Preparation of High-Strength/High-Modulus Regenerated Cellulose Fibers from Lyotropic Mesophases

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SYNOPSIS

Cellulose triacetate (CTA) fibers were spun from a 35% (w/v) solution of CTA (molecular weight, 95,000) in trifluoroacetic acid (TFA)/CH_2CL_2 (60/40, v/v) using laboratory-scale spinning equipment, an air gap, and cold MeOH as the coagulant. The resulting fibers, of large diameter (ca. 80 μm) were saponified with a variety of reagents. The regenerated cellulose fibers had tenacities and moduli as high as 1.6 and 50 GPa, respectively. The fiber properties did not show a dependence on which cellulose polymorph was present. It is suggested that, for highly oriented fibers, the cellulose molecular weight is the primary parameter that determines the strength and modulus. This emphasizes the advantages of using a lyotropic cellulosic mesophase which permits relatively low solution viscosities at high concentrations and high polymer molecular weights. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Since Werbowyj and Gray[1] first reported that a cellulose derivative, viz., hydroxypropyl cellulose, forms a mesophase in water, investigations of cellulosic mesophases (both lyotropic and thermotropic) have expanded rapidly. Investigators appear to have two main motivations: to study mesophase formation primarily from a purely scientific approach and/or to examine cellulosic mesophases from a technological viewpoint, specifically as a route to high-strength, high-modulus (compared to viscose rayon) regenerated cellulose fiber.

There are two main reasons for using lyotropic mesophases from which to spin fibers with improved properties:

1. The molecular order of the mesophases in solution is transmitted to the solid fiber phase [this is exemplified by spinning of poly-(phenylene terephthalamide) fibers]. How-ever, cellulosics form chiral nematic mesophases. Thus, it is necessary to unwind the superhelicoidal structure during the fiber-extrusion phase.
2. High polymer concentrations of low solution viscosity are possible with lyotropic mesophases, which is an obvious advantage compared to isotropic solutions. Unfortunately, cellulose mesophases, regardless of the solvent, do not exhibit the viscosity maximum typical of polymeric lyotropic mesophases.

There have been a number of reported attempts to directly spin cellulose fibers with improved properties from lyotropic mesophases. Quenin et al.[2] prepared dry-jet, wet-spun fibers from a lyotropic mesophase of cellulose in NMMO—H_2O. The Young's modulus of the fiber was 35 GPa and the tenacity was 0.9 GPa, values which are comparable to the highest reported modulus and tenacity values of viscose rayon fiber. Tencel® (a regenerated cellulose fiber commercially produced by Courtaulds) is reported to have a 0.5–0.8 GPa tenacity, which is spun from a NMMO—H_2O solution at a polymer concentration that is probably below the critical concentration for mesophase formation. It is pro-

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Table I   CTA Fiber Spinning Parameters[a]

	Experiment				
	1	2	3	4	5
Extrusion rate (m/min)	0.84	0.89	2.94	2.94	2.94
Take-up speed (m/min)	2.93	3.00	6.75	10.5	14.4
Draw ratio	3.47	3.34	2.29	3.57	4.89
Coagulant	CH_3OH	H_2O	CH_3OH	CH_3OH	CH_3OH
Bath temp (°C)	−7	3	−10	−20	−20

[a] Spinnerette: 6 holes of 0.25 mm i.d.; air gap: 6.5 cm.

duced only in staple form as the filaments fibrillate extensively on bending. Bianchi et al.[3] spun fibers from both isotropic and anisotropic solutions of cellulose in DMAC/LiCl mixtures. They reported initial moduli as high as 21.3 GPa—again, comparable to viscose rayon. Yang et al.[4] spun cellulose fibers from an anisotropic solution in NH_3/NH_4SCN. Tenacities of ∼ 0.4 GPa and moduli of ∼ 20.5 GPa were obtained. The morphologies of the cellulose were not reported by Bianchi et al. or Yang et al., although in both cases it was probably Cellulose II (or III in fibers spun from NH_3/NH_4SCN). Recently, we spun cellulose dissolved in TFA/CH_2Cl_2 above the critical concentration.[5] The fiber tenacity was 0.4 GPa and the resulting morphology was II. There is some controversy in the literature regarding the maximum theoretical or calculated elastic modulus of a cellulose fiber depending on whether the crystal polymorph is Cellulose I or II.

Northolt[6] and Northolt and de Vries[7] concluded that it is unlikely that the highest possible elastic extension with a corresponding additional stress buildup can be achieved for a cellulose fiber having the Cellulose II morphology. They suggest that if a fiber-formation process could be developed such that only the Cellulose I polymorph is obtained, then "an increase in strength of at least 60% may be expected." Kroon-Batenburg et al.,[8] based on a com-

parison of experimental values and molecular mechanics calculations with cellobiose, concluded that the essential difference between Cellulose I and II, as regards their elastic modulus, is the number of intramolecular hydrogen bonds per anhydroglucopyranose unit. In Cellulose I, there are two intramolecular hydrogen bonds parallel to the chain axis while there is only one in Cellulose II.[8,9] The presence of two intramolecular hydrogen bonds per structural unit in Cellulose I is cited as the reason for its higher elastic modulus compared to Cellulose II.

Kroon-Batenburg et al.[8] calculated the following elastic moduli and compared them with experimental moduli:

Cellulose Fiber	Crystal Form	Elastic Modulus (GPa)	
		Calcd	Obsvd
Native	I	136 ± 6	130–137
Regenerated	II	89 ± 4	71–90

The Tashiro and Kobayoshi[9] calculated values are

I   167.5 GPa

II   162.1 GPa.

Crystalline elastic moduli observed by the X-ray diffraction method were reported by Sakurada et al.[10]: I, 130–138 GPa; II, 90 GPa; and Matsuo and Sawatari[11]: I, 120–140 GPa; II, 106–112 GPa.

The values calculated by Kroon-Batenburg et al. agree closely to the experimental values and those obtained by Sarurada et al. The values calculated by Tashiro and Kobayoshi, while higher than those of Kroon-Batenburg et al., the experimental value,

Table II   Properties of As-spun CTA Fiber

Expt #	Average Diameter (μm) of 6 Fils	Tenacity (GPa) Max
2	74	0.60
4	74	0.51
5	43	0.77
3	116	1.05
—	116	9.3
1	76	1.05

Table III   Filament Eveness Data

Sample	Diameter of Individual Fibers (μm)						Av
CTA, as-spun	78.2	81.3	81.3	81.3	79.9	75.2	79.5
Saponified, (NaOCH$_3$/CH$_3$OH)	67.7	67.7	74.1	70.9	66.6	68.8	69.3

and those from X-ray diffraction analyses indicate a smaller difference in the modulus of forms I and II compared to the data from other investigators except the data of Matsuo and Sawatari.

Kroon-Batenburg,[12] using β (1 → 4) glucopyranose oligomers as model compounds performed molecular dynamics simulations for the compounds in various solvents. The results showed that the tg conformation of the C$_5$—C$_6$—OH bonds in Cellulose I is unstable in the presence of polar solvents indicating Cellulose I is converted to the II polymorph is such solvents.

The Kroon-Batenburg et al. studies[8,12] suggest that the failure to date to directly spin ultrahigh-strength/high-modulus regenerated cellulose fibers from liquid crystalline solutions of cellulose is that, in the presence of polar coagulation agents, Cellulose II is formed. However, the results of Tashiro and Kobayashi[9] and Matsuo and Sawatari[11] indicate that the modulus of a regenerated cellulose fiber is little influenced by which polymorph results.

Bheda et al.,[13] Roche et al.,[14] and Hong and co-workers[15] have spun cellulose triacetate (CTA) fibers from anisotropic solutions. Lyotropic mesophases

of CTA do exhibit the typical low concentration viscosity maximum for the viscosity vs. concentration plot of a mesomorphic solution, permitting high concentrations of CTA in the spin solvent. Second, in each case,[13-15] the fibers consisted of the CTA I polymorph.

O'Brien[16] spun CTA fibers from mesomorphic solutions of specially prepared CTA (MW ~ 300,000) in either TFA-CH$_2$Cl$_2$ or TFA-H$_2$O solvent mixtures. Tenacities as high as 2 GPa were obtained. The triacetate fibers were saponified with NaOMe. The regenerated cellulose fibers had tenacities as high as 2.6 GPa, moduli of 52.8 GPa, and elongations of about 10%. These are the highest strength and modulus values reported to date for regenerated cellulose fibers.

Here, we report the spinning of CTA fibers from a mesomorphic solution (35% w/v) in TFA-CH$_2$Cl$_2$ (60/40 v/v) using commercially available CTA (Eastman Chemical) with a molecular weight of ~ 95,000, and their conversion into cellulose fibers using a variety of saponification reagents. In all cases, fibers were formed with strengths and moduli superior to those of viscose rayon fibers.

Table IV   Regenerated Cellulose Fiber Properties

ID #	CTA Annealing Time (min)	Annealing Temp (°C)	Saponification Reagent	Conditions	Fiber Diameter (μm)	Tenacity (GPa)	Modulus (GPa)	Cellulose Morphology
1	10	235	NaOCH$_3$/MeOH (0.005 m)	116 h RT	72	1.5	50.6	I (IV)
1A	—	—	NaOCH$_3$/MeOH (0.005 m)	72 h RT	48	1.5	30.8	—
2	10	235	NaOEt/EtOH (2.85%)	118 h RT	78	1.1	37.5	II
3	8	235	NaOEt/EtOH (2.8%)	1.5 hr RT	66	1.1	24.6	II (I, IV)
4	8	235	NaOAc/NaOH/H$_2$O (10%, 1%)	16 h 80°C	44	0.87	35.6	II (I, IV)
5	8	235	NaFormate/NaOH/H$_2$O (10%, 1%)	118 h RT	48	1.6	46.6	II (I, IV)
6	8	235	NaFormate/NaOH/H$_2$O (10%, 1%)	20 h RT	66	1.2	31.0	II
7	—	—	NH$_4$OH/H$_2$O (28%)	72 h RT	25	1.4	31.4	—

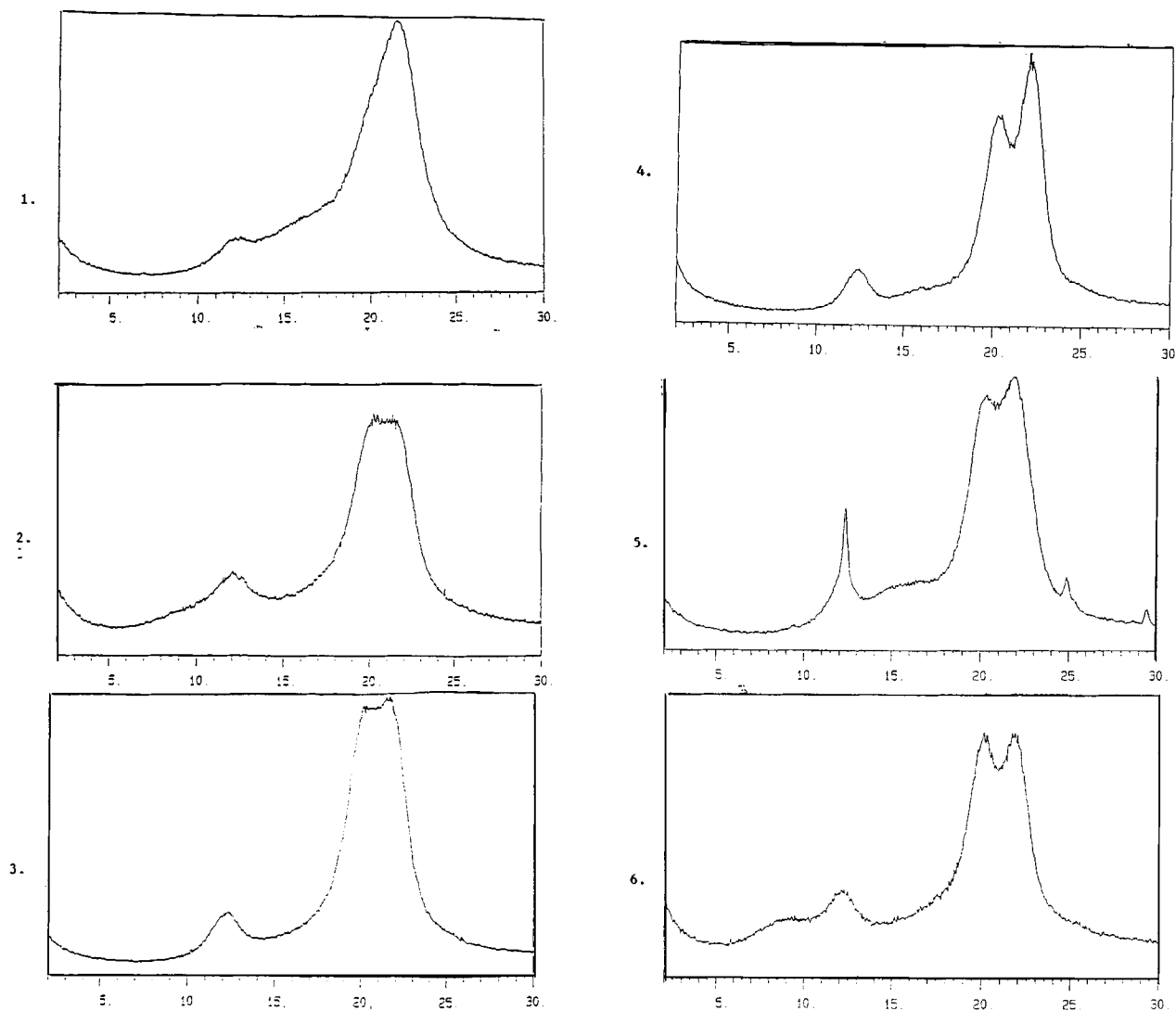**Figure 1** Cellulose X-ray diffractograms: (1) after saponification of CTA with NaOCH₃/ MeOH, 116 h, RT; (2) after saponification of CTA with NAOEt/EtOH, 118 h, RT; (3) after saponification of CTA with NaOEt/EtOH, 1.5 h, RT; (4) after saponification with NaOAc/NaOH, 16 h, 80°C; (5) after saponification with NaFormate/NaOH, 118 h, RT; (6) after saponification with NaFormate/NaOH, 20 h, RT.

EXPERIMENTAL

CTA (Eastman Chemical, D.S. ~ 2.9) was air-dried, a weighed amount added to a glass-stoppered Erlenmeyer flask (250 mL), and a mixture of TFA and CH₂Cl₂ (60/40 v/v) added to give a solution containing 35 wt % CTA. The flask and contents were slowly mixed by inverting the flask and contents daily for 7 days, at which time dissolution was complete. The solution viewed under crossed polars was highly irridescent and birefringent. It was pneumatically forced through a six-hole (0.25 mm i.d.)

spinneret into a coagulation both containing cold MeOH or H₂O and the resulting fibers wound on a godet which was sprayed with water. An air gap of 6.5 cm between the spinneret and the coagulant was used. The fibers were immersed in distilled water overnight and then oven dried at 40°C. Weighed amounts of CTA fiber were immersed in the various saponification reagents for various time periods (Table V), removed, washed with water, dried and reweighed.

WAXS diagrams were obtained with nickel-filtered CuKα radiation on a Siemens X-ray diffraction

Table V   20 Values of Peaks in Diffractograms

Diffractogram	20 Values	Polymorph Assignment
1	12.24, 16.21, 21.52	I (II, IV)
2	12.16, 20.5, 20.95, 21.61	II
3	12.07, 20.33, 21.34	II (I, IV)
4	12.33, 16.00, 20.24, 22.05	II (I, IV)
5	12.33, 16.09, 20.28, 21.80	II (I, IV)
6	12.11, 20.50, 21.74	II

system. The X-ray tube was operated at 30 kV and 20 mA. Stress–strain data were measured at 25°C and 65% relative humidity with an Instron Model 1123 tester using an extension rate of 50.8 cm/min and a gauge length of 2.54 cm.

RESULTS AND DISCUSSION

The CTA spinning parameters are in Table I. With the available spinning equipment, it was only possible to spin large diameter filaments (ca. 43–116 μm Table II) with filament cross sections that were quite variable (Table III). Additionally, only low winding speeds were possible, so that very high molecular orientations were not achieved. The large fiber diameters and less than perfect orientations can only result in lower than optimal fiber properties. Nevertheless, the CTA fibers had relatively high strengths (Table II). The CTA fibers were annealed at 235°C and then saponified with various reagents and conditions (Table IV). The resulting cellulose fibers had tenacities as high as 1.6 GPa and moduli up to 50 GPa.

In view of the large and uneven cross sections of the fibers, only the maximum tenacities and moduli are listed as those values represent fiber properties that may be obtained by the simple process employed here. The mechanical properties are significantly higher than commercially available regenerated cellulose fibers. They are lower than those obtained by O'Brien[16] who employed a markedly higher molecular weight CTA but are higher than those obtained by directly spinning cellulose from a mesomorphic solution.[1–4] Weight changes in the fibers before and after saponification showed that complete deacetylation was achieved.

Table VI   Tenacities vs. Molecular Weights for Regenerated Cellulose Fibers

Fiber	Molecular Weight	Tenacity (GPa)
Viscose rayon	60,000	0.5
Cellulose[16]	300,000	2.6
Cellulose (present data)	95,000	1.6

X-ray diffractograms of the fibers are in Figure 1. An attempt was made to analyze the diffractograms using curve-fitting techniques, but the results were not definitive with respect to establishing cellulose morphologies. The 2θ values of the peaks in Figure 1 (diffractograms 1–6) are summarized in Table V. These peak positions were compared with those of Cellulose I, II, III, and IV. Fibers labeled as 2 and 6 were very probably Cellulose II and the remaining fibers 3, 4, 5, mixtures of II, and either I or IV. Nevertheless, excellent tenacities and moduli were realized with different saponification reagents. Meridian X-ray scans suggested that fiber 1 (regenerated with $NaOCH_3/MeOH$) belongs to either the Cellulose I or IV_1 family but Cellulose II was also present. Though not studied, it is likely that fibers 3, 4, and 5 had Cellulose IV_1 present.

However, the tenacity and moduli were relatively unaffected by which polymorph was present. Indeed, the highest tenacity was obtained with the fibers with only II present (#6). O'Brien[17] reported that his regenerated cellulose fibers were mixtures of II
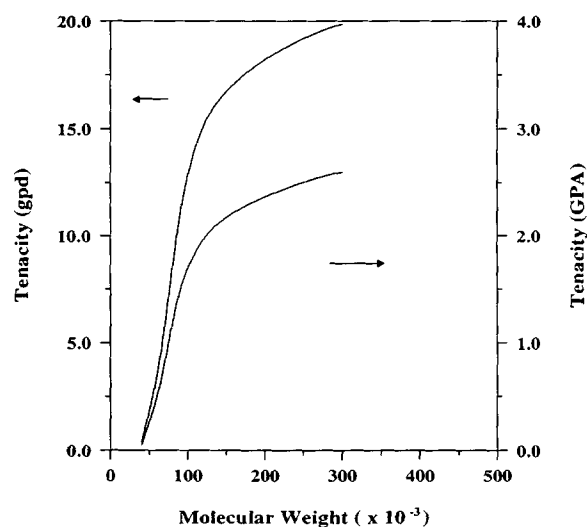
Figure 2   Tenacity vs. molecular weight.

and IV. Certainly, his fiber properties are higher than those reported here, which, in turn, are superior to those for viscose rayon. The latter is composed of Cellulose II. This comparison suggests that the cellulose molecular weight rather than the polymorph is the principal factor controlling the fiber properties. In Table VI are listed the approximate molecular weights[‡] and corresponding tenacities for viscose rayon, the O'Brien fibers, and those reported here. The data are plotted in Figure 2. In each case, the maximum tenacity value is used. The plot clearly shows that the fiber strength is dependent on the cellulose molecular weight and that the polymorph has little or no influence. In addition, the plot is typical of that for a polymer mechanical property vs. molecular weight.

The present results support the theoretical calculations of Tashiro and Kobayashi[9] and the strength data from X-ray diffraction results reported by Matsuo and Sawatri,[11] i.e., the cellulose fiber strength is little influenced by which polymorph predominates.

O'Brien's and the present study do emphasize the advantage of employing a cellulosic mesophase that exhibits a maximum in the solution viscosity vs. polymer concentration plot, i.e., it is possible to spin from solutions of high concentration but low viscosity and high cellulose molecular weights. However, based on the present results, those of O'Brien[16] and typical tenacity values for viscose rayon, an important factor determining the strength and moduli of regenerated cellulose fibers may be the polymer molecular weight. Finally, it is particularly gratifying that a commercial grade of CTA can be utilized to produce high cellulose fiber strengths and moduli, particularly, in view of the less than optimal fiber spinning conditions.

[‡] As noted in the Experimental section, the CTA dissolution time in TFA/CH₂Cl₂ was 7 days. The CTA molecular weight does decrease with time in TFA/CH₂Cl₂, but the change is modest after 7 days.[18] It is unlikely that any ester interchange occurred in view of the data in Ref. 18.

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