Modified Cellulose Fibers Prepared by the *N*-Methylmorpholine-*N*-oxide (NMMO) Process

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ABSTRACT: Cellulose fibers with modified properties have been prepared from cellulose solutions in *N*-methylmorpholine-*N*-oxide (NMMO). Poly(ethylene oxide) as a hydrophilic modifier and polyethylene as a hydrophobic modifier were added to the spinning solution. Based on microscope examination and measurements of such properties of fibers as porosity, moisture absorption, water retention, and tensile strength, structural changes as well as physical and

mechanical properties of the resultant fibers depending on the amount of modifier added to the spinning solution were analyzed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 907–916, 2002

Key words: fibers; modification; additives; FT-IR; differential scanning colorimetry (DSC)

INTRODUCTION

The process of cellulose fiber spinning using N-methvlmorpholine-N-oxide (NMMO) as a solvent is a new alternative method to the viscose process, as it is wasteless, environmentally friendly, and used in a closed production cycle. The lyocell fibers currently manufactured by this process are biodegradable fibers with good physical and mechanical parameters, showing high dry and wet tensile strengths, high stability of dimensions, low shrinkage in washing, good moisture absorption, and susceptibility to fibrillation. The latter feature is, however, undesirable when using these fibers for the production of textiles with good performance properties, as it is necessary to use additional treatments to prevent this phenomenon. On the other hand, the susceptibility of lyocell fibers to fibrillation also makes it possible to obtain special surface effects such as soft handle and the "peach skin" effect.¹⁻³ Cellulose fibers obtained by the NMMO process can be used to produce all types of flat textile fabrics. They can be blended with natural and synthetic fibers to spin thin yarns with high strength and twist, which allows one to produce thin and light fabrics. Lyocell fibers are also appropriate for technical purposes, such as reinforcing fibers in composites and building materials, and replacing glass fibers because of their high strength parameters and good capability to be mixed with resins and polymers.⁴ Because of their properties, cellulose fibers prepared by the NMMO process are

also perfect raw material for producing non-wovens.^{5,6}

These properties indicate that the process has a potential and certainly will be widely developed commercially. All manufacturers are concerned with enriching their range of produced fibers and therefore continue working on improving the NMMO process, especially with the goal of modifying fiber properties. Many research centers have been carrying out studies and obtaining interesting results on a laboratory scale, some of which will certainly soon find practical implementation.7-12 Possibilities for modification are extensive, and this process of fiber manufacture is particularly suitable because the solvent used dissolves not only cellulose but also many other polymers, such as poly(ethylene oxide), polyvinylopyrrolidone, poly-(vinyl acetate), silk, wool, aliphatic polyamides, cellulose mono- and diacetate, polyethylene, polyacrylonitrile, and some low molecular weight compounds. Because of such a wide range of possible modifications, the NMMO process may become a base technology for the manufacture of new generation cellulose fibers, especially superabsorptive, high-performance, or special composite fibers.

Several papers have recently appeared in the literature indicating that other polymers may be added to cellulose to change the structure and properties of fibers obtained by the NMMO process. Morgenstern and co-workers¹³ have obtained fibers from a homogeneous solution of cellulose and aromatic polyamide [poly(2,6-dichloro-1,4-phenylenephthalamide)]. Most of the estimated textile physical properties of blend filaments containing ≤ 10 wt % of that polymer do not differ significantly from those of pure cellulose filaments. However, wet abrasion resistance showed a

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maximum at that polymer content of 10 wt %. When the polymer content is >10 wt %, the fibrillation tendency of examined fibers is increased. Coincidentally, a decrease of tensile strength and wet abrasion resistance was obtained.

At the Thuringian Institute of Textile and Plastic Research, studies are being carried out to obtain new properties of this type of cellulose fibers. Fibers have been prepared from solutions containing cellulose and other polymers, such as carboxymethylchitin, chitosan, and polyethyleneimine, as well as starch and carbon black. The addition of carboxymethylchitin, chitosan, or polyethyleneimine makes the resultant fibers fungicidal and antibacterial. On the other hand, polyethyleneimine causes improved dyeability for acidic dyes. The addition of starch or heteropolysaccharides to the cellulose solution in NMMO considerably improves the hydrophilic properties of the fiber. It is also possible to prepare fibers with interesting properties by including insoluble substances, such as pigment dyes, carbon black, and ceramic materials, in the cellulose-NMMO system. The addition of carbon black allows electroconductive fibers to be prepared.¹⁵

The Man-Made Fiber Department at the Technical University of Łódź has long carried out studies on the manufacture of cellulose fibers by the NMMO process, especially to modify the fiber properties. Using the addition of linear synthetic polymers, antibacterial agents, or surface-active agents to the spinning solution, fibers with increased or decreased hydrophilicity and electroconductive or antibacterial properties have been obtained.^{16–18}

The aim of the present study was to prepare fibers from the cellulose solution in NMMO with modified properties by the addition of hydrophilic [poly(ethylene oxide)] and hydrophobic (polyethylene) modifiers. The use of polyethylene waxes as plasticizers in the industry is well known, whereas poly(ethylene oxides) with a molecular weight of up to 6000 are used as pore-forming agents.

EXPERIMENTAL

Spinning solutions were prepared with spruce cellulose with DP = 809. A 50% aqueous solution of Huntsman NMMO was used as solvent. Tenox PG (propyl ester of gallic acid) was used as an antioxidant, and poly(ethylene oxide) (PEO) from Fluka, with a molecular weight (MW) of 6000, was used as a hydrophilic modifier. Polyethylene wax (PE), with a MW of 6214 and manufactured by the Blachownia Chemical Company (Poland), was used as a hydrophobic modifier.

Fibers were spun from 15% solutions of cellulose in NMMO containing 2–20 wt % PEO or 2–20 wt % PE in relation to the content of α -cellulose. Cellulose was dissolved in NMMO using an IKAVISK blender. The prepared spinning solutions were used to spin fibers

by the dry-wet method on a laboratory spinning machine, using a spinneret with 18 orifices; the orifice diameter (*d*) is 0.4 mm and the capillary length (*l*) is 6 mm (l/d = 15). The spinning solution flow rate was 0.38 m/min, and the temperature of the spinneret during spinning was 105 °C. Fibers were spun to an aqueous bath at a temperature of 20 °C. The distance between the spinneret and the aqueous bath surface was 15 cm. The plasticization of fibers took place in an aqueous bath at 80 °C. The plasticization bath also served as a washing bath.

The moisture absorption of the obtained fibers at 65 and 100% RH was determined according to Polish standard PN-71/P-04635. Water retention was measured in accordance with PN-72/P-04800. Samples of fibers were immersed in distilled water containing a surface-active agent (Rokafenol N-8, 0.1%) for 24 h and then centrifuged off for 10 min at 324 rad/s.

Fiber density was determined by the flotation method, using a thermostat-controlled gradient column at 25 °C filled with a mixture of carbon tetrachloride and toluene.

Fiber porosity was examined by the mercury porosimetry method using a Pascal 440 apparatus coupled to a computer system and recorder. Using mercury porosimetry, the following parameters were determined: the total cumulative volume of pores, the internal volume of the set of capillaries with definite radius and their percentage content, the total specific surface, the percentage share of the internal surface of the set of capillaries with definite radius, and the total porosity. The total porosity expresses the ratio between the volume of pores (volume of internal cavities) and the external volume occupied by the sample.

Fiber cross-sections and the specific birefringence index were measured with an optical Biolar microscope coupled to the computer image analyzer. The data was analyzed using Screen Measurement 32G/ Mutech software. Surface and cross-sections of selected fiber samples were examined with a Jeol 35C electron microscope.

Fiber linear density was determined according to PN-ISO 1973. Tensile strength and elongation at break under conditioned and wet conditions, as well as loop strength were measured according to PN-85/P-04761/04.

Differential scanning calorimetry (DSC) measurements of the obtained fibers were carried out with a Du Pont TA2000 differential scanning colorimeter. Fiber samples were examined at a heating rate of 10 $^{\circ}$ C/min under a nitrogen stream in the temperature range 50–400 $^{\circ}$ C.

Fourier transform infrared (FTIR) spectra were obtained with a Mattson IR spectrophotometer. The potassium bromide (KBr) pellet technique was employed.

Cellulose Solutions Containing Various Amounts of Modifiers							
Sample code	Content of modifier	Moisture absorption at 65% R:H, %	Moisture absorption at 100% R:H, %	Retention, %	Total cumulative volume, mm ³ /g	Total specific surface area, m ² /g	Total porosity, %
B-144	_	12.66	24.96	77.20	18.00	0.787	5.47
B-151	2% PEO	12.66	25.94	79.27	23.00	2.203	4.94
B-154	5% PEO	12.68	25.86	80.77	24.51	1.486	5.42
B-155	10% PEO	12.72	25.96	82.93	29.41	4.309	7.08
B-156	15% PEO	13.01	25.92	85.02	34.00	3.69	8.54
B-157	20% PEO	13.23	26.03	87.80	53.00	5.01	14.64
B-169	2% PE	12.30	23.48	64.18	38.61	4.36	6.18
B-167	5% PE	12.04	22.39	62.99	31.13	1.46	4.44
B-166	10% PE	11.72	22.79	62.03	33.33	5.50	8.83
B-165	15% PE	10.83	22.47	61.45	40.39	4.55	7.94
B-158	20% PE	10.71	22.05	58.61	30.69	5.59	4.16

TABLE I Characteristics of Porosity and Hygroscopic Properties of Fibers Prepared from Cellulose Solutions Containing Various Amounts of Modifiers

RESULTS AND DISCUSSION

Porosity and hygroscopic properties

Experiments were carried out with hydrophilic (PEO) and hydrophobic (PE) compounds. The addition of these polymers to the material of cellulose fibers brings about a change in fiber porosity and hygroscopic properties. The latter depend on the total fiber porosity, its character, internal surface, and moisture transport possibilities. The capillary system developed in fibers facilitates the transport of moisture and liquid penetration of fibers during the dyeing and finishing processes. As for fiber properties, not only is the total internal surface of fiber important, but so is the radius of the pores and the distribution of their dimensions. Sets of capillaries with a definite size were divided conventionally¹⁹ into four groups, described as small pores with a radius of 4–15 nm, medium pores with a radius of 15-150 nm, large pores with a radius of 150-1875 nm, and very large pores with a radius of 1875–7500 nm. The results of porosity measurements are given in Table I and in Figures 1 and 2. Based on



Analyzing the effect of the modifiers used on the porosity parameters such as total cumulative volume,



Figure 1 Distribution of the relative volume of pores versus their radius for fibers prepared from cellulose solutions containing various content of PE.

1003 80% Relative Pore Volume [%] 70% 60% 50% 40% 30% 20% 105 15.09 without PEO 2%PEO 5%PEO 10%PE0 15%PE0 20%PEO Content of Modifier [%] Pore Radius Ranges [nm] 7500 - 1875 1875 - 150 **R** 150 - 15 N15-4

Figure 2 Distribution of the relative volume of pores versus their radius for fibers prepared from cellulose solutions containing various content of PEO.

		Evaporatio	n of adsorbed	Thormal do	amposition	
		W	ater			
Sample code	Content of modifier	<i>T</i> ₁ , ℃	ΔH_1 , J/g	$T_{2 \max} \circ C$	ΔH_2 , J/g	
B-144		67.78	186.2	338.79	56.41	
B-151	2% PEO	75.83	219.3	335.40	20.62	
B-154	5% PEO	67.74	151.4	330.95	49.50	
B-155	10% PEO	81.47	246.1	336.27	24.21	
B-156	15% PEO	79.59	250.6	338.87	37.17	
B-157	20% PEO	72.74	143.5	338.49	73.99	
B-164	2% PE	77.09	254.2	333.73	105.1	
B-167	5% PE	87.29	242.7	337.78	92.81	
B-166	10% PE	86.40	231.6	335.54	103.2	
B-165	15% PE	91.25	151.6	331.51	71.74	
B-158	20% PE	80.81	222.1	332.76	65.49	

TABLE II Thermal Analysis (DSC) of the Fibers Obtained from the Cellulose Solutions with Various PE and PEO Contents

total specific surface, and total porosity, one observes an increase in the total cumulative volume of the fibers obtained from solutions containing PEO or PE. The highest increase was obtained in fibers spun from a spinning solution containing 20 wt % PEO or 10 wt % PE, whereas the total cumulative volumes of these fibers were 53.00 and 40.39 mm³/g, respectively (Table I). On the other hand, the total cumulative volume of unmodified fibers is $18.00 \text{ mm}^3/\text{g}$. The addition of modifiers to the spinning solution also brings about an increase in the total specific surface of fibers compared with unmodified fibers. The highest increase in the total specific surface was observed in fibers obtained from the cellulose solution containing 20 wt % PEO or 20 wt % PE. In both cases, the value of the total specific surface was at a level of 5 m^2/g , whereas in unmodified fibers, the corresponding value is only 0.787 m^2/g . The total porosity of unmodified fiber amounts to 5.47%, whereas in fibers obtained from spinning solutions containing PEO this parameter shows an upward trend with increasing amount of PEO, reaching 14.64% for fibers obtained from solutions containing 20 wt % PEO. In the case of fibers obtained from solutions with various amounts of PE, the fiber obtained with the addition of 10 wt % PE shows the highest porosity (8.83%).

The measurement of moisture absorption by the obtained fibers at 65 and 100% RH (Table 1) show that the moisture absorption of fibers containing PEO under normal conditions is only slightly affected, whereas that of fibers containing PE is distinctly decreased with an increase in the amount of PE added. The lowest moisture absorption under normal conditions was observed for fibers obtained from the solution containing 20 wt % PE. Similar trends in moisture absorption were observed at 100% RH. The results of porosimetric measurements (Table I) show that the slight increase in moisture absorption by the fibers containing PEO is probably associated with the increased proportions of small pores in the fiber struc-

ture and with the increase in the total internal volume. On the other hand, the drop in moisture absorption in the fibers obtained with the addition of PE results from the hydrophobic character of this polymer (Table II, Figures 3–6).

Examining the water retention by fibers obtained from cellulose solutions containing PEO (Table I) and comparing the results with those obtained for unmodified fibers, one can see that this parameter increases considerably with an increase in the amount of modifier, reaching a level of 87.80% for fibers obtained with 20 wt % PEO in solution. This result is probably due to the increase in the total internal volume of pores and their total internal surface. On the other hand, the fibers modified with PE show decreased water retention with an increasing amount of this modifier. The drop to a value of 58.61% is observed in fibers obtained with the use of 20 wt % PE, whereas unmodified fibers show water retention at a level of 77.20%. This effect is probably due to the hydrophobic character of the PE present in the modified fibers.

Thermal analysis

Thermal studies of the fibers obtained from cellulose solution with various contents of PEO or PE were carried out by examining DSC thermograms of these fibers (Figures 5 and 6, Table II). It is clearly seen in all the DSC thermograms that there is an endothermic peak at ~ 100 °C that shows the evaporation of adsorbed water (i.e., the water absorbed by fibers during standard conditioning of 65% RH and 20 °C). The second endothermic peak, in the region of ~ 330 to 340 °C, is due to decomposition of the fiber. Comparison of the DSC thermograms of fibers obtained with PEO with those of unmodified fibers (Figure 5) indicates that no new peaks are observed.

The thermograms of fibers obtained with 10 wt % PE (Figure 6) show a new distinct endothermic peak at a temperature ~ 105 °C. According to the literature,²⁰



Figure 3 IR spectra of fibers obtained from cellulose solutions with various content of PE: (1) without PE, (2) 2 wt % PE, (3) 5 wt % PE, (4) 10 wt % PE, (5) 15 wt % PE, (6) 20 wt % PE.

this peak is connected with the melting of the crystalline phase PE. Analysis of the effect of the modifiers under investigation on the thermal properties of the modified fibers indicates that water evaporates with more difficulty and at higher temperatures than in the case of unmodified fibers. This result seems to be associated with the formation of a fine porous structure and the high content of small pores in the fiber



Figure 4 IR spectra of fibers obtained from cellulose solutions with various content of PEO: (1) without PEO, (2) with 20 wt % PEO.



Figure 5 DSC thermograms of fibers prepared from cellulose solutions with various content of PEO.



Figure 6 DSC thermograms of fibers prepared from cellulose solutions with various content of PE.

 TABLE III

 Mechanical Properties of the Fibers Obtained from the Cellulose Solutions with Various PE and PEO Contents

	Content modifier, % wt										
	Without modifier		Poly(e	ethylene	oxide)			Po	olyethyle	ene	
Fiber property	0	2	5	10	15	20	2	5	10	15	20
Linear density, dtex	6.54	5.95	5.79	7.14	5.85	5.34	5.97	5.82	5.63	5.98	5.95
Conditioned tensile strength, cN/tex	31.5	30.6	31.4	30.7	29.5	33.1	30.9	31.4	27.1	29.5	26.4
Conditioned elongation at break, %	15.4	13.5	13.8	14.0	14.7	13.4	14.4	17.0	14.6	16.5	14.8
Wet tensile strength, cN/tex	18.2	20.5	21.4	16.9	21.9	21.7	19.9	23.4	19.5	20.2	19.8
Wet elongation at break, %	15.7	16.0	15.0	14.1	16.0	15.4	16.1	20.4	18.4	18.4	15.8
Loop tensile strength, cN/tex	5.24	5.34	6.68	5.97	5.56	6.32	5.46	6.54	5.64	6.69	5.54

material. Regarding the thermal decomposition of the obtained fibers, the addition of modifiers to the spinning solution brings about a decrease in the temperature of fiber decomposition by a maximum of 8 °C. This decrease seems to be due to the drop in fiber orientation and a decreased degree of crystallinity. Only fibers obtained from solutions containing 15 and 20 wt % PEO have the same temperature of decomposition as the unmodified fibers (i.e., 338.79 °C). From the thermal measurements it also follows that in the case of the fibers containing PE, the decomposition process proceeds with considerably more difficulty than in the case of unmodified or PEO-modified fibers.

Mechanical properties

Mechanical properties of the fibers obtained from solutions containing PEO or PE are given in Table III. The fibers containing PE show a decreased tensile strength in the conditioned state, especially when the PE content is 20 wt %. In the case of the fibers modified with PEO, this parameter is similar to that for unmodified fibers, but when the addition of PEO is 20 wt %, the fiber tensile strength increases up to 33.1 cN/tex. The modified fibers also show lower values of conditioned elongation at break than those of unmodified fibers, with the exception of fibers obtained from the solutions containing 5 or 15 wt % PE whose elongation is 17.0 and 16.5%, respectively. On the other hand, all the modified fibers show higher wet tensile and elongation in comparison with unmodified fibers. The highest values of these parameters are observed for the fiber obtained from the solution containing 5 wt %PE. An increase in the loop tensile strength is also observed for all the modified fibers. The highest value of this strength, 6.69 cN/tex, is shown by the fibers obtained from the solution containing 15 wt % PE and from fibers obtained from the solution containing 5 wt % PEO, whose loop tensile strength is 6.68 cN/tex. The modified fibers also show decreased linear densities compared with unmodified fibers. This result is probably associated with a partial washing-out of the added modifiers.

Spectrophotometric measurements

To examine more precisely the changes taking place in the fiber material under the influence of the modifiers, IR spectra were taken and analyzed (Figures 3 and 4). The IR spectra of fibers obtained from the cellulose solutions containing PE (Figure 3) show bands at wavelengths characteristic of cellulose. A significant difference in the IR spectra can be observed at the wavelength of 2900 cm⁻¹. In the spectrum of unmodified fibers at this wavelength, a single peak appears with a medium intensity associated with CH stretching vibrations and CH₂ asymmetrical stretching vibrations. In the IR spectra of the fibers obtained with PE, starting from the fiber with the lowest PE content, in addition to the band at 2900 cm^{-1} , a new band appears at 2850 cm⁻¹. The intensity of this new band increases considerably with increasing amount of PE added to the cellulose solution. This band is associated with CH₂ symmetrical stretching vibrations from PE. This fact confirms the presence of PE in the fiber material. It is interesting to note that even repeated rinsing of the fiber in hot water does not wash out this polymer from the modified fiber. The IR spectrum of PE also shows a band at 1469 cm⁻¹ associated with CH₂ bending vibrations, and this band is also observed in the IR spectra of the fibers under discussion. On the other hand, the IR spectra of fibers prepared from cellulose solutions containing various amounts of PEO (Figure 4) show no band that could be ascribed to PEO. The most characteristic band of PEO is that at 1150 cm⁻¹ corresponding to the vibration of -C-O-C-, but this band is also present in the IR spectrum of cellulose and therefore the presence of PEO cannot be confirmed by examination of IR. It is most likely that PEO has been washed out from the fiber material during repeated rinsing with hot water.

Fiber density

As seen from the results of fiber density (Table IV), the fibers prepared from cellulose solutions containing various amounts of PEO have a similar density to that

/10

Birefringence Index							
Sample code	Content of modifier	Specific birefringence index	Density, g/cm ³				
B-144		0.0373	1.5272				
B-151	2% PEO	0.0370	1.5239				
B-154	5% PEO	0.0377	1.5232				
B-155	10% PEO	0.0365	1.5236				
B-156	15% PEO	0.0366	1.5235				
B-157	20% PEO	0.0358	1.5245				
B-164	2% PE	0.0358	1.5005				
B-167	5% PE	0.0333	1.4841				
B-166	10% PE	0.0309	1.4402				
B-165	15% PE	0.0289	1.4161				
B-158	20% PE	0.0259	1.3785				

TABLE IV Effect of the Amount of Modifier Added to the Spinning Solution on the Fiber Density and Specific Birefringence Index

of unmodified fibers (i.e., ~ 1.5272 g/cm³). It seems then that PEO has been really washed out and the fiber material consists exclusively of cellulose, but with a modified structure as already discussed. On the other hand, in the case of the fibers prepared from solutions containing various amounts of PE, one can observe a considerable decrease in the fiber density with an increase in the amount of the modifier. The lowest density of 1.3785 g/cm³ was obtained for the fiber obtained from the solution containing 20 wt % PE. These results are consistent with the IR measurements, which confirm the presence of PE in the fiber material. The considerable decrease in the density of fiber containing PE is because the PE used for the modification has a density of 0.920 g/cm³.

Microscope examination

Microscope examination of the obtained fibers indicates they are characterized by a regular round shape of cross-section similar to those of synthetic and



Figure 8 Cross-sections of fibers prepared from the cellulose solution containing 20 wt % PE (magnification of 2000 \times).

polynosic fibers. The pictures of fiber cross-sections prepared from solutions containing PEO show the presence of pores in the fiber material (Figure 7), whereas those of fibers with PE show irregularly distributed domains of PE, indicating a bicomponent fiber material (Figure 8). A scanning electron microscopy (SEM) micrograph of the unmodified fibers was examined (Figure 9) indicates clear scratches and fractures on the surface of modified fibers, which were probably caused by partial washing-out and passing the modifiers with NMMO to the spinning bath.

Examination of the overall orientation, expressed by the specific birefringence index (Table IV), shows that the values of this index are slightly decreased in comparison with those of unmodified fibers with increasing amounts of PEO (from 0.0373 for unmodified fibers to 0.0358 for fibers prepared with 20 wt % PEO). Considerably greater changes are observed in the fiber containing PE. The addition of 2 wt % PE to the spinning solution causes the resultant fiber to have a birefringence index of 0.0358, whereas the addition of



Figure 7 Cross-sections of fibers prepared from the cellulose solution containing 20 wt % PEO (magnification of 2000×).



Figure 9 Cross-sections of unmodified cellulose fibers prepared by NMMO process (magnification of $2000 \times$).

20 wt % PE results in a birefringence index of 0.0259. The results obtained show that the addition of PE to the spinning solution brings about a considerable drop in the overall orientation of the fiber material.

CONCLUSIONS

Based on the examinations performed, one may state that the addition of PE or PEO to the spinning solution of cellulose brings about a change in the fiber structure towards a fine-porous structure. As a hydrophobic polymer, the presence of PE in the fiber material makes it more hydrophobic in comparison with unmodified fibers. At the same time, the applied PE wax with relatively low molecular weight brings about a decrease in the overall orientation of the fibers and consequently some deterioration in the strength properties of the fiber. On the other hand, PEO, as a hydrophilic and water-soluble compound is removed from the fiber material during washing. However, despite the removal of PEO, the fiber modified with PEO becomes more porous in relation to unmodified fibers. The addition of PEO to the spinning solution causes the resultant fibers to have a considerably higher total volume of pores and total internal surface, with the total fiber porosity being increased three times.

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