

# ***Wet Spinning of Liquid Crystalline Solutions of Cellulose Acetate Butyrate and Cellulose Triacetate***

## **INTRODUCTION**

In recent years, various research teams have found concentrated solutions of cellulose derivatives to be liquid crystalline.<sup>1-7</sup> This has also been found for solutions of cellulose itself.<sup>8,9</sup> While the solution spinning of cellulose derivatives dates back a century,<sup>10,11</sup> it was only in 1976 that Panar and Willcox<sup>2</sup> applied for a patent on the solution spinning of fibers from liquid crystalline solutions of cellulose derivatives. Recently, Shimamura, White, and Fellers<sup>12</sup> have shown bulk hydroxypropyl cellulose acts like a thermotropic liquid crystal and studied the melt spinning of fibers from it.

No reports of basic studies of fiber spinning from anisotropic solutions of cellulose derivatives are in the literature. We begin such a study in the present paper. Specifically we investigate the spinning of solutions of cellulose acetate butyrate (CAB) in dimethylacetamide (DMA) and of cellulose triacetate (CTA) in trifluoroacetic acid (TFA). These solutions have previously been identified as being liquid crystalline in the literature.<sup>2,6,7</sup> We present evidence that relates liquid crystalline features<sup>7</sup> to solid state properties.

## **EXPERIMENTAL**

### **Materials**

The cellulose acetate butyrate (CAB) used in these studies was obtained from the Tennessee Eastman Company. It was 13.5% acetate and 37.5% butyrate with an intrinsic viscosity of 2.12 dL/g in dimethylacetamide at 25°C. The cellulose triacetate (CTA) was supplied by the Celanese Fibers Company. It had a degree of substitution of 2.92 and an intrinsic viscosity in dichloroacetic acid of 3.57 dL/g at 25°C.

The solvent for the CAB was dimethylacetamide (DMA) and the coagulation bath was a 50/50 solution of DMA and H<sub>2</sub>O. The coagulation bath content was chosen so as to avoid the occurrence of Marangoni instabilities due to high heats of solution.<sup>13</sup> These lead to fluted void structures which strongly influence fiber properties.<sup>13</sup> The solvent for the CTA was trifluoroacetic acid (TFA) and the coagulant was methanol. The systems investigated, including concentrations, are summarized in Table I.

### **Determination of Liquid Crystalline Character**

The solutions were placed in Fisher Scientific Littman slides which contain a built-in cavity and covered with thin microscope slide covers. The optical character was studied using a Leitz ortholux polarizing light microscope with crossed polarizer and analyzer. The passage of light defines a birefringent character.

### **On-Line Birefringence**

An Olympus polarizing light microscope was used to investigate the birefringence of vertical filament from CAB/DMA solutions of various concentrations. These were extruded vertically downward from the Harvard infusion withdrawal pump used in the wet spinning studies. There was no takeup and the filaments descended under gravity. These studies were similar to the experiments reported by Onogi et al.<sup>5</sup>

### **Wet Spinning**

The wet spun fibers were produced using a dry jet method of the type introduced by Blades<sup>14</sup> for liquid crystalline solutions of *p*-linked aromatic polyamides. The wet spinning apparatus used was essentially that of Hancock, Spruiell, and White, which was described in an earlier paper.<sup>15</sup> A single

TABLE I  
Cellulose-Derivative Solutions Spun into Fibers

Polymer	Solvent	Concentration (g/mL)	Solution phase behavior	Coagulant
Cellulose acetate butyrate (CAB)	Dimethyl acetamide (DMA)	0.35	Isotropic	50/50 DMA/H <sub>2</sub> O
		0.40	Two phase, isotropic/anisotropic	
		0.45	anisotropic	
		0.50	anisotropic	
Cellulose triacetate (CTA)	Trifluoroacetic acid (TFA)	0.25	isotropic	CH <sub>3</sub> OH
		0.30	anisotropic	

hole spinneret of diameter 0.08 cm was used with an air gap of 2 cm between the spinneret and the coagulant. The coagulated fibers emerging from the bath were washed with water before taking them up on a rotating spool. These fibers were subsequently immersed in a water bath for 2 h and air dried for a subsequent 48 h.

#### Fiber Characterization

Wide angle X-ray diffraction (WAXS) patterns were carried out on fibers using a Philips X-ray generator. CuK $\alpha$  radiation of wavelength 1.542 Å was used.

Birefringences of fibers were determined using an Olympus microscope with a Berek compensator.

An AMR Model 900 high resolution scanning electron microscope was used to study the fiber. Fracture surfaces were formed in liquid nitrogen. The samples were coated with a gold palladium alloy.

Force-elongation curves were obtained on a Table Model Instron tensile testing machine.

#### OPTICAL AND WET SPINNING BEHAVIOR

The most dilute of the CAB/DMA and CTA/TFA solutions allowed no passage of light through the crossed polars in the quiescent state. This was not the case for the more concentrated solutions. The 0.40 g/mL CAB solutions indicated a two-phase structure and 0.45 and 0.50 solutions showed a completely birefringent field. The detailed character of this birefringent structure and a comparison to other cellulose derivative solutions has been considered in some detail by the authors in an earlier paper.<sup>7</sup> Suffice it to say that the birefringent morphology was not as well developed as observed in solutions of hydroxypropyl cellulose, CTA, and ethyl cellulose studied. The 0.25 CTA solution was isotropic and the 0.30 solution was completely anisotropic. The CTA/TFA system showed a well-defined birefringent morphology similar to CTA in dichloroacetic acid reported earlier.<sup>7</sup>

Diameter and birefringence profiles for the CAB/DMA solutions are shown in Figure 1. The birefringences are negative. The birefringence values of the 0.40 and 0.45 solutions are substantially higher than for the 0.25 solution. These observations certainly reflect enhanced molecular orientation in the 0.40 and 0.45 solutions. They are undoubtedly due to the liquid crystalline characteristics of the solutions and are similar to the observations of Onogi et al.<sup>5</sup> The high levels of orientation may also be associated with the orientation developed in the spinneret as found for hydroxypropyl-cellulose melts.<sup>12</sup>

There was a marked difference in the spinability of isotropic and anisotropic CAB solutions. With the 0.35 g/mL solution, it was not possible to take up the fiber with or without an air gap. The other solutions were wet spun over a range of conditions. The results for the CTA/TFA solutions are similar. The 0.25 solution could be wet spun only with difficulty. The anisotropic 0.30 solution could be wet spun over a wide range of conditions. The results of the above paragraph bring to mind

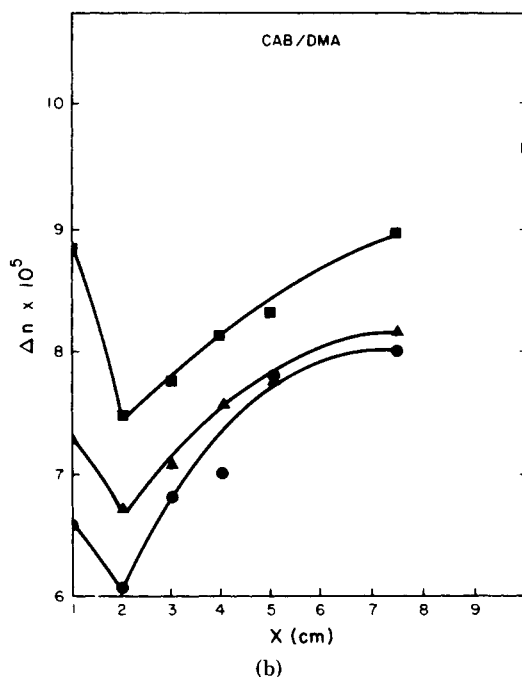
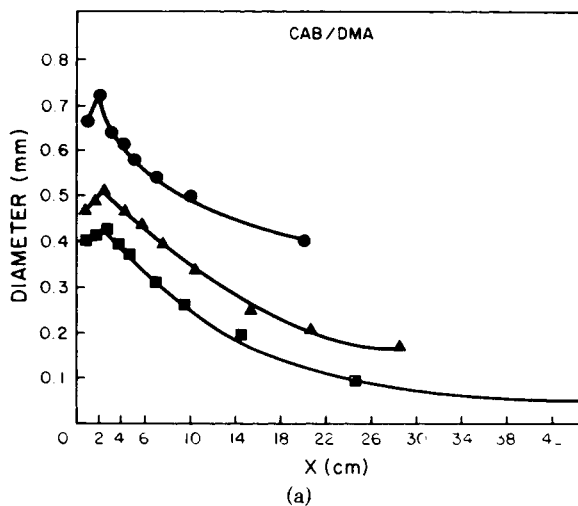


Fig. 1. (a) Diameter profile. (b) Birefringence profile for cellulose acetate butyrate/DMA solutions on a descending spinline. (●) 25%; (▲) 40%; (■) 45%.

the patent of Ballard and his co-workers<sup>16</sup> on polypeptide solutions, where liquid crystalline characteristics are claimed to greatly improve the spinnability.

## FIBER STRUCTURE AND PROPERTIES

### Cellulose Acetate Butyrate

Figure 2 shows an SEM photomicrograph typical of a CAB fiber fractured in liquid nitrogen. Three distinct superstructures can be seen. These are (a) an outer skin, (b) a fibrillar structure, and (c) an inner core. Skin core superstructures are well known in wet spun fibers.<sup>13,15</sup> Fibrillar structures

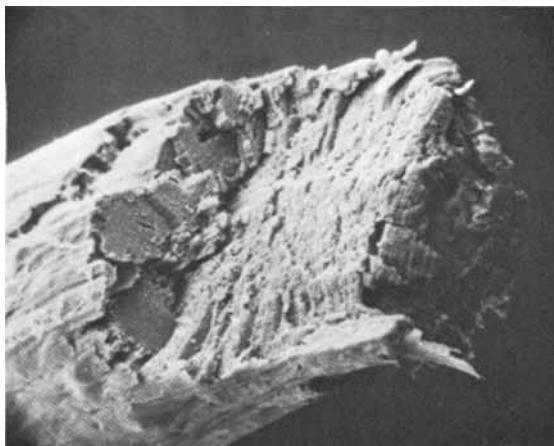


Fig. 2. SEM photomicrograph of fracture surface of wet spun cellulose acetate butyrate (CAB) fibers.

are usually not seen in undrawn wet spun fibers. It must be associated with the liquid crystalline spinning solutions and the "dry jet" procedure. The general characteristics of the wet spun CAB fibers are summarized in Table II.

A WAXS pattern for a typical wet spun fiber is shown in Figure 3. The WAXS pattern shows three "d" spacings. These are somewhat diffuse reflections at 3.10 Å, 4.256 Å, and 5.47 Å. It is of interest to note that CAB solidified from the melt forms a glass with an amorphous halo at 5.45 Å.<sup>17</sup> Apparently the only pathway to forming a solid state crystalline CAB fiber then is via the spinning of a liquid crystalline solution. The 5.47-Å reflection in the wet spun fiber would appear to represent the amorphous halo. Crystallinity has been found in CAB precipitated from an acetone solution by Boy, Schulken, and Tamblyn.<sup>18</sup>

The wet spun CAB fibers exhibit birefringence levels as shown in Table II. The birefringence of the fibers is negative, as was the case for the filaments as they were being spun. The negative birefringence of an oriented fiber must correspond to the polarizability perpendicular to the chain being greater than that parallel to the chain. This would appear due to the bulky butyrate and acetate groups. A similar situation exists with polystyrene,<sup>19</sup> which leads to negatively birefringent fibers.<sup>20</sup>

Force-elongation curves were determined for the wet spun fibers. Young's modulus, tensile strength, and elongations to break were measured. The results are summarized in Table II. There is unfortunately no comparison possible with fibers spun from an isotropic solution.

TABLE II  
Structure and Properties of Wet Spun Cellulose Acetate Butyrate Fibers

Solution concentration (g/mL)	Draw-down ( $V_L/V_0$ )	Fiber diameter ( $\mu\text{m} = 10^4 \text{ cm}$ )	Birefringence ( $\Delta n \times 10^4$ )	Young's modulus $\times 10^{-9}$ (dynes/cm <sup>2</sup> )	Tensile strength $\times 10^{-8}$ (dynes/cm <sup>2</sup> )	Elongation to break (%)
0.40	3.4	390	1.05	8	4.2	10
0.45	3.4	320	1.28	9	11	10
	5.2	260	1.57	15	11	10
0.50	3.4	340	1.20	8	6.75	10
	5.2	300	1.36	10	7	10
	6.8	230	1.78	17	6.5	10
	8.5	200	2.10	23	9	10

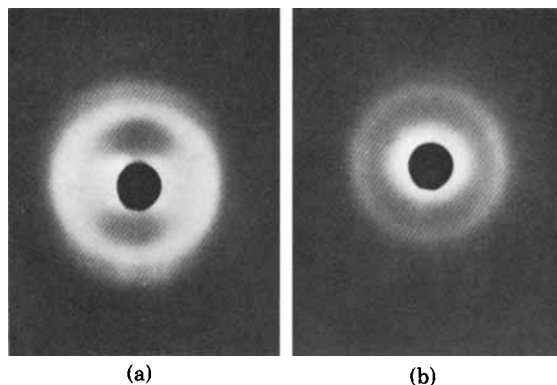


Fig. 3. WAXS pattern for CAB fibers: (a) wet spun; (b) melt spun.

TABLE III  
Structure and Properties of Wet Spun Cellulose Triacetate Fibers

Solution concentration (g/mL)	Draw-down ( $V_L/V_0$ )	Fiber diameter ( $\mu\text{m} = 10^{-4} \text{ cm}$ )	Birefringence ( $\Delta n \times 10^4$ )	Young's modulus $\times 10^{-9}$ (dynes/cm <sup>2</sup> )	Tensile strength $\times 10^{-8}$ (dynes/cm <sup>2</sup> )	Elongation to break (%)
0.25	3.9	520	3.72	32	8.8	22.5
0.30	3.9	400	2.34	27	15	10
	7.8	270	4.40	75	20	10
	15.6	140	6.8	75	50	10

### Cellulose Triacetate

Figure 4 is an SEM photomicrograph showing the fracture surface of a CTA fiber spun from a liquid crystalline solution. It shows a skin core structure but not as much fibrillar character as the CAB fiber of Fig. 2. The fiber characteristics are summarized in Table III.

WAXS patterns for the CTA fibers indicated the occurrence of crystallinity; peaks are observed at spacings corresponding to 3.74 Å, 4.06 Å, 5.43 Å, and 11.64 Å. These appear to correspond to values described by Sprague, Riley, and Noether<sup>21</sup> for the Triacetate I structure.

The CTA fibers exhibit birefringences as shown on Table III. The birefringences are positive and generally correlate to the mechanical strength properties, which are also shown in Table III. The CTA fibers from the more concentrated liquid crystalline solutions exhibit a significantly enhanced Young's modulus and tensile strength compared to those spun from isotropic solutions. These enhanced properties are only obtained at draw ratios greater than 4. Such spinning conditions were only attainable for liquid crystalline solutions.

### DISCUSSION

Certain conclusions may be drawn from this study. The most specific of these relates to CAB. Liquid crystalline CAB solutions can be spun into a fiber with solid state crystallinity. This is the only known mechanism for developing this structure as CAB will not crystallize by cooling from the melt state. This suggests a strong relationship between fiber structure and the character of the spinning solution. Recalling our earlier study,<sup>7</sup> the level of structural perfection in the liquid crystal is determined both by the chemical structural regularity of the polymer and its interaction with the solvent. It would appear that the better this development of liquid crystalline structure, the more highly developed the structural features of the solid state fiber: viz., CAB vs. CTA.

This suggests the general proposition that the structural character of the solid state fiber and its mechanical properties are intimately related to the structure developed in the liquid crystalline state.

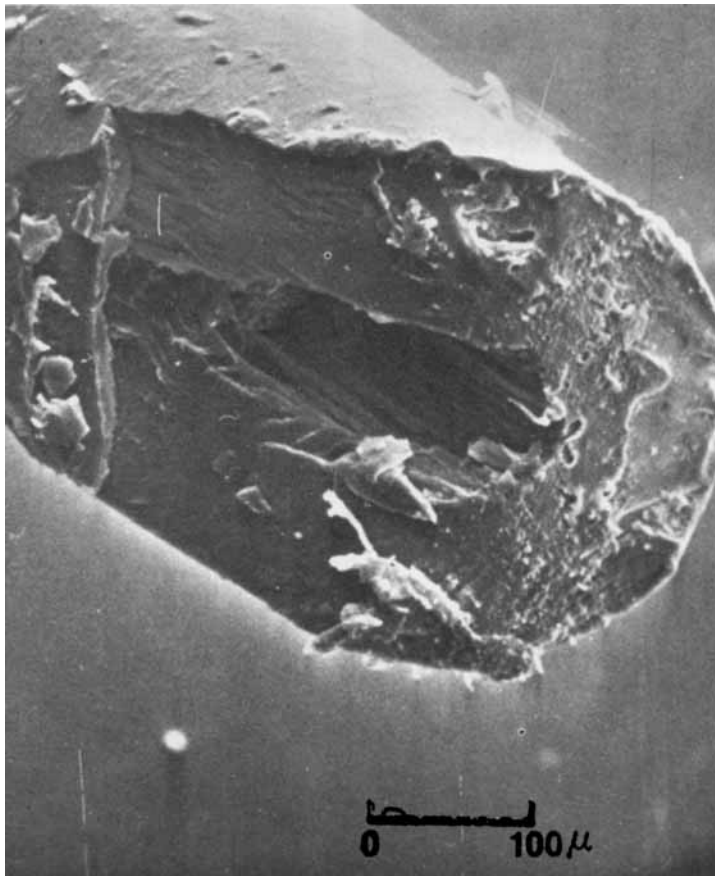


Fig. 4. SEM photomicrograph of fracture surface of wet spun cellulose triacetate (CTA) fiber spun from a liquid crystalline solution.

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Received May 18, 1981  
Accepted June 22, 1981