Electrospun Polyethylene Oxide/Cellulose Nanocrystal Composite Nanofibrous Mats with Homogeneous and Heterogeneous Microstructures

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Supporting Information

ABSTRACT: An electrospinning process was successfully used to fabricate polyethylene oxide/cellulose nanocrystal (PEO/CNC) composite nanofibrous mats. Transition of homogeneous to heterogeneous microstructures was achieved by tailoring the concentration of PEO/CNC mixture in the solution from 5 to 7 wt %. Morphology investigation of the obtained nanofibers demonstrated that rod-shaped CNCs were well-dispersed in the as-spun nanofibers and highly aligned along the nanofiber long-axis. PEO/CNC nanofibers became more uniform and smaller in diameter with increased CNC-loading level. The heterogeneous composite mats were composed of rigid—flexible bimodal nanofibers. Results of structure characterization indicated that the incorporated CNCs interacted strongly with the PEO matrix through hydrogen bonding. Mechanical properties of both types of mats were effectively improved by using CNCs, with heterogeneous mats being stronger than their homogeneous counterparts for all compositions (0–20 wt % CNC contents). When a smaller diameter needle was used to form homogeneous mats, enhanced thermal and mechanical properties were obtained.

1. INTRODUCTION

Electrospinning of polymer solutions or melts driven by a high-voltage electric charge is a highly versatile technique that can be used to generate continuous 1D polymeric fibers with diameters ranging from several micrometers to tens of nanometers.1 Electrospun nanofibrous materials possess a variety of interesting characteristics such as small dimension, large specific surface area, wide-range porosity, unique physicochemical property, and excellent flexibility for chemical/physical surface functionalization. Hence, electrospun nanofibrous materials not only are being used in research laboratories but also are increasingly applied in industry.2 Their application includes, but is not limited to, optoelectronics, sensors, catalysis, filtration, and medicine. They are of particular interest in regenerative medicine and tissue engineering because nanofibers can be potentially tailored to mimic natural extracellular matrix (ECM) in terms of structure, chemical composition, and mechanical properties.3,4 Electrospun polymeric nanofibers, however, are not sufficiently strong for many applications because of low molecular chain orientation along the fiber long-axis resulting from low stretching forces in the process of fiber formation.5 During the past several years, a large number of studies has been conducted to improve mechanical properties of electrospun polymeric nanofibers. Incorporating nanoparticles into polymer matrices is one technique that has been developed and used as one of the most effective methods for reinforcing electrospun nanofibers.6–9

Cellulose nanocrystals (CNCs), one of the strongest and stiffest natural biopolymers, with an estimated elastic modulus of 130 GPa and a tensile strength of 7 GPa,10 are a suitable candidate for tailoring mechanical properties of polymer materials.11 They have been successfully used as highly effective reinforcing nanofillers for various electrospun polymer nanofibers including poly(ε-caprolactone) (PCL),12 poly(vinyl alcohol) (PVA),13 poly(acrylic acid) (PAA),14 polyethylene oxide (PEO),15 poly(lactic acid) (PLA),16,17 polystyrene (PS),18 and ethylene-vinyl alcohol copolymer (EVOH).19 Furthermore, because CNCs are nontoxic, biocompatible, and biodegradable, they have a significant potential in developing fully biodegradable polymer nanocomposites for biomedical applications. Considering excellent dispersion of CNCs in water,20 the development of an all-aqueous system for electrospinning based on a combination of CNCs with water-soluble polymers offers advantages in avoiding the use of organic solvents. The residual solvents can detract from the biocompatibility of the electrospun fibers when they are exposed to cells in vitro or in vivo. PEO was chosen for this study because of its high solubility in water. More importantly, PEO is also a nontoxic, fully biodegradable, and

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biocompatible polymer. It has attracted tremendous attention in the biomedical field for controlled drug release and tissue engineering.\cite{21,22} Over the past few years, extensive studies have been done on electrospun PEO fibers produced from PEO/water solutions to study the effects of process conditions and solution compositions.\cite{23-25} One of the most interesting findings was a bimodal diameter distribution for PEO fibers spun from higher concentration solutions.\cite{26} Although the electrospun PEO nanofibers loaded with a low content of bacterial cellulose whiskers were reported,\cite{15} the effect of processing variables on their morphology and mechanical properties has not been fully investigated. To the best of our knowledge, the bimodal fiber morphology of composite nanofibrous mats and its effect on mechanical properties have not been previously reported.

In this study, a series of PEO/CNC composite nanofibrous mats with different CNC contents was fabricated via an electrospinning process from two suspensions with different PEO/CNC loading levels. The specific objective was to investigate the influence of solution concentration on morphology and mechanical properties of bead-free electrospun PEO nanofibers reinforced with wood-based CNCs. Moreover, the long-term goal of the study is to develop an all-aqueous process for preparing biomimetic fully biodegradable and biocompatible (both matrix and fillers) composite mats with homogeneous and heterogeneous microstructures for their potential applications in biomedical fields.

2. EXPERIMENTAL SECTION

2.1. Raw Materials and Processing. PEO with a viscosity molecular weight (Mn) of 900,000 g mol$^{-1}$ was purchased from Sigma-Aldrich (St. Louis, MO). CNCs were isolated from commercial microcrystalline cellulose (Avicel FD-100 MCC, FMC Biopolymer, Philadelphia, PA) by combined acid hydrolysis with 64% H$_2$SO$_4$ and high-pressure homogenization process, as described in our previous papers.\cite{27,28} The obtained aqueous CNC suspension had a CNC concentration of ~1 wt %. Figure 1 shows a transmission electron micrograph (TEM) micrograph of manufactured CNCs, having a rod-shape structure with a diameter of 10 ± 3 nm and a length of 112 ± 26 nm. The aqueous solutions/suspensions in all experiments were prepared with distilled water.

2.2. Electrospinning Process. A certain amount of powder PEO was added to distilled water or fresh CNC suspension. The resulting mixtures were kept under vigorous magnetic stirring overnight at room temperature to obtain homogeneous pure PEO solutions or PEO/CNC suspensions, which were stored in a refrigerator for no longer than 1 week prior to their use. The concentrations of the PEO/CNC mixture in the solutions prepared were 5 and 7 wt %. The CNC loading percentage in relation to the total PEO/CNC weight was chosen as 0, 5, 10, and 20 wt %. The samples were designated as x-PEO or x-PEO/CNC-y, where x (wt %) is the total concentration of PEO and CNCs in water and y (wt %) is the concentration of CNCs in the mixture. The detailed composition information is shown in Table 1.

Pure PEO solutions or PEO/CNC suspensions were loaded in a 5 mL BD plastic syringe with either a 20 gauge (inner diameter [ID] = 0.584 mm) or a 25 gauge (ID = 0.241 mm) stainless steel needle. The needle was connected to a high voltage power supply (Gamma High Voltage Research, Ormond Beach, FL), which generates positive DC voltages up to 30 kV. The flow rate of the solution was controlled by a Chemxy Fusion 100 syringe pump (Stafford, TX). A piece of grounded aluminum foil was placed under the capillary needle tip as a collector. The obtained mats were vacuum-dried at 40 °C for 12 h and then stored in a desiccator prior to characterization.

2.3. Measurement and Characterization. Conductivity and surface tension of the electrospinning solutions were determined at room temperature using a Jenway Model 4330 conductivity and pH meter (Bath, U.K.) and a Thermo Fisher Scientific DCA Radian 322 analyzer (Newington, NH), respectively. Shear viscosities of the solutions were measured using an AR2000ex Rheometer (TA Instruments, New Castle, DE). A 40-mm cone—plate geometry with a cone angle of 1°59′42″ and a truncation of 56 μm was used for the flow measurements. The temperature of test samples was kept at 25 °C with a Peltier device, and the shear rate was varied from 0.1 to 100 s$^{-1}$. To avoid the evaporation of water in the sample, we sealed the 56 μm gap between cone and parallel plate with a solvent trap cover, and the coat on the top of the cover was filled with low-viscosity silicon oil.

Fourier transform infrared (FTIR) spectra of electrospun mats were measured using a Bruker FTIR analyzer (Tensor-27, Bruker Optics, Billerica, MA) with attenuated total reflectance (ATR) mode. Each spectrum was acquired in a transmittance mode on a Zn/Se ATR crystal cell by accumulation of 64 scans with a resolution of 4 cm$^{-1}$ and a spectral range of 4000–600 cm$^{-1}$. Differential scanning calorimetry (DSC) measurements were performed with a TA Q2000 system (TA Instruments) at a 5 °C min$^{-1}$ heating rate from −65 to 110 °C in a 50 mL min$^{-1}$ dynamic nitrogen atmosphere. Samples of ~5 mg were loaded into DSC pans sealed using a crimping tool. All tests were carried out in duplicate. Wide-angle X-ray diffraction (WAXD) patterns of PEO and PEO/CNC nanofibrous mats were recorded using a Bruker Siemens D5000 X-ray diffractometer (Bruker AXS, Madison, WI) with Cu Kα radiation ($λ = 0.154$ nm) at 40 kV and 30 mA. X-ray diffraction data were collected from 2θ = 5 to 35° at a scanning rate of 0.02° s$^{-1}$ at room temperature. Surface morphologies of the nanofibers sputter-coated with gold for Table 1. Compositions, Conductivity, and Surface Tension of Electrospinning PEO Solutions and PEO/CNC Suspensions

<table>
<thead>
<tr>
<th>sample</th>
<th>concentration (wt %)</th>
<th>CNC content (wt %)</th>
<th>conductivity (µS cm$^{-1}$)</th>
<th>surface tension (mN m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-PEO</td>
<td>5</td>
<td>0</td>
<td>84.2 ± 2.5</td>
<td>67.6 ± 1.4</td>
</tr>
<tr>
<td>5-PEO/CNC-5</td>
<td>5</td>
<td>5</td>
<td>127.8 ± 4.1</td>
<td>64.8 ± 1.0</td>
</tr>
<tr>
<td>5-PEO/CNC-10</td>
<td>5</td>
<td>10</td>
<td>212 ± 6.6</td>
<td>65.2 ± 1.0</td>
</tr>
<tr>
<td>5-PEO/CNC-20</td>
<td>5</td>
<td>20</td>
<td>399 ± 14.3</td>
<td>67.3 ± 1.6</td>
</tr>
<tr>
<td>7-PEO</td>
<td>7</td>
<td>0</td>
<td>92.4 ± 3.0</td>
<td>70.2 ± 1.8</td>
</tr>
<tr>
<td>7-PEO/CNC-10</td>
<td>7</td>
<td>10</td>
<td>247 ± 7.2</td>
<td>68.8 ± 1.6</td>
</tr>
<tr>
<td>7-PEO/CNC-20</td>
<td>7</td>
<td>20</td>
<td>481 ± 19.7</td>
<td>69.1 ± 1.6</td>
</tr>
</tbody>
</table>
2 min were examined by a Hitachi S-3600N scanning electron microscope (SEM, Hitachi High Technologies America, Schaumburg, IL) at 25.0 kV. The distribution of nanofiber dimensions was obtained from the analysis of SEM images using the Adobe Photoshop software (version CS2). Fifty nanofibers were randomly selected from each image and measured using the ruler tool. The morphology of the CNCs in the nanofibers was observed using a JEOL 100CX TEM (JEOL USA, Peabody, MA). Samples were prepared for the TEM analysis by directly electrospinning PEO/CNC suspension onto a carbon-coated 400-mesh copper grid. The parameters used for electrospinning included 15 kV voltage, 0.1 mL·h⁻¹ flow rate, and 20 cm distance from the needle tip to the collector plate. The obtained material was allowed to dry and was then stained with 2% uranyl acetate for TEM observation.

Mechanical properties of the nanofibrous mat samples were measured using an AR2000ex rheometer with a solid clamp in tension mode at room temperature and a loading rate of 1.2 mm·min⁻¹. The thickness of the mats was measured using a Mitutoyo digimatic indicator with ±1 μm accuracy. To avoid any direct touch on mat surfaces during sample preparation, we carefully peeled off each mat from the surface of aluminum foil. The mat was placed between two pieces of weighing paper and then cut into rectangular pieces (20 mm in length and 5 mm in width). The ends of each obtained sample were fixed onto the top and bottom areas of a “T”-shape paper template (Figure S1 of the Supporting Information) using adhesive tape to strengthen the sample ends for clamping. The effective loading area had a planar dimension of 5 mm (width) × 10 mm (gauge length). After specimens were mounted onto the solid clamp by firmly tightening the clamp screws, the vertical holding side in the paper template was cut. The stress and strain values were calculated from the machine-recorded force and displacement based on initial cross-section area and original gauge length (10 mm) of each sample, respectively. The Young’s modulus for each sample was calculated from the initial linear portion of stress-strain curves through a linear regression analysis. Three replicates were performed for each sample group.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Electrospinning Solutions. It is well known that surface tension, conductivity, and viscosity of spinning solutions play important roles in determining the morphology of electrospun nanofibers. Table 1 shows changes in the surface tension and conductivity data of pure PEO solutions and PEO/CNC suspensions with different concentrations of CNCs. The surface tension of the PEO/CNC suspensions decreased slightly compared with that of CNC-free PEO solutions. Their conductivity significantly increased because of the presence of uronic acid and sulfate ester groups on the CNC surface from the sulfuric acid hydrolysis during CNC production. Furthermore, the conductivity of both 5- and 7-PEO/CNC suspensions increased with increased CNC content. This behavior can effectively prevent the formation of beads and promote the continuous spinning of smaller diameter fibers for PEO/CNC systems because of increased charge density in the ejected jets. Compared with the 5-PEO/CNC suspension, the 7-PEO/CNC suspension had higher conductivities.

Figure 2 shows measured viscosity of pure PEO solutions and PEO/CNC suspensions with the total concentrations of 5 and 7 wt % under different shear rates. The 5-PEO solution displayed a Newtonian fluid characteristic at low shear rates. Above ~1.0 s⁻¹ shear rate, the viscosity of the 5-PEO solutions decreased with increased shear rate due to breaking the intermolecular interactions and entanglements among the PEO chains by shear stresses. In contrast, all PEO/CNC suspensions exhibited a typical shear-thinning behavior through the whole range of shear rates. The obtained material was allowed to dry and was then stained with 2% uranyl acetate for TEM observation.

Figure 3. SEM images of as-spun 5-PEO (a), 5-PEO/CNC-5 (b), 5-PEO/CNC-10 (c), 5-PEO/CNC-20 (d), 5-PEO/CNC-20D (e), 7-PEO (f), 7-PEO/CNC-10 (g), and 7-PEO/CNC-20 (h) nanofibers at an electrical field strength of 0.75 kV·cm⁻¹ and a flow rate 0.1 mL·h⁻¹.
222 from 0.1 to 100 s⁻¹. The shear-thinning behavior of the 7-PEO/CNC suspensions was more apparent than that of the 5-PEO/CNC suspensions. From Figure 2, it can also be found that the viscosity of PEO/CNC suspensions decreased significantly after CNCs were added to the PEO solution because CNCs disrupted the PEO chain interactions and entanglements, which allowed the PEO molecules to align much easier. In addition, PEO/CNC suspensions exhibited more shear thinning behavior with increased CNC contents attributed to the strong interaction between PEO and CNCs (confirmed by FTIR and WAXD analysis below) increasing the solution inertia. 31 It is well known that the wall shear rate of non-Newtonian fluids is inversely proportional to the inner radius of the needle at a fixed volumetric flow rate. 32 When PEO/CNC suspensions flow in a smaller needle, they would bear a higher shear rate, thereby showing lower viscosities (Figure 2) owing to the orientation of the CNCs at the high shear rate, especially in solutions with high CNC loadings. 33 This result suggests that the electrospinning process of PEO/CNC suspensions could be performed facilely with a low-diameter needle.

The operational conditions were carefully examined by performing a series of electrospinning runs with varying electric field strengths, distances from the tip of the needle to the collector plate, and flow rates. Suitable electrospinning parameters for PEO solutions and PEO/CNC suspensions included a 15 kV voltage with a needle tip to collector distance of 20 cm (equivalent to an electric field strength of 0.75 kV·cm⁻¹) and a flow rate of 0.1 mL·h⁻¹. To obtain test samples with structures matched as much as possible, all electrospun nanofibrous mats reported later in this Article were produced from 0.6 mL of the corresponding electrospinning solutions with the spinning conditions stated above at 60% relative humidity and 25 °C.

3.2. Microstructure of Nanofibrous Mats. Figure 3 shows typical SEM images of as-spun pure PEO and PEO/CNC nanofibrous mats. The corresponding fiber diameter histograms are given in Figure 4. All fibers produced were in the nanoscale range, and beads within single fibers were rarely visible. Fibers electrospun from the 5 wt % PEO solution and PEO/CNC suspensions (Figure 3a–d) were almost homogeneous and exhibited decreased average diameters and diameter deviations with increased CNC contents attributed to the strong interaction between PEO and CNCs (confirmed by FTIR and WAXD analysis below) increasing the solution inertia. 31 It is well known that the wall shear rate of non-Newtonian fluids is inversely proportional to the inner radius of the needle at a fixed volumetric flow rate. 32 When PEO/CNC suspensions flow in a smaller needle, they would bear a higher shear rate, thereby showing lower viscosities (Figure 2) owing to the orientation of the CNCs at the high shear rate, especially in solutions with high CNC loadings. 33 This result suggests that the electrospinning process of PEO/CNC suspensions could be performed facilely with a low-diameter needle.
Figure 6. FTIR spectra of electrospun nanofibrous mats and CNC film.

Figure 7. DSC curves of electrospun PEO and PEO/CNC nanofibrous mats.

5 mL of 1 wt % CNC suspension was cast in a plastic Petri dish and dried overnight under vacuum at 40 °C to produce CNC films of ~30 µm in thickness. Characteristic absorbance peaks for the CNC film were attributed to the hydrogen-bond O–H stretching at ca. 3700–3100 cm⁻¹ (~3342 cm⁻¹), the O–H bending of adsorbed water at 1651 cm⁻¹, the C–H stretching at 2900 cm⁻¹, the C–OH deformation mode at 1034 cm⁻¹, and the C–OH out-of-plane bending mode at 667 cm⁻¹. Typical absorption bands for pure PEO nanofibrous mats were detected at 2882 cm⁻¹, attributed to CH₂ stretching, which overlapped with observed bands for the CNCs. Some other characteristic bands for the pure PEO nanofibrous mats were observed at 1148,1101,1062, and 958 cm⁻¹, assigned as C–O–C stretching vibration, at 1467 cm⁻¹ assigned as C–H bending mode, and at 1358 and 1340 cm⁻¹ assigned as C–H deformation modes. Because PEO used in the experiment had a relatively high molecular weight, the O–H absorption bands were not obvious and thus can be neglected. FTIR spectra of all as-spun 5-PEO/CNC nanofibrous mats showed absorption bands related to cellulose O–H peaks such as 3342, 1034, and 667 cm⁻¹, and these characteristic peaks broadened and strengthened gradually with increased CNC contents in the 5-PEO/CNC composite nanofibrous mats, which reflected the strength of the hydrogen bonding predominantly attributed to that primary hydroxyl groups at the position C6 of the glucose unit of cellulose interacting with ether oxygen in PEO. In addition, the FTIR spectra of 7-PEO/CNC nanofibrous mats (not shown) showed similar trends compared with those of the 5-PEO/CNC nanofibrous mats. Analysis of the above-mentioned FTIR spectra indicated that electrospun nanofibers consisted of both components initially presented in the polymer solution (i.e., no component was selectively excluded during the electrospinning process).

3.4. Thermal Behavior of Nanofibrous Mats. To investigate the effect of CNCs on the thermal behavior of PEO matrix, a DSC study was performed on the pure PEO and PEO/CNC nanofibrous mats (Figure 7). The thermal parameters, including glass-transition temperature (Tg defined as the midpoint temperature of glass transition), melting temperatures (Tm), enthalpy of fusion (ΔHm), and weight fractional crystallinities (XC), were measured from the DSC curves, and the data are summarized in
WAXD Analysis of Nanofibrous Mats.

Table 2. Thermal and Tensile Properties of Electrospun Nanofibrous Mats

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_g/°C</th>
<th>T_m/°C</th>
<th>ΔH_m/J g⁻¹</th>
<th>X_c/%</th>
<th>T/μm</th>
<th>σ_max/MPa</th>
<th>E/MPa</th>
<th>ε₀/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-PEO</td>
<td>-47.3</td>
<td>65.3</td>
<td>157.7</td>
<td>76.9</td>
<td>9 ± 1</td>
<td>2.50 ± 0.06</td>
<td>15.2 ± 0.3</td>
<td>200 ± 12</td>
</tr>
<tr>
<td>5-PEO/CNC-5</td>
<td>-46.5</td>
<td>65.5</td>
<td>131.9</td>
<td>67.7</td>
<td>10 ± 2</td>
<td>5.08 ± 0.14</td>
<td>38.1 ± 0.7</td>
<td>122 ± 8</td>
</tr>
<tr>
<td>5-PEO/CNC-10</td>
<td>-46.3</td>
<td>63.4</td>
<td>121.4</td>
<td>65.8</td>
<td>9 ± 1</td>
<td>5.96 ± 0.16</td>
<td>37.9 ± 0.6</td>
<td>103 ± 7</td>
</tr>
<tr>
<td>5-PEO/CNC-20</td>
<td>-46.0</td>
<td>60.1</td>
<td>103.7</td>
<td>63.2</td>
<td>9 ± 1</td>
<td>7.04 ± 0.21</td>
<td>35.3 ± 0.5</td>
<td>166 ± 10</td>
</tr>
<tr>
<td>5-PEO/CNC-20D</td>
<td>-44.6</td>
<td>62.7</td>
<td>104.0</td>
<td>63.4</td>
<td>8 ± 1</td>
<td>7.01 ± 0.18</td>
<td>38.3 ± 0.4</td>
<td>106 ± 7</td>
</tr>
<tr>
<td>7-PEO</td>
<td>-47.4</td>
<td>65.4</td>
<td>158.0</td>
<td>77.1</td>
<td>13 ± 2</td>
<td>4.00 ± 0.10</td>
<td>23.8 ± 0.9</td>
<td>168 ± 10</td>
</tr>
<tr>
<td>7-PEO/CNC-10</td>
<td>-46.9</td>
<td>64.2</td>
<td>138.9</td>
<td>75.3</td>
<td>14 ± 3</td>
<td>6.68 ± 0.20</td>
<td>43.3 ± 1.5</td>
<td>141 ± 9</td>
</tr>
<tr>
<td>7-PEO/CNC-20</td>
<td>-46.1</td>
<td>63.0</td>
<td>118.7</td>
<td>72.4</td>
<td>13 ± 2</td>
<td>8.52 ± 0.25</td>
<td>59.6 ± 3.8</td>
<td>125 ± 8</td>
</tr>
</tbody>
</table>

See Table 2. X_c was calculated using eq 1

\[
X_c = \frac{\Delta H_m}{\Delta H_0(1 - C_{CNC})} \times 100
\]  

where \(\Delta H_0 = 205\) J/g is the enthalpy of fusion for 100% crystalline PEO and \(C_{CNC}\) is the weight concentration of CNCs in the PEO/CNC mixture. As shown in Table 2, \(T_g\) of both 5- and 7-PEO/CNC nanofibrous mats slightly increased with increased contents of CNCs from 0 to 20 wt %. The results can be explained by the fact that the interaction between the PEO and CNCs was gradually improved with the addition of CNCs because of the strong hydrogen bonding between them, which limits the molecular chain movement of PEO. From Figure 7 and Table 2, it can also be seen that the incorporation of CNC decreased the melting temperatures and enthalpies of nanofibers and also decreased the crystallinities of PEO in the composites, similar to the results found in the investigation on electrospun EVOH/bacterial cellulose nanowhiskers composite nanofibers. Moreover, this effect became more obvious with increased CNC content. This result indicates that the presence of CNCs hindered the organization of PEO molecular chains into ordered structures during the electrospinning process. Interestingly, the 7-PEO/CNC nanofibrous mats showed relatively higher \(T_m\) and \(X_c\) than those of the 5-PEO/CNC nanofibrous mats, which is likely ascribed to the different primary microstructures of nanofibrous mats. Because the secondary nanofibers made up the majority of the heterogeneous mats, which barely contained any CNCs, it could be deduced that the organization of fewer PEO molecular chains in the 7-PEO/CNC systems were interrupted by CNCs during electrospinning process. In addition, compared with the 5-PEO/CNC-20 nanofibrous mats, the 5-PEO/CNC-20D nanofibrous mats had higher values in all thermal parameters, suggesting the fact that more uniform distributions of PEO/CNC nanofibers improved the thermal properties of nanofibrous mats.

### 3.5. WAXD Analysis of Nanofibrous Mats

WAXD diffraction patterns of the electrospun PEO and PEO/CNC nanofibrous mats are shown in Figure 8. Before plotting, data were smoothed over 35 adjacent points and were then normalized so that the main peaks had the same y-axis values for a direct comparison. Two typical diffraction peaks at \(2θ = 19°\) and \(23°\) for the as-spun PEO nanofibrous mats are attributed to (120) and (112) crystal plane, respectively. For all composite nanofibrous mats, no new diffraction peaks were observed. However, with increased CNC content, the peak at \(2θ = 23°\) for composite mats broadened and strengthened gradually, indicating the presence of CNCs because the primary peak around \(2θ = 22.5°\) attributed to the CNC (200) plane overlapped with that peak of PEO (112) crystal plane. Moreover, the slight shift of diffraction peaks for composite mats suggested that CNCs influenced the crystalline structure of PEO. Apparent crystal size \(L_{hkl}\) of PEO was computed using Scherrer’s equation

\[
L_{hkl} = \frac{K\lambda}{(B \cos \theta_{hkl})}
\]

where \(\lambda\) is the wavelength of the Cu Kα beam (1.54 Å), \(K\) is a constant of 0.89, and \(B\) is the half width of the \((hkl)\) reflection at a scattering angle \(2θ_{hkl}\) prior to smoothing. As shown in Figure 8, apparent crystal sizes were obtained using eq 2 from the most prominent diffraction peaks (120). It can be seen that \(L_{120}\) in composite mats is lower than that in pure PEO mats, suggesting that the introduction of CNCs is deleterious for the packing of PE molecular chains. The results were in an agreement with the results of DSC runs shown above. It illustrated adversely the good compatibility between PEO and CNCs through the strong hydrogen interaction. With increased CNC content, \(L_{120}\) for both types of mats decreased gradually. Moreover, the 5-PEO/CNC-20D nanofibrous mats had the smallest \(L_{120}\), indicating that the compatibility between PEO and CNCs was improved by decreasing needle diameter likely due to a better dispersion and orientation of CNCs in electrospinning solution at higher shear rates. Compared with the 5-PEO/CNC composite nanofibrous mats, the 7-PEO/CNC composite nanofibrous mats showed...
from 200 ± 17 to 103 ± 7%. Upon further increasing of the CNC content, however, decreased $E$ and increased $\varepsilon_b$ of the 5-PEO/CNC nanofibrous mats was observed. This phenomenon was likely attributed to the decreased fiber size uniformity (Figure 4). Therefore, a CNC loading of 10 wt % was the optimal content for the 5-PEO/CNC nanocomposite mats based on the $E$ values. With decreased needle diameter from 0.584 to 0.241 mm, the 5-PEO/CNC-20 nanofibrous mats showed improved $E$ and $\varepsilon_b$ values (as shown in 5-PEO/CNC-20D), which indicates that homogeneous mats composed of more uniform nanofibers had better mechanical properties because of the higher crystallinity. For the 7-PEO/CNC nanofibrous mats (Figure 9b), the values of $\sigma_{\text{max}}$ and $E$ increased with increased CNC contents (from 0 to 20 wt %) from 4.00 ± 0.10 to 8.52 ± 0.25 MPa and 23.8 ± 0.9 to 59.6 ± 3.8 MPa, respectively. Although the changes in $\sigma_{\text{max}}$ and $E$ for the 7-PEO/CNC nanofibrous mats were similar to those of the 5-PEO/CNC mats, these values of the 7-PEO/CNC nanofibrous mats were higher than that of the 5-PEO/CNC nanofibrous mats throughout all compositions. These results indicated that the especially heterogeneous network microstructure was beneficial to the mechanical properties of electrosyn spun composite nanofibrous. To interpret the effect of heterogeneous microstructures on mechanical properties of composite mats, we investigated SEM-based morphologies of heterogeneous 7-PEO/CNC-20 nanofibrous mats in different stages of the tensile process. The results are shown in Figure 10. Before the yield point (i.e., the initial stage of tensile testing), mat morphology (Figure 10a) did not have obvious changes compared with that of the mats before tensile testing (Figure 3h), showing the behavior of elastic deformation. Both Figure 10a and Figure 3h show the ultrafine secondary fibers attached to the primary fibers. In general, mechanical properties of electrosyn composite nanofibrous mats are influenced by factors including component properties, nanofiber structure, and the interaction among the nanofibers. Therefore, the measured morphological result suggests that the nanofibers in mats hardly moved at the beginning of tensile process, which was attributed to the strong interaction among the nanofibers originating from the strong polar of PEO and CNCs. The modulus $E$ was determined from the initial stress-strain curve (i.e., linear portion). The improved Young’s modulus of heterogeneous mats (compared with homogeneous mats) could be ascribed to secondary ultrafine nanofibers interacted strongly with primary nanofibers through the bonding points and entanglement between them. (Insert Figure 10a.) In contrast, the nanofibers in the homogeneous mats were separate fibers with the absence of entangling ultrafine secondary fibers, resulting in less interaction among them and less overall mat modulus. After the yield point and before mat fracture, with increased tensile stress, most of the nanofibers in the mats gradually reached their tightened state and aligned along the tensile direction (Figure 10b) attributed to the bonding points between nanofibers that were destroyed. In addition, a few of the primary nanofibers were necked and fractured (insert of Figure 10b). In this stage, many ultrafine secondary fibers were also broken off from the primary fibers, which could defer the rupture of primary nanofibers and thus increase the elongation at break for heterogeneous mats (as shown in Table 2). As stress levels were increased, more primary nanofibers were gradually necked and broken. At the maximum tensile stress level (Figure 10c), most nanofibers were necked and fractured, leading to the final mat rupture. Because the diameters and relative CNC content of the primary nanofibers in the heterogeneous composite mats were larger than those of the
nanofibers in the homogeneous composite mats (as depicted in Section 3.2), the heterogeneous mats could bear higher stresses, leading to higher tensile strength of the heterogeneous mats in comparison with their homogeneous counterparts. To the best of our knowledge, this is the first time when the bimodal microstructure of electrospun composite nanofibrous mats was directly correlated with their mechanical properties.

4. CONCLUSIONS

A series of PEO/CNC composite nanofibrous mats with different CNC loadings were successfully fabricated via an electrospinning process. Morphology investigation of obtained nanofibrous mats demonstrated that the transition from homogeneity to heterogeneity in their microstructures was achieved by tailoring the concentration of electrospinning solutions from 5 to 7 wt %. PEO/CNC nanofibers became more uniform and finer with the increased CNC content because of the enhanced electric conductivity of electrospinning solutions. With the decrease in the needle diameter, as-spun nanofibers showed improved size uniformity. The heterogeneous composite mats were composed of rigid-flexible bimodal nanofibers. It was also indicated that CNCs effectively improved the mechanical properties of both types of nanofibrous mats. This was ascribed to the efficient stress transfer from PEO to CNCs originating from their strong interactions and the uniform dispersion and high alignment of CNCs in the electrospun fibers. When a smaller diameter needle was used in the spinning of homogeneous network mats, enhanced thermal and mechanical properties were obtained. Moreover, the mechanical properties of heterogeneous nanofibrous mats were better than those of their homogeneous counterparts for all compositions (0–20 wt % CNC contents). It was demonstrated for the first time that the especially heterogeneous nanofibrous microstructure made of rigid-flexible bimodal nanofibers is beneficial to the mechanical properties of electrospun composite nanofibrous mats.

ASSOCIATED CONTENT

Supporting Information. Paper template for preparing tensile specimens. This material is available free of charge via the Internet at http://pubs.acs.org.

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