

# Melt Spinning of Thermotropic Cellulose Derivatives

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**ABSTRACT:** The melt spinning of two thermotropic cellulose derivatives—trimethyl silyl cellulose and phenyl acetoxy cellulose—is described in this article. Removal of the substituents was facile, rapid, and essentially complete. Both the melt-spun and regenerated fibers had banded textures typical of fibers spun from a liquid crystalline phase. The regenerated cellulose fibers had high strengths and moduli compared to viscose rayon and Lyocel cellulose fibers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 418–423, 2000

**Key words:** cellulose, cellulose derivatives, lyotropic and thermotropic cellulose mesophases, melt spinning, regenerated cellulose fibers

## INTRODUCTION

Melt spinning offers several advantages compared to solvent or wet-fiber spinning; for example, no spin solvent and recovery are required, there are no toxic by-products, and there are lower energy demands. The present-day formation of regenerated cellulose fibers involves either solvent or wet spinning.

The melt spinning of cellulose triacetate<sup>1,2</sup> and proprionate<sup>2</sup> has been reported but never practiced commercially. Shimamura et al.<sup>3</sup> melt-spun hydroxy propyl cellulose. However, it would be difficult to remove the hydroxyl propyl groups to regenerate the cellulose. Cooper et al.<sup>4</sup> melt-spun trimethyl silyl cellulose [TMSC; degree of substitution (DS) 2.2–2.6 from cellulose of degree of polymerization (DP) 2600], melt-extruded the fiber at 320°C, and regenerated the cellulose using 2-propanol/H<sub>2</sub>O/HCl(60/40/2.5 v/v/v). The regen-

erated cellulose fiber properties were similar but not superior to those of the rayon fibers. Differential thermal analysis of the TMSC gave no evidence of a K→N transition.

Pawlowski et al.<sup>5</sup> synthesized phenyl acetoxy cellulose (PAC), 4-methoxy phenyl acetoxy cellulose, *p*-tolyl acetoxy cellulose, and TMSC and showed that these materials were thermotropic by using differential scanning calorimetry (DSC) and hot stage microscopy. The substituent groups were readily removed under mild conditions.

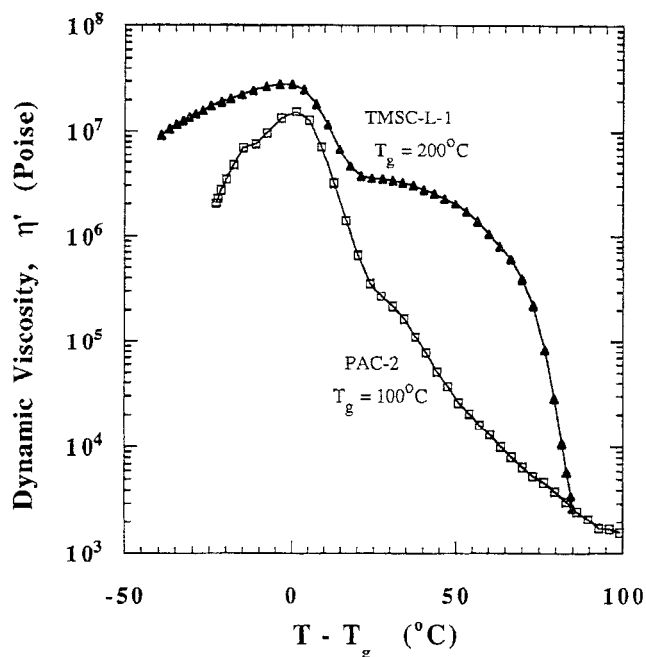
Here we describe the melt spinning of PAC and TMSC, the physical properties of the PAC and TMSC fibers, their desubstitution, and the properties of the regenerated cellulose fibers.

## EXPERIMENTAL

TMSC was synthesized using the procedures of Pawlowski et al.<sup>5,6</sup> from cellulose, DP 202 (Avicel, type PH-105, FMC Corp., Princeton, NJ), and DP 855 (Buckeye Cellulose, Memphis Tenn.). PAC was prepared using the Pawlowski et al. procedure from cellulose DP 202, but triethylamine

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**Figure 1** Dynamic viscosity versus temperature for TMSC and PAC. The  $x$  axis has been shifted for each material with respect to the corresponding  $T_g$ . The shoulders in the data above  $T_g$  indicate transitions in the liquid state. The frequency of oscillation was 1.0 rad/s, and the strain was 5%.

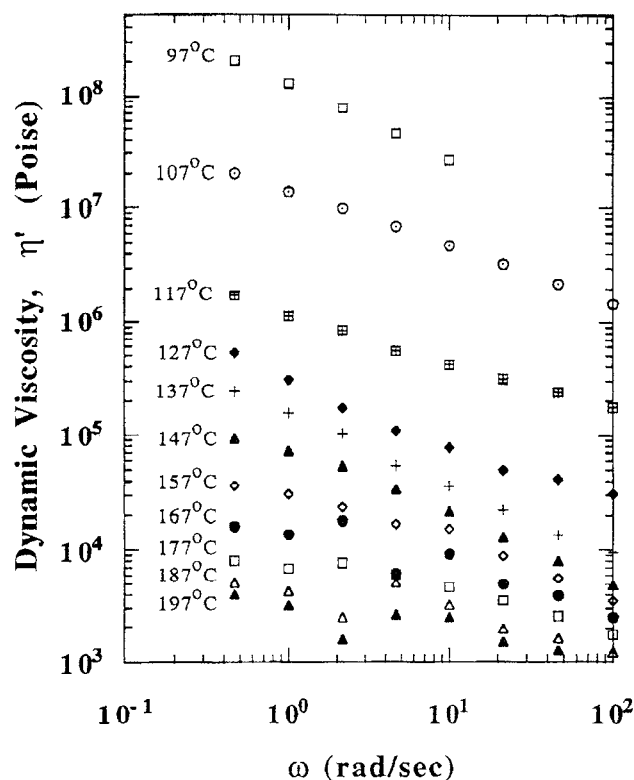
was used in place of pyridine as an acid acceptor. In each case the derivatives were shown to be thermotropic by DSC and hot stage microscopy. The K→N transition temperatures for PAC and TMSC were 110°C and 247–284°C, respectively. The TMSC decomposed at 323°C.

Fibers were melt-spun using a Sieglaff–Mckevy capillary rheometer with a 2.5 mL volume cylinder, a spinneret diameter of 0.25 mm, L/D of 100, 20 psig air pressure, and windup speeds of 18–62 m/min. For the spinning of TMSC, the cylinder was heated to 270°C, and TMSC powder was added under nitrogen. The temperature was in-

**Table I** Desubstitution of TMSC Fibers (DS 2.7)

| Fiber Denier      | Time (min) | Weight Loss (%) | Si (%)        |
|-------------------|------------|-----------------|---------------|
| 11.7 <sup>a</sup> | —          | —               | 21.1 (DS 2.7) |
| 58                | 1          | 48.6            | —             |
| 11.7              | 2          | 47.4            | 3.2 (DS 0.02) |

<sup>a</sup> Melt-spun TMSC fibers.



**Figure 2** Dynamic viscosity versus frequency at several temperatures for PAC (at low strain). The  $x$  axis has been normalized with respect to  $T_g$ . The liquid shows a shear-thinning viscosity, which is common for materials with a domain-type structure such as liquid crystalline polymers. Similar behavior was observed for TMSC.

creased to 275°C and the TMSC extruded under air pressure. The fibers were desubstituted both with and without tension using a mixture of

**Table II** Effect of Processing on Cellulose Molecular Weight

|  | Intrinsic Viscosity (dl/g) | Average Molecular Weight | Average DP |
|--|----------------------------|--------------------------|------------|
| Cellulose  | 1.17                       | 32,000                   | 202        |
| Regenerated cellulose from TMSC before extrusion | 1.07                       | 29,600                   | 183        |
| Regenerated cellulose from TMSC after extrusion  | 0.95                       | 26,000                   | 160        |

**Table III Physical Properties of TMSC and Regenerated Cellulose Fibers<sup>a</sup>**

| Fiber Type               | Take-Up Speed<br>(m/min) | Fiber<br>Denier | Tenacity<br>(g/d) | Modulus<br>(g/d) | Elongation<br>(%) |
|--------------------------|--------------------------|-----------------|-------------------|------------------|-------------------|
| TMSC                     | 18                       | 35.8            | 1.7               | 59               | 14                |
|                          | 31                       | 17.5            | 1.3               | 40               | 15                |
|                          | 62                       | 11.7            | 2.4               | 76               | 14                |
| Regenerated<br>Cellulose |                          | 12.6            | 2.2               | 129              | 24                |
|                          |                          | 7.5             | 2.9               | 108              | 15                |
|                          |                          | 3.9             | 4.8               | 208              | 17                |

<sup>a</sup> Desubstituted under tension.

2-propanol/H<sub>2</sub>O/HCl (37%; 60/40/5 v/v/v) at 75°C for 2 min, washed with methanol, dried at room temperature, and then further dried at 100°C for 5 min. The intrinsic viscosity of the cellulose before and after derivatization, extrusion, and desubstitution was determined using cupriethylene diamine and a Ubbelohde viscometer at 25°C. Silicon analysis was used to determine the DS of TMSC and the C and H analysis for PAC. The stress-strain properties of the TMSC and regenerated cellulose fibers were measured at 25°C and 75% RH with an Instron SinTECH tester using gauge lengths of 10 and 20 mm and extension rates of 15 and 24 mm/min.

PAC was prepared from 202 DP cellulose and melt spun using the same procedure as for TMSC but with a barrel temperature of 175°C. The fibers were desubstituted with 0.1 N MeONa in methanol at 60°C with and without tension.

The TMSC, PAC, and regenerated cellulose fibers were examined with a polarizing microscope. Rheological data for TMSC and PAC were obtained using a parallel plate shear viscometer (Rheometrics RMS-800).

## RESULTS AND DISCUSSION

Ordered melts have lower viscosities compared to similar isotropic materials and exhibit a stress

thinning behavior.<sup>7</sup> TMSC and PAC behave in a similar manner.

The dynamic shear viscosity of both polymers versus temperature relative to their glass transition temperatures is shown in Figure 1. The shoulders in the data above are  $T_g$ , that is, for both materials at  $T - T_g$ , approximately equal to 25°C, indicate the polymers have some ordered structure. It was also found by measuring the dynamic viscosity versus frequency that both materials behaved as a power law fluid (i.e., constant slope of the log viscosity versus log frequency) with shear thinning behavior. Figure 2 is an example of the data for PAC. Shear thinning behavior is common for polymers with domain-type structures, such as liquid crystalline polymers.

The desubstitution of TMSC (DS 2.7) prepared from cellulose, DP 202, was fast, with nearly complete desubstitution realized in 2 min or less, as shown in Table I. The preparation of TMSC followed by fiber extrusion and desubstitution does result in cellulose depolymerization (Table II). Hu et al.<sup>8</sup> have shown that the strength and moduli of regenerated cellulose fibers prepared by spinning a lyotropic mesophase of cellulose triacetate followed by desubstitution are dependent on the cellulose molecular weight. However, even at a relatively low cellulose molecular weight (26,000), the fiber properties reported herein are noteworthy (Table III). In this and subsequent tables only

**Table IV Fiber Physical Properties**

| Fiber                                 | Take-Up Speed<br>(m/min) | Denier | Tenacity<br>(g/d) | Modulus<br>(g/d) | Elongation<br>(%) |
|---------------------------------------|--------------------------|--------|-------------------|------------------|-------------------|
| TMSC                                  | 31                       | 21.2   | 7.0               | 69               | 19                |
|                                       | 62                       | 16.4   | 5.5               | 86               | 16                |
| Regenerated<br>Cellulose <sup>a</sup> |                          | 11.4   | 5.7               | 101              | 20                |
|                                       |                          | 9.3    | 6.4               | 108              | 15                |

<sup>a</sup> Without tension.

**Table V Effect of Measurement Parameters on Regenerated Cellulose Fiber Properties**

| Fiber Denier   | Tenacity (g/d) | Modulus (g/d) | Elongation (%) |
|--|----------------|---------------|----------------|
| Test parameters: 10-mm gauge length, 15 mm/min extension speed |                |               |                |
| 13.1   | 5.9            | 80            | 16             |
| Test parameters: 20 mm gauge length, 24 mm/min extension speed |                |               |                |
| 31.5   | 4.6            | 281           | 6              |
| 25.3   | 4.6            | 408           | 6              |
| 17.3   | 4.0            | 275           | 6              |

the maximum values are given, as the fiber extrusion parameters are not optimized. The maximum values illustrate the potentially excellent regenerated cellulose fiber properties that may be realized by melt spinning of thermotropic cellulose derivatives followed by desubstitution.

As expected, the tenacity and moduli of the fibers increased as the fiber denier was decreased by increasing the fiber take-up speed. At 3.9 denier, the tenacity and modulus of the regenerated fiber exceeds that of viscose rayon (molecular weight ~60,000) and equals the highest reported values for Lyocel fibers. The results of another melt-spinning experiment of TMSC followed by desubstitution without tension are shown in Table IV. Again, excellent physical properties were obtained. The question of whether tension during desubstitution is desirable needs further study. The physical property data in Tables III and IV were obtained using a gauge length of 10 mm and an extension speed of 15 mm/min. Table V compares the properties of the regenerated cellulose

fibers measured at 15- and 20-mm gauge length and at extension speeds of 15 and 24 mm/min. The latter values were obtained courtesy of Allied/Signal. Obviously, increasing the gauge length and extension speed resulted in an increase in fiber modulus. It is well known that moduli values are dependent on the rate of deformation. There is also the possibility that some fiber orientation occurred by increasing the extension speed.

TMSC (DS 1.8) prepared using cellulose from wood pulp of DP 855 was melt-spun using the same spinning equipment and procedure as described above. The fibers were desubstituted using 2-propanol/H<sub>2</sub>O/HCl for 2 min at 75°C without tension. Fiber properties are shown in Table VI. The physical test parameters were: gauge length 10 mm and extension speed 15 mm/min. As expected, the tenacities and moduli of the regenerated cellulose fibers are higher than those obtained with the lower DP cellulose, even though the fiber deniers were higher. Changing the test

**Table VI Fiber Physical Properties (DP = 855)**

| Fiber  | Take-Up Speed (m/min) | Fiber Denier | Tenacity (g/d) | Modulus (g/d) | Elongation (%) |
|--|-----------------------|--------------|----------------|---------------|----------------|
| Test parameters: 10-mm gauge length, 15 mm/min extension speed |                       |              |                |               |                |
| TMSC   | 31                    | 21.2         | 7.0            | 86            | 19             |
|  | 62                    | 16.4         | 5.5            | 69            | 16             |
| Regenerated cellulose under tension slack                      |                       | 11.4         | 5.7            | 101           | 20             |
|  |                       | 9.3          | 6.4            | 108           | 15             |
|  |                       | 16.2         | 6.8            | 95            | 24             |
| Test parameters: 20-mm gauge length, 24 mm/min extension speed |                       |              |                |               |                |
| Regenerated cellulose under tension slack                      |                       | 31.5         | 4.6            | 408           | 6              |
|  |                       | 25.3         | 4.6            | 281           | 6              |
|  |                       | 17.3         | 4.0            | 275           | 6              |
|  |                       | 20.7         | 5.8            | 347           | 9              |

**Table VII Fiber Physical Properties**

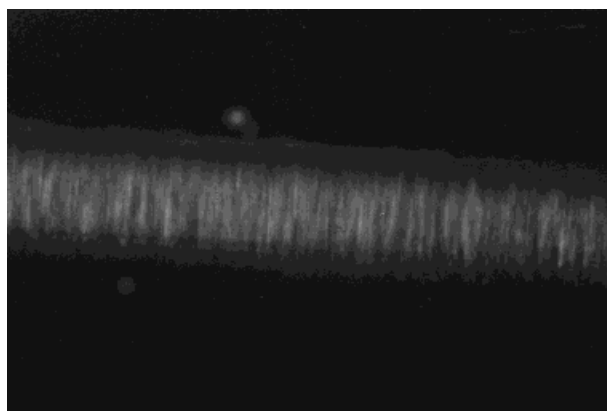
| Fiber                 | Take-Up Speed<br>(m/min) | Fiber<br>Denier | Tenacity<br>(g/d) | Modulus<br>(g/d) | Elongation<br>(%) |
|-----------------------|--------------------------|-----------------|-------------------|------------------|-------------------|
| PAC                   | 62                       | 25.3            | 3.0               | 54               | 24                |
| regenerated cellulose |                          | 12.4            | 4.2               | 97               | 14                |

parameters to the 20-mm gauge length and 24 mm/min again increased the fiber modulus (Table VI).

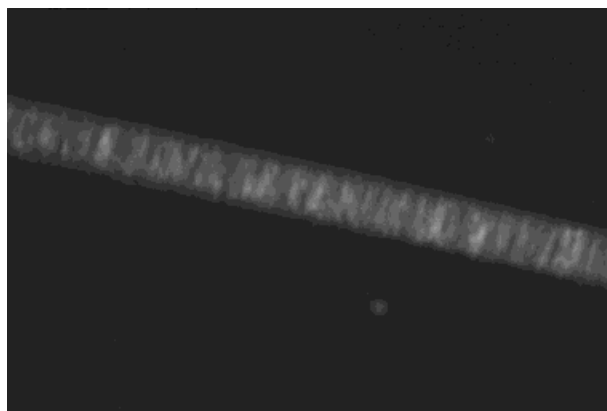
PAC (DS 2.8) was synthesized using DP 202 cellulose and melt spun. The fibers were desubstituted using 0.1N  $\text{CH}_3\text{ONa}$  in methanol at 60°C without tension. The desubstitution was essentially complete within 30 min. Physical properties are summarized in Table VII. The test parameters were 10-mm gauge length and 15 mm/min

extension speed. The properties of regenerated cellulose from PAC, while preliminary, are comparable to rayon fiber.

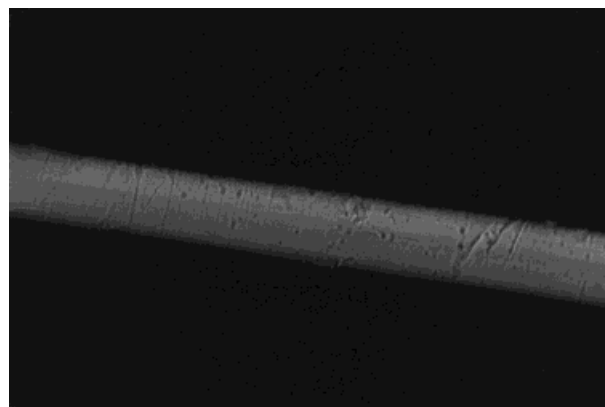
The above results are gratifying and demonstrate that melt spinning of thermotropic cellulose derivatives followed by desubstitution provides a route to regenerated cellulose fibers in filamentary form with excellent physical properties. Optimization of the spinning parameters will



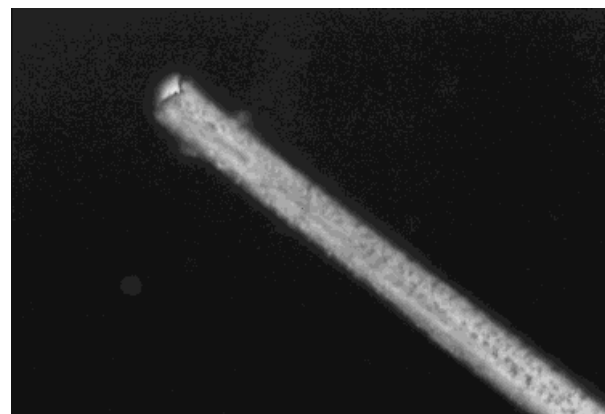
**Figure 3** Photomicrograph of TMSC fiber under crossed polars; 400× magnification.



**Figure 4** Photomicrograph of desubstituted TMSC fiber under crossed polars; 400X magnification.



**Figure 5** Photomicrograph of PAC fiber under crossed polars; 400× magnification.



**Figure 6** Photomicrograph of regenerated cellulose fiber (from TMSC) under crossed polars; 400× magnification, after fracture.

lead to improvements in fiber uniformity and give a combination of both high strength and modulus. This is exemplified by the effect of the physical test parameters on fiber moduli.

Many fibers spun from a liquid crystalline phase exhibit a banded texture.<sup>9</sup> The formation of a banded fiber texture has been observed in Kevlar fibers and is attributed to a pleated structure.<sup>10</sup> Peuvrel and Navard<sup>11</sup> provide an explanation of the formation of the banded texture on extrusion of liquid crystalline polymers.

The TMSC fibers and cellulose fibers regenerated thereof were examined under crossed polars at 400X (Figs. 3 and 4). A banded texture is evident in both cases, confirming that the mesomorphic nature of TMSC is preserved during extrusion and desubstitution. Optical photomicrographs of PAC fibers under crossed polars at 400X show a banded texture (Fig 5). Similarly, the regenerated cellulose fibers from PAC also have a banded texture, but the fibers have a porous structure. The porosity probably occurred during the desubstitution reaction, suggesting that a modification of the procedure is required. A photomicrograph of a fractured cellulose fiber regenerated from TMSC shows a clean break (Fig. 6). Fibrillation of Lyocel fiber occurs on fracture, which prevents their use in filament form.

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