

# Cellulose Nanofibers Prepared by the *N*-Methylmorpholine-*N*-oxide Method

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**ABSTRACT:** The process of electrospinning is very suitable for obtaining fibers with a diameter on a nanometer scale. Such fibers can be spun from almost all kinds of known polymers, copolymers, and polymer blends. In this work, we present cellulose nanofibers obtained by the electrospinning process from spinning dopes containing cellulose dissolved in an *N*-methylmorpholine-*N*-oxide/water system. Under different electrospinning process conditions,

cellulose fibers, a nonwoven fiber network, and a cellulose membrane were obtained. The fibers were examined with scanning electron microscopy. The diameters of the fibers were in the submicrometer range. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1855–1859, 2005

**Key words:** fibers; nanotechnology; polysaccharides

## INTRODUCTION

The idea of fiber formation with an electrostatic field has been known for about 70 years. This method was first described by Formhals<sup>1</sup> in 1934, but a constant growth in interest in nanofiber production has only been observed for about the last 2 decades. Electrospinning is a very useful and relatively simple method for producing fibers with a submicrometer diameter range. With this method, it is possible to obtain nanofibers from various kinds of polymers. Electrospinning is applied in the production of ultrafine fibers from such polymers as polyolefins,<sup>2</sup> polyamides,<sup>3</sup> polyesters,<sup>4</sup> polyurethanes,<sup>5</sup> polypeptides, and DNA<sup>6,7</sup> as well as polymers with special properties, such as conductive polymers.<sup>8</sup> In recent years, probably more than 100 different polymers, copolymers, and mixtures of polymers have been successfully used to obtain fibers with diameters of less than 500 nm.

However, most of these fibers were obtained by the method of electrospinning from solution,<sup>9</sup> and only a few were spun from molten polymers.<sup>2</sup> In fact, from a practical point of view, the easiest way to obtain nanofibers by the electrospinning process is to spin the polymer solution with a solvent that is sufficiently polar and volatile. In addition, there are still some other important factors, such as the molecular weight of the polymer, polymer concentration, applied voltage, net charge density, surface tension of the polymer solution, and electric conductivity, all of which are crucial to the process of fiber formation.<sup>10,11</sup> Concerning the specific properties of natural polymers, the process of manufacturing fibers by the electrospinning

method appears much more complex. There are several articles in the literature dealing with this subject that suggest the complexity of this problem.<sup>12–14</sup>

Cellulose is a natural polysaccharide with a unique molecular structure. This biodegradable and nontoxic polymer has wide applications for fiber production. The presence of numerous hydroxy groups along the polymer chain establishes relatively strong hydrogen bonds between adjacent cellulose macromolecules; this results in the formation of a specific submolecular structure and specific chemical and physical properties. The presence of a large number of hydrogen bonds means that cellulose is not soluble in most organic or inorganic solvents. However, several efficient cellulose solvent systems are known,<sup>15–19</sup> but from the point of view of their application to the electrospinning process, only a few solvent systems may be successfully used for this purpose.<sup>20,21</sup> One of the most promising cellulose solvents is *N*-methylmorpholine-*N*-oxide (NMMO).<sup>22,23</sup> This compound has been known as a direct cellulose solvent since the 1930s. This excellent solvent is used for producing standard cellulose fibers on an industrial scale. Now it can be successfully applied for obtaining cellulose nanofibers. The basic principles of cellulose nanofiber formation are similar to those of the electrospinning of other polymer solutions, but the fact that NMMO is not volatile, causing certain problems linked to the coagulation process collecting the fibers or others, makes the process more sophisticated.<sup>24–26</sup>

## EXPERIMENTAL

### Materials

For the preparation of cellulose nanofibers, spruce cellulose (polymerization degree (DP) 800, 96.8%  $\alpha$ -cellulose) and  $\alpha$ -cellulose (DP 700) were used.

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A 50% water solution of NMMO was purchased from Hustman Holland BV (Rotterdam, the Netherlands). The antioxidant propyl ester of gallic acid (Tenox PG) was purchased from Aldrich (Gillingham Dorset, UK).

V-5002 Berol Nobel AB (Stenungsand, Sweden) was added to the coagulation bath as a surfactant.

All chemicals were used without further purification.

### Instrumentation

The spinning dopes were made with an IKA-VISC laboratory-scale knitter (Heitersheim, Germany), and a small, oil-heated glass electrospinning device was used for the preparation of cellulose nanofibers. The high voltage was supplied by a Meratronik P435 isolation meter (Lodz, Poland), with an adjustable high voltage range of 0–10 kV, capable of measuring the value of the flowing current during the spinning process.

The process of electrospinning the cellulose fibers was observed in laser light (coherent, 532 nm, 150 mW) and recorded with a FinePix S602Zoom digital camera (Fuji Photo Film Co., Ltd., Tokyo, Japan).

A JEOL 5200 LV scanning electron microscope (Tokyo, Japan) was used to examine the structure of the fibers obtained.

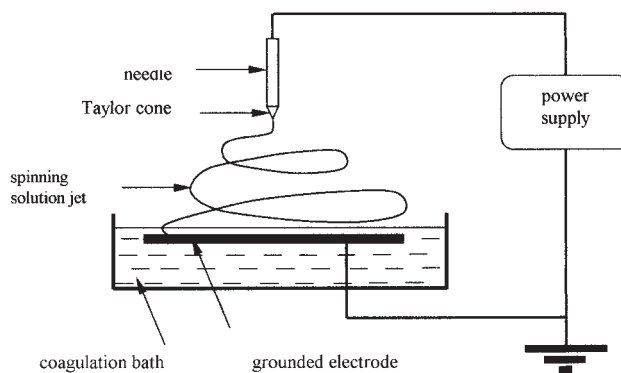
### Cellulose spinning dope preparation

$\alpha$ -Cellulose from spruce cellulose pulp was prepared by the mercerization of a 17.5% NaOH water solution. After treatment, the pulp was filtered, neutralized, washed, and dried.

The cellulose spinning dopes were prepared by the NMMO method. The solutions were prepared as follows. The appropriate amount of cellulose was mixed with a 50% water solution of NMMO, and then the antioxidant (1% w/w calcd. for the  $\alpha$ -cellulose content) was added. The mixture of the cellulose and 50% water solution of NMMO was vigorously stirred and heated, and the excess water was removed under low-pressure conditions. The process was continued until a sufficient quantity of water was collected, and a homogeneous, transparent solution of cellulose was obtained. Cellulose solutions in NMMO were applied to the electrospinning process without any further filtration.

### Electrospinning experiments

Cellulose nanofibers were obtained by the dry-wet electrospinning method with the apparatus described in ref. 25 and shown in Figure 1. The cellulose solution in NMMO was placed in the glass spinning device and heated to melting. The spinning solution was spun from a vertically fixed metal needle with a diameter of 0.45 mm. A high voltage of 9–10 kV was applied to the metal needle.



**Figure 1** General scheme of the apparatus for electrospinning cellulose nanofibers.

The process of electrospinning was carried out between 80 and 100°C. The electrospun nanofibers were collected on the surface of a grounded coagulation bath containing water or water with a surfactant. In some cases, the continuously moving surface of the coagulation bath was used. The distance from the needle to the coagulation bath surface varied from 10 to 15 cm. The solidified cellulose nanofibers were collected on metal mesh, glass-fiber mesh, or fabrics; they were then carefully washed in distilled water, dried, and examined.

## RESULTS AND DISCUSSION

Two kinds of cellulose solutions in NMMO were used for the electrospinning process: (1) solutions containing 1, 2, or 4 wt %  $\alpha$ -cellulose prepared from mercerized cellulose pulp and (2) solutions containing 1, 2, or 4 wt %  $\alpha$ -cellulose prepared from raw spruce cellulose pulp.

The parameters of the electrospinning process are shown in Table I.

The solutions containing 1 wt %  $\alpha$ -cellulose were spun within the temperature range of 80–85°C. However, for the solution containing 1% polymer, the spinning process was very stable, and no significant disturbances were observed; unfortunately, no continuous fibers were formed. Apparently, the concentration of the polymer was too low to create fibers. It seems that during the electrospinning process, the polymer solution jet was torn off into very short sections. In both cases, the product was a dustlike water dispersion.

The spinning solutions containing 4 wt %  $\alpha$ -cellulose were too viscous even within the temperature range of 125–130°C to obtain any fibers. In this case, the solution emerging from the metal needle created a drop; that is, its shape did not change under the strong electrostatic field. A relatively high concentration of cellulose in the solution showed too high a viscosity and surface tension of the solution to form fibers. It

**TABLE I**  
Parameters of the Electrospinning Process for Different Cellulose Solutions

Type of solution	Solution temperature (°C)	Applied voltage (kV)	Stability of process <sup>a</sup>	Range of fibres diameter (nm)
1% (mercerized) <sup>b</sup>	80–85	9.0	+++	–
1% (raw) <sup>c</sup>	80–86	9.0	+++	–
2% (mercerized)	90–95	9.0	++	200–400
2% (raw)	95–100	9.5	+++	200–400
4% (mercerized)	125–130	10.0	–	–
4% (raw)	125–130	10.0	–	–

<sup>a</sup> +++ = very stable jet, continuous process; ++ = stable process with some jet disturbances; + = quite stable process with many jet disturbances; – = no jet formation observed.

<sup>b</sup> Solutions made of mercerized cellulose.

<sup>c</sup> Solutions made of raw spruce cellulose.

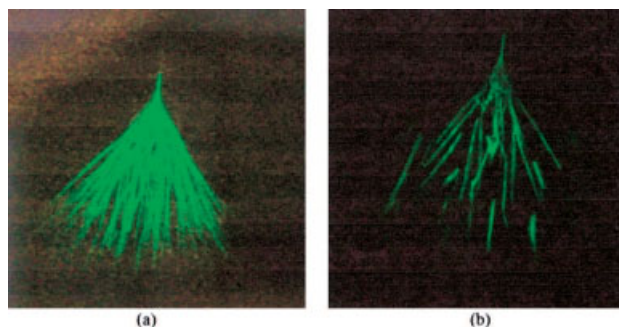
would probably be possible to reduce the viscosity of the solution to a level suitable for spinning by a further increase in the temperature of the spinning solution. Nevertheless, too high a temperature of the spinning solution could cause uncontrolled degradation of both cellulose and NMMO. In extreme cases, the overheated solution could even explode. The aforementioned failure in producing cellulose nanofibers from 4 wt % solutions does not prejudice the fact that when, for example, a much higher voltage than 10 kV is applied or substances are introduced that reduce the viscosity of the spinning solution, it is possible to obtain cellulose nanofibers from the NMMO solvent containing higher concentrations of cellulose.

From an experimental point of view, it seems that the most suitable solutions for electrospinning process are those that contain 2 wt %  $\alpha$ -cellulose. The process was usually carried out within the temperature range of 90–100°C. The potential between the metal needle and the coagulation bath surface was 9.0–9.5 kV. However, even though some jet disturbances were observed, the electrospinning process of the cellulose solutions was very stable and could be continuously carried out for several hours. For the solution containing 2% cellulose, the calculated yield of the electrospinning process under the aforementioned condi-

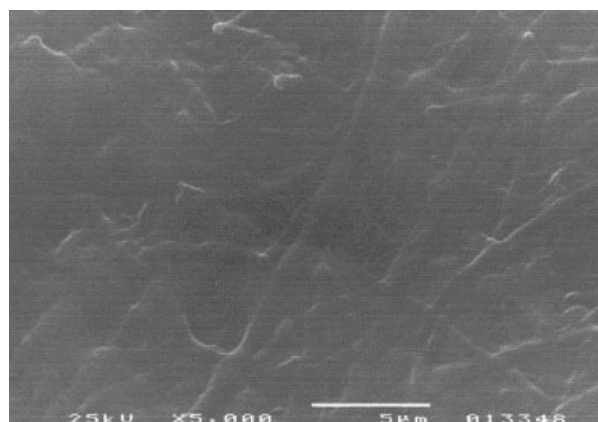
tions was about 8 mg of cellulose nanofibers per hour. An example of the spinning process of a 2 wt % cellulose solution is shown in Figure 2.

According to the data reported in this article, the way in which the spun cellulose solution coagulates is very important for the morphology of the fibers obtained. In the first step of this research, the cellulose fibers were collected on the still surface of water. In that case, only a membranelike shape was obtained (Fig. 3). The scanning electron microscopy (SEM) image in Figure 3 clearly shows that the obtained film was made of single fibers. The film formation was caused by three main factors: (1) the surface tension of the coagulation bath was too high, (2) the process of removing the solvent from the spinning jet was too slow, and (3) the process of piling up the new layers of the non-jet-solidified spinning solution was too fast. All these factors resulted in the fibers sticking together and the creation of films. Some electrospinning processes were carried out on the coagulation bath containing water with a surfactant, but filmlike products were also obtained.

The single fibers were obtained by the electrospinning of fibers on the continuously moving surface of the coagulation bath (Fig. 4). The moving surface of the coagulation bath removed the fibers from the spin-



**Figure 2** Images of an electrospinning jet of a 2 wt % cellulose solution with exposure times of (a) 10.0 and (b) 1.25 ms. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** Cellulose membrane made of single fibers.



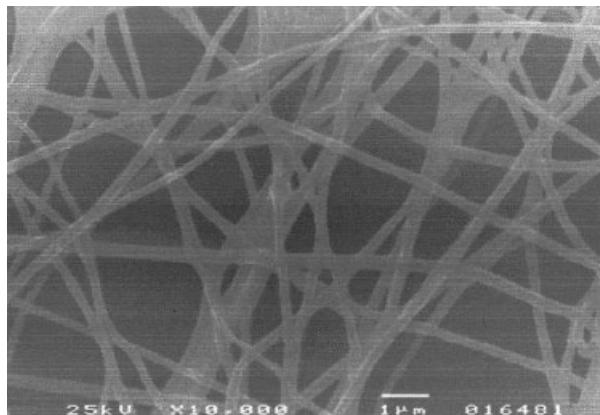


Figure 4 Cellulose nanofibers.

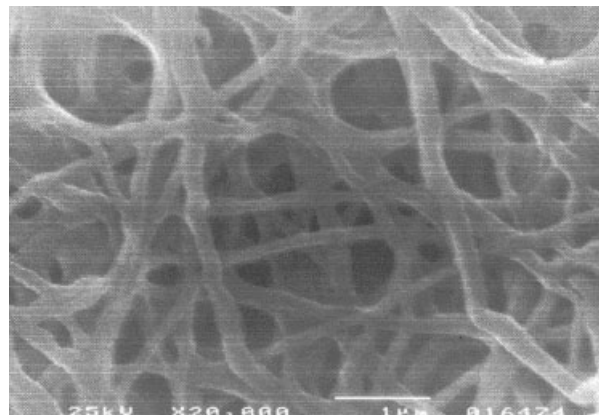


Figure 6 Spaghetti-like cellulose nanofibers.

ning zone and prevented the film from being formed. On the basis of these tentative experiments, it seems that the factors that mainly influence the morphology of the product are the manner of coagulation and the take-up method of the fibers obtained.

In Figure 5, cellulose nanofibers in a cablelike shape are shown. This kind of product was drawn from the coagulation bath.<sup>22,23</sup> Even though the fibers were glued together, their orientation was obvious.

An entirely different product was obtained when the spinning process was carried out on the moving surface of the coagulation bath, and the fibers were taken up on the rotating drum. In this case, a spaghetti-like product was obtained (see Fig. 6).

The fibers shown in Figure 5 were not oriented, and the structure of the product seemed to be a nonwoven material. However, some fibers stuck together; usually, though, they created a netlike structure, in which the single fibers were easily recognizable. In fact, we did not observe any significant differences between the nanofibers obtained from the NMMO solution containing raw cellulose and that containing mercerized cellulose.

On the basis of the SEM images of the obtained cellulose fibers, the frequency distribution of the fiber diameters was estimated, as shown in Figure 7.

According to Figure 7, there was a tendency for the formation of fibers with diameters of about 200 and 400 nm. The fraction of the fibers with a diameter above 500 nm was relatively small.

CONCLUSIONS

Cellulose nanofibers were obtained by the electrospinning process. Raw spruce cellulose pulp and  $\alpha$ -cellulose were dissolved in NMMO to prepare the spinning solutions. The NMMO method allowed homogeneous cellulose spinning solutions to be obtained in a relatively simple way. The obtained cellulose solutions were transparent and showed a honeylike consistency at the spinning temperature.

The solutions containing 1, 2, or 4%  $\alpha$ -cellulose were applied for the electrospinning process. The cellulose nanofibers were only obtained when the solutions containing 2 wt % cellulose were applied to the electrospinning process. From an experimental point of view, there were no significant differences between the cellulose solutions containing raw cellulose and those containing mercerized cellulose. The spinnability of the solutions containing raw cellulose and those containing mercerized cellulose were similar. The

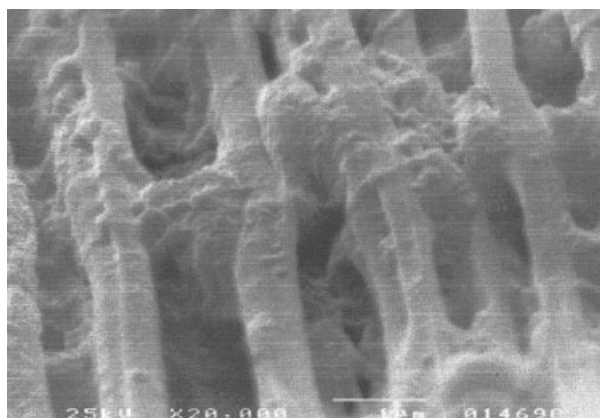


Figure 5 Cablelike cellulose nanofibers.

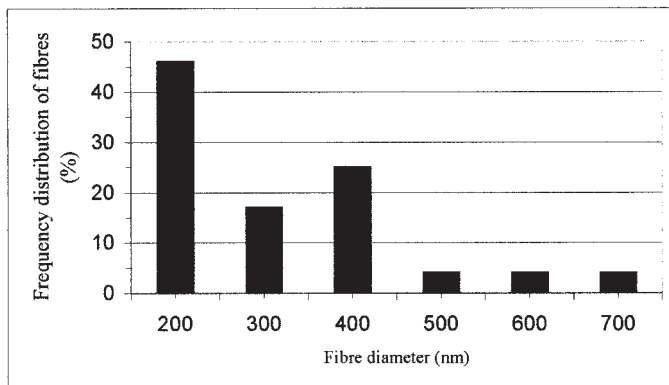


Figure 7 Frequency distribution of cellulose fibers.

morphologies of the nanofibers obtained from both types of solutions showed no distinguishable differences.

The very stable spinning process of the solutions containing 1 wt % cellulose yielded a dustlike product. This was probably caused by too low a concentration of the polymer.

For the solutions containing 4 wt % cellulose, its too high viscosity made the spinning process impossible even at a relatively high temperature. However, from a technological point of view, increasing the concentration of cellulose in the solution was not the essential problem, but some difficulties in spinning more concentrated solutions could be solved by the addition of substances that reduced the viscosity or by the application of a much higher voltage.

Most of the cellulose fibers obtained from the solutions containing 2 wt % cellulose had diameters below 500 nm.

According to the experimental data, the shapes of the obtained products strongly depended on the way in which the fibers were collected and solidified. Electrospinning the cellulose solutions containing 2% polymer onto the still surface of the coagulation bath yielded a filmlike product, whereas the formation of the fibers on the moving surface of the coagulation bath yielded a product in the shape of fibers, a non-woven material, or cables. According to the conditions of coagulation (e.g., the velocity of the surface of the coagulation bath, the way in which the coagulation medium flows, and the temperature) and the way in which the fibers are taken up, it is possible to produce various kinds of materials from cellulose nanofibers with precisely designed properties. In this article, some preliminary results are shown. Deeper and more detailed research should be conducted to answer the numerous questions about the process of electrospinning cellulose nanofibers, methods of jet solidification, and also the methods of taking up the obtained fibers.

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