Nanocomposite Fibers Electrospun from Biodegradable Polymers

Chunhui Xiang, Margaret W. Frey

Department of Fiber Science & Apparel Design, Cornell University, Ithaca, NY 14853, USA

Abstract

Cellulose fibrils were prepared by sulfuric hydrolysis and incorporated into dimethylfomamide (DMF) by ultrasonicaiton to obtain a stable suspension. The morphology of cellulose nanofibrils in DMF was studied by TEM and the results indicated that cellulose nanofibrils were able to disperse into DMF. Nanocomposite fibers were electrospun from PLA-cellulose nanofibrils/DMF suspension at elevated temperature and collected as randomly oriented non-woven fabrics. Effects of the cellulose nanofibril content on the electrospun non-woven fabrics on the fabric physical properties and morphology were studied. As the concentration of cellulose (on the weight of PLA) increased, the uniformity of the electrospun nanocomposite fibers changed. Crystallinity of the electrspun non-woven fabrics was determined by wide angle diffraction (XWRD). The addition of cellulose nanofibrils increased the crystallinity of the electrospun PLA non-woven fabrics.

Key words: Cellulose; Nanofibrils; Poly(lactic acid) (PLA); Electrospinning; Biodegradable.

Introduction

Electrospinning provides a method to produce nanofibers with high specific surface area and great surface to mass ratio. Moreover, a significant implication of the mechanism of electrospinning is that it allows a bicomponent system that will have properties from each of the polymeric components, e.g., one of the polymers could contribute to hydrophilicity while the other could enhance the hydrophobicity of the resulting non-woven fabrics.

Poly(lactic acid) (PLA) is a highly versatile, biodegradable, aliphatic polyester derived from 100% renewable resources, such as corn and sugar beets. PLA offers great promise in a wide range of commodity applications. PLA has been investigated widely via electrospinning techniques. [1-3] Additionally, a wide variety of materials have been incorporated in electrospun PLA fibers to tailor the fibers for particular end uses. [4] Frey et al. reported that the average diameter of PLA electrospun from 22 wt. % PLA/DMF solution at 70 ºC was 281 nm. [5]

Cellulose in the form of nanofibrils is the load-bearing constituent in plants. Cellulose nanofibrils are arranged in bundles of 10 – 50 nm width. Cellulose nanofibrils have fine diameter, large aspect ratio (fiber length divided by diameter), biocompatibility, high strength and modulus as well as other favorable physical properties associated with the highly crystalline extended chain conformation. Advanced materials based on this constituent are therefore likely to be developed in the near future. [6]

Researchers have successfully produced cellulose micro/nano fibrils with an average length smaller than 200 nm. [7] A problem is that once the micro/nano fibrillated cellulose is dried, it is very difficult to disperse since hydrogen bonds cause strong adhesion between the individual micro/nano fibrils. Marcovich et al. [8] reported that a stable suspension of cellulose nanocrystals was obtained in DMF. After the hydrolysis treatment, the cellulose nanocrystals were freeze-dried and re-dispersed by ultrasonic agitation in DMF.

In this study, cellulose micro/nano fibrils hydrolyzed from cellulose microcrystalline was produced and incorporated into PLA/DMF solution before electrospinning. Nanocomposite fibers were electrospun from PLA-cellulose/DMF suspension at elevated temperature. The morphology of cellulose nanofibrils and the electrosopun non-woven fabrics was studied. The effect of cellulose content on the crystallinity of the electrospun PLA non-woven fabrics was explored by wide angle X-ray diffraction.

Experimental

A. Materials

Microcrystalline cellulose powder (MCC, extra pure, average particle size 90 μm) was purchased from Acros Oganics. Poly(lactic acid) (PLA) (Mw = 211, 332 Da, Mn = 109,337 Da, density = 1.25 g/cm^3) were supplied by Cargill Dow (Minnetonka, MN). Ion exchange Rexyn I-300 (H-OH) was purchased from Acros Oganics. Sulfuric acid (96.1%, density = 1.84 g/cm^3) was purchased from J. T. Baker. N, N – dimethylformamide (DMF) was purchased from Mallinckrodt Laboratory Chemicals (Phillipsburg, NJ). All regents were used without further purification.

B. Methods and techniques

1. Preparation of cellulose nanofibrils

The starting material to produce cellulose nanofibrils was cellulose microcrystalline powder. The MCC was treated by acid hydrolysis in a concentrated sulfuric acid solution (64 wt.% sulfuric acid in water). The ratio of MCC to acid solution was 1 – 8.75 g/ml. The treatment was conducted at 45˚C for 1hr under strong stirring. After the hydrolysis treatment, the cellulose suspension was further dispersed by an ultrasound treatment (10 min at full power) with an ultrasonic liquid processor (Misonix Sonicator® 3000) in an ice bath. This hydrolysis condition was

based on the work Dong et al. [7]. After the hydrolysis treatment, the hydrolyzed cellulose was washed twice with distilled and deionized water, separating the cellulose nanofibrils from the suspension by centrifugation (13500 rpm, 10min) after each wash.) Then the cellulose suspension was dialyzed against distilled and deionized water with some ion-exchange (Rexyn I-300 (H-OH)) for 3 days with 12 – 14K molecular weight cutoff dialysis tubing. After dialysis, the pH value of the cellulose suspension was close to netural (3 ~ 4). Then the dialyzed suspension was ultrasonicated for further dispersion. The final aqueous suspension was centrifuged and freeze–dried (Labconco Freeze Dry System/ Freezone® 4.5) to avoid re-agglomeration of the cellulose crystals. The dried cellulose nanofibrils were re-dispersed by ultrasonication in DMF.

2. Preparation of electrospinning solution and nanofiber non-woven fabrics

After the cellulose was dispersed in DMF, PLA was added to the cellulose/DMF suspension and the mixture was brought to 70˚C for full the dissolution of PLA in DMF. 25 wt.% PLA/DMF solution was prepared. 0, 1 wt.% and 10 wt.% cellulose (on the weight of PLA) was added to the PLA/DMF solution. The PLA-cellulose/DMF suspension was electrospun at 70˚C, 15 kV voltage, 10 μL/min feed rate, 10 cm collection distance, 0.57 mm (O.D.) needle size, and using aluminum foil as the collector. During electrospinning, the suspension temperature in the syringe was controlled by a shielded heating unit pre-heated to 70 ˚C and controlled to ± 1˚C with a Watlow controller (St. Louis, Missouri) [9]. The needle was heated with a Varitemp® heat gun (Master Applicance Corp., Racine, WI) to 70 ± 5˚C. All samples were collected for 3 hours.

3. Microscopy

One drop (8μL) of a 0.1 wt.% cellulose/DMF suspension of the cellulose nanofibrils was allowed to dry on a Formvar and carbon coated grid (200 mesh). The cellulose nanofibrils were stained with 0.2% aqueous uranyl acetate. TEM micrographs were taken at 120 kV with a transmission electron microscope (TEM, Technai T12). The morphology of electrospun non-woven fabrics was observed by a scanning electrotron microscope (SEM, LEICA 440). The fibers were coated with gold and platinum and observed under 25 kV accelerating voltage.

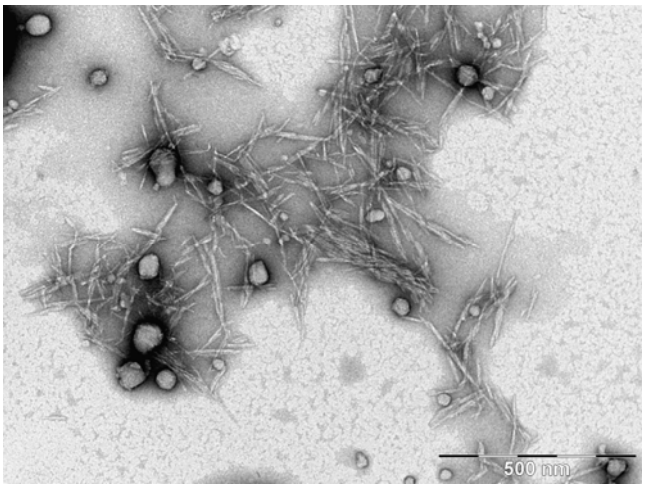
4. X-ray diffraction

Wide angle X-ray diffraction (WAXD) was conducted with a Scintag PADX diffractometer using an incident X-ray wavelength of 1.542 Å. Samples were scanned from 2θ = 2 º to 39.98 º at a step rate of 0.03 º to qualitatively analyze cellulose nanofibril and its addition to PLA non-woven fabrics. The resulting plot of X-ray intensity versus 2θ was analyzed by the profile-fitting program DMSNT ThermoARL. Areas of the peaks obtained from the analysis were used to estimate the degree of crystallinity of each phase, i. e., the ratio of the area of the crystalline reflections to that of the total area of the crystalline and amorphous phases.

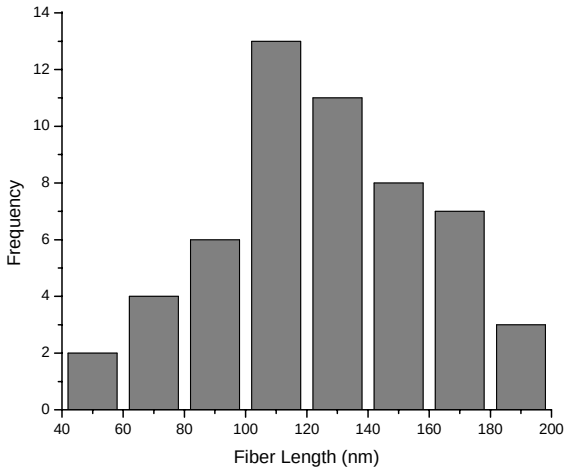
Results and discussions

1. Characterization of cellulose nanofibrils

The morphology of cellulose nanofibrils in DMF after re-dispersion with ultrasonication is shown in Figure 1 (a). Cellulose was re-dispersed into DMF by ultrasonication. The average length of cellulose nanofibrils is 123.8 ± 34.7 nm by measuring 54 single cellulose nanofibrils from the TEM pictures. The size distribution of cellulose nanofibrils is shown in Figure 1 (b). The length of cellulose nanofibrils is between 40nm and 200nm. This provides the possibility of adding cellulose nanofibrils into the electrospun PLA fibers.



(a)



(b)

Figure 1. (a) TEM picture of cellulose nanofibrils re-dispersed in DMF by ultrasonication. (b) The size distribution of cellulose nanofibrils.

The X-ray patterns of the cellulose samples are shown in Figure 2. Sample A is cellulose microcrystallines, the starting material, and sample B is the products. The X-ray pattern did not change after the treatment. Both show strong peaks at 2θ = 16.7 º and 22.6 º, which are the characteristic peaks of cellulose. The principal reflections in a native cellulose (cellulose I) is that the 2θ locates at 14.4 º, 16.6 º, and 22.5 º. [10] The diffraction patterns of the hydrolyzed samples still showed the typical reflections to cellulose I, which indicated that the crystal integrity of cellulose had been maintained during the hydrolysis process. However, the degree of crystallinity of cellulose microcrystalline obtained from wide angle X-ray diffraction pattern is 63.02%. The degree of crystallinity of cellulose nanafibrils from the X-ray pattern is 47.7%. The decrease of the degree of crystallinity indicates that the hydrolysis not only occurred in the amorphous regions but also affected the cellulose crystals.

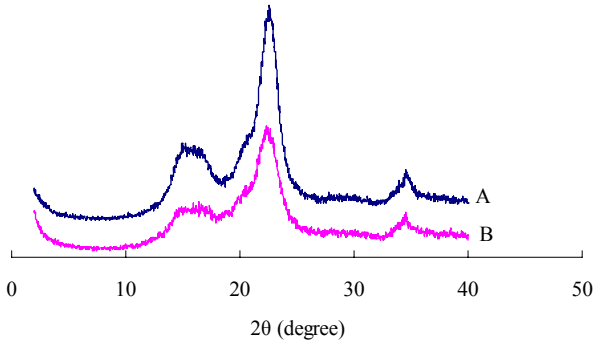
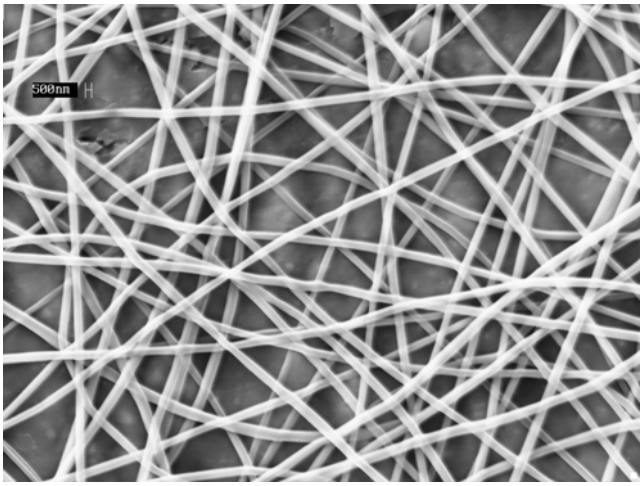
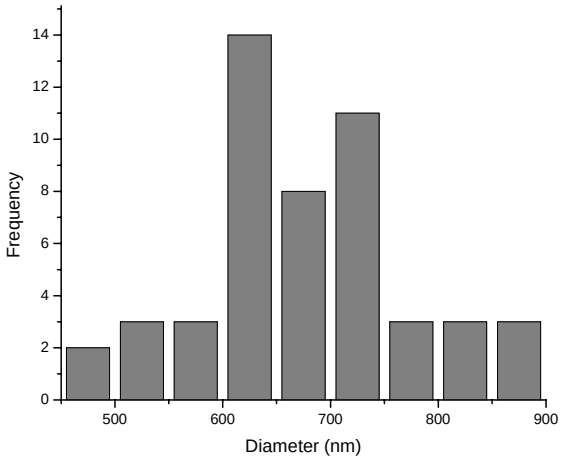


Figure 2. X-ray diffraction patterns of cellulose samples: A: microcrystallines; B: nanofibrils.

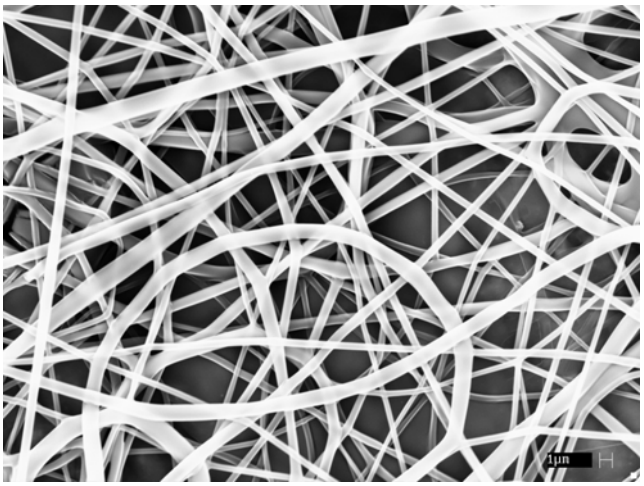
2. Morphology of electrospun non-woven fabrics

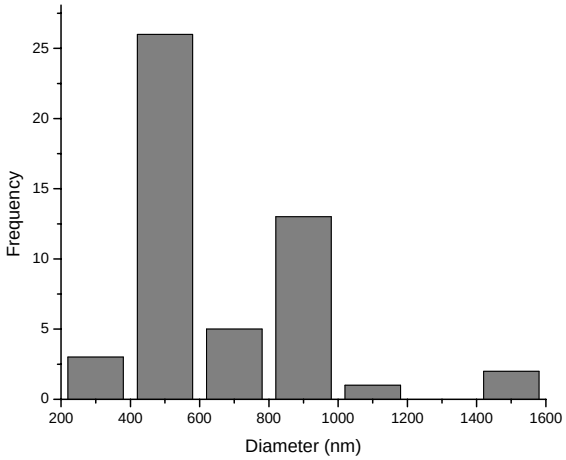
The morphology and diameter distribution of the electrospun non-woven fibers is shown in Figure 3. As the cellulose concentration increased, the diameter uniformity of the electrospun fibers changed. Figure 3 (a) shows the morphology diameter distribution of pure the PLA fibers electropun from dimethylformamide (DMF) solution at 70˚C. The average fiber diameter is 675.4 ± 95.0 nm by measuring 50 electrospun fibers from the SEM pictures. Figure 3 (b) and (c) show the morphology and diameter distribution of the nanocomposite fibers electrospun from 1 wt.% cellulose and 10 wt.% cellulose added to PLA/DMF respectively. Nanocomposite fibers electrospun from 1 wt.% cellulose-PLA/DMF suspension have an average diameter of 650.4 ± 253.7 nm, and the fibers from 10 wt.% cellulose nanofibrils have an average diameter of 662.2 ± 188.4 nm. The addition of cellulose nanofibrils broadened the fiber diameter distribution. This may be because cellulose nanofibrils changed the viscosity of the PLA/DMF solution and hence influenced the morphology of the electrospun nanocomposite fibers.



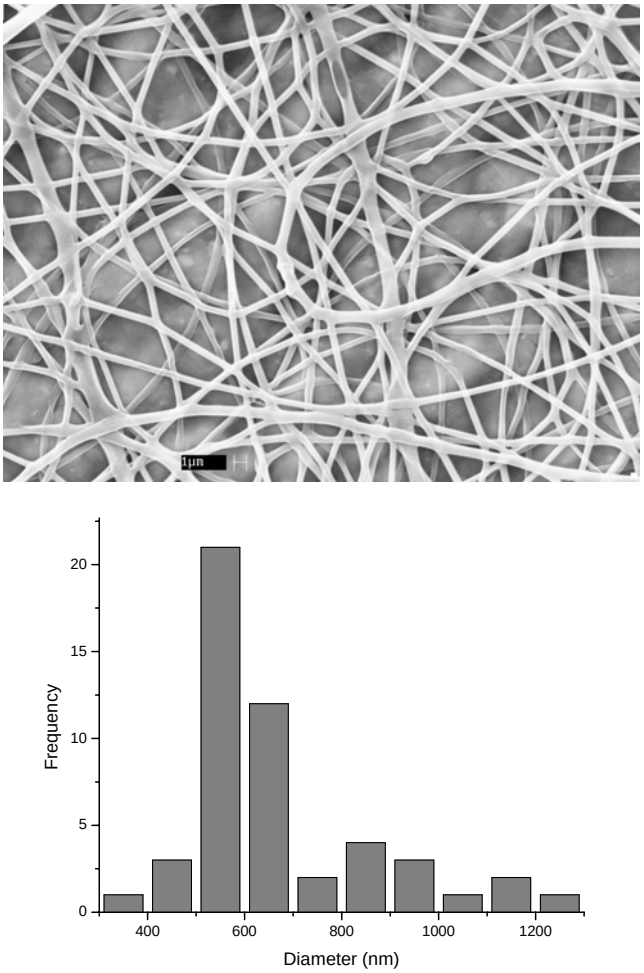


(a) The morphology and diameter distribution of the fibers electrospun from 0 wt% cellulose in 25 wt.% PLA/DMF solution at 70˚C.





(b) The morphology and diameter distribution of fibers electrospun from1 wt.% cellulose in 25 wt.% PLA/DMF suspension at 70˚C.



(c) The morphology and diameter distribution of fibers electrospun from 10 wt.% cellulose in 25 wt.% PLA/DMF suspension at 70˚C.

Figure 3. The morphology and fiber diameter distribution of the electrospun non-woven fabrics.

3. X-ray diffraction

Figure 4 shows the X-ray pattern of the electrospun PLA non-woven fabrics and the electrospun PLA non-woven fabrics contained 10 wt.% (on the weight of PLA) cellulose nanofibrils. The electrospun PLA non-woven fabrics showed a broad diffraction pattern, which indicated the amouphous state of PLA. As our expected, the electrospun PLA non-woven fabrics containing 10 wt.% cellulose exhibited strong peaks at 2θ = 16.9 º and 22.8 º. These two peaks are the characteristic peaks of cellulose. The addition of cellulose nanofibrils into the electrospun PLA nanofibers changed the crystallinity of the PLA non-woven fabrics.

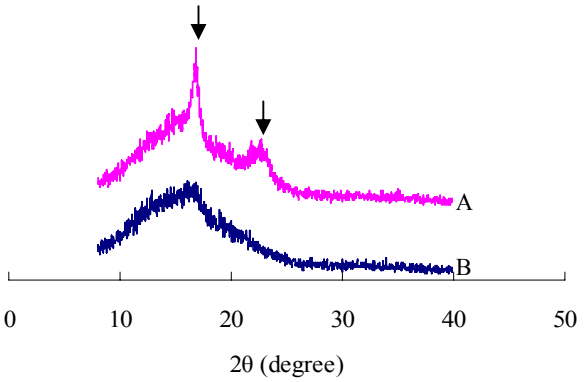


Figure 4. X-ray diffraction patterns of the electrospun non-woven fabrics. A: 10 wt.% cellulose nanofibrils in the electrospun non-woven fabrics; B: pure PLA electrospun non-woven fabrics.

Conclusion

Cellulose nanofibrils were successfully produced by sulfuric hydrolysis. PLA non-woven fabrics containing 1 wt.% and 10 wt.% cellulose nanofibrils were successfully electrospun at 70˚C. As the cellulose concentration increased in PLA, the morphology of the cellulose changed. Nanocomposite fibers containing 10 wt.% cellulose nanofibrils were flatter than the fibers containing 1 wt.% cellulose nanofibrils.

Acknowledgements

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