Liquid crystalline solutions of cellulose in phosphoric acid for preparing cellulose yarns
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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7 Structure and properties of cellulose fibers spun from an anisotropic phosphoric acid solution
Reproduced in part from M.G. Northolt, H. Boerstoel, H. Maatman, R. Huisman, J. Veurink, H. Elzerman (to be published)

Abstract
A new process is described for the preparation of high tenacity and high modulus cellulose yarns. Liquid crystalline solutions of cellulose in phosphoric acid are spun via an air gap. The structure and mechanical properties of the yarn referred to as fiber B are discussed and compared with those of existing regenerated cellulose fibers. The crystal structure of the fiber is of the cellulose II modification and the highly oriented and crystalline fibers have a an initial filament modulus of 44 GPa, a sonic modulus of 58 GPa, and a tenacity of 1.7 GPa.

7.1 Introduction
Regenerated cellulose fibers have long been made by various processes yielding fibers with a wide range of mechanical properties. They include textile fibers with a low modulus and tenacity but a high elongation at break, fibers for industrial applications such as tire yarns with an intermediate modulus and tenacity, as well as fibers with a high modulus and tenacity but a low elongation at break for technical applications.

Here we will compare some structural and mechanical properties of a highly oriented cellulose fiber spun from an anisotropic solution in phosphoric acid using an air gap. There are a variety of processes for the production of cellulose yarns, both for textile and industrial application. The commercial types all have a limited tenacity. Among the (former) commercial yarn types are those prepared by the viscose, cuprammonium, Fortisan®, and N-methylmorpholine N-oxide (NMMO) processes. Two processes from the patent literature have demonstrated the great potential of cellulose in manufacturing high tenacity, high modulus yarns.

In the viscose process, cellulose xanthate (Cell-O-CS₂Na) is dissolved in an alkali solution and spun into a coagulation bath of diluted sulfuric acid, during which drawing may optionally be applied. These yarns, referred to as Enka® Viscose and Cordenka®, serve textile and industrial applications, respectively. A high modulus variant is Cordenka® EHM, which was prepared by adding formaldehyde either to the spinning bath or the spinning dope. This will slow down coagulation, as a result of which the yarns can be drawn further. In the cuprammonium process cellulose is dissolved in a mixture of copper sulfate and ammonium hydroxide. As early as in 1931 the possibility of spinning this solution via an air gap was claimed in a Bemberg patent. Fortisan® is a saponified cellulose acetate prepared by dry spinning a solution of cellulose acetate in acetone. In a post-treatment use is made of the thermoplastic properties of cellulose acetate by drawing in steam under pressure in order to improve orientation.
Subsequently, the cellulose acetate is saponified in caustic soda or sodium acetate. In the NMMO-process, cellulose and an aqueous NMMO-solution are mixed. Water is then evaporated and the cellulose starts to dissolve. As an explosive mixture can be formed, the solution is stabilized by adding propyl gallate. The solution is spun via an air gap, in which drawing is applied, into an aqueous coagulation bath. Whereas Courtaulds has commercialized the process for staple fiber production (Tencel®), Akzo Nobel operates a pilot plant for filament yarns (NewCell®). The Lenzing staple fibers are known as Lenzing® Lyocell. In patent applications by DuPont the preparation of high tenacity filaments is described. Cellulose is dissolved in trifluoroacetic acid to form a liquid crystalline solution, which is spun via an air gap into a methanol coagulation bath. The cellulose acetate is optionally steamdrawn to improve orientation and subsequently saponified with an alkali solution. The patents mention filament tenacities of 2.7 GPa for a test length of one inch for a number of filaments, which is indicative of the high potential when a yarn is produced from an anisotropic cellulose solution. A Michelin patent application describes another process for preparing high tenacity cellulose yarns. Cellulose is introduced into a mixture of formic acid and phosphoric acid. In situ derivatization occurs, as a result of which cellulose formate is formed, which dissolves in phosphoric acid and the excess formic acid. The resulting liquid crystalline solution is spun via an air gap, in which drawing is applied, into an acetone coagulation bath. Subsequently, the cellulose formate yarn is saponified to form high tenacity and high modulus yarns.

The last two processes demonstrate that liquid crystalline solutions of cellulose (derivatives) are good precursors for high tenacity cellulose yarns. A new process was developed for preparing high tenacity yarns by making use of liquid crystalline cellulose solutions in phosphoric acid. Isotropic solutions of cellulose in phosphoric acid have long been known. But, it was only recently discovered that anisotropic solutions can also be formed. Until then it was assumed that either cellulose had to be derivatized or a cosolvent as sulfuric acid was needed to form anisotropic solutions in phosphoric acid. As we have demonstrated in the previous chapters, superphosphoric acid (P₂O₅ concentration in the solvent of 72-76 % w/w) is an excellent solvent for cellulose. Cellulose rapidly dissolves in superphosphoric acid. Liquid crystalline solutions are formed in a wide range of cellulose concentrations, the lower limit being a cellulose concentration of 8 % w/w, which is extremely low, taking into account the semiflexible nature of the cellulose chain.

Structure and mechanical properties of cellulose fibers
The cellulose chain can adopt two conformations. Whereas in the cellulose I form there are two intramolecular hydrogen bonds between the successive anhydroglucose units O(2')...O(6) and O(3)...O(5'), in the cellulose II form only a bifurcated intramolecular hydrogen bond O(3)...O(5'),O(6') is found parallel to the ether bridge, as shown in Figure 7.1. Whereas Cellulose I is only found in natural fibers, viz. in a rather pure fiber form in flax, manila, ramie
and sisal, the cellulose II form is observed in regenerated fibers. The two different conformations of the hydroxymethyl group that cause the difference in intramolecular hydrogen bonding are of considerable effect on the ultimate tensile properties of the fibers. The modulus of the cellulose I chain is 140 GPa and that of cellulose II only 90 GPa.\textsuperscript{25,26}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cellulose_conformations.png}
\caption{The chain conformation of cellulose I (left) and cellulose II (right)}
\end{figure}

Northolt and De Vries derived that the modulus $E$ of the fiber relates to the orientation parameter $\langle \sin^2 \phi \rangle$, the average shear modulus $g$, and the chain modulus $e_c$ as\textsuperscript{27}:

$$
\frac{1}{E} = \frac{1}{e_c} + \frac{\langle \sin^2 \phi \rangle}{2g} 
$$

(7.1)

The birefringence is given by:

$$
\frac{\Delta n}{\Delta n_{\text{max}}} = 1 - \frac{3}{2} \langle \sin^2 \phi \rangle 
$$

(7.2)
where $\Delta n_{\text{max}}$ is the maximum birefringence. A more detailed description is given by Northolt. Figure 7.2 shows the different modes of chain packing in two cellulose crystal modifications as viewed along the chain axis. The difference in lateral hydrogen bonding is likely to be the cause of the different values of the shear modulus $g$ for cellulose I and rayon fibers, viz. 1.5 and 2.5 GPa, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{cellulose.jpg}
\caption{The crystal structure of cellulose I and cellulose II viewed along the chain axis}
\end{figure}

7.2 Experimental

7.2.1 Preparation of the yarns

Orthophosphoric acid was supplied by Font Electrique SA Bex (99 % w/w $\text{H}_3\text{PO}_4$), and polyphosphoric acid by Albrite (appr. 84 % w/w $\text{P}_2\text{O}_5$). Cellulose V60 was purchased from Buckeye and powdered by International Filler.

Orthophosphoric acid and polyphosphoric acid were mixed in a thermostated vessel at a ratio such that the presolvent had a $\text{P}_2\text{O}_5$ concentration of approximately 74 % w/w. During mixing the temperature was kept above 42°C in order to melt the phosphoric acid crystals and equilibrate the mixture. Powdered cellulose containing approximately 5 % w/w and the solvent were thoroughly mixed in a ZSK 30 twin screw extruder. The solution containing 19 % w/w of
dry polymer was filtered, heated, and extruded through an assembly of spinnerets jointly containing 1500 capillaries of 65 μm. The filaments passed through an air gap, in which they were subjected to drawing and went through a falling jet coagulation bath containing acetone. The acid was further removed from the yarn by washing with water in jet washers to achieve a phosphorus level of 0.43 % w/w, part of which appeared to be bonded to the cellulose. The yarns were neutralized with a 2 % w/w Na₂CO₃ solution, washed to a sodium content of 0.53 % w/w, finished, and dried on heated godets at a speed of 100 m/min. The degree of polymerization (DP) of the raw material, as determined by a viscosity measurement in a copper II ethylene diamine/water mixture was approximately 800⁵. Because of the high rate of dissolution, in contrast with the slow rate found in the preparation of viscose, short process times can be realized, which is very advantageous for economic processing.

7.2.2 Evaluation of the yarns
The structure and mechanical properties of the new fibers, coded B, are compared with the following cellulose fibers: a textile yarn Enka® Viscose, Cordenka® 660 and 700 tire yarns, a high modulus Cordenka® EHM yarn, which are all prepared according to the viscose process, and with an old sample of Fortisan® yarn prepared by spinning a cellulose acetate yarn, which was drawn up to 2000% in saturated steam and subsequently saponified in sodium acetate, washed, and dried⁵.

A short description of the structural and mechanical analysis is given here; for a more detailed description of the various measuring techniques the reader is referred to Northolt.²⁸ Tensile measurements were performed with the Zwick 1445 Tensile Tester at 21°C and 65 % R.H. Test lengths of 25 mm and 100 mm with a strain rate of 10 %/min. were applied. The filament linear density was determined with a vibroscope.

The axial birefringence of the fibers was determined by making use of either the De Senarmont method (for perfectly circular cross sections) or interference microscopy (noncircular cross sections)²⁸. The results are presented in table 7.2. Wide-angle X-ray diffraction patterns were recorded.

7.3 Results and discussion
Figure 7.3 shows the tensile curves of filaments typical of the group of strongest filaments from the bundles for the test length of 100 mm of the fibers prepared by the viscose process and fiber B produced by air gap spinning a liquid crystalline solution of cellulose in phosphoric acid. The values found for the ten strongest filaments out of 50 filaments of fiber B having a test length of 25 mm, with sample standard deviations added in parentheses, are: tenacity σ₀=1.70 (0.03) GPa, initial modulus Eᵢ= 44 (3) GPa, elongation at break εᵢ=6.5 (0.3) %, and the linear density is 1.43 (0.16) dtex. Table 7.1 lists the average filament tensile properties of the fibers.
The filament tensile curve for a test length of 100 mm of a variety of viscose fibers and fiber B.

The shear modulus $g$ was derived from the curve of the sonic modulus as a function of strain. By drying the fiber B its sonic modulus increased from 58 to 67 GPa, which is caused by a higher shear modulus of 6 GPa in the dry state. From equation 7.1 it follows that at equal orientation a higher modulus is found at augmented shear modulus. Figure 7.4 compares the mechanical properties of yarns of fiber B and Cordenka® 700.
Figure 7.4: Mechanical properties of yarns of fiber B and Cordenka® 700

Figure 7.5 shows the X-ray diffraction pattern taken with a flat plate camera and Cu Kα radiation of fiber B and Cordenka® 700. The differences in orientation and crystallinity are striking. Both patterns are characteristic of the cellulose II crystal modification. Table 7.2 presents some structural parameters of the various cellulose fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>$10^4\Delta n$</th>
<th>crystal width (nm)</th>
<th>crystal height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enka® Viscose</td>
<td>260</td>
<td>2.9</td>
<td>9.0</td>
</tr>
<tr>
<td>Cordenka®660</td>
<td>330</td>
<td>3.6</td>
<td>10.3</td>
</tr>
<tr>
<td>Cordenka®700</td>
<td>390</td>
<td>3.7</td>
<td>9.6</td>
</tr>
<tr>
<td>Cordenka®EHM</td>
<td>510</td>
<td>4.3</td>
<td>15</td>
</tr>
<tr>
<td>Fortisan®</td>
<td>480</td>
<td>5.5</td>
<td>15.6</td>
</tr>
<tr>
<td>B</td>
<td>502</td>
<td>3.9</td>
<td>17.8</td>
</tr>
</tbody>
</table>

The modulus and tenacity of the cellulose fiber B are considerably higher than obtained by the Fortisan® process and the viscose process.

Figure 7.6 shows an optical micrograph of a section of fiber B, indicative of a lateral structure.
Figure 7.5: X-ray diffraction patterns taken with a flat plate camera of fiber B (left) and Cordenka® 700 tire yarn (right).

Figure 7.6: Optical micrograph of sections of fiber A between crossed polars showing positive lateral birefringence, indicative of a radial texture. Use was made of a λ retardation plate with the slow direction at 45° with the polars. The dark fields were blue and the light fields yellow when viewed through the microscope.
Figure 7.7 compares the hysteresis loss of the cellulose B fiber with that of poly (para-phenylene terephthalamide) (PpPTA), polyamide (PA) and polyester (PET) fibers. It should be noted that for the cellulose types and for PpPTA the hysteresis loss is much smaller than for polyester and polyamide. Whereas polyester and polyamide can be applied in a very limited temperature range, the cellulose and PpPTA yarns can also be applied at elevated temperatures. As a result, the cellulose yarns can be used advantageously in processes exhibiting dynamic loading.

![Graph showing tan delta vs temperature for cellulose B, PA, PET, Fiber B, and PpPTA fibers.]

**Figure 7.7:** The hysteresis losses as a function of the temperature for the cellulose B fiber as compared with PpPTA, polyamide and PET fibers.

**Table 7.3:** Comparison of the average filament tenacity and moduli, normalized by the chain modulus, for fiber B, PpPTA and PBO fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>$e_{c}$ (GPa)</th>
<th>$E_{in}$ (GPa)</th>
<th>$E_{in}/e_{c}$ (-)</th>
<th>$\sigma_{b}$ (GPa)</th>
<th>$\sigma_{b}/e_{c}$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (cellulose II)</td>
<td>90</td>
<td>44</td>
<td>0.49</td>
<td>1.3</td>
<td>0.0144</td>
</tr>
<tr>
<td>PpPTA (Twaron® 1055)</td>
<td>240</td>
<td>120</td>
<td>0.50</td>
<td>3.2</td>
<td>0.0133</td>
</tr>
<tr>
<td>PBO</td>
<td>475</td>
<td>280</td>
<td>0.59</td>
<td>5.8</td>
<td>0.0122</td>
</tr>
</tbody>
</table>

Table 7.3 shows that the tenacity and modulus normalized by the chain modulus of high modulus fibers such as PpPTA, polybenzoxazole (PBO), and of fiber B are almost equal. This underlines the similarity of the structure and morphology of these fibers. The origin probably
lies in the similar processing of these yarns. For, they are all produced by air gap spinning liquid crystalline solutions. The high local orientation typical of these solutions is transformed into a global orientation due to shear and elongational flows in the process, as described in the Chapters 4, 5, and 6. Due to the application of this technology, the new cellulose yarn can be ranged in the group of high modulus and high tenacity yarns similar to PpPTA and PBO as far as structure and properties are concerned.

7.4 Conclusions
A process was developed for the preparation of high modulus and high tenacity cellulose yarns by air gap spinning liquid crystalline solutions of cellulose in phosphoric acid. The modulus and tenacity are much higher than obtained by the commercial processes. Due to fast dissolution and environmentally friendly processing, economically advantageous fiber production can be realized.

The crystal structure of the new fiber has the cellulose II modification, which is also found in all other regenerated cellulose fibers. When the fiber tenacity and modulus of the new cellulose fiber are normalized by the chain modulus, the values thus obtained are almost equal to the normalized values of the PpPTA (Twaron) and PBO fibers.

The new cellulose II fiber with high strength and modulus values has a very low \( \tan \delta \) value in a wide temperature range, which implies little energy dissipation during dynamic loading. Whereas polyester and polyamide can only be used in a limited temperature range, fiber B, as the other cellulose yarns and the PpPTA, can be applied in much wider temperature range. The combination of a tenacity higher than the conventional cellulose yarns and a smaller energy dissipation than that of polyester at elevated temperature, makes this yarn very special.

7.5 Acknowledgment
The authors wish to thank Mr. B. Koenders and Mr H. Lammers for carrying out the numerous spinning experiments, Dr E. Klop and Mr. R. van Puijenbroek for the X-ray diffraction characterization and the drawings of the crystal structures, Mr. F. Elkink for the hysteresis measurements and Ms B. Schaffers-Korff for the mechanical measurements.

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