

Institute of Biopolymers and Chemical Fibres
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland
E-mail: nanotech@ibwch.lodz.pl

Abstract

Electrospinning and melt-blown techniques were harnessed to the investigation into the preparation of textile materials of thin cellulose fibres. The spinning was performed by using spinning solutions with cellulose concentration of 3wt% and 6 wt% in N-methylmorpholine-N-oxide (NMMO). By adopting suitable spinning conditions for both of the applied techniques, laboratory lots of the textile materials were prepared with fibres having an average diameter of 0.66 μm to 10.6 μm from electrospinning and 1.37 to 1.50 μm from melt-blowing, respectively, for increasing concentration of cellulose in the spinning solutions. It was found by SEM inspection that the fibres obtained by both techniques are of irregular shape and often stick to each other at certain length. In the electrospinning it was observed that thin and thick fibres joined together may take an original shape resembling a tailor seam. In extremities, the fibres are deformed to such degree and combined on such large surface as to form a sort of film with discernible only fibre fragments.

Key words: electrospinning, melt-blown, NMMO, cellulose, microfibres.

Introduction

The preparation of micro- and nanofibres may be accomplished by a variety of physical-chemical methods. It must, however, be noted that cellulose is neither fusible nor dissolvable in most common solvents which implies specific methods of its processing to fibre. Best known amongst the applied physical-chemical methods are two: electrospinning [1 - 3] proceeding in an electrostatic field, and air blowing spinning [4 - 6] (inclusive melt-blown) where the fibre is formed in a stream of compressed air. The use of the methods in relation to cellulose carries a problem: the applied solvents are not easy to evaporate and attempts to form the fibre according to the methods end up in producing an extended stream of the cellulose solution. Coagulation of the extended spinning solution stream is still needed to form the fibre. During the coagulation, the solvent travels to a fluid which does not dissolve cellulose and the remaining cellulose material is formed into a fibre. The final form of the cellulose in such fibres (so called regenerated cellulose) differs greatly in supermolecular structure from native cellulose [7, 8]. Nonetheless, the advantageous properties of cellulose are maintained and the fine shape of the fibre adds new interesting features absent in natural cellulose fibres. Therefore, materials made of micro- and nanofibres are frequently designed for advanced applications in medicine and hygiene [3, 9]. Investigations into the production of thin cellulosic fibres are not restricted to the fibre formation but include the preparation of the spinning solution. Though cellulose is one of the oldest polymers applied in the manufacture of fibres, its processing still poses

environmental, work safety and economic problems. Based on world-wide long term R&D work, three promising solvents may be indicated as suitable for the preparation of cellulose spinning solutions on a large scale, notably:

- NMMO (N-methylmorpholine-N-oxide) in Lyocell process [10, 11]
- NaOH (sodium hydroxide-water) in Celsol technology [8, 12]
- Imidazole salts and other ionic liquids [12, 13].

An industrial use of the solvents is far behind expectations. Despite advanced research, the Celsol process has not yet been up-scaled from laboratory trials to industry. Ionic liquids that have better cellulose dissolving potential and higher thermal resistance than NMMO still remain in the labs. It is only the Lyocell process exploiting NMMO as a solvent (Tencel fibres, Lenzing Lyocell) that has found its way to industrial manufacturing with the amount of well over one hundred thousand tonnes of fibres turned out annually world-wide. The solvent emerges as suitable in the preparation of spinning solutions for the spinning of thin fibres by electrospinning [14 - 16] and melt-blowing [17, 18]. Only a few publications in that specific field could be found; knowledge concerning the use of textile material based on thin cellulose fibres is rather limited.

The aim of the present work is the preparation of thin cellulosic fibres in the micro- and sub-micro range from NMMO solution by electrospinning and melt-blow techniques on a laboratory scale. Equal spinning solutions were adopted in both techniques to better assess the difference in use. Investigation into the

preparation of microfibres from such solutions by melt-blowing on a larger scale will be reported in a separate publication.

Experimental part

Materials

- Cellulose - Columbus Pine produced by Weyerhaeuser Co. (USA) with DP = 1400 (producer's data) both untreated and hydrothermally pretreated was used in the preparation of spinning solutions. The hydrothermal processing (HT) resulted in a decrease in the cellulose polymerization degree to the level of 370 [18, 19].
- NMMO N-methylmorpholine-N-oxide (NMMO), in a 50% aqueous solution was delivered by BASF, Germany. It was characterized by $n_D^{26} = 1.4198$ and bulk density of 1.14 g/cm³
- Propyl gallate by Fluka Co. with a 98% content of the active substance. It was used as antioxidant in the cellulose/NMMO solutions.

Preparation of the cellulose solutions

The NMMO solution was first concentrated to the 70 wt% content. Crumbled cellulose after the HT pretreatment or untreated was added to the NMMO solution at 40 °C with stirring. The antioxidant (propyl gallate) was added in the amount of 0.1 wt % on cellulose. About 1 - 2 l of such mixture was put into a 5 l vacuum autoclave, preheated to 40 °C. The autoclave was equipped with an illuminated sight glass enabling the inspection of the cellulose pulp surface in the course of dissolving. The reactor content was slowly (1 - 2 hours) heated up to 120 °C with a step-wise pressure reduction from

atmospheric to about 8 mmHg enabling the evacuation of a sufficient amount of water to reach its content in the mixture below 13.3 wt%, thus enabling the dissolution of the cellulose in the NMMO or more precisely in the monohydrate NMMO \times 1H $_2$ O. At that point, the hitherto white and opaque pulp began to darken and acquire transparency. The process was continued at a pressure of 3 - 5 mmHg and temperature of 120 °C usually no longer than half an hour. Samples were taken for microscopic inspection and the amount of the delivered water was controlled to prevent its drop in the mixture to below 10 wt%. At such conditions, except for the monohydrate, the NMMO anhydrate appears to largely augment the dissolving ability. The conditions are seen as optimum with regard to work safety. It must be noted that beyond 150 °C cellulose undergoes an exothermic decomposition in the presence of NMMO. In adverse conditions like big mass, and excessive water evacuation, temperature may increase causing an explosive decomposition of the solvent [21]. It, therefore, seems that the water content during the dissolutions must not be reduced to below 10%. Also important is the inspection of the pulp surface in the autoclave through the sight glass to control and prevent effervescent boiling which may occur at an excessive decrease in the pressure, high temperature and presence of a large amount of water.

Spinnable solutions were prepared from both kinds of cellulose at its variable concentration in the range of 3 - 16 wt%.

In microscopic inspections, the solutions of the untreated cellulose revealed fragments of fibres that could not be dissolved and were therefore classified as unsuitable for spinning. The prepared spinning solutions were characterized in respect of:

- Viscosity – by measuring the melt flow index MFI at 120 ± 0.5 °C and piston pressure of 2170 G, plastometer Brignole, Italy
- Thermal properties DSC measurements, differential scanning calorimeter Diamond (Perkin-Elmer, USA), at a scanning speed of 20 K/min
- Microscopic inspection in visible light to assess the dissolution degree of the cellulose – microscopes Biolar (PZO, Poland) and Boetius (Germany) with heated table.

Note that the cellulose/NMMO spinning solutions are alkaline and hygroscopic and, therefore, must be stored in sealed and chemically resistant containers.

Electrospinning

For the electrospinning of cellulose fibres by the Lyocell process the solutions solidified at ambient temperature (some solutions solidify with delay) must be heated up to at least the melting point, i.e. above 80 °C [21, 14]. The thin cellulose solution streams formed in the electrostatic field must be quickly coagulated to become fibres. The process is mostly accomplished in water where it proceeds rapidly in less than 1 second. The device used for such electrospinning is schematically presented in *Figure 1*. The

earthed spinning head has two temperature-controlled heating zones. The spinning solution is melted in the cylindrical chamber (2 ccm of volume) and pressed with nitrogen to a steel pipe (inner dia of 0.8 mm) where the temperature of the beginning of spinning is adjusted. The spun fibrous material is taken up on the surface of the water in which a metallic mesh is immersed, connected to the high potential of the high voltage power supply ES50P-20W Ormond Beach, (USA). The fibrous material is collected on the mesh and then transferred onto a plastic mesh on which it is washed many times with distilled water and, then, slowly dried at ambient temperature (20 °C) .

Melt-blown

Figure 2 presents a schematic of the device for the preparation of fibrous materials by melt-blowing from the cellulose/NMMO solutions. As in electrospinning, the spinning head is electrically heated with a thermostat control usually above 80 °C. The spinning solution is melted in a cylindrical chamber (4 ccm of volume) and pressed by nitrogen to a steel pipe (inner diameter of 0.8 mm). The pipe is centrally fixed along nearly its entire length in a conical opening in the bottom part of the spinning head. Compressed heated air is fed through that opening. The air stream is controlled with a rotameter before heating. In these conditions, the stream of the spinning solution is entrained and drawn by the streaming hot air till it reaches the surface of the water used as a coagulation agent. The fibrous material is collected on a plastic mesh,

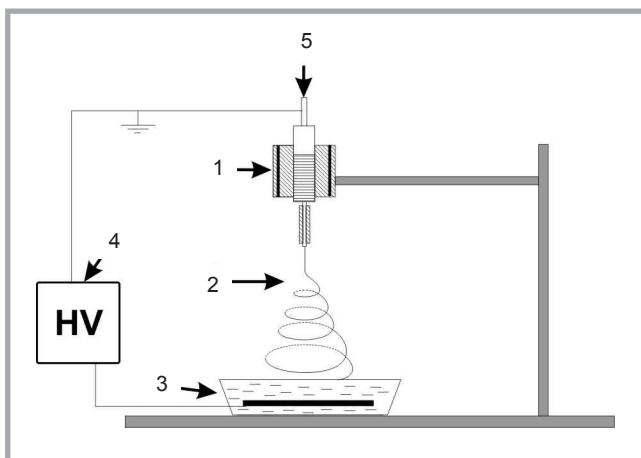


Figure 1. Simplified scheme of electrospinning device for the spinning of cellulose fibres from cellulose/NMMO solutions: 1 – heated electrospinning head (cross-section) with a separately heated needle (earthed); 2 – electrospinning area 3 – coagulation tray with metallic mesh connected to positive high electric potential; 4 – high voltage power supply; 5 – nitrogen inlet for the out-pressing of the spinning solution.

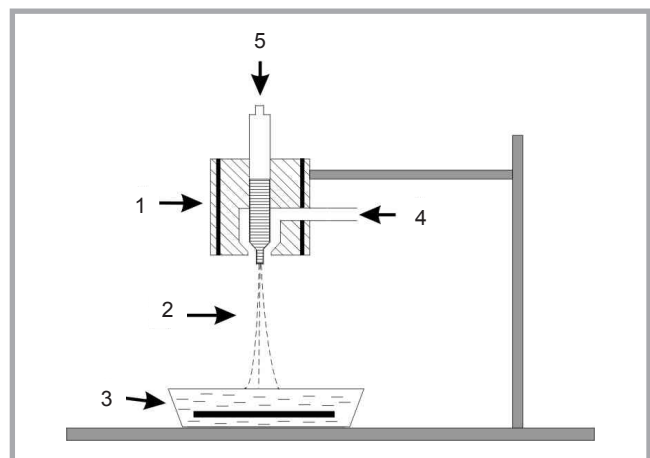


Figure 2. Simplified scheme of melt-blowing device for the spinning of cellulose fibres from cellulose/NMMO solutions: 1 – heated melt-blown head (cross-section); 2 – area where the stream is formed by the action of hot air flow; 3 – coagulation tray with plastic mesh 4 – hot air inlet; 5 – nitrogen inlet for the out-pressing of the spinning solution.

washed with distilled water many times and eventually slowly dried at ambient temperature (20 °C).

■ Results and discussion

From a variety of spinning solutions with different cellulose concentration, two were selected for the electrospinning and melt-blowing processes. The remaining ones will be reported in a separate publication. Characteristics of the two selected solutions can be found in **Table 1**. From the DSC measurements it appears that the solutions are prone to thermal crystallization (from the melt, T_c , or by a secondary heating, T_{cc}) hence they will turn crystalline when stored at ambient temperature. For the process, they must be heated up to beyond 82 °C to get the melt, and further if a lower viscosity is needed. As mentioned earlier, heating up to above 150 °C is hazardous. The ability

for thermal crystallization of the cellulose solutions could contribute to a faster solidification in the course of the stream forming if it were not for the proneness to supercooling (low temperature T_c). Furthermore, the speed at which the stream travels the short distance of several centimetres between the electrodes in the electrospinning is quite high, amounting to many metres per second [22], and hence the travelling time is too short to enable crystallization. Now, the solution stream, still liquid, reaches the water surface where it coagulates. High kinetic energy of the solution streams may cause fragmented joining of the streams with the earlier collected, not entirely coagulated ones. Favouring the undesired phenomenon is a short distance between the electrodes when the collected streams are still relatively thick and insufficiently quenched, thus maintaining a low viscosity. The case is illustrated with **Figure 3.A**

where fragments of the thick fibres stick to each other. The strange bonds between thin and thick fibres resembling a tailor's seam are also seen in the photo. The thin fibres represent the thread while the thick ones the sewn fabric. The observed effect is allegedly a result of the high speed attained by the thin fibres in the course of electrospinning - 200 m/s and higher [22, 23] and by the uneven (fibrillar) structure of the thick fibre material which can be seen in the photo. The thin swift fibres may be driven into the soft part of the thicker fibre or stop on the surface of harder fragments. The integration of the streams on the take-up surface is an extreme phenomenon occurring when the distance between the electrodes is very small, of about 5cm, and spinning solutions of low viscosity are used (e.g. solution with concentration of 3 wt% - **Table 1**). In such conditions, a film is collected where the fibre form appears in fragments only (see **Figure 3.B**). The forming of similar membranes was also reported in other works [14, 16], where it was explained by a too slow coagulation. Similar results were also obtained in this study in the part of the melt-blowing technique when the spinning head was situated only 5 cm above the water level. The reasons for the forming of the quasi-continuous structures are the same as in electrospinning. The spinning solution streams are carried off by the hot air and promptly reach the water surface; moreover, in the hot air they give out their heat much more slowly and persist longer in a plastic condition. Therefore, spinning solutions of low viscosity were avoided in the trials as well as a short distance between the spinning head and the take up.

Table 1. Properties of cellulose/NMMO spinning solutions used in electrospinning and melt-blowing: T_m and ΔH_m – temperature and enthalpy of melting during first heating, T_c and ΔH_c – temperature and enthalpy of crystallization from the melt, T_{cc} and ΔH_{cc} – temperature and enthalpy of cold crystallization (all were estimated at scanning speed of 20 K/min); c^* - Dissolution degree was assessed in terms of quality based on microscopic inspection in visible light. Dissolution was considered complete if no more than one undissolved fibre fragment appeared in the field of view.

Solution number	Cellulose content, wt%	Flow index 120 °C, g/10 min	T_m , °C	ΔH_m , °C	T_c , °C	ΔH_c , °C	T_{cc} , °C	ΔH_{cc} , °C	Dissolution degree*, %
1	3	1345	81.4	122.9	12.5	103.7	50.7	17.6	100
2	6	887	75.8	110.4	-9.2	0.9	9.1	97.5	100

Table 2. Parameters of the electrospinning device in trials during which fibrous materials were obtained. Average diameter of the fibre is given; * - distance between the end of the spinning pipe (needle) and the take-up surface (water surface in the coagulation tray).

Trial number	Solution number	Air gap*, cm	Voltage, kV	Temperature, °C		Fibre average diameter, μ m
				spinning head	needle	
E1	2	5	11	100	96	10.6
E2	2	5	11	100	130	4.88
E3	1	9.5	29	100	100	0.96
E4	1	11	30	110	100	0.66

The parameters adopted in the electrospinning are shown in **Table 2**. **Figure 4** presents the results of the SEM inspections. From the results it may be concluded that thinner fibres can be spun with a longer way of electrospinning, lower viscosity of the spinning solution and higher voltage/ Fibres prepared in the E4 trial are 16 times thinner than those from E1; they may be classified as sub-micron fibres. In none of the trials fibres could have been made with a regular cross-section.

Parameters quoted in **Table 3** (see page 56) apply to the melt-blowing. **Figure 5** (see page 56) presents the results of the SEM inspections. Although in both trials similarly thin materials were obtained, in the B2 trial a fibrous material was pre-

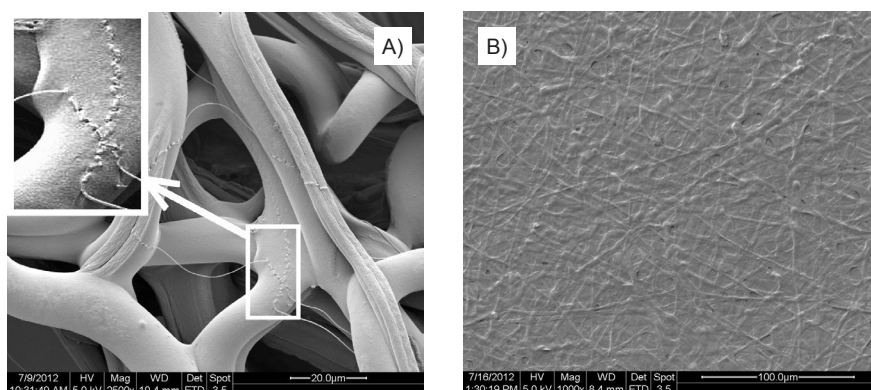


Figure 3. Fibrous materials obtained by electrospinning from cellulose/NMMO solution. A-fibrous material with discernible fragments of joint fibres; B- material collected in the form of a membrane with visible fibres.

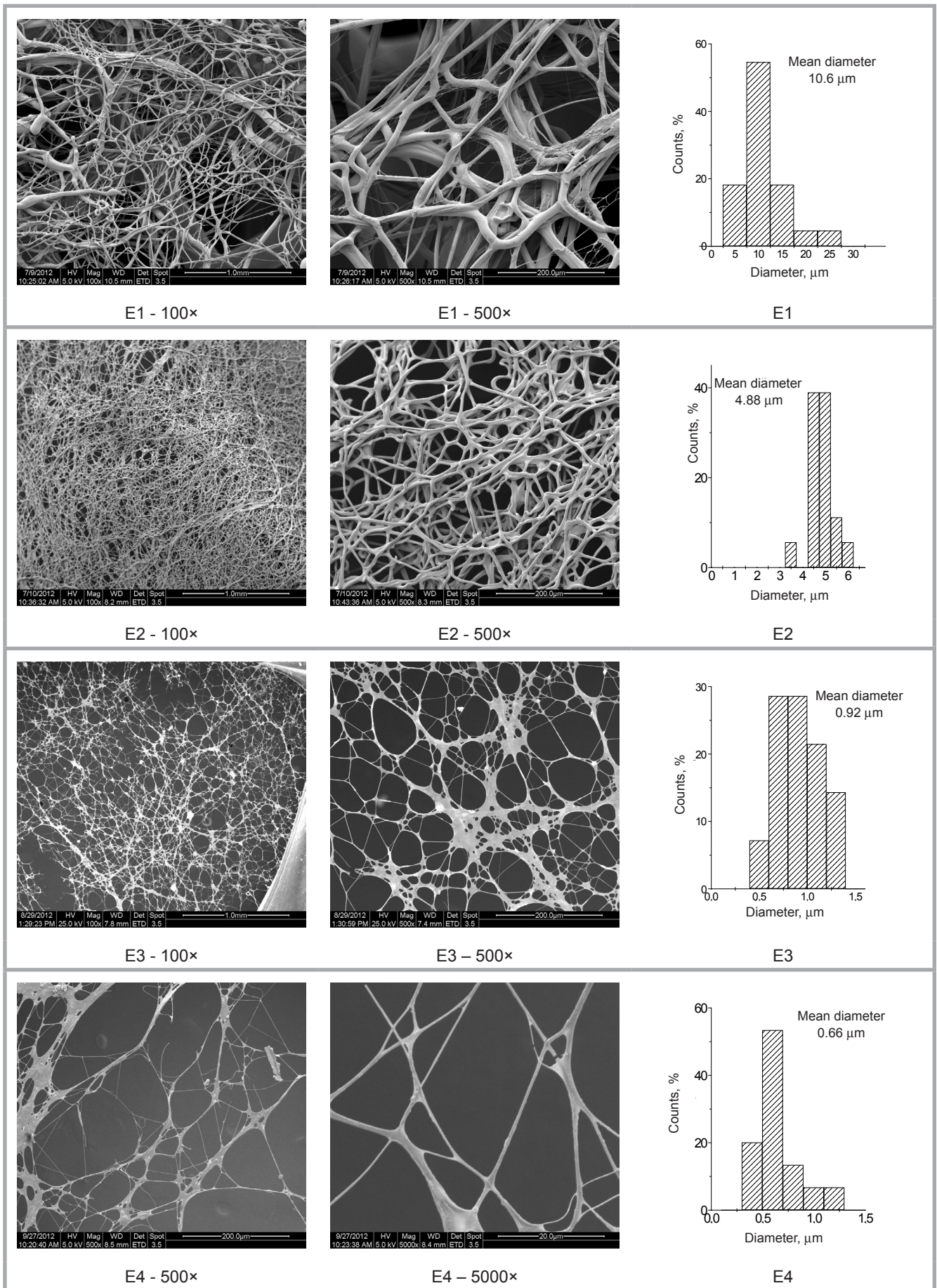


Figure 4. SEM images at 100x, 500x, and 500x and 5000x magnification of cellulose fibrous mats obtained by electrospinning from molten cellulose/NMMO solutions in trials E1 – E4 at conditions quoted in Table 2. Also shown are the histograms of fibre diameter.

Table 3. Parameters of the melt-blown device in trials during which fibrous materials were obtained. Average diameter of the fibre is given; * - distance between the end of the spinning pipe and the take-up surface (water surface in the coagulation tray).

Trial number	Solution number	Air gap*, cm	Compressed hot air		Extrusion pressure, MPa	Head temp., °C	Average fibre diameter, µm
			Temperature, °C	Flow, l/h			
B1	1	10	82	700	0.005	110	1.37
B2	2	31	82	700	0.005	120	1.50

pared with the best shape regularity of all attempts made in the study. Optimum conditions for the preparation of thin fibres have so far not been established in both of the applied processes.

Summary

Spinning solutions were prepared with varied cellulose concentration (3 - 16 wt%) in the NMMO solvent and reduced cellulose polymerization degree. Quality of the solutions of the regular cellulose (no HT pretreatment) was unsatisfactory. Therefore, only solutions of the HT-pretreated cellulose were used in the spinning. Electrospinning and hot air melt-blowing techniques were harnessed

in the investigations aimed at the preparation of fibrous materials. Spinning was accomplished from solutions with 3 wt% and 6 wt% concentration of cellulose with DP reduced to 370. Solutions with higher cellulose concentration were too viscous for the spinning. By selecting suitable spinning parameters in both techniques applied, experimental lots of the fibrous material were prepared and characterized by: average fibre diameter in the various trials of 0.66 µm to 10.6 µm in electrospinning, and 1.37 to 1.50 µm in melt-blowing, respectively, for increasing cellulose concentration. SEM inspection revealed irregular shapes of the prepared fibres which often stick to each other in fragments. The joints be-

tween the thin and thick fibres in electrospinning may take a curious shape resembling a tailor seam.

Acknowledgments

- Thanks go to Dr Dariusz Wawro for providing the HT pretreated cellulose.
- This work was carried out as a part of research project no. 1306/7.PR UE/2010/7 which has been supported financially by the Ministry of Science and Higher Education (Poland).

References

1. Frey M W. Electrospinning cellulose and cellulose derivatives. *Polymer Reviews*, 2008; 48: 378–391.
2. Huang Z-H, Zhang Y-Z, Kotaki M, Ramakrishna S. A review on polymer nanofibres by electrospinning and their applications in nanocomposites. *Composites Science and Technology* 2003; 63: 2223–2253.
3. Lee KY, Jeong L, Kang YO, Lee SJ, Park WH. Electrospinning of polysaccharides for regenerative medicine. *Advanced*

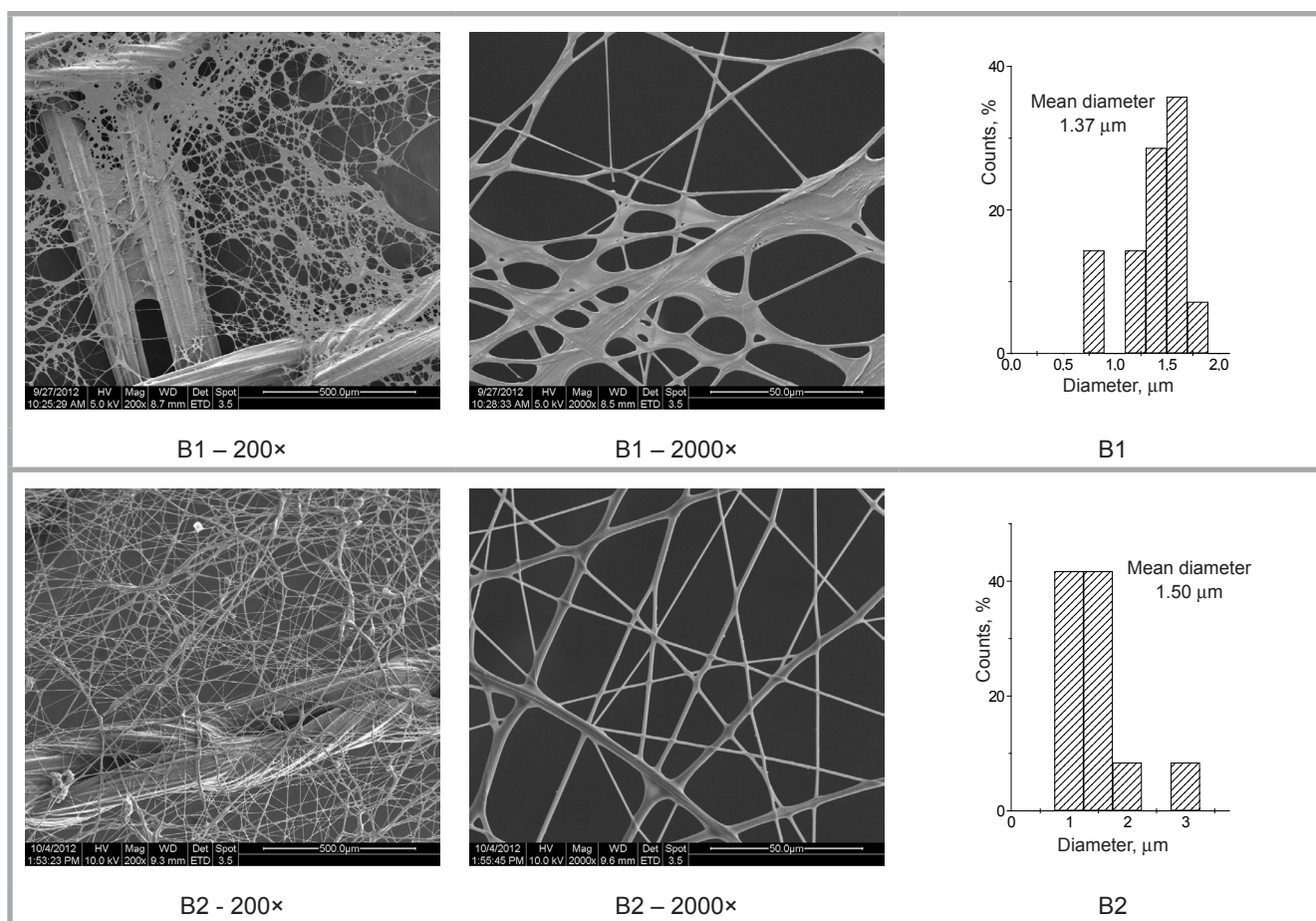


Figure 5. SEM images at 200× and 2000×, magnification of cellulose fibrous mats obtained by melt-blowing method from molten cellulose/NMMO solutions in trials B1 and B2 at conditions quoted in Table 3. At the magnification of 200×, the thick elements of the mesh supporting the fibrous mat are discernible. Also shown are the histograms of fibre diameter.

- Drug Delivery Reviews* 2009; 61: 1020–1032.
4. Zhuang X, Yang X, Shi L, Cheng B, Guan K, Kang W. Solution blowing of submicron-scale cellulose fibres. *Carbohydrate Polymers* 2012; 90: 982–987.
 5. Medeiros ES, Glenn GM, Klamczynski AP, Orts WJ, Mattoso LHC. Solution blow spinning: A new method to produce micro- and nanofibres from polymer solutions. *Journal of Applied Polymer Science* 2009; 113: 2322–2330.
 6. Zhang LF, Kopperstad P, West M, Hedin N, Fong H. (). Generation of polymer ultrafine fibres through solution (air-) blowing. *J Appl Polym Sci* 2009; 114: 3479–3486.
 7. Fink HP, Weigel P, Purz H, Ganster J. Structure formation of regenerated cellulose materials from NMMO-solutions. *Prog Polym Sci* 2001; 26: 1473–1524.
 8. Chen X, Burger C, Fang D, Ruan D, Zhang L, Hsiao BS, Chu B. X-ray studies of regenerated cellulose fibres wet spun from cotton linter pulp in NaOH/thiourea aqueous solutions. *Polymer* 2006; 47: 2839.
 9. Schiffman, J.D. and Schauer, C.L., A Review: Electrospinning of Biopolymer Nanofibres and their Applications. *Polymer Reviews*, (2008), 48:2, p.317-352
 10. Mortimer SA, Peguy AA. The formation of structure in the spinning and coagulation of Lyocell fibres. *Cellulose Chem Technol* 1996; 30: 117-132.
 11. White P. Lyocell: The production process and market development. In: *Regenerated cellulose fibres*. Ed. C.Woodings, Woodhead Publishing, Cambridge, (2001), p. 62-87.
 12. Wendler F, Meister F, Wawro D, Wesolowska E, Ciechańska D, Saake B, Puls J, Le Moigne N, Navard P. Polysaccharide Blend Fibres Formed from NaOH, N-Methylmorpholine-N-oxide and 1-Ethyl-3-methylimidazolium acetate. *FIBRES & TEXTILES in Eastern Europe* 2010; 18, 2 (79): 21-30.
 13. Wang H, Gurau G, Rogers RD. Ionic liquid processing of cellulose. *Chem. Soc. Rev* 2012; 41: 1519-1537.
 14. Kulpinski P. Cellulose Nanofibres Prepared by the N-Methylmorpholine-N-oxide Method.. *J Appl Polym Sci* 2005; 98: 1855-1859.
 15. Han SO, Son WK, Youk JH, Park WH. Electrospinning of Ultrafine Cellulose Fibres and Fabrication of Poly(butylene succinate) Biocomposites Reinforced by Them. *J Appl Polym Sci* 2008; 107: 1954–1959.
 16. Kim C-W, Kim D-S, Kang S-Y, Marquez M, Joo YL. Structural studies of electrospun cellulose nanofibres, *Polymer* 2006; 47: 5097-5107.
 17. Ebeling H, Fink HP. Cellulose meltblown nonwovens using the lyocell process. *Lenzinger Berichte* 2006; 86: 124–131.
 18. Tang S, Mukhopadhyay SK. Melt-blown lyocell: Influence of solution characteristics on fibre properties. *Journal of the Textile Institute* 2006; 97: 39–47.
 19. Wawro D, Stęplewski W, Bodek A. Manufacture of Cellulose Fibres from Alkaline Solutions of Hydrothermally - Treated Cellulose Pulp. *FIBRES & TEXTILES in Eastern Europe* 2009; 19, 3 (74): 18-22.
 20. Struszczyk H, Wawro D, Urbanowski A, Mikołajczyk W, Starostka P, Tomaszewski W, Ciechańska D. Process for producing modified cellulose pulp. 2001: Pat. Appl: WO 2001030855.
 21. Laszkiewicz, B. *Wytwarzanie włókien celulozowych bez udziału dwusiarczku węgla*, Ed. Lodart S.A. Lodz, 1997.
 22. Tomaszewski W, Kudra M, Cieciana D, Szadkowski M, Gutowska A. Electrospinning of aligned fibrous materials on inner rapidly rotating cone surface. *Fibres & Textiles in Eastern Europe* 2012; 20, 6B (96): 46-53.
 23. Tomaszewski W, Kudra M. *Research report IBWCh*, P23, 2012.

Received 09.05.2012 Reviewed 29.11.2012

Lodz University of Technology
Faculty of Material Technologies and Textile Design
 Department of Man-Made Fibres

Research:

The Department of Man-Made Fibres has more than 50 years of history and experience in man-made fibres. The main scientific interest of the Department can be divided into several fields: composite interactive cellulose fibres based on NMMO, nanofibres from biodegradable polymers, advanced materials based on biodegradable polymers for medical and technical applications, special fibres based on advanced polymers.

The Department is equipped with advanced devices for spinning solution preparation and fabrication of fibres and nanofibres by different methods (melt state, dry-wet, wet spinning).

Cooperation:

The Department is currently looking for partners from academia or industry.

We offer:

The Department is equipped with various devices for the determination of the properties of fibres and polymers: thermal analysis (TGA and DSC), rheometers and devices to determine the melt flow rate, devices for determining the mechanical properties of fibres (e.g. tensile tester), spectrometers (FTIR, UV-vis), optical microscopes.

For more information please contact:

Department of Man-Made Fibres
 Lodz University of Technology
 ul. Zeromskiego 116, 90-924 Łódź, Poland
 tel.: (48) 42-631-33-59 e-mail: Piotr.Kulpinski@p.lodz.pl website: <http://www.k41.p.lodz.pl/>