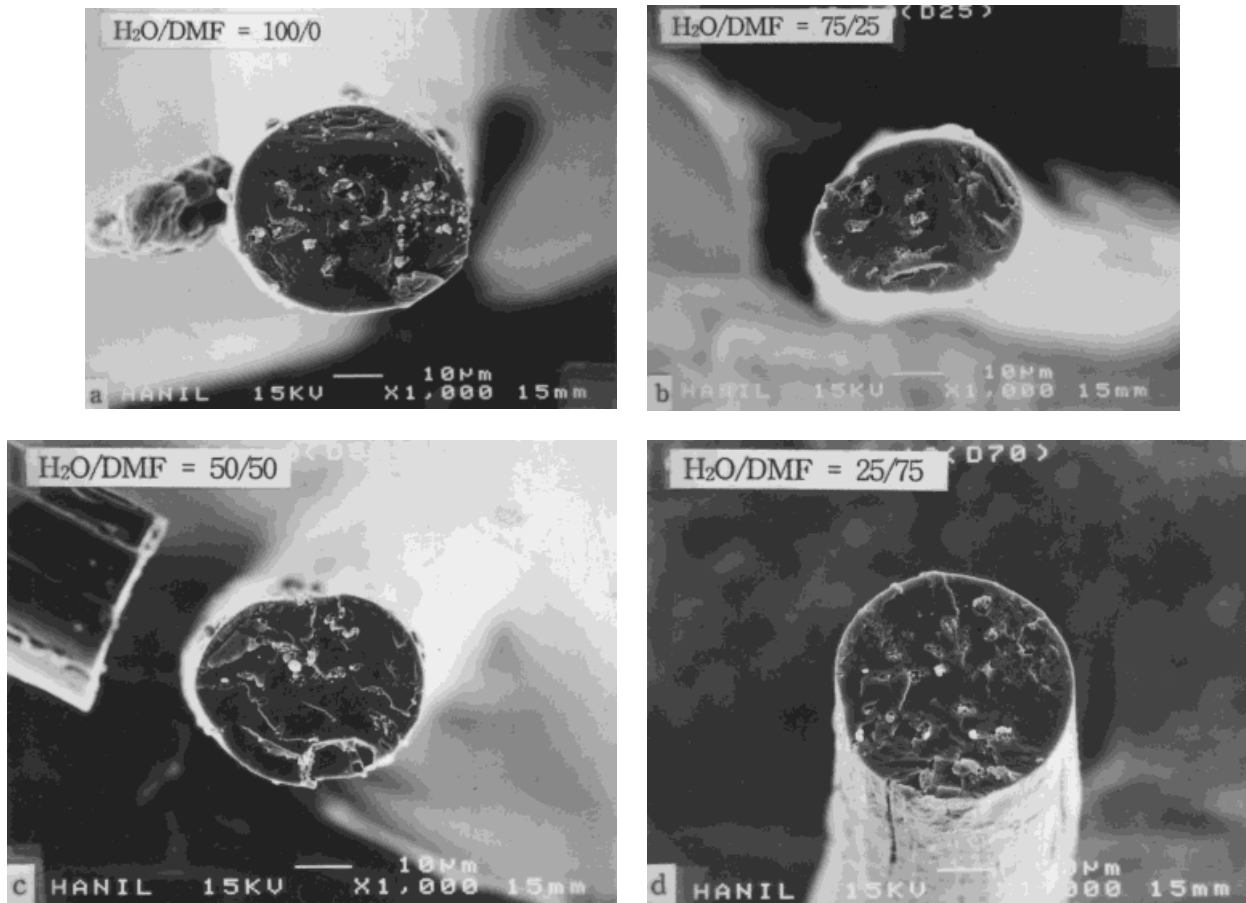
**Figure 6** SEM micrographs of a cross-section of AP-PAN fibers obtained at various CBC: (a) D0, (b) D25, (c) D50, and (d) D75.

with the addition of CA for AP-PAN/CA blend fibers and by the microvoid generation due to the accelerated coagulation of CA and the difference of compressibilities between CA and PAN for MA-PAN fibers, as mentioned above. In addition, all fibers obtained at higher CBC, except MA-PAN fibers, clearly show lower WRV because their structures become denser due to the retardation of coagulation rate. However, in the case of MA-PAN fibers, the fiber obtained from D50 shows a lower WRV than that from D75 because of less macrovoid formation through the occurrence of indentation on it.

#### Tensile Properties of Fibers

Tensile properties of fibers are shown in Table II, and their typical stress-strain behavior are shown in Figures 8 to 11. Tenacities and initial moduli

of all fibers except the AP-PAN fiber generally increase as CBC increases, i.e., as the rate of coagulation decreases. MA-PAN fiber obtained from D50 shows the least porosity and superior tensile properties, including tenacity, elongation, and initial modulus, to those obtained from D0, D25, and D75, leading to the superior final fiber properties. MA-PAN/CA blend fiber shows poorer tensile properties, especially tenacity and elongation, than MA-PAN fiber since the macrovoids were spread over all cross-sectional regions; consequently, the intermolecular cohesive force is decreased, as shown in Figure 4. In AP-PAN fibers, the tensile properties, especially elongation at break, are more pronounced than those of MA-PAN fibers. This could be related to the homogeneity of the structure caused by the low porosity (Fig. 5). AP-PAN/CA blend fibers show inferior tensile properties to those obtained from parent polymer.



**Figure 7** SEM micrographs of a cross-section of AP-PAN/CA blend fibers obtained at various CBC: (a) D0, (b) D25, (c) D50, and (d) D75.

On the other hand, optimum CBC to attain better tensile properties moved to higher values in both blend dope spinnings. This implies that coagulation speed of CA is faster than that of PAN copolymers.

## CONCLUSIONS

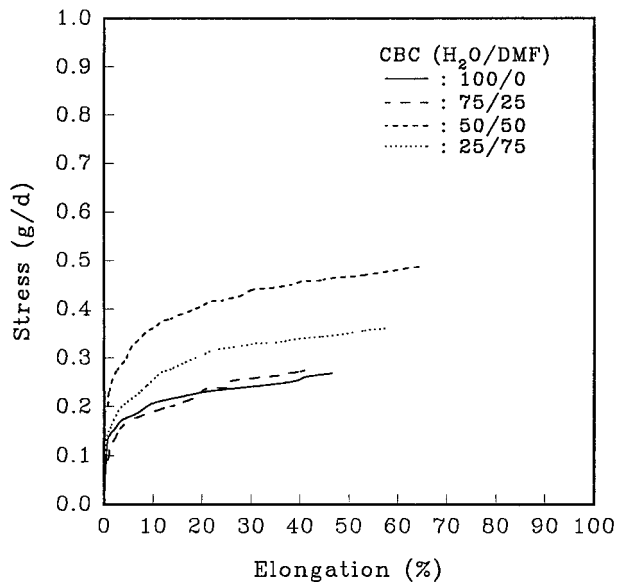
We have prepared several experimental fibers of MA-PAN, AP-PAN, and their blends with CA through wet-spinning in DMF/water to investigate the effect of hydrophilicity on moisture regain and water content, in addition to the coagulation condition on the characteristics of the fibers. From these experiments, we obtained the following results.

1) In the cases of MA-PAN/CA blend fibers,

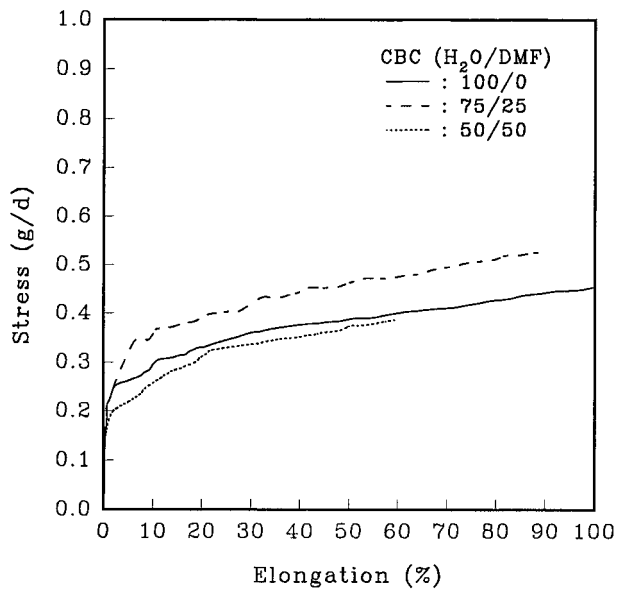
the cross-sections were transformed from unsymmetrical shape to circular one, and the number of macrovoids was increased with CA content (3–10 wt %) due to the acceleration of coagulation rate by CA. However, MA-PAN/CA blend (10 wt % of CA) fibers showed circular shapes regardless of CBC.

- 2) AP-PAN and AP-PAN/CA blend fibers obtained at all CBC showed dense and circular cross-sections without voids due to the retardation of coagulation by the hydrophilic AP in PAN copolymer.
- 3) AP-PAN fibers showed the highest moisture regain (about 7%) due to the hydrophilicity of AP; whereas the moisture regain of AP-PAN/CA blend fiber was decreased by 5%, based on AP-PAN fiber.
- 4) Water retention values of blend fibers were





**Figure 8** Effect of DMF concentration of coagulation bath on the stress-strain curves of MA-PAN fibers.

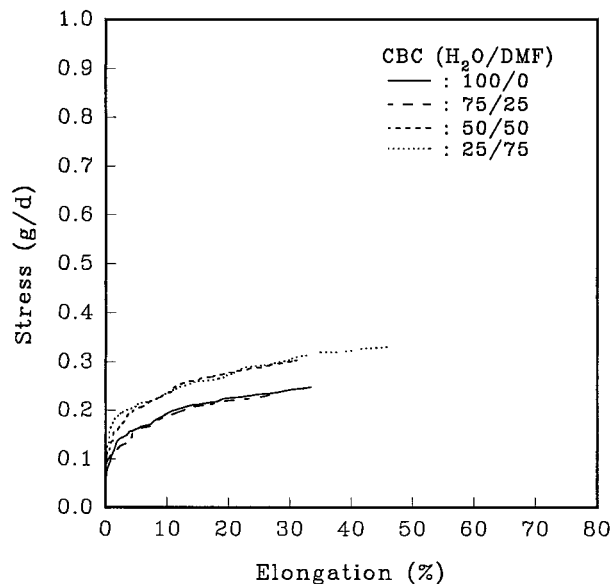


**Figure 10** Effect of DMF concentration of coagulation bath on the stress-strain curves of AP-PAN fibers.

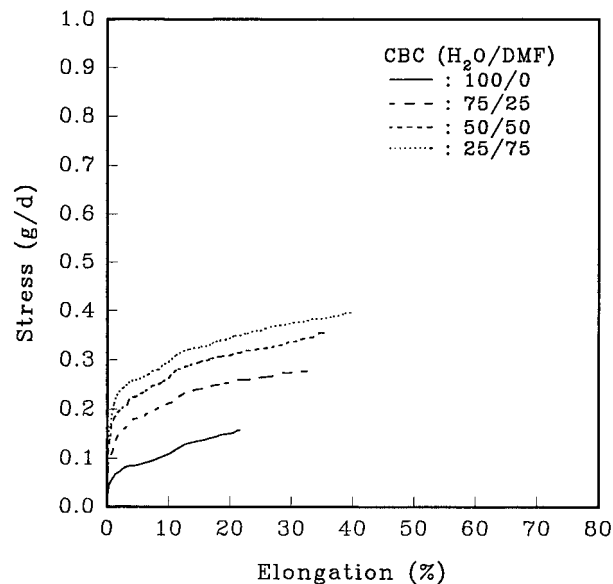
higher than that of unblended PAN fibers due to the generation of more pore sites by CA.

5) All AP-PAN fibers have excellent tensile

properties; whereas only MA-PAN fiber obtained at D50, and AP-PAN/CA blend fibers obtained at D75, showed relatively good tensile properties.



**Figure 9** Effect of DMF concentration of coagulation bath on the stress-strain curves of MA-PAN/CA blend fibers.



**Figure 11** Effect of DMF concentration of coagulation bath on the stress-strain curves of AP-PAN/CA blend fibers.

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