Electrospinning of Cellulose-Based Nanofibers

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ABSTRACT: Cellulose derivatives of carboxymethyl cellulose sodium salt (CMC), hydroxypropyl methylcellulose (HPMC), methylcellulose (MC), and enzymatically treated cellulose have been electrospun, and the microstructure of the resulting nanofibers has been analyzed by scanning electron microscopy (SEM). Before electrospinning, the solutions were characterized by viscometry and surface tension measurements, and the results were correlated with spinnability. Four different CMC derivatives, varying in molecular weight (M_w), degree of substitution (DS), and substitution pattern, have been electrospun in mixtures with poly(ethylene oxide) (PEO), and nanofibers of various characteristics have formed. The CMC-based nanostructures, i.e., the nonwoven sheet and individual nanofibers, proved to be independent of M_w and DS but largely dependent on the substitution pattern. The nonwoven sheets varied in homogeneity, and beads appeared on the individual fibers. Depending on the chemical nature of the CMC, the extraction of PEO resulted in pure CMC nanostructures of varying appearance, indicating that the distribution of PEO and CMC in the nanofibers also varied. Two different HPMC derivatives, varying in DS, were electrospun into nanofibers. Homogeneous nonwoven sheets based on nanofibers of similar appearance are formed, independent of the substitution content of the HPMC sample. Preliminary fibers were obtained from enzymatically treated cellulose in a solvent system based on lithium chloride dissolved in dimethyl acetamide (LiCl : DMAc). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1473–1482, 2007

Key words: electrospinning; nanofibers; cellulose cellulose derivatives

INTRODUCTION

Electrospinning is a technique used to spin fibers with diameters of <100 nm up to micrometer level from a wide range of polymers. This electrostatic processing method uses a high-voltage electric field to form solid fibers from a polymeric fluid stream (solution or melt) delivered through a millimeter-scale nozzle. Formhals[1–3] patented this process as early as the 1930s. At the time, the technology did not develop any further due to low-output, inconsistent, and low-molecular orientation, as well as poor mechanical properties and high-diameter distribution. The electrospinning technique was revitalized by Taylor[4] during the 1960s through theoretical and experimental activities. Reneker and coworkers[5–7] were pioneers in this field and investigated the mechanism and theories of electrospinning. A few review articles and reports on electrospinning of nanofibers and related applications have been recently published.[8,9] Nanofiber-based materials have a large surface area and small pore sizes compared with conventional textiles, which makes their properties unique when used in applications. Nanofibers are useful in various applications, such as filtration applications;[10–12] protective clothing;[12,13] electronics;[14] biomedical applications, including tissue engineering, wound dressings, and drug delivery systems;[15–18] space materials; and reinforced composites.[19,20]

Cellulose is an abundant and renewable resource found in most parts of the world, which makes it a cheap raw material for various applications. However, little research has been done on the use of cellulose and cellulose derivatives as a raw material within electrospinning. Electrospun nanostructures based on cellulose and its derivatives are potential candidates for applications within the field of pharmaceuticals. For instance, several reports deal with the investigation of electrospun fiber mats as delivery vehicles, showing dosage forms with useful and controllable dissolution properties.[15,21–25] Verreck et al.[24] reported electrospinning of hydroxypropoxy methylcellulose (HPMC) and simultaneous encapsulation of a medically active compound for use as a drug-release system. The drug studied, itraconazole, is poorly water-soluble. The fibers obtained were compared with a physical mixture, a solvent-cast film and melt-extruded samples. The physical mixture of itraconazole and HPMC gave very little drug release. The solvent-cast film and the melt-extruded samples showed rapid release of the itraconazole. Electrospun samples dissolved completely over time, with the rate of dissolution depending on

the formulation presentation and drug to polymer ratio, at a lower rate than the solvent-cast film and melt extrudate. Hence, electrospun fibers show good potential in drug delivery application, since complete release of the drug was achieved and the release rate could be controlled by, for instance, the drug-to-polymer ratio, and the fiber diameter with the help of process parameters and the presentation of fibers used.

Except for cellulose acetate,[26,27] only a limited number of publications can be found on the electrospinning of cellulose and its derivatives.[25,28,29] Kessick and Tepper[27] have reported the formation of nanofibers of carboxymethyl cellulose sodium salt (CMC). A low-concentration CMC solution (0.01%) was sprayed into positively and negatively charged droplets using electrospraying. Nanoscale fibers were spontaneously formed between the droplets of opposite charge. However, it must be noticed that the length of the fibers between the micro-droplets was very short, ~1 μm. It seemed that fiber formation was promoted at reduced dimensions thanks to electric field concentration effects. The only paper published so far dealing with electrospinning of cellulose is a preprint by Frey et al.,[28] at the Department of Textiles and Apparel, Cornell University, in which preliminary electrospun cellulose fibers from cellulose dissolved in an ethylene diamine/thiocyanate salt system is reviewed.

The complications involved in electrospinning of cellulose are mainly due to the many difficulties ascribed to the material, one being its reluctance to interact with conventional solvents. Therefore, the choice of solvent systems is very important. Enzyme-treated cellulose may be dissolved in alkali solutions, but the fibers need to be coagulated. Other solvent systems worth mentioning are direct dissolution in cuprammonium hydroxide (cupro) for silk production, the Lyocell process (the solvent is an amine oxide, NMMO, N-methyl morpholine oxide), the viscose process (treatment with alkali and carbon disulfide) and dissolution via cellulose nitrate. Cellulose may also be dissolved in dimethylacetamide containing lithium chloride (LiCl : DMAc).[30–32] This solvent system is very powerful and is often used in molecular-weight measurements of cellulose and was the system chosen for further studies in this work.

This study deals with the electrospinning of cellulose derivatives HPMC, CMC, methylcellulose (MC), and enzymatically treated cellulose. The influence of the molecular weight (Mw), degree of substitution (DS) and substitution content and pattern of the derivatives on the electrospinning process and the resulting fibers was investigated.

EXPERIMENTAL

Materials

Electrospinning of the cellulose derivatives carboxymethyl cellulose sodium salt (CMC), hydroxypropyl methylcellulose (HPMC), and methylcellulose (MC), and of enzymatically treated cellulose was investigated. The enzymatically treated cellulose was provided by Tampere University of Technology (TUT), Finland. The cellulase mixture used was a culture filtrate from genetically modified *Trichoderma reesei* strain and was obtained from Primalco Ltd, Biotec, Rajamäki, Finland. The genes producing cellobiohydrolase (CBH) proteins were removed from the culture and the production of endoglucanase II (EG II) protein was enriched. The dosage used in enzymatic treatment was 500 ECU/g.

The cellulose derivatives are listed in Table I, together with their characteristics. Polyethylene oxide (PEO) with a molecular weight (M_w) of 400 000g/mol (Sigma-Aldrich, Stockholm, Sweden) was used in the mixture with CMC.

Solution preparation and characterization

The cellulose and cellulose derivatives were dissolved in different solvent systems, at different concentrations (w/w). Air bubbles in the solutions were removed prior to electrospinning by ultrasound treatment.

The CMC powder was mixed with the PEO powder, at a ratio of 1 : 1, before dissolution in water. The HPMC and MC were dissolved in water and ethanol mixtures, at a ratio of 1 : 1. The cellulose was soaked in water for at least 2 h. The wet cellulose was then filtered and soaked in dimethyl acetamide (DMAc) for 1 h. The cellulose was filtered and soaked once again in pure DMAc to minimize the presence of water.

TABLE I
Material, Producer, and Material Characteristics

| Material	Abbreviation	Producer	Approximate molecular weight (g/mol)	DS	Methoxy content (%)	Hydroxypropoxy content (%)
CMC Cekol 30	CMC A	CP Kelco, Sweden	120,000	0.72	—	—
CMC Cekol 700	CMC B	CP Kelco, Sweden	280,000	0.77	—	—
CMC Cekol 2000S	CMC C	CP Kelco, Sweden	350,000	1.24	—	—
CMC Cekol 500T	CMC D	CP Kelco, Sweden	250,000	0.72	—	—
HPMC 60SH4000	HPMC A	Shin—Etsu, Japan	350,000	—	29.2	8.8
HPMC 90SH4000	HPMC B	Shin—Etsu, Japan	350,000	—	22.9	9.4
MC SM4000	MC	Shin—Etsu, Japan	350,000	—	22.9	0

Before dissolution, the excess of DMAc was filtered off. The cellulose was then dissolved in DMAc containing 8% lithium chloride (Scharlau, Barcelona, Spain) (LiCl : DMAc), a procedure that took ∼15 min.

The viscosity of the CMC/PEO and HPMC solutions was characterized by stress sweeps between 10-740Pa. The measurements were performed in a rheometer, a Bohlin Rheometer CS 30 (Malvern Instruments Ltd., Worcestershire, UK), using a cone-and-plate geometry with a diameter of 25 mm and a cone angle of 5.4°.

The surface tension of the HPMC solutions was measured using a tensiometer of model Krüss Tensiometer K9 (Krüss GmbH, Germany) equipped with a Wilhelmy plate as measuring geometry.

Electrospinning of nanofibers

The solution was poured into a syringe fitted with a metal needle of 18 gauge. The distance between the needle tip and the grounded collector (aluminum foil) was set at 20 cm. The needle was connected to a high-
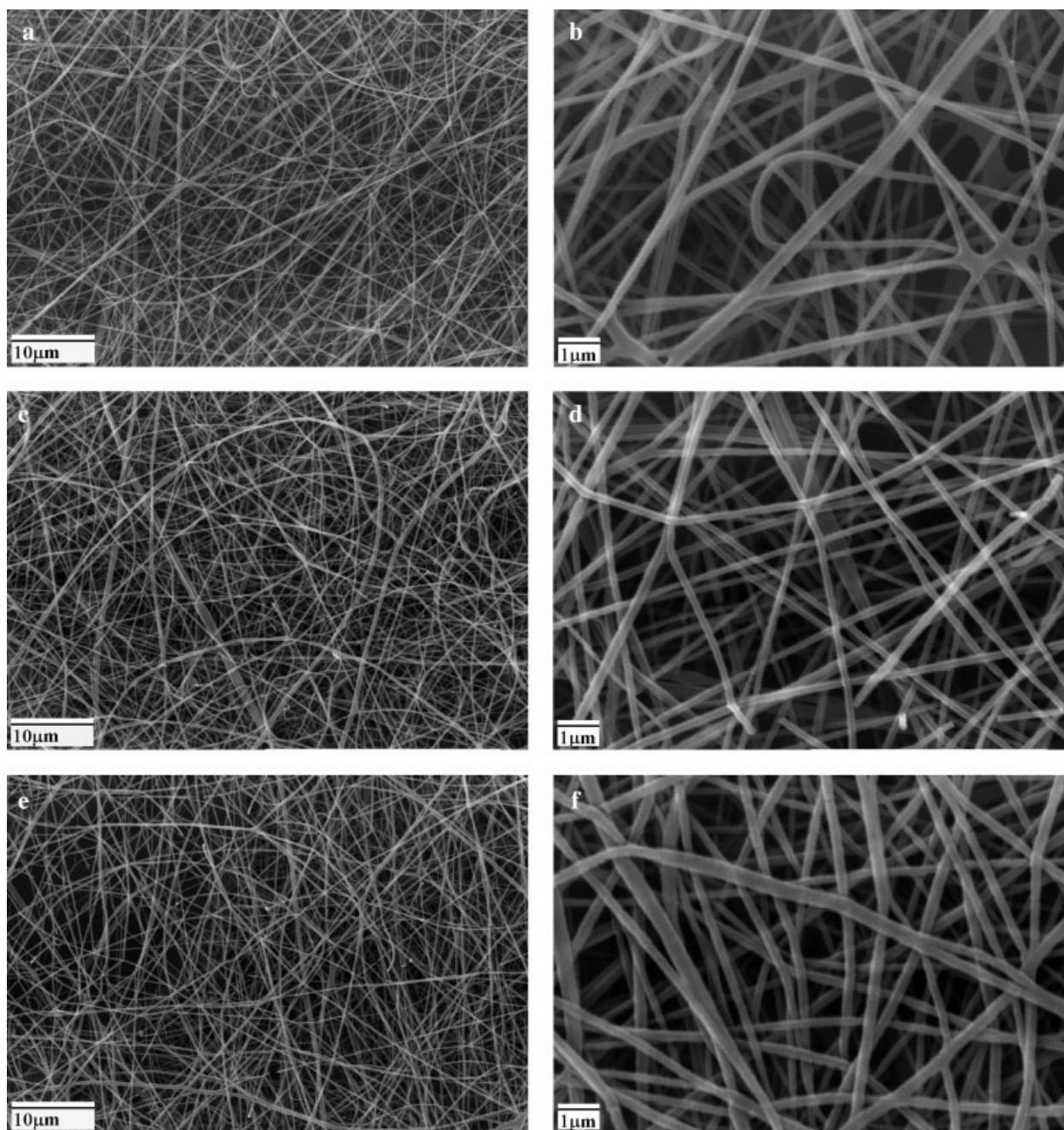
Figure 1 SEM images at two different magnifications of electrospun CMC : PEO nanofibers. (a,b) 4% CMC A, 4% PEO; (c,d) 4% CMC B, 4% PEO; (e,f) 4% CMC C, 4% PEO The electrospinning was conducted under 35 kV except for CMC B- and C-based solutions that were electrospun at 40 kV.

voltage supply from Gamma High Voltage, Ormond Beach, FL, USA, capable of delivering DC voltages up to 50 kV. The fibers were electrospun under a voltage of 35 kV unless other values are given.

Characterization of nanofibers

The morphology of the electrospun nanofibers was observed with a scanning electron microscope (SEM). The resulting nonwoven sheet of nanofibers was mounted with carbon tape and sputtered with a thin layer of gold in a Fine Coat Ion Sputter JFC-1100

(JEOL Ltd., Tokyo, Japan). The examination was done in a JSM-T300 (JEOL Ltd., Tokyo, Japan) by means of digital picture acquisition, using the software SemAfore 4.02 from JEOL Ltd. This software was also used to make a rough estimate of the diameter of the fibers. About 20 fibers from each of the samples were measured and the mean diameter calculated.

Extraction of PEO

Electrospun nanofibers of CMC/PEO were treated with an accelerated solvent extractor, ASE 200 (Dionex,
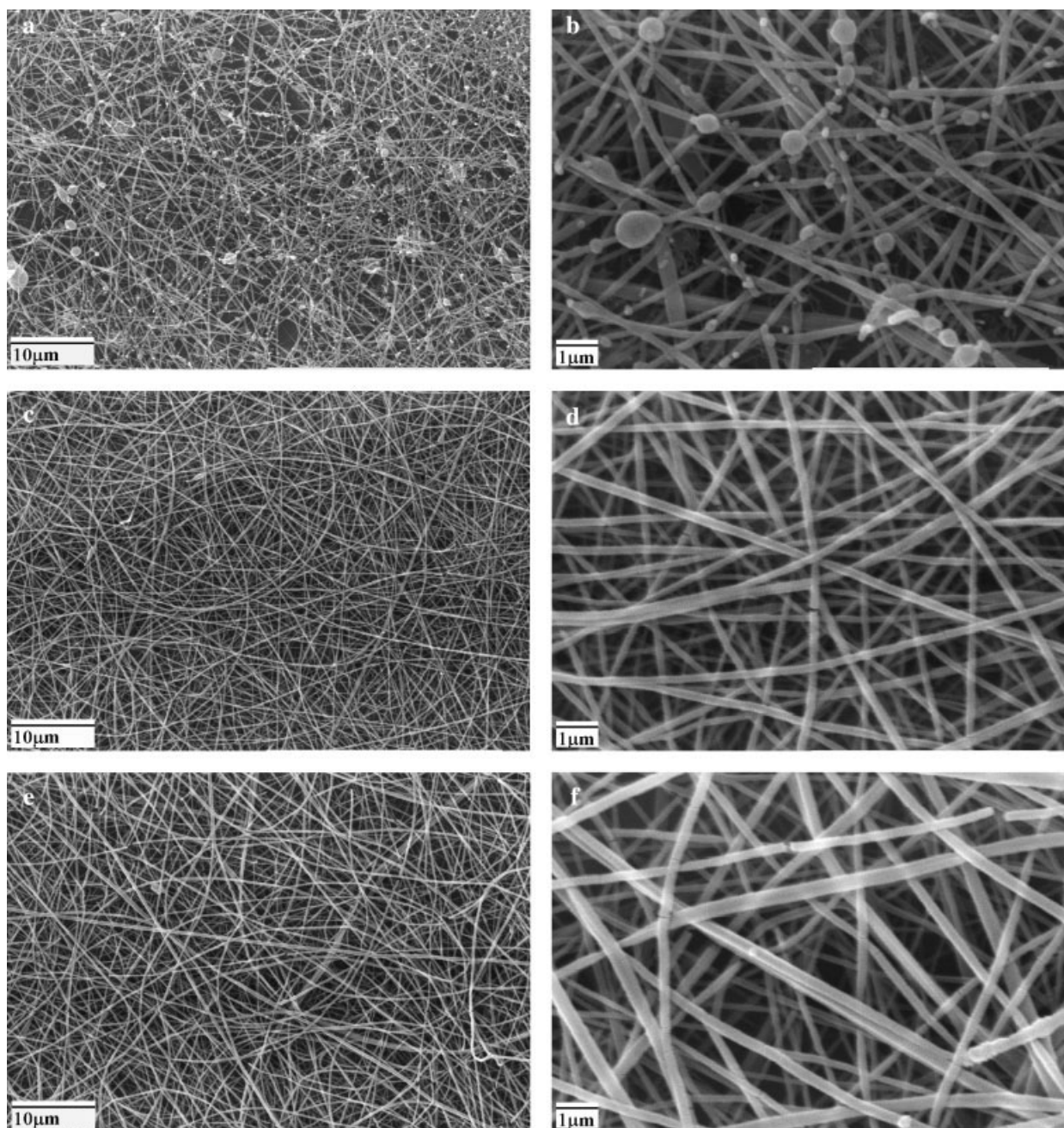
Figure 2 SEM images at two different magnifications of electrospun CMC : PEO nanofibers. (a,b) 3% CMC D, 3% PEO; (c,d) 3% CMC A, 3% PEO; (e,f) 3% CMC B, 3% PEO.

Västra Frölunda, Sweden), to extract the PEO from the fibers. Ethanol was used as extractor medium at a pressure of 2000 bars and a temperature of 80°C for 10 min. The treatment extracts the PEO in the nanofibers, while leaving the CMC part intact. The extraction of PEO in the nanofibers was verified by a Spectrum One Fourier-Transform Infrared Spectroscope, from Perkin-Elmer, Wellesley, MA, USA.

RESULTS AND DISCUSSION

Blend systems of CMC and PEO

Nanofibers from different CMC derivatives with different M_w, DS, and substitution patterns were successfully electrospun in a mixture with PEO (1 : 1 ratio) as a spinnable carrier.

SEM images of CMC/PEO-based nanofibers, at a total concentration of 8%, are shown at two different magnifications in Figure 1. The CMC derivatives CMC A, B, and C vary in M_w and DS (see Table I for material characteristics). A comparison of the SEM images in Figure 1 shows that the nanofibers formed are very similar, at both magnifications. At the lower magnification [Fig. 1(a), (c), and (e)], homogeneous nonwoven sheets of fibers of similar appearance are found. At the higher magnification [Fig. 1(b), (d), and (f)], individual nanofibers are shown. The individual fibers are rather straight with an even diameter over the length covered by the image. The mean diameter of the individual fibers lies between 200 and 250 nm, independent of the M_w and DS of the CMC derivative. The result suggests an independence of M_w and DS of the CMC derivatives on the morphology of the electrospun nanostructures, i.e., both nonwoven sheet and individual nanofibers.

CMC D has a documented blocky substitution of carboxymethyl groups, and a strong association between nonsubstituted parts on the CMC chain in solution, via intramolecular interactions, has been foreseen (G. Kloow, at C. P. Kelco, Skoghall, Sweden, personal communication; see also brochure CEKOL Cellulose Gum for Toothpaste 47110 by C. P. Kelco). A more random substitution of carboxymethyl groups is true for the other CMC derivatives investigated. As a result of its blockiness, a lower concentration (total concentration of 6%) had to be used to ensure that the viscosity of the solution was sufficient for electrospinning. SEM images of CMC D/PEO-based nanofibers are shown at two different magnifications in Figure 2(a,b). For comparison, CMC A and B have been electrospun at a total concentration of 6% [Fig. 2(c,d) and 2(e,f), respectively]. CMC A has a DS similar to that of CMC D, while CMC B has a M_w close to that of CMC D (see Table I).

It is clear from a comparison that the substitution pattern of the CMC molecule is crucial for the morphology of the nanofibers formed (see Fig. 2). The CMC D-based system forms an inhomogeneous and coarse nonwoven sheet [Fig. 2(a)], comprising dense fiber regions as well as looser regions with few fibers. Beads are also present in the nonwoven sheet, most likely a result of pre-aggregation in the solution before electrospinning, outlasting the elongation forces acting during fiber formation. At the higher magnification [Fig. 2(b)], the beads are clearly seen. The beads are more or less spherical in shape, and the SEM image suggests that they are both positioned on the fibers and integrated within the fibers. The CMC A and CMC B-based systems form homogeneous nonwoven sheets and straight nanofibers with individual fibers of even diameter [Fig. 2(c,f)], i.e., similar in appearance to the corresponding nanofibers in Figure 1 at a higher concentration. The similarity indicates that the concentration is of minor significance within the range studied.

The viscosity of the CMC/PEO solutions studied is shown in Figure 3 as a function of the shear rate. All solutions are shear thinning. The highest viscosity is found for the 4% CMC D : 4% PEO solution, which was nonspinnable. High viscosity was also found for 4% CMC B and 4% CMC C-based solutions and, as a consequence, these two systems required a slightly higher voltage to initiate jet formation during electrospinning, i.e., 40 kV compared with 35 kV for the other solutions. The viscosity of a solution is one of several factors that is crucial for spinning ability. A decrease in concentration for the CMC D-based solution results in a lower viscosity and, thus, a spinnable system. It is interesting to note that a higher slope is true for the curve representing the nonspinnable system 4% CMC D (i.e., 4% PEO), indicating a higher shear sensitivity (''unspinnable'' appears to be used in texts referring to politics).
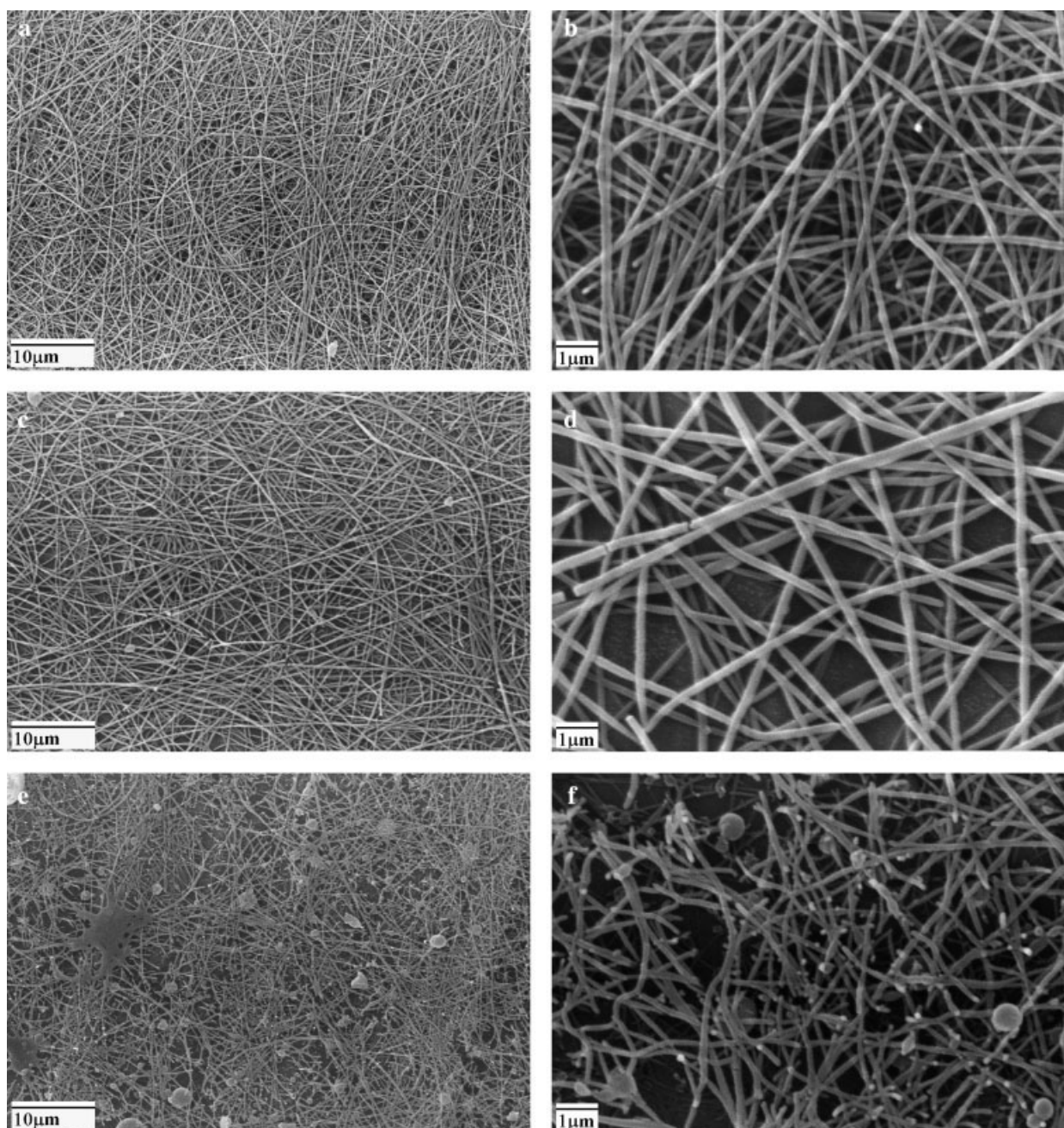
Extraction of PEO

Nanofibers of pure CMC were created by extracting PEO from the CMC/PEO nanofibers described above.
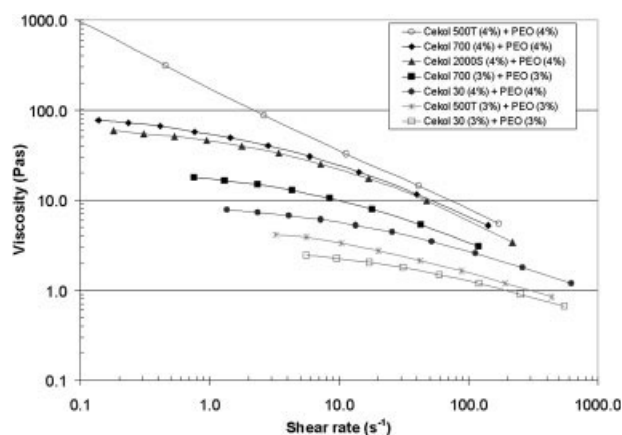

Figure 3 Viscosity as a function of shear rate of the CMC solutions.

The microstructure of extracted nanofibers (6% total concentration) based on CMC A, B, and D is shown in Figure 4 at two different magnifications. The extraction of PEO had different effects on the nanofibers, depending on the CMC derivative. The CMC A- and B-based nanofibers are more or less unaffected by the extraction of PEO [cf. Fig. 4(a,d) with Fig. 2(c,f). Neither the nonwoven sheet nor the individual nanofibers are affected by the extraction. Furthermore, PEO extraction was not found to affect nanofibers based on higher concentrations or on CMC C either (not shown). In contrast,

CMC D-based fibers are highly influenced by the extraction of PEO [cf. Fig. 4(e,f) with Fig. 2(a,b)]. As a result of the extraction, the nonwoven sheet has collapsed, showing dense regions of merged fibers, and the image gives a two-dimensional impression rather than three-dimensional one [cf. Fig. 2(a) and Fig. 4(e)]. At the higher magnification, it is evident that extraction led to disintegrated, individual nanofibers [cf. Fig. 2(b) and Fig. 4(f)]. The findings suggest a different phase distribution of PEO in the fibers, which may most likely be attributed to the different nature of the CMC

Figure 4 SEM images at two different magnifications of fibers made of CMC A (a and b), CMC B (c,d), and CMC D (e,f) after extraction of PEO. The total concentration prior extraction was 6%, and the ratio between CMC and PEO was 1 : 1.
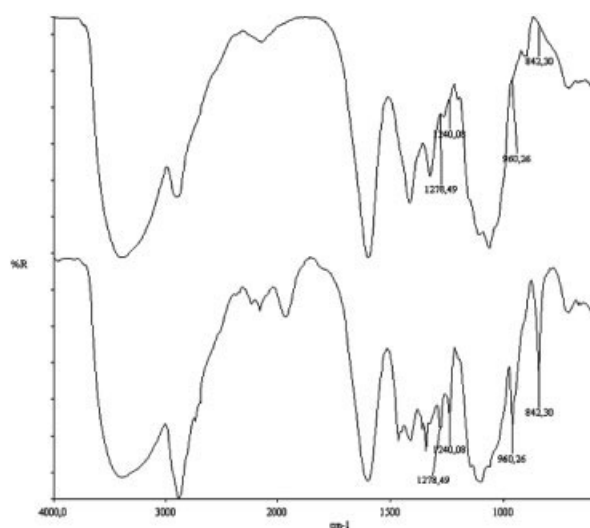
Figure 5 FTIR spectra of fibers made of CMC A before (lower curve) and after extraction (upper curve) of PEO.

derivatives, in particular the substitution pattern, as discussed above. Furthermore, the fact that the beads are found in the extracted nanofibers supports the interpretation that they consist of CMC rather than PEO (see discussion above). The phase distribution in a multicomponent solution may be a crucial factor in

determining the structure of the individual nanofibers. In an investigation on multicomponent systems based on poly(lactic acid) and polyvinylpyrrolidone, Bognitzki et al.[32] found that the phase distribution had completely different effects on the morphologies of the individual nanofibers. Ongoing experiments by the authors are targeting the influence of solution phase behavior of CMC/PEO on the morphology of electrospun nanofibers.

The removal of the PEO in the nanofibers was confirmed by FTIR analysis, and an example is shown in Figure 5. Peaks assigned to the CH_2 groups of PEO,[33] which are at 842, 960, 1240 and 1278 cm^{-1}, disappear after extraction, indicating removal of PEO. This is valid for all the CMC grades used in this study.

Hydroxypropyl methylcellulose

Nanofibers from two different HPMC derivatives with similar M_w and varying DS of the substitution groups were successfully electrospun (see Fig. 6 for SEM images and Table I for characteristics). The two derivatives vary mainly in methoxy content. At the lower magnification [Fig. 6(a,c)], homogeneous nonwoven sheets are shown independent of the substitution content of the HPMC sample. At the higher
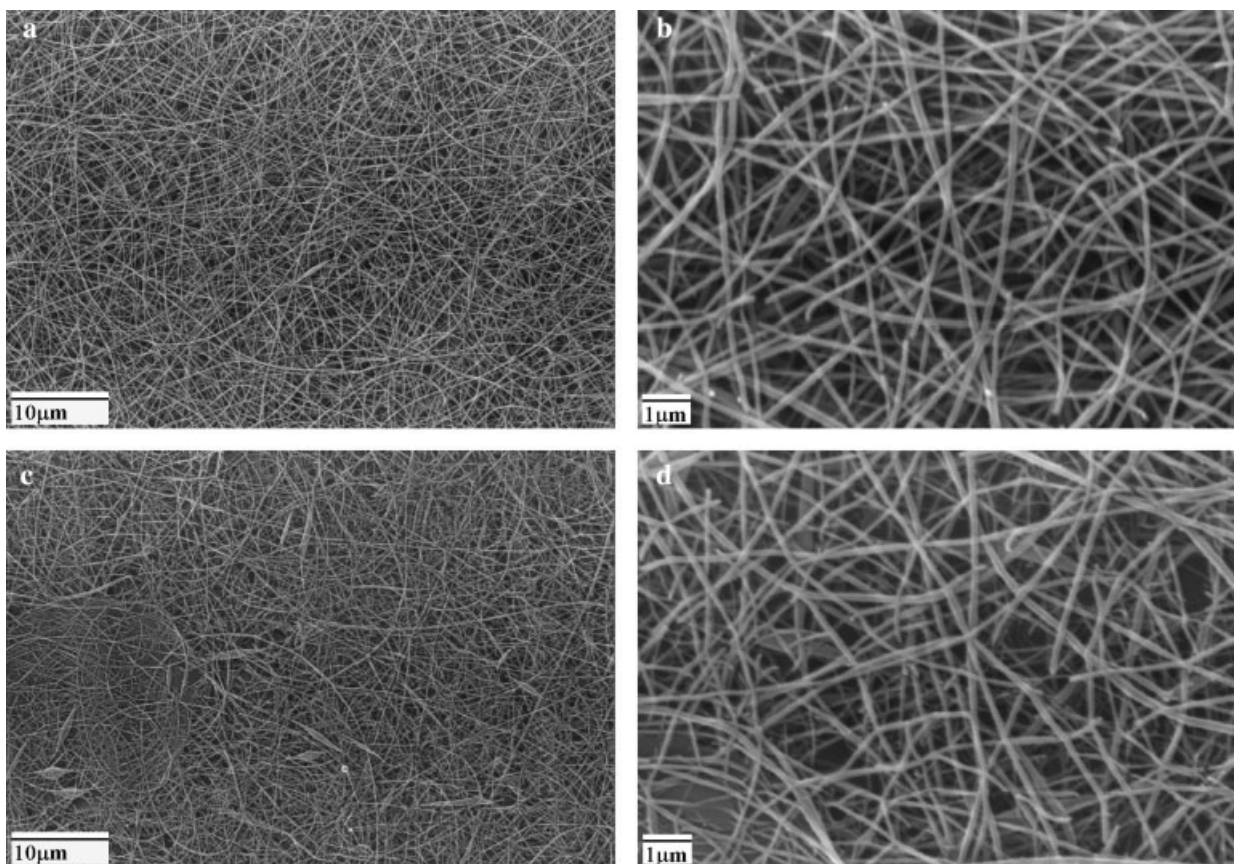
Figure 6 SEM images at two different magnifications of electrospun nanofibers of HPMC in 1 : 1 water/ethanol. (a,b) 2,86% HPMC A; (c,d) 2,14% HPMC B.
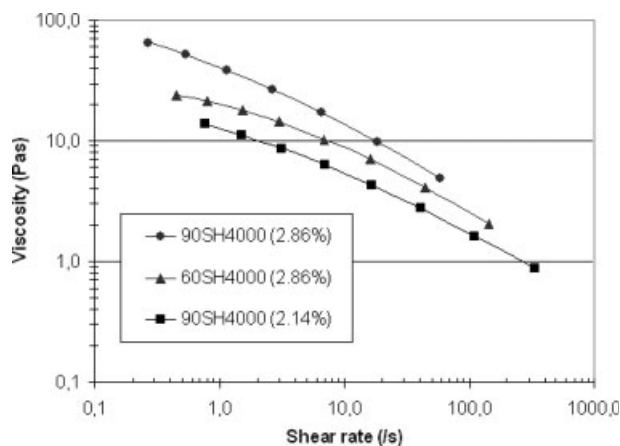
Figure 7 Viscosity as a function of shear rate of HPMC solutions.

magnification [Fig. 6(b,d)], it is also noted that the individual nanofibers are alike. The measured mean diameters of the HPMC A sample [Fig. 6(a,b)] and HPMC B [Fig. 6(c,d)] are 128 nm and 127 nm, respectively. The similarity in nanostructures indicates that the methoxy content of the HPMC only exerts a minor influence on the nanofibers. The behavior of the HPMC is surprisingly similar to that of the CMC, discussed above; i.e., M_w and DS are of no significance for the electrospun nanostructures. Since an influence was found on the nanostructures of the substitution pattern of CMC, it would also be interesting to study the effect of the substitution pattern of HPMC.
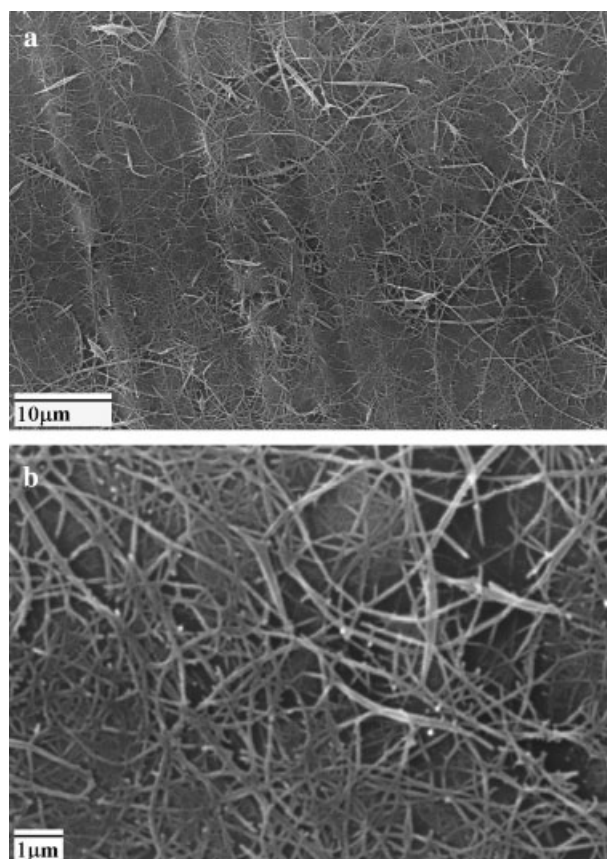
A lower concentration had to be used for the HPMC B-sample (2.14% instead of 2.86% used for the HPMC A sample) to have a spinnable solution. Electrospinning is strongly influenced by the viscosity and the surface tension of the solution. The viscosity during a rate sweep and the surface tension of the HPMC systems at the different concentrations are shown in Figure 7 and Table II, respectively. At a concentration of 2.86%, the HPMC B-solution is not spinnable due to high viscosity and surface tension (see Fig. 7 and Table II). As a consequence, a Taylor cone is not formed during electrospinning since the electrical field strength is too low to overcome the viscous forces and the surface tension. A decrease in concentration to 2.14% adjusts the viscosity and surface tension of the

HPMC B to values that are spinnable and similar to those for HPMC A (concentration of 2.86%) (see Fig. 7 and Table II). The difference in chemical nature (see Table I) between the samples probably accounts for the difference in surface tension and viscosity, thus, influencing the spinnability to a high degree.

To investigate further the influence of the chemical nature of the samples on electrospinning of nanofibers, MC was electrospun under the same conditions as the HPMC (see Fig. 8 for SEM images and Table I for the MC characteristics). Comparison showed that the MC sample has a zero hydroxypropoxy content, while its methoxy content and viscosity are similar to those of the HPMC B. At the lower magnification [Fig. 8(a)], a nonwoven sheet is found comprising dense areas of merged fibers, giving a two-dimensional impression. At the higher magnification [Fig. 8(b)], uneven, coarse fibers with a broad diameter distribution are shown. Areas with merged fibers are mixed with areas of individual, coarse fibers. The nanostructures formed are typical when electrospun fibers that are not dry land on the collector. A voltage of 40 kV was required to initiate electrospinning. Comparison with the nanostructures created for the

TABLE II
Surface Tension and Spinnability of the Different HPMC Solutions in 1 : 1 Water : Ethanol

Material	Concentration (%)	Surface tension (mN/m)	Spinnable
60SH4000	2.86	36.3	Yes
90SH4000	2.86	41.8	No
	2.14	36.6	Yes

Figure 8 SEM images at two different magnifications of electrospun preliminary nanofibers, based on 2.86% MC in 1 : 1 water ethanol. The electrospinning was conducted under 40 kV.
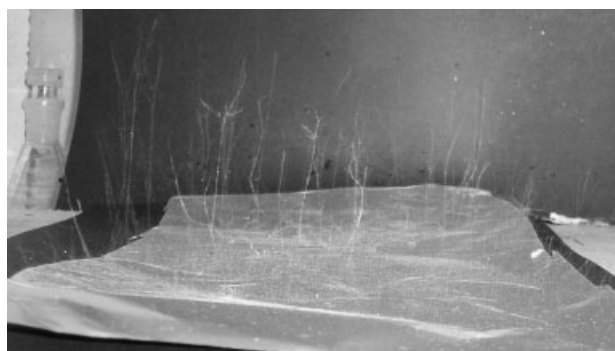
Figure 9 Standing fibers observed during electrospinning of cellulose dissolved in LiCl : DMAc. The electrospinning was conducted under 15 kV.

HPMC derivatives (Fig. 6) suggests that the hydroxypropoxy content influences the spinnability of the systems. Further in-depth studies are required to confirm these suggestions.

### Preliminary fibers from systems of cellulose and LiCl : DMAc

Preliminary fibers were electrospun from solutions containing 3% enzymatically treated cellulose in a solvent of 8% LiCl in pure DMAc solution using a voltage of 15 kV. The spun fibers did not form the general nonwoven sheet resulting from electrospinning, but rather stood straight up in the electrical field (see Fig. 9). The phenomenon may be related to the high amount of salt, mainly Li^+ and Cl^-, present in the nanofibers. The high charge may cause a positive charge on the nanofibers that forces them to stand up in the negative field. Upon speculation, a positive overall charge of the fibers may indicate that the Li^+ ions are more strongly connected to the cellulose molecules than the Cl^- ions, or that the Cl^- ions are pulled toward the grounded plate by the electrical field whilst the Li^+-ions prefer the high negative charge at the tip of the nozzle. If the fibers have a positive charge that corresponds to the inverse of the field in which they are situated, they will be affected as if they were in a field with the potential zero. In this case, the fibers will have no desire to go to the grounded plate and will stand straight up in the electrical field between the nozzle and the collector. Of course, these are only suppositions and would need deeper investigation to be confirmed.

When the electric field is turned off, the fibers collapse on the collector and lose their shape. The loss of shape is believed to occur due to the fact that DMAc is not volatile enough, which results in non-solidified fibers. Several fibers contract into drops on the collector, but it is still possible to observe some fibers remaining [see Fig. 10(a)]. When a plastic film was used as a collector instead of aluminum foil, the same standing fibers were obtained, but some fibers managed to keep their shape even after the field was turned off [Fig. 10(b)]. The appearance of these fibers is very similar to those produced by Frey's group using a solvent system of ethylene diamine/thiocyanate salt.[28] The different behavior of the preliminary fibers on the two collector materials can be due to the interfacial tension. The wettability of the plastic film is low, but the aluminum foil has an oxygenated surface and thus has a much higher wettability. An additional explanation could be that the different collectors vary in their ability to transport the electrical charges, resulting in slightly different experimental conditions in the electrospinning process. This might influence the surface tension, the drying process or other important mechanisms.

CONCLUSIONS

Solutions of enzymatically treated cellulose and cellulose derivatives HPMC, CMC, and MC have been electrospun, and nonwoven sheets of nanofibers with different morphologies have formed. The influence of the M_w and DS of the CMC and HPMC derivatives proved to be of no significance for the electrospin-
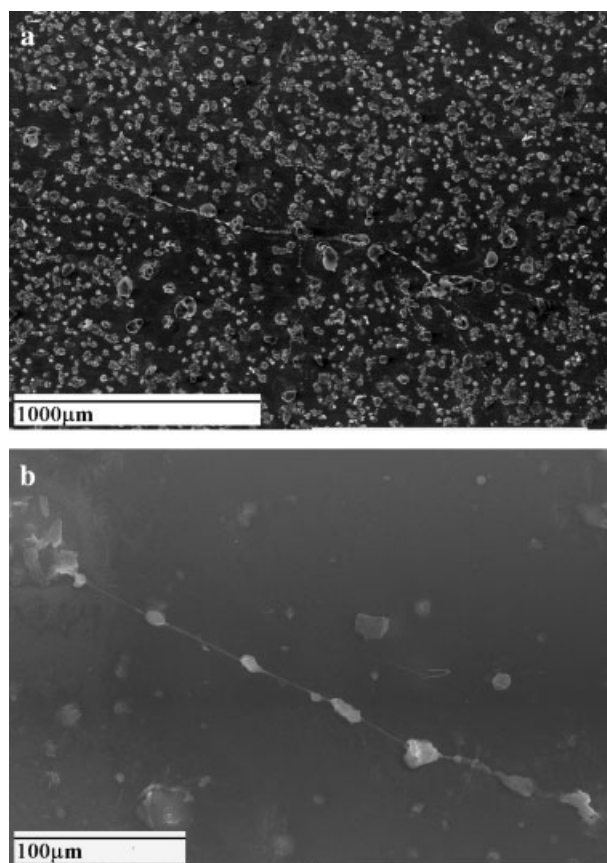
Figure 10 SEM images of electrospun cellulose in LiCl : DMAc. (a) Aluminum foil as collector. (b) Plastic film as collector.

ning process, and the resulting nanostructures, i.e., homogeneous nonwoven sheets, were formed from even nanofibers. In contrast, the substitution pattern of carboxymethyl groups on the CMC derivatives proved to be crucial for the appearance of the nanofiber web as well as the morphology of individual nanofibers. A blocky substitution resulted in the formation of an inhomogeneous and coarse nonwoven sheet with spherical beads, which seemed to be positioned on the fibers or integrated within the fibers. Four different CMC derivatives were electrospun in a mixture with PEO. Extracting PEO resulted in pure CMC nanofibers that varied in appearance according to the substitution pattern, indicating a different distribution of PEO in the bicomponent nanofibers. Preliminary fibers were electrospun from enzymatically treated cellulose with LiCl : DMAc as the solvent system.

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