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Evaluation of Diluted Cellulose Solutions for Nanofibre Production Using the Electrospinning Method

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Abstract
This paper discusses the possibility of nanofibre formation in an electrostatic field from cellulose solutions in different solvent systems. Additionally when investigating solutions of various cellulose content, an attempt was made to evaluate these solutions from the viewpoint of their usability for nanofibre formation. The spinnability of the solutions examined was assessed based on observation of the stability of nanofibre formation by the simplest single needle spinning device. The morphology of the samples obtained by electrospinning was studied by Scanning Electron Microscopy (SEM). Spinning dopes were obtained using well-known technologies for cellulose solution preparation applied in the cellulose fibre industry, namely N-Methylmorpholine N-oxide (NMMO) and viscose methods, as well as a mixture of phosphoric acids, which is relatively cheap, easily available and yet not used in industry. Based on the research conducted, it may be concluded that the cellulose solutions in NMMO proved to be the best system for exceptionally stable formation of nanofibres in an electrostatic field.

Key words: *cellulose, cellulose nanofibres, electrospinning, cellulose solvents.*

Introduction

Cellulose nanofibres are still being intensively investigated, including their formation by pure mechanical [1] and chemical [2] methods as well as by formation in an electrostatic field [3, 4]. The major reason for such a strong interest in this type of fibres is, among other things, the cellulose itself as it is a widely available and renewable raw-material. Additionally specific properties of nanofibres make them potentially suitable for use in filters for gas and liquids [4], wound-dressing materials with antibacterial activity [7] and even as bio-bacteria [8]. It was also reported that, due to their extremely high specific surface area, cellulose nanofibres exhibited a very high water retention level, amounting even to 14500%, which means that the weight of water absorbed was approx. 150 times larger than the weight of dry fibres [9]. Nevertheless there are two serious constraints on more effective development of cellulose nanofibre production in an electrostatic field. The first one is related to the specific properties of cellulose, especially to its lack of volatile solvents which could be used to prepare spinning dopes suitable for formation in an electrostatic field, and to the necessity for low cellulose content in the solution because of their relatively high viscosity. The second constraint is linked to the specifics of electrospinning, which is a process of extremely low efficiency, *i.e.* of several dozen milligrams of fibres per hour [9]. The lack of cellulose low volatile solvents has been partly overcome by the application of a solidifying bath. Shortly after the spinning solution jet reaches the surface of the solidifying bath, the solvent is removed, and nanofibres solidify [3, 10]. Therefore, at present, it is essential to find a suitable solvent for cellulose. Such a solvent is expected to produce concentrated spinning dopes of low viscosity which would exhibit good spinnability in an electrostatic field. In addition, the cellulose dissolving process should be easy to apply. The search for new cellulose solvent systems should also address such factors as the lowest possible price, availability, and low or none toxicity. In fact, it seems extremely difficult to find a solvent system that fulfils all the above- mentioned requirements. Over the past few years, a considerable number of reports on so-called ionic liquids of cellulose have been published in scientific literature [11]. However, low solvent stability, the limited solubility of cellulose, the high viscosity of solutions obtained, and difficulties associated with their recovery are the major drawbacks as regards the application of ionic liquids in the formation process of cellulose nanofibres [12, 13].

The objective of this work was to investigate the possible application of cellulose solutions in the electrospinning method. Special interest was given to both the preparation of spinning dopes and the formation of nanofibres. The research presented was limited to three, well-known, solvent systems of cellulose which were selected based on their ability to recover, market availability as well as the economics of their production at an industrial level. Two direct solvents of cellulose, *i.e.* NMMO [14] and phosphoric(V) acid [15], were used to obtain spinning solutions of cellulose. Under laboratory conditions, it is relatively easy to obtain such solutions. The cellulose solution in NMMO is chemically stable even at an elevated temperature of spinning. Even though concentrated phosphoric (V) acid is known as a cellulose solvent [16-18], it is not used in real industrial applications because of cellulose degradation caused by this solvent at temperatures above 0 °C. Solution of cellulose xanthate in NaOH, commonly known as a viscose, was the third spinning dope studied. For over one hundred years, this method has been used in industry to produce viscose rayon.

According to the literature, cellulose solution in NMMO is not very often used for the electrospinning process. For this

system, the main difficulty is the necessity of applying the solidification bath, which makes the process and equipment used relatively sophisticated. The first scientific article about the electrospinning of cellulose solution in NMMO was published in 2005 [3]. Since that time a few publication have appeared describing the process in more detail. Kim el al. [4] studied the process of electrospinning of cellulose solution in NMMO and compared it with the spinning of cellulose solution in the lithium chloride/DMAc system. They found that the crystallinity of cellulose fibres spun from the NMMO can be controlled by the spinning conditions. Recently several organic solvents (N-methylpyrrolidinone [5], DMSO [6]) were applied to obtain lower viscosity cellulose solutions in NMMO.

Uppal et al. [5] obtained a solution of α-cellulose in 85% phosphoric acid, but the process of electrospinning was not successful. According to the Authors, the solution was not spinnable in the conditions applied.

Until now, viscose has not yet been studied as a solution for the electrospinning process.

In this paper, the applicability of diluted cellulose solutions for nanofibre production by electrospinning is discussed.

Experimental

Materials

Cellulose (Rayonier Ltd.) of polymerisation degree DP = 1800, α-cellulose content of 97.6%, and moisture content of 5.7% was used to prepare spinning dopes. Technical NMMO in the form of 50% water solution was produced and supplied by Hustman Holland BV (Rotterdam, Holland). Propyl ester of gallic acid (Tenox PG) (Sigma – Aldrich) was used as an antioxidant. Other reagents used in research were produced by Avantor Performance Materials (Poland).

Methods

Cellulose nanofibres were prepared as follows: cellulose was dissolved in one of the solvent systems chosen, and then spun by means of electrospinning methods. In all cases, water was used as a solidification bath. During the spinning, the stability of the process was observed. Nanofibres obtained were washed in distillated water, dried and examined by the SEM method.

Preparation of cellulose solutions in NMMO

Cellulose solutions of a concentration of 2% and 5% were prepared using a rotary evaporator. The initial mixture contained cellulose, antioxidant at a level of 0.01% based on the α-cellulose weight, and water solution of NMMO. The composition of this mixture was such that the cellulose concentration required would be obtained after the water evaporation process. Under reduced pressure, the excess of water was evaporated from the mixture to the final water content of about 17%. The resulting homogenous, transparent, straw yellow solutions crystalised relatively fast after cooling to room temperature.

Preparation of cellulose solutions in phosphoric acids

Cellulose solutions in phosphoric(V) acid were prepared in a kneader (IKA-VISC) with a working capacity of 350 ml, equipped with two horizontal stirrers and a heating jacket. The first stage involved the mixing of phosphoric (V) and polyphosphoric acids in such a ratio that the P_2O_5 content was about 74.4%. The acid mixture was stirred for 30 minutes at a temperature of 40 °C, then the mixture was cooled to a temperature of 10 °C, and cellulose was added to obtain solutions of a cellulose concentration of 2% or 5%. The entire mixture was stirred for another 30 minutes until a transparent solution was obtained. The solutions prepared were clear and colorless. The cellulose solutions were stored in airtight containers at a temperature of -18 °C.

Preparation of sodium cellulose xanthate solutions

In order to obtain sodium cellulose xanthate in NaOH, cellulose pulp was mercerised in aqueous sodium hydroxide solution of a concentration of 19% at room temperature for 6 hours. After the mercerisation, the alkali-cellulose obtained was pressed to remove the excess of NaOH, and then it was disintegrated and subjected to the xanthation process, carried out at room temperature in an airtight glass vessel. During the xanthation, alkali-cellulose was treated with CS_2 to obtain sodium cellulose xanthate of substitution degree SD = 1.0. The resulting sodium cellulose xanthate was dissolved in 4% NaOH aqueous solution to obtain spinning dopes of a cellulose content of 2% or 5%. The solutions produced were transparent and light brown in colour.

The quality of solutions was evaluated by optical microscopy, inspecting the samples for the presence of undissolved cellulose fibrils.

Determination of the real content of cellulose in the spinning solutions

In order to determine the real content of cellulose in the solutions produced, a sample of spinning dopes of about 5 g was spread between two glass plates to obtain a thin and uniform layer on the plate surface. Afterwards these layers were immersed in a solidifying bath. The sample of cellulose solutions in NMMO was solidified in water, and sodium xanthate in the NaOH sample was coagulated in a diluted aqueous solution of sulfuric (VI) acid, whereas for the sample of cellulose in phosphoric acid, this was performed in acetone. The films obtained were rinsed several times in distilled water to remove solvent residue and then dried in a dryer to a constant weight at a temperature of 105 °C.

Formation of nanofibres

The cellulose solutions obtained were placed in the glass ampoule of a nanofibre spinning device. For NMMO solutions of cellulose, the ampoule was heated to such a temperature as to get an appropriate viscosity of the solution, whereas for viscose and phosphoric acid solutions, formation was carried out at room temperature. Due to the device construction, which enabled to produce nanofibres continuously, spinning dope outflow from the capillary was driven by gravity forces. In the electrospinning device, no additional pumps enforcing continuous solution flow were used. To compare the results for all the solvent systems used, the spinning conditions were set as follows: the applied voltage was 10, 15 and 20 kV, and the distance between the capillary and solidifying bath surface (air gap) was kept at 5, 10 and 15 cm. The spinning dope jet formed in the electrostatic field was applied onto the surface of the flowing water solidifying bath. Subsequently the solidifying bath with nanofibres was transferred onto a rotating cylindrical mesh with the surface covered by polypropylene nonwoven fabric, on which nanofibres were deposited. After washing out the solvent residue with distilled water and the drying process, the nanofibres were visually inspected for their distribution uniformity on the nonwoven fabric. Visual inspection was also used to control the process stability by determination of the number

of spinning dope jet breaks during 30 minutes of continuous processing. In order to eliminate subjective evaluation of nanofibre formation, the following criteria were adopted for a 30 minute continuous process:

- no breaks or rare breaks of the solution jet were observed (not more than 3 breaks) – „+ + +”,
- minor instability of formation and breaks of the solution jet were observed (3-10 breaks) – „+ +”,
- quite a few breaks of the solution jet were observed (more than 10 breaks), but fibres were formed – „+”,
- solutions from which a jet was not formed at all or was formed for a very short time – „–”.

Spinning process observations were conducted using a 20 watt halogen lamp.

Morphology evaluation of the nanofibres produced was carried out using a scanning electron microscope – TESCAN Vega3 SB Easyprobe.

Results and discussion

Six spinning dopes based on three different solvent systems were used during the trials of cellulose nanofibre formation in an electrostatic field conducted. For each solvent system, two solutions of a concentration of 2% and 5% were prepared.

The real content of cellulose in the spinning solutions was determined using the procedure described hereinbefore. The results obtained are presented in ***Table 1***.

Based on the results presented in ***Table 1***, it can be stated that the concentrations of all solutions prepared are nearly the same as the cellulose contents calculated theoretically. Some differences between those values result from the specifics of the solution preparation procedure and cellulose degradation, occurring usually upon its dissolution, as well as from the fact that the cellulose pulp used had not been dried prior to the dissolution process. However, it should be mentioned that the values of cellulose content in the spinning dopes determined were very close to the ones expected.

The spinning process of nanofibres was carried out choosing parameters in such a way they would be comparable for each solution system. In each case, for the three different air gaps selected, three different values of voltage were applied.

Table 1. *Theoretical and real content of cellulose in the spinning dopes.*

Solution type	Theoretical content of cellulose, %	Real content of cellulose, %
NMMO	2.0	1.95
	5.0	4.92
phosphoric acid	2.0	1.87
	5.0	4.81
viscose	2.0	1.74
	5.0	4.67

Table 2. *Electrospinning conditions and stability evaluation of fibre formation from NMMO solutions.*

Cellulose content, %	Voltage, kV	Air gap, cm	Evaluation of spinning process stability
2	10	5	+ + +
		10	+ + +
		15	+ +
	15	5	+ +
		10	+ + +
		15	+ + +
	20	5	+
		10	+ +
		15	+ + +
5	10	5	+ +
		10	+
		15	–
	15	5	+ +
		10	+ +
		15	–
	20	5	+
		10	–
		15	–

Nanofibre formation from NMMO solutions

All cellulose solutions in NMMO, regardless of the cellulose content, were solids at room temperature. Therefore fibre formation by both conventional methods and that using an electrostatic field required solution melting and spinning at temperatures ranging from about 95 °C to 130 °C. For the purpose of this research, a heated glass ampoule was used for fibre spinning from NMMO solutions. The results of cellulose nanofibre formation from NMMO solutions are given in ***Table 2***.

The results in ***Table 2*** indicate that solutions containing 2% of cellulose have better spinability than those containing 5% of cellulose when considering nanofibre formation from NMMO solutions. For 2% cellulose spinning dope, the formation process was very stable at a voltage range of 10-15 kV and air gap of 5-10 cm. Very good effects were also obtained using a voltage of 20 kV and air gap equal to 15 cm. For such values of the process parameters, a very stable formation (without any breaks) was observed even for a spinning time longer than 1 hour.

It seems that good selection of the spinning solution temperature, which affected liquid viscosity and, hence, the velocity of the outflow from the capillary, was an important parameter, having a vital effect on nanofibre formation stability. The voltage applied and the distance from the solidifying bath also affected the formation of the solution jet. The higher the voltage and the lower the air gap, the faster the solution take-up from the capillary tip. For the low voltage applied, the rate of jet formation was insufficient and a drop was formed which disturbed the formation process. On the other hand, when the voltage applied and resulting jet stretching forces were too high, the spinning dope outflow was too slow, and in extreme cases formation stopped. Consequently suitable selection of the parameters mentioned above was crucial for the stability of solution jet formation.

Table 3. *Electrospinning conditions and stability evaluation for cellulose solutions in phosphoric acids.*

Cellulose content, %	Voltage, kV	Air gap, cm	Evaluation of spinning process stability
2	10	5	+
		10	+
		15	–
	15	5	+
		10	+
		15	–
	20	5	–
		10	–
		15	–
5	10	5	–
		10	–
		15	–
	15	5	–
		10	–
		15	–
	20	5	–
		10	–
		15	–

For the solutions containing 5% of cellulose, the nanofibre formation process was much less stable. Although the fibres were electrospun at a temperature of 130°C, the solution viscosity could not be lowered sufficiently to maintain process stability within a longer span of time. It should be noted that in this case process parameters such as the low voltage and wide air gap were entirely unsuitable.

Nanofibre formation from cellulose solutions in phosphoric acids

The cellulose solutions in phosphoric acids were electrospun under almost the same operating conditions as were used for the cellulose solutions in NMMO. The only exception here resulted from the cellulose degradation at elevated temperatures, for which reason the spinning process was carried out at room temperature. The results of cellulose nanofibre formation from phosphoric acid solutions are presented in ***Table 3***.

Based on the experiments conducted, it may be stated that cellulose solutions in phosphoric acids were a much more demanding system. In this case, the viscosity of the solutions constituted a major difficulty in the formation of nanofibres. A viscosity of 2% in the system was already quite high, whereas solutions containing 5% of cellulose could not be ejected from the capillary. It should also be emphasised that for a voltage of 15 and 20 kV and rather narrow air gaps, electric flashovers were observed. Even though the tests carried out did not produce the results desired, it cannot be stated categorically that solutions of this type are unsuitable for the electrospinning of nanofibres. The authors believe that the application of lower polymerisation degree cellulose or lower cellulose concentrations would allow to prepare solutions of lower viscosity and, thus, would allow to achieve a range of parameters enabling stable jet formation.

Nanofibre formation from viscose solutions

The same process conditions as were applied for the solutions described above were also used in attempts to form cellulose nanofibres from viscose solutions. It should be mentioned that the attempts undertaken were unsuccessful as under no experimental conditions were solution jet formation and fibre electrospinning observed. For smaller air gaps (5 cm) and lower voltages (10 kV), a forming mist was seen, which could have been a result of spraying of the viscose solution in the electrostatic field. However, that process was also unstable and stopped after a few minutes. The formation of drops at the capillary tip, followed by those drops falling into the bath were the most common phenomena. The presence of flammable carbon disulfide, which was used to produce viscose, was an additional process difficulty. Therefore the concern was that too high voltage applied would result in electric flashover and could even have caused a fire. The high toxicity of viscose solutions was another limitation of this process.

Despite the fact that the tests conducted failed and there was no evidence that cellulose nanofibres could be electrospun from viscose solutions, the authors believe that viscose could turn out to be a suitable system for manufacturing *e.g.* cellulose nanoparticles. Even though a continuous and stable jet of solution was not observed, it is possible that the solution sprayed in an electrostatic field could form (in air) staple fibres or spherical objects with diameters in the nanometer range. At the current stage of our research, we were unable to isolate such objects from the solidifying bath to confirm their existence using SEM examination. The main difficulty in isolating such small objects lies in the fact that the baths used in the device for nanofibre formation have volumes of a few litres and the production rate of electrospinning is very low (about a few milligrams per hour). Research aiming at confirmation of the above thesis has already started and will continue in the future.

SEM analysis of cellulose nanofibres

Thorough observation of nanofibres is direct confirmation of the effectiveness of nanofibre formation. After solidifying in the bath, the nanofibres were transferred by the water stream onto a rotating cylindrical mesh with polypropylene nonwoven fabric on its surface. Due to the extremely low number of nanofibres in comparison to the volume of the solidifying bath flowing in the electrospinning device, it was very difficult to control the deposition of spun fibres on the nonwoven fabric. Nevertheless a thin layer of nanofibres was obtained for a stable electrospinning process.

For nanofibres electrospun from NMMO solutions, the product deposited on nonwoven fabric was visible as a thin, quite uniform white layer, which – after drying – had a tendency to break along the axis of fibre deposition.

For nanofibres spun from cellulose solutions in phosphoric acid, the samples obtained exhibited quite high heterogeneity and did not form a cohesive layer.

On the other hand, no formation of a nanofibre layer was observed during electrospinning from viscose solutions, which probably resulted from the washing out of deposited objects from the nonwoven fabric.

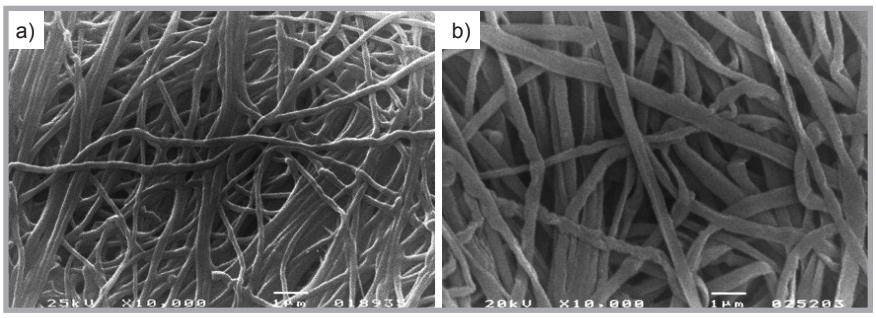

Figure 1. *SEM images of cellulose nanofibres electrospun from NMMO solutions of cellulose contents of 2% a) and 5% b) (10 kV and 10 cm).*

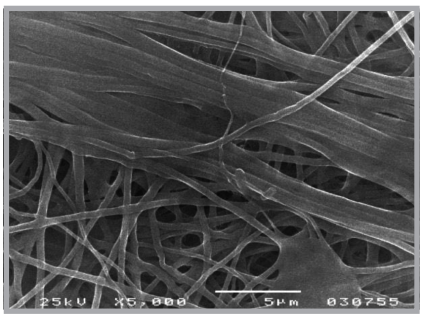

Figure 2. *SEM image of cellulose nanofibres electrospun from phosphoric acid solution of a cellulose content of 2% (10 kV and 10 cm).*

The samples of cellulose nanofibres obtained were examined as to their appearance and diameter using electron scanning microscopy (SEM). For nanofibre morphology comparison, nanofibre samples spun under the same conditions, *i.e.* at a voltage of 10 kV and distance between the capillary and bath surface of 10 cm, were selected.

Figures 1.a and ***1.b*** show images of the cellulose nanofibres electrospun from NMMO solutions of a concentration of 2% and 5%, respectively.

Analysis of the SEM images indicates that the average thickness of fibres formed from both 2% and 5% solutions was practically within a similar range of values. The distribution of diameter values for nanofibres obtained from 2% solutions was between approx. 200 and 350 nm, whereas that for nanofibres obtained from 5% solutions, this ranged from about 200 nm to 550 nm.

It can be also stated that the nanofibres produced were stuck together, which was an outcome of both their taking-up and drying methods. Based on the results, which have not yet been published, it can be said that the drying method of cellulose nanofibres also has a significant impact on their tendency to stick to each other and, in consequence, on their final morphology.

In the case of nanofibres produced from the phosphoric acid system, the samples examined exhibited a relatively large number of fibres stuck together, which probably resulted from the solidification rate of the solution jet. Nanofibres stuck together may suggest fairly slow washing out of the solvent from the solution jet. ***Figure 2*** presents an exemplary SEM image of the nanofibres electrospun from cellulose solutions in phosphoric acid.

SEM analysis was also applied to nonwoven fabrics which were used during nanofibre formation from viscose solutions. However, neither spherical objects nor objects similar in shape to the nanofibres were detected on the surface of the nonwoven material.

Conslusions

Diluted spinning solutions of cellulose in three different solvents were prepared, namely cellulose solutions in NMMO and in phosphoric acids, and cellulose xanthate solution in NaOH. Attempts to form nanofibres in an electrostatic field were made using different formation conditions and evaluating process stability. Based on the research conducted, it may be concluded that 2% cellulose solution in NMMO is particularly suited to the production of cellulose nanofibres using electrospinning. This system allows stable formation for a relatively wide range of operating parameters, varying for the applied voltage – from 10 to 20 kV, and for the air gap – from 5 to 15 cm. NMMO solutions of 5% cellulose content exhibit quite high viscosity and can be spun at elevated temperatures (130 °C). However, it should be remembered that the thermal degradation processes of the cellulose-NMMO system occur much faster at this temperature, which is disadvantageous for the process itself.

Cellulose solutions in phosphoric acid have relatively high viscosity and, thus, only solutions of a concentration of 2% in a very limited range of process parameters can be used to form nanofibres. However, the formation is unstable and should be run in chilled ampoule due to the fast degradation of the polymer at temperatures above 0 °C. Because of the high viscosity, 5% cellulose solutions in phosphoric acids cannot be used for fibre formation in an electrostatic field when the equipment described above is employed.

It was impossible to produce cellulose nanofibres from viscose solutions containing 2% or 5% of cellulose by weight. Under the conditions studied, the jet formation is not stable and resembles solution spraying rather than nanofibre spinning. However, it is not excluded that after some equipment modifications, it would be possible to produce staple nanofibres or cellulose of spherical shape and of a size in the nanometer range. Also the modification of such parameters as the surface tension and viscosity of viscose solutions should ensure the outcome expected, *i.e.* nanofibre formation. It seems that this direction of research looks promising and should be developed in the near future.

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