High-Performance Nanofibers and Nanostructures for New Generation Multifunctional Materials

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Abstract

The recent interest in nanotechnology has triggered research on nanofibers and nanostructures. Here we present our work on fiber-based multifunctional materials including nanofibers obtained via electrospinning processes. Such nanofibers are of potential value given the highly porous structures they form and their large surface area-to-volume ratio which is often required in high performance applications. We investigated cellulose-based microstructures that may offer unique opportunities due to its high stiffness and strength as well as the possibility of subsequent surface chemical modification.

Our research involved first the isolation of cellulose whiskers from filter paper followed by the incorporation of the whiskers in hydrophobic polymer (polystyrene) matrices. The overall aim is to tailor the functionalities and properties of the resulting composites. Cellulose filler and polymer matrices were casted as composite films. These films together with electrospun webs were characterized using scanning electron microscopy (SEM).

The preliminary results show that the nanofibers produced had average diameters of 250 - 300 nm. Also, there is a significant effect on the cellulose whiskers concentration on the storage modulus of the composite (MPs). As the concentration of cellulose whiskers is increased a significant increase on the storage modulus is observed, compared with a control film (no cellulose whiskers added). We used surfactants to increase the stability of the dispersion. However, it was found that there is an optimum surfactant concentration to obtain films with the highest strength.

Introduction

Cellulose based microstructures offer unique opportunities due to its high stiffness/ strength, hydrophilicity, biocompatibility, stereoregularity, biodegradability, chemical stability, and the ability to form superstructures as well as the possibility of subsequent surface chemical modification. Depending on their origin, cellulose nanocrystals have diameters ranging from 3 to 20 nm with a high aspect ratio [1-3]. In spite of the abundance of cellulose as a biological raw material, the utilization of cellulose as a component in microcomposites is largely unexplored. Several uses have been identified for such nanocrystals to work as fillers of composite materials [4-8], food products (non-caloric thickening agents) [9], edible coatings [10], drug delivery agents [11], etc. Current interest in the development of sustainable bio-based economies as well as the emerging shortage of fossil fuels is expected to promote further study into these alternatives.

In utilization of cellulose microfibrils as an additive or filler, a homogenized dispersion of the cellulose filler within the matrix materials should be pursued in order to obtain uniform properties of the final product. The aggregation of filler or additive would have undesirable effect on the final products including poor mechanical properties due to the load transfer

mechanism failure as well as non-uniform appearance [12, 13]. However, it is not trivial to obtain the product without aggregation of cellulose fibrils, especially when they are used with hydrophobic matrices, mainly due to the intrinsic filler attraction and incompatibility with the hydrophobic polymer matrix. In order to keep the cellulose from aggregation and improve dispersion in the matrix material, modification of hydrophilic surface of cellulose has been studied including the method of graft polymerization [13-15], silylation of –OH group in cellulose [16-20], surfactant treatment [13, 21], etc. Among those, surfactant treatment is of particular interest due to its simplicity of application to enhance the compatibility between the hydrophilic fillers and the hydrophobic matrices or solvent. Here the hydrophilic group of the surfactants may be adsorbed on the cellulose whiskers whereas hydrophobic groups would be present in the hydrophobic solvent or matrices, deterring formation of aggregation.

Electrospinning is a novel processing techniques for the production of nonwoven mats of which fibers in a few nanometers to tens of micrometer diameter [22-26]. Electrospinning as a nano-scale fabrication process will be attempted with the polymer solution containing micro or nano sized cellulose fillers in this study.

The specific purpose of this study include the isolation of cellulose fibrils of micro or nano size (cellulose whiskers) from cellulose paper and the integration of cellulose whiskers with a hydrophobic polymer matrix, polystyrene (PS), in order to tailor the functionalities and properties of the resulting composites. For fine-tuning adhesion of cellulose fibrils to surrounding matrices, surfactant was used to stabilize the dispersion of hydrophilic cellulose whiskers in hydrophobic solvent and matrices. Cellulose filled PS matrices were casted as composite films and also electrospun to form nonwoven mats. Electrospinning allowed for unique control over the fiber formation process and facilitated the development of fundamental relationships between process operating parameters and micro or nano fiber properties.

Experimental Protocols

Materials

Polystyrene (Mn = 140,000/Mw = 230,000 and Tg = 94.0 ^{o}C), Whatman$^{®}$ No.1 cellulose filter paper, hydrochloric acid (HCl) and sorbitan monostearate (Span 60) were purchased from Sigma-Aldrich (St. Louis, MO).   Tetrahydrofuran (THF) was obtained from B&J Brand^{TM} (Muskegon, MI). All chemicals and solvents were stored and used as received.

Protocols

Preparation of cellulose whiskers

Cellulose microfibrils whiskers were obtained by HCL acid hydrolysis of Whatman$^{®}$ cellulose filter paper. A volume of 700 mL of 1.5 M HCL was added to 20 g of filter paper, and the cellulose was hydrolyzed at 100˚C for ~4 hrs after being ground by 10 Speed Osterizer$^{®}$ Blender. After the hydrolysis, the cellulose solution was diluted with deionized water and centrifuged at 2800 rpm, afterwards clear upper layer of acid was removed. After four to five times of acid rinsing, fine cellulose microfibrils become dispersed in water solution. The turbid layer with small sizes of microfibrils of centrifuged solution was collected. This turbid layer would include the cellulose particles (whiskers) with small sizes, up to several micrometer lengths. In order to remove very small particles with small aspect ratio, the collected turbid

solution was further centrifuged at 8,000 rpm for 30 min and then at 14,000 rpm for the following 30 min, using Automatic Servall® Superspeed Centrifuge. Very fine particles in the upper layer were removed, and the microfibril deposits after the high speed centrifugation were freeze dried using a Labconco system (Kansas City, MU).

Preparation of composite film

Composite films were prepared by solvent casting, using polystyrene (PS) as a matrix polymer and cellulose whiskers (C.W.) as a filler material. A solution of 10 wt % of PS and C.W. in tetrahydrofuran (THF) was prepared and cast in a Fisher brand® weighing dish made of aluminum (Fisher Scientific, Pittsburgh, PA). The composite film was prepared by evaporating the solvent in ambient condition under hood. The wt. ratio of PS to C.W. used in composite films was 97:3 and 94:6. In order to investigate the effect of Span 60 on the degree of dispersion of C.W. in composite film, different ratios of C.W. to Span 60 were used as: 1:0, 1:1, 1:2 and 1:4. Prepared composite films were analyzed by using optical microscopy (Olympus BH2-UMA, Japan, equipped with a video camera Sony® DXC-970 MD) at 100X.

Electrospinning experiments

Electrospinning of composite materials were carried out using custom made electrospinning equipment [25, 26]. Our setup was designed to ensure operation in a uniform electric field that is generated between two parallel plates. The bottom plate is aligned vertically with the top plate, thus forming the geometry of a small capacitor with parallel field lines. The reservoir (Luer-Slip Plastic Sryinges, National Scientific Co.) of polymer solution is loaded into the plastic syringes (between 25 ml and 50 ml) using the syringe pump (Model No. NE-500, New Era Pump System Inc.). Then, the polymer solution is delivered to the aluminum capillary tube located on the stationary top plate using C-Flex Teflon tubing (inside diameter of ~ 0.125 inches) and the polymer solution is exposed to a high electrical field. The flow rate solution is adjusted and controlled by Pupmterm software. The electrical charge that develops at the fluid's free surface interacts with the external electric field, resulting in the emission of a steady fluid jet that thins as it accelerates downfield. A power device (Series EL, Model No. PS/EL50P00.8, Glassman High Voltage, Inc.) supplies up to 50 kV (range from 0 to 50 DV Kilovolts) to the lower plate used as a target to collect the nano-fibers. Measurements were reproducible to within + 0.5 kV. The applied voltage was changed and repeated to cover a large range of low and high flow rates in order to map out bounds for each transition region. Also, the electric current between plates was measured with the same instrument within a range from 0 to 1 DC Milliamperes (Glassman High Voltage, Inc.). A Digital Stroboscope (Model No. DT-301 SHIMPO, Shimpo Industrial Co., LTD) helped to enhance the images of rapidly varying jets as they show instabilities. The stroboscope was placed close to the apparatus to have a better dynamic visualization of the nano-fibers before reached the collection plate.

Solution concentration was changed in order to find the optimum condition for electrospinning of the material. Weight concentrations of PS and C.W. solution were changed from 10 to 20 %. Electrospinning parameters including flow rates (ml/min), spinning voltage (kV), and working distance (cm) were varied depending on the material compositions and whipping motion during electrospinning experiments.

Scanning Electron Microscopy analysis

The resulting composite nanofibers were characterized using scanning electron microscopy (SEM). A Hitachi S-3200N variable pressure SEM was used to obtain the

microphotographs (images) of the nanofibers formed during the electrospinning experiments. This instrument is a conventional high resolution thermionic SEM that used an accelerating voltage from 0.3 to 30 kV with a working distance between 3 mm and 60 mm. The nanofibers collected on to aluminum foil were shadowed with a layer (~150 A^o thick) of gold-palladium (Au/Pd) in order to prevent charging of the nanofibers.

Results and Discussion

Isolation of cellulose whiskers in micro/nano-scale sizes

Cellulose fibrils (micro or nano size) or cellulose whiskers were obtained from cellulose filter paper. Amorphous regions at the interface of microcrystalline domains in these fibers (along the microfibril length) were removed by acid treatment to produce microcrystals. Cellulose microfibrils obtained by HCl hydrolysis had rod-like shape. The cellulose whiskers are expected to have high mechanical modulus and therefore are expected to be excellent candidates in the manufacture of composite materials. The characterization of the cellulose whiskers was accomplished via atomic force microscopy (AFM). The length and the width of the whiskers were determined to range from 0.80 to 5.3 μm; and from 0.16 to 0.51 μm, respectively as shown in Figure 1.
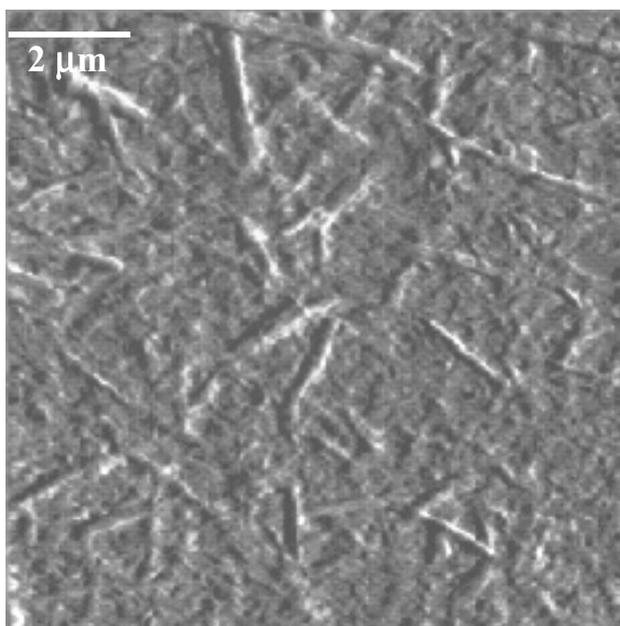
Figure 1. AFM images of cellulose whiskers obtained from acid hydrolysis of cellulose paper.

Electrospinning of composite mixture

The operating electrospinning conditions such as flow rate, distance between the two parallel plates, capillary inner diameter size and applied voltage were initial screened to determine the conditions that would ensure the formation of nanofibers [26]. Polymer solutions

in THF containing 6 wt % of cellulose fillers were prepared for electrospinning. The concentration of polymer solution was varied from 10 to 30 wt % to achieve the optimum condition in electrospinning. The 20 wt % polymer solution with cellulose whiskers was found to produce beadless nonwoven fibers. For later preparation of sample solution, 20 wt % of polymer and filler solutions were employed with or without of Span 60 or without Span 60 (0.6 wt %) This concentration was found to show the best dispersion properties in composite films. Figures 2 - 4 show the fibers produced by different experimental electropinning conditions.

Dynamic Mechanical Analysis (DMA)

DMA tests were performed on the polystyrene films obtained by film casting. The determination of the storage modulus (G') of the cast films (Figures 5 and 6) were performed instead of the measurements of the mechanical properties of fibers obtained by electrospinning due to the limitation of the DMA's instrument.

Figure 5 shows the effect of adding cellulose whiskers. Note that the curve with the lowest storage modulus corresponds to polystyrene film with no added cellulose whiskers. G' is related with the elastic energy of the material. As the cellulose content is increased the storage properties are improved. On the other hand, Figure 6 illustrates the detrimental effect of excess surfactant. As more surfactant is added to the composite lower storage modulus are observed.
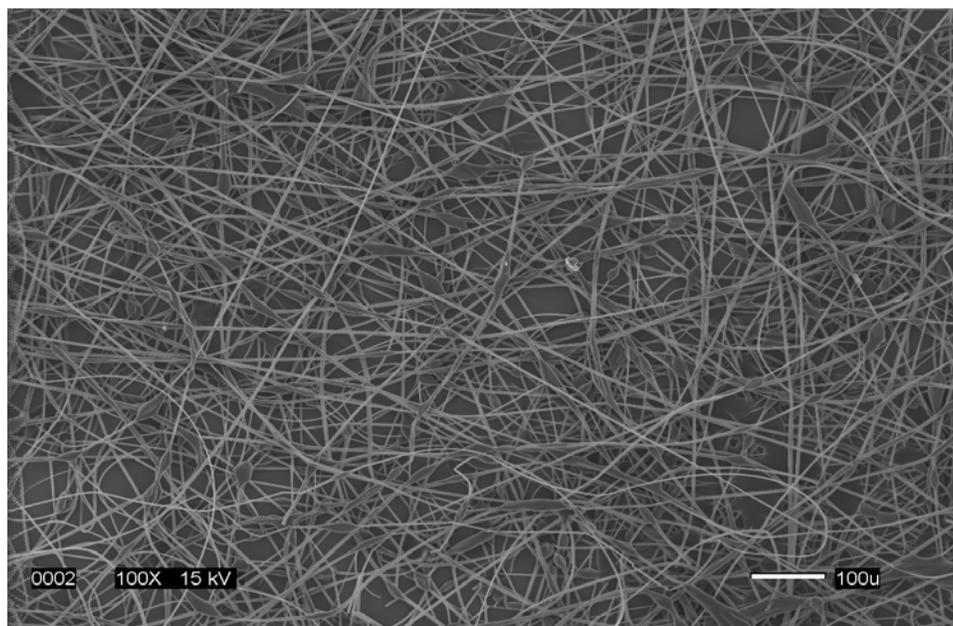
Figure 2. SEM micrographs of polystyrene electrospun webs (fibers diameter of 2 – 7 μm). Experimental conditions included polystyrene in THF (15 wt %), 30 KV voltage, plates separation of 20 cm and volumetric flow rate of 0.35 ml/min.
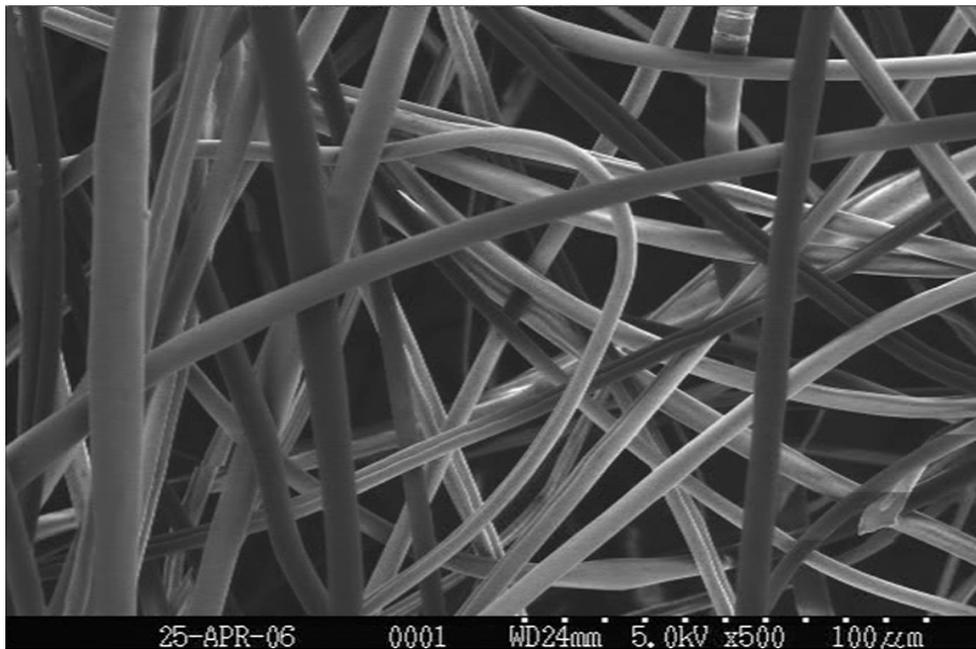
Figure 3. SEM micrographs of composite electrospun webs (fibers diameter of 2 – 9 µm). Experimental conditions included polystyrene (15 wt %) in THF (Ratio:PS:C.W. = 97:3), 35 KV voltage, plates separation of 20 cm and volumetric flow rate of 0.30 ml/min.
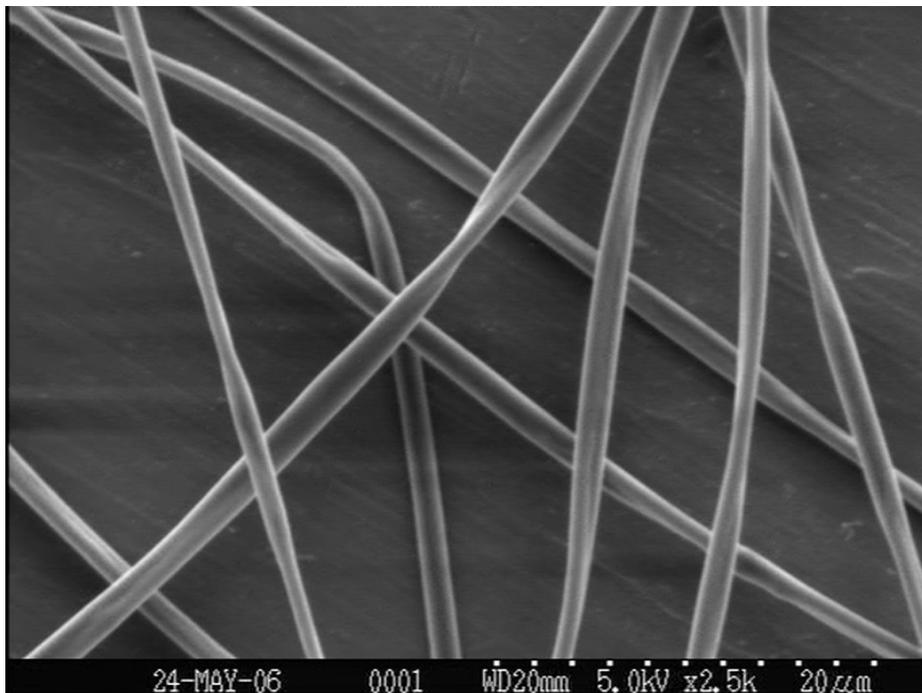
Figure 4. SEM micrographs of composite electrospun fibers (fibers diameter of 1 – 6 µm). Experimental conditions included polystyrene (20 wt %) in THF (Ratios:PS:C.W.:Span = 94:6:3), 35 kV voltage, plates separation of 20 cm and volumetric flow rate of 0.15 ml/min.
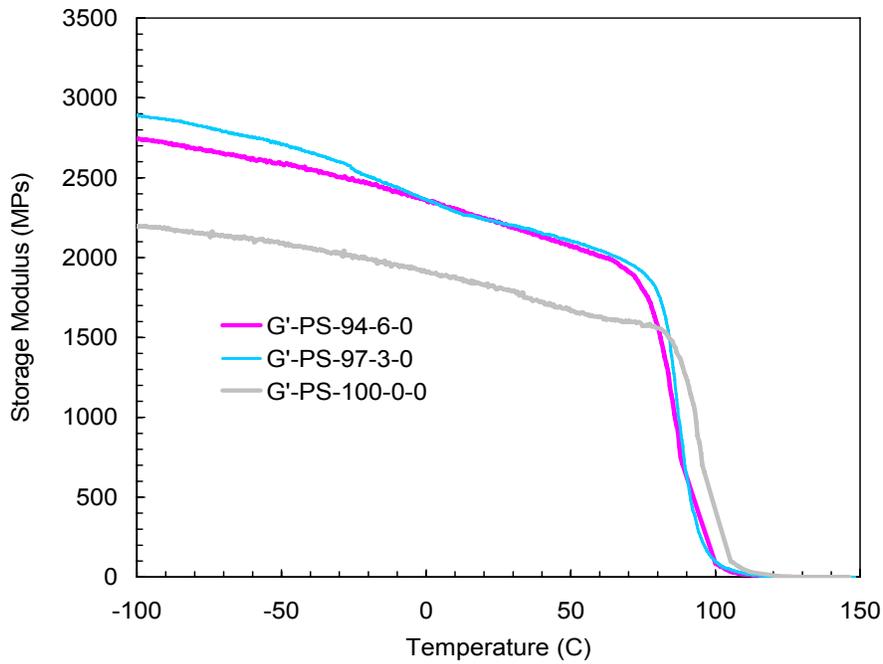
Figure 5. DMA analysis shows the effect of the addition of cellulose whiskers to the polymer solution. G' increases by increasing cellulose whiskers concentration (Ratios:PS:C.W.:Span = Polystyrene:Cellulose Whiskers: Surfactant).
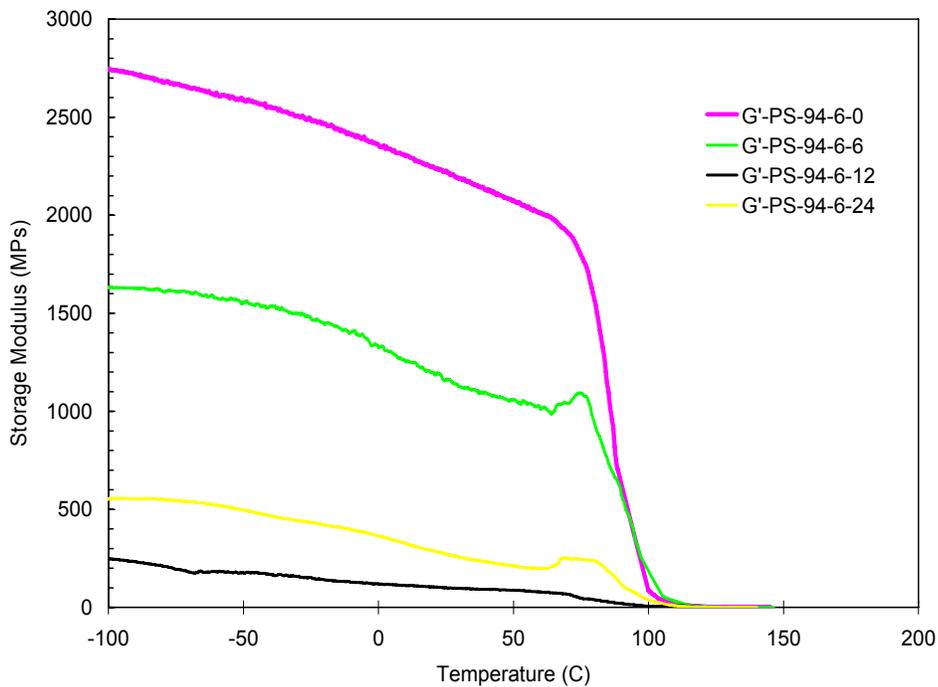
Figure 6. DMA analysis shows the effect of the addition of surfactant. G' decreases by increases surfactant concentration (Ratios:PS:C.W.:Span = Polystyrene:Cellulose Whiskers: Surfactant).

Conclusions

A major challenge in the performance of the targeted cellulose biocomposites is their compatibility with hydrophobic polymer matrix. With adding surfactant, we expected to overcome this issue and further produce materials with tailored surface properties. From the optical microscope observation of composite films, Span 60 appears to enhance the dispersion of cellulose whiskers in hydrophobic PS matrix. Electrospinning was performed to obtain web-structured composite material with disperse phase consisting of nano or micro sized fibers. SEM micrographs show that fibers produced by electrospinning processes were ~1 to 10 μm in diameter.

The intended composite materials, including micro or nano structures, are expected to have potential applications as reinforcing fillers for synthetic polymer matrices. Additionally, potential applications of the composites include the manufacture of strong lightweight textile nonwovens, super hydrophobic natural materials or production of bioactive filters and lightweight novel barrier materials for protection against chemical and biological agents.

Acknowledgements

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