WILL THE CELLULOSE FIBRE PRODUCTION PROCESS BECOME GREENER?

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Abstract:
More than 30 years research experience of the Laboratory of Cellulose Solutions and Products of Their Treatment in the field of the production of hydrocellulose fibres without using carbon disulfide is discussed. Dimethylformamide-dinitrogen tetroxide system, aqueous solutions of zinc chloride and orthophosphoric acid were developed and tested. They are all direct solvents for cellulose as opposite to the viscose process where indirect cellulose solvent is used. Fibre production processes have been implemented in the laboratory, pilot and prototype production scales. The properties of the spinning solutions and physical-mechanical properties of the hydrocellulose fibres are given.

Keywords:
cellulose solutions, fibres, dimethylformamide, dinitrogen tetroxide, zinc chloride, orthophosphoric acid

Introduction

There is a paradox in the manufacture of man-made fibres that one of the cleanest fibre types, i.e. hydrocellulose fibre, is not produced by environmentally acceptable methods. The historically first viscose process is famous by air and water pollution and the use of hazardous carbon disulfide.

Several alternative processes have been proposed throughout the last century. Their main advantage is the absence of toxic gases such as CS₂ and H₂S. However disadvantages touch on high cost, complicated dissolving procedure, extreme when recovering solvents and poor industrial application.

We started green strategy in the cellulose fibres production in the late 80s before the founding fathers of Green chemistry P.Anastas and J.Warner enunciated its principles. Since that three hydrocellulose fibre production processes have been developed.

Camilon process: Dimethylformamide-dinitrogen tetroxide system
ten times higher, and the filtration and de-aeration stages took much less time. The total time for preparing a spinning solution was reduced to three times. A technological evaluation showed that cellulose dissolution in DMF-N₂O₄ is much simpler than in the viscose process, since mercerization, xanthation, and ripening were not required in the new process. The number of filtrations was reduced to one because there were practically no gels in the solutions. As a whole there were eleven stages of the spinning solution preparation in the viscose process in comparison with five in the Camilon process.

Despite of the fact that the highest Newtonian viscosity of cellulose solutions in DMF-N₂O₄ was five to seven times higher than the viscosity of the viscose solutions, the effective viscosity at the spinning channel, corresponding to a velocity gradient of 10⁴ to 10⁵ s⁻¹, was practically the same. The maximum spinning rate of the fibre, named Camilon, was 70 to 80 m/min compared to 48 m/min for viscose fibres at equal solution flow rates in a spinneret (20 m/min). The maximum spinneret drawings was also higher: 250 to 300 % compared 140 %. The more severe precipitation conditions resulted in the higher spinning rates for Camilon process. The lower ability to orientation drawing (20 to 50 % compared to 100 to 200 % in the viscose process) was determined by this reason as well.

In addition, Camilon process was distinguished by lower energy consumption, since coagulation and washing baths had the lower temperature than in viscose process (respectively, 20 °C and 50 °C). According to the proposed scheme, the spun product was extruded into a spinning bath consisting of DMF, H₂O and inorganic salt. The complete absorption and coupling of nitrogen oxides took place in the spinning bath. For this reason there were no gaseous evolutions in the spinning zone.

The data of Table 1 show that the strength and elongation of Camilon fibres are at the same level as conventional viscose fibres, while modulus, recovery angle, and elastic recovery are 1.5 to 2.0 times higher for Camilon than for viscose fibres. The molecular mass distribution of cellulose was the same at the experimental and viscose fibre produced by Lenzing AG (Figure 1).

<table>
<thead>
<tr>
<th>Fibre Property</th>
<th>Viscose</th>
<th>Camilon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength, cN/tex</td>
<td>15-25</td>
<td>15-25</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>15-25</td>
<td>15-20</td>
</tr>
<tr>
<td>Modulus, kg/mm²</td>
<td>200-300</td>
<td>400-500</td>
</tr>
<tr>
<td>Wet strength, % of strength under standard conditions</td>
<td>45-55</td>
<td>40-50</td>
</tr>
<tr>
<td>Wet modulus, kg/mm²</td>
<td>50-70</td>
<td>60-80</td>
</tr>
<tr>
<td>Recovery angle, degrees</td>
<td>50-60</td>
<td>100-120</td>
</tr>
<tr>
<td>Deformation constituents, %</td>
<td>60-70</td>
<td>85-95</td>
</tr>
<tr>
<td>elastic</td>
<td>30-40</td>
<td>5-10</td>
</tr>
<tr>
<td>plastic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double flexure</td>
<td>3,000-10,000</td>
<td>2,000-4,000</td>
</tr>
</tbody>
</table>

Camilon fibres had a characteristic luster, were more resilient, and had better dye ability than viscose fibres. Thus, Camilon had 3.5 times higher color intensity acquired under the same dyeing conditions. The technological process of fibres production was implemented on the prototype production scale. Camilon has been processed into carded
yarns, which were used to produce knitted fabrics. The samples of fabrics have been turned into clothes (shirts, dresses et. al.).

![Graph showing molecular-mass cellulose distribution](image)

Figure 1. Molecular-mass cellulose distribution in experimental hydrocellulose (1) and viscose fibre of Lenzing AG (2)

Green features of this process as compared to the viscose process are the use of the ambient temperature and pressure for the solution preparation, the reduction of atmospheric emissions in almost ten times, the waste water discharges in almost 100 times. The only disadvantage was the usage of gaseous dinitrogen tetroxide at the solvent preparation stage.

**Zinc chloride-water system**

Numerous attempts to produce the fibre or film from cellulose solutions in aqueous zinc chloride solutions were unsuccessful in most cases due to the strong destructive action of this system. We have developed the procedure for the wood cellulose dissolution by the preliminary treatment with ZnCl₂ solutions of non-dissolving composition (75-84 % of ZnCl₂) at 70-80 °C and the following dissolution in ZnCl₂ – H₂O system with 63-67 % content of ZnCl₂ at 65-75 °C [2]. Spinning cellulose solutions prepared by this procedure had significantly high viscosity which was rapidly increased when cooling. Cellulose solutions transformed into transparent thermo-convertible gels at 18-20 °C. After 20-40 hours of storage gels become dimmed and regulated supermolecular structures formed in the gels’ volume. They looked like spherulites and were crystal/solvates by nature (Figure 2). The dimension of spherulite were from a dozen of micrometers to 1-2 millimeters. Spherulites had a legibly expressed ring structure with a Maltese cross. When heating the spherulite separated from the original solution during the temperature interval 45-50 °C, their congruently melting occurred with the formation of transparent homogeneous solution with the cellulose concentration for about 10 %. The viscosity of the solutions and cellulose degree of polymerization has been shown to decrease after 3-8 hours. The degree of polymerization fell to a value lower than 300. The solution “life” has been increased by keeping the solution at a reduced temperature (10-20 °C). This delays the destruction processes considerably, and when it is time to mould the solutions have to be heated to the viscose-flow condition. The solutions of cellulose in ZnCl₂·H₂O system are slightly sensitive to shear deformation.
They manifested almost Newtonian behavior in the wide range of the strength tension and then the viscosity reduced (Figure 3).

Figure 2. Spherulites, arised in 5% solution of sulphite cellulose in aqueous solutions of zinc chloride (x290)

![Graph](image)

Figure 3. The flow curves of 5% solutions of sulphate cellulose in zinc chloride at 50 °C (1) and 70 °C (2) an the first and sixth days (they are figured in brackets) of their keeping at 20 °C and of 7% solutions of cotton cellulose at 50 °C (3) and 70 °C (4).

The remaking of cellulose solutions into rayons was carried out at the pilot spinning plants by the wet and dry-wet method of moulding. The most stable results were obtained by the wet shallow-bath method of moulding when using the horizontal spinning units. Water-alcohol mixtures were determined as the best coagulation baths. The better complex of physical-mechanical properties was provided by water-isopropanol coagulation medium. Physical-mechanical fibres properties were closed to the conventional viscose fibres but with higher strength in the loop and elasticity modulus. The cross-section of the experimental fibre has a correct round shape such as viscose high modulus and polynose fibres. The main disadvantage of this process is the necessity of the corrosion-resistant equipment using.

This process is greener than viscose one owing to a large reduction of toxic fallout in the atmosphere and water, due to the exemption of high toxic, inflammable and explosive carbon disulfide.
Greencell process: $\text{H}_3\text{PO}_4\cdot\text{H}_2\text{O}$ system

The novel process of cellulose dissolution in aqueous solutions of orthophosphoric acid has been proposed as a quite real alternative to the viscose process. Non-toxic and almost completely regenerated solvent makes the process environmentally friendly. The main features of the new process are lack of sewage contaminating reservoirs and low water consumption (less than 16 m$^3$ of water per 1 ton of fibre, see Figure 4). The distillation of setting baths makes it possible to reuse solvent and provide closed technological water cycle.

![Figure 4. Water consumption for viscose process and Greencell process](image)

Based on modern concepts of the stepwise dissolving process (see Figure 5) optimal temperature and time conditions for the initial stage has been established. The first stage involves the cellulose activation in phosphoric acid. It has been found that prolonged high-temperature activation of cellulose in aqueous solutions of phosphoric acid leads to degradation of the polymer chains, which adversely affects physical and mechanical properties of the spun fibres. Low-temperature activation is free of this shortcoming, but it appears a number of technological challenges associated with high viscosity of cellulose dispersion at the activation stage, and during the subsequent dissolution process. The results of our latest research in this area made it possible to obtain highly concentrated spinning solutions of cellulose (7-9 wt. %) with minimal polymer degradation. On the extruded samples the degree of polymerization has been determined (DP = 400-600). The dissolution time does not exceed 3 hours.

It has been found that rheological behavior of the concentrated cellulose solutions in orthophosphoric acid considerably differs from pseudo plastic behavior [3]. With increasing shear stress the intermediate part of the flow curve remains on a quasi-Newtonian plateau of viscosity. It has been explained in terms of shear-induced anisotropy.

A pilot plant machine for fibres spinning from polymer solutions has been developed. The 4 dm$^3$ capacity machine reservoir allow to spin a continuous or periodic mode. The fibre tensile strength (15-25 cN/tex), and the fibre elongation at break (10-25%) have been tested.
A bundle of filaments was observed by using optical microscopy. The cross section of the cellulose filaments (see Figure 6) has a rounded shape that is typical for high-wet modulus or polynosic rayon cross sections. This correlates with the results of measuring the elastic modulus (600-800 cN/tex), that are far exceed the elastic modulus of conventional viscose fibres, cotton and wool.

For fibres and yarns produced by the new technology of spinning solutions of phosphoric acid, proposed common name "Greencell". The name of the process reflects the fact that it is considered to be an environmentally friendly process and it complies with modern sustainability principles of creating new technologies, i.e. the principles of "green" chemistry.

Thus, the novel technology of cellulose fibre production from orthophosphoric acid solution differs from typical viscose process by high ecological compatibility, and can be referred to "green chemistry" approach.

References