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Preparation and Characterization of Core–Shell Structured Nanofibers by Coaxial Electrospinning

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Abstract: Functional core–shell structured composite nanofibers were prepared by electrospinning two polymer solutions in a coaxial system. The core–shell structured nanofibers were comprised of varying concentrations of polyurethane (PU, shell) and a Nylon-6 (core). The resultant nanofibers were characterized by means of scanning electron microscopy, transmission electron microscopy, fourier transform infrared spectroscopy and tensile mechanical test. Furthermore, water vapor transmission rate and pliability of cotton fabrics coated with non-woven mats of the core–shell structured nanofibers were also measured. The results indicated that it is feasible to attach composite nanofibers onto a textile substrate.

Key Words: nylon-6/polyurethane core shell nanofibers, coated textiles, water vapor transmission rate, pliability

1. INTRODUCTION

Electrospinning is a straightforward technique that produces continuous polymer fibers, with diameters from a few nanometers to micrometers, by the action of an external electric field imposed on a polymer solution or melt [1]. The technique provides the capacity to lace together a variety of types of polymers to produce ultrathin fibers arranged randomly as a mat or membrane that are potentially useful as protective clothing [2]. Fibrous materials obtained by this technique could be used for filter media, providing the advantages of high filtration efficiency (FE) and low air resistance, or chemical protective clothing, depending on the specific polymer being used. Gibson et al. [2] have investigated the performance measurements of electrospun Nylon-6,6 fiber mats and found that they had comparable transport properties to the textiles and membranes currently used in protective...
clothing systems. The results further indicated that the electrospun nanofibers presented both minimal impedance to moisture vapor diffusion and extreme efficiency in trapping aerosol particles compared with conventional textiles [2–4]. Aerosols and hydrosols of structured or core–shell particles, each of which is comprised of a certain substance surrounded by another, are of particularly important for encapsulating food additives [5–9], targeted drug delivery [10] and special material processing [11].

One route to achieve a core/shell structure in nanofibers is by coaxial electrospinning [12] with two miscible or immiscible polymeric components. The combination of a Nylon-6 core with a PU shell was anticipated to be attractive from the viewpoint of being able to achieve a good combination of transport and mechanical properties. Such core–shell nanostructures are attractive for textile applications because by judicious choice of the constituent polymer components, they have the potential to provide protection from an aggressive environment, are potentially capable of neutralizing chemical agents, and the outer surface can be functionalized without affecting the core material [12].

In the present work, coaxial electrospinning [13–16] of Nylon-6 core and PU shell nanofibers were investigated. It was postulated that a non-woven nanofibrous fabric of Nylon-6 (core)–PU (shell), may exhibit an attractive combination of properties derived from each polymer, (i.e., better surface properties and adhesion from the PU shell, and excellent mechanical performance from the Nylon-6 core). The aim of this research was to develop composite nanofibers that exhibit exceptionally good breathability, elasticity, mechanical strength and filtration efficiency for potential textile applications in protective garments, filters and flight suits.

2. EXPERIMENTAL

2.1. Coaxial electrospinning

Nylon-6 ($M_w = 52,800$) and polyurethane (PU, elastomeric, $M_n = 2000$, with glass transition temperature ($T_g$) of –65 °C) were purchased from JINGJIAN plastic Ltd (Shanghai, China). Tetrahydrofuran (THF, purity ≥ 90%), dimethylformamide (DMF, purity ≥ 99.5%) and $m$-cresol, were all obtained from Chemical Reagent Co. Ltd (Shanghai, China) and used without further purification.

Two immiscible solutions were prepared for coaxial electrospinning in the following way. Nylon-6 was dissolved in $m$-cresol at 6% by weight in room temperature for 6 h, whereas PU was dissolved in tetrahydrofuran (THF)/dimethylformamide (DMF) (1/1, ratio by volume) at different concentrations (4, 6, 8, and 10 wt.%) at 80 °C with stirring for 10 h. It should be noted that the concentration of Nylon-6 in solution was kept constant throughout this work.

The basic experimental setup used is shown in figure 1, which is essentially the same as that of a conventional electrospinning setup [14–16]. It consisted of a DC voltage generator (Beijing Machinery & Electricity Institute), two syringe pumps (model WZ-50C2; Zhejiang University Medical Instrument Co., Ltd), and a self-made spinneret system with
an inner needle (inner diameter: 0.51 mm, outer diameter: 0.8 mm) coaxially placed inside an outer one (inner diameter: 1.6 mm). The core and shell solutions were delivered by syringe pumps through Teflon tubes connecting the syringes with the inner and outer spinnerets (needles), respectively. The high DC voltage was introduced into the inner solution. The PU (shell)/Nylon-6 (core) nanofibers were obtained at 27 kV with a tip-to-collector distance of 12–13 cm. The flow rates of the outer and the inner fluids were 2.00 mL h\(^{-1}\) and 0.20 mL h\(^{-1}\), respectively. The electrospinning process was carried out at room temperature in air.

The nanofibers were electrospun directly onto double-faced retinitis glue, which had already been affixed onto a cotton fabric sample. The glue is widely used to bond textiles, sponges and non-woven fabrics. Figure 2 shows the cotton fabric covered with the electrospun non-woven nanofibers. The nanofibers were bonded by thermal treatment at 120 °C under 300–500 gf cm\(^{-2}\) of pressure for 5–10 s.

2.2. Characterization

2.2.1. Morphology

The morphological characteristics of the composite nanofibers were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM (HITACHI S-2360N machine at an accelerating voltage of 15 kV) samples were sputtered with gold prior to imaging. The core–shell structure was observed through a HITACHI H-600 TEM machine, at an accelerating voltage of 75 kV.
2.2.2. Infrared spectroscopy

Infrared spectroscopy was conducted on the nanofiber membranes using an EQUINOX 55 (Bruker, Germany) instrument operating with a scanner velocity of 6.10 kHz. The number of sample scans and the background scans were 64 and 32, respectively.

2.2.3. Mechanical testing

The mechanical behavior of the membranes was characterized by tensile property measurement using a small-size tester (Model CSS-44020; Changchun Research Institute for Testing Machines, China) with a load cell of 10 N. A cross-head speed of 10 mm min$^{-1}$ was used for all of the specimens tested. The diameters of the electrospun fibers were measured using visualization software ImageJ 1.34s (National Institutes of Health, Bethesda, MD, USA). For each sample, the diameter distribution was obtained from about 100 measurements on the random nanofibers obtained from SEM images. The nanofiber membranes were very thin and could be damaged even by a slight touch, thus the tensile samples were affixed with end-tabs in order to achieve sufficient grip (figure 3). All samples were rectangular with dimensions of 50 cm × 10 cm as described by Huang et al. [17].

2.2.4. Water vapor transport testing

Water vapor transmission of the cotton fabric covered with composite nanofibers was measured by a dish method following a Chinese National Standard GB/T 12704-91. The specimen thickness was 0.12 ± 0.03 mm, which was obtained by controlling the elec-
trospinning time for 1 h. The constant temperature and relative humidity was determined using a humidistat HWS-150 (Jinghong Laboratory Instrument Co., Ltd, Shanghai, China) and was 39 °C and 94%, respectively.

2.2.5. Pliability testing

Pliability testing was conducted to determine the conformability of the nanofibrous non-woven fabrics. The pliability test on the nanofibrous fabrics was conducted according to GB/7689.4-2001 standard using a set-up as shown in figure 4. The fabric sample was placed between two wood blocks, A and B, and the front of the fabric was located at the intersect line of the planar and inclined surfaces of the block B. The block A was then pushed to drive the fabric to slide slowly on block B in such a way that there was no sliding between the block A and the fabric. Due to gravity, the fabric droops towards the inclined surface of block B. As soon as the fabric touched the inclined surface, the pushing force was stopped. The distance the fabric travels on the planar surface is an index of the fabric pliability. A key parameter in such an experiment is the sample thickness as it will affect the experimental results to a significant degree. The membrane thickness was controlled to 0.12 ± 0.03 mm, and the test was repeated six times and averaged to give a meaningful statistical result.
3. RESULTS AND DISCUSSION

3.1. Morphology

Figure 5 shows a TEM image of a composite nanofiber. The core–shell structure is evident by the lighter (surface) and darker areas (center). The core diameter was about 250 nm and the fiber diameter was about 435 nm. The shell wall thickness was about 93 nm. The boundary region between the core and shell polymers is reasonably well defined in the image. Nylon-6 has been shown to be an electrospinnable polymer [18]. Until now, there have been no reports on electrospun PU/Nylon composite nanofibers. Initially, the coaxial electrospinning of Nylon-6 in 2,2,2-trifluoroethanol [19] and PU in a mixture of DMF/THF was attempted. This polymer/solvent system did not lead to a Taylor cone and usually resulted in polymer precipitation and clogging of the co-axial needles. Consequently, a different approach was used in which a solution of Nylon-6 in m-cresol was employed instead. This approach was successful in producing core–shell nanofibers, but the Nylon-6/m-cresol solution by itself could not be spun into nanofibers. It appears from the image in figure 5 that the shell polymer served as a template for the formation of the core Nylon-6 fiber.

The diameter ranges of the nanofibers prepared from different PU/Nylon-6 concentrations are listed in table 1. The diameter ranges did not differ radically within the concentration ranges studied. The PU by itself gave the smallest diameter nanofibers. The SEM photographs and size distributions of the electrospun PU (shell)/Nylon (core) fibers with different shell solution concentrations are shown in figure 6. The size distribution of every kind of the electrospun fibers was obtained from about 200 fiber measurements. Figure 6(a) shows the image of the electrospun PU fibers with 8 wt.% concentration, which exhibited the finest morphology in this work. Some beads could be seen on the electrospun fibers prepared from PU (shell, 6 wt.%)/Nylon-6 (core, 4 and 6 wt.%), as shown in figure 6(b) and (c). As the concentration of the PU solution increased, the beads gradually
Figure 5. Transmission electron microscopy of a PU (shell)/Nylon-6 (core) fiber.

Table 1. Diameters of electrospun PU (shell)/Nylon-6 (core) composite nanofibers.

<table>
<thead>
<tr>
<th>Shell solution</th>
<th>4 wt.% PU</th>
<th>6 wt.%PU</th>
<th>8 wt.%PU</th>
<th>10 wt.%PU</th>
<th>8 wt.%PU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core solution</td>
<td>6 wt.%Nylon-6</td>
<td>6 wt.%Nylon-6</td>
<td>6 wt.%Nylon-6</td>
<td>6 wt.%Nylon-6</td>
<td>6 wt.%Nylon-6</td>
</tr>
</tbody>
</table>

disappeared and the shape of the beads gradually changed from spherical to spindle-like (figure 6(d)). Only a very few beads could be found on the fibers that were electrospun from PU (shell, 10 wt.%)/Nylon-6 (core) system (figure 6(e)). Continuous and smooth fibers could be formed with an 8 wt.% PU concentration (figure 6(d)). It has been reported that the formation of beaded fibers is related to the instability of the jet of polymer solution, the solution viscosity, net charge density carried by the electrospinning jet and surface tension of the solution [16]. Higher viscosity favors the formation of fibers without beads [20]. Many parameters such as solution concentration, surface tension, solvent used, voltage, temperature, and relative humidity can influence the formation of fibers by electrospinning. The effect of different PU concentrations on the morphology of the core–shell structure was investigated by keeping the other conditions such as voltage, and the outer and inner flow rates unchanged. It can be seen that there were many more beads in figure 6(c) than in figures 6(b) and (e). At a magnification of 1000, the diameters of the fibers are quite uniform in figure 6(a) and figure 6(d), with those in figure 6(a) being
Figure 6. SEM images of electrospun fibers of (a) PU, 8 wt.% and PU (shell)/Nylon-6 (core) which have the concentrations of (b) 4 wt.%/6 wt.%; (c) 6 wt.%/6 wt.%; (d) 8 wt.%/6 wt.%; (e) 10 wt.%/6 wt.%.

smaller. The difference of the morphologies in fiber diameters between figure 6(a) and figure 6(b) to 6(e) may suggest the existence of a core–shell structure in the latter.

3.2. Infrared spectroscopy

From the spectra in figures 7 and 8, the configuration of the core–shell construction for the coaxially electrospun nanofibers was identified. According to figures 7 and 8, adsorptions emanating from the aliphatic constituents are evident (CH$_2$—2925 ± 10 cm$^{-1}$, C–H, 2850 ± 10 cm$^{-1}$ asymmetrical flexing vibration).
Figure 7. FT-IR spectra of various fiber samples of PU (shell)/Nylon-6 (core): (I) 4 wt.%/6 wt.%; (II) 6 wt.%/6 wt.%; (III) 8 wt.%/6 wt.%; (IV) 10 wt.%/6 wt.%

On the basis of figure 8(b), it can be seen that the peaks of Nylon-6 bulked at 3100 cm\(^{-1}\), which is indicative of the characteristic peak of polyamide, and 1639 cm\(^{-1}\), which is from the amide carbonyl group. It is clear from figures 7 and 8(b), that the amide carbonyl group emanating from the Nylon-6 is present in the samples (I, II, III, and IV). In addition, evidence of the N–H group appears in the 1545 cm\(^{-1}\) region and 3299 cm\(^{-1}\). All of these bands did not appear in figure 8(a) but do appear in figures 7 (I)–(IV) and 8(b), this further suggests the existence of Nylon-6 in the composite nanofibers.

From figure 8(a), the FT-IR spectra of the PU polymer, the following characteristics are observed: a strong absorption in the 1700–1670 cm\(^{-1}\) region due to the stretching vibration of the carbonyl group in the carbamate (R–O–C(=O)–NHR). In general, strong absorbing peaks corresponding to a mono-substituent and to a di-substituted compound may occur in the region of 1736 to 1700 cm\(^{-1}\). A combination of these two gave rise to a peak at 1730 cm\(^{-1}\). There was also a peak around 1701 cm\(^{-1}\) that was attributed to the carbonyl group of the amido ester. The characteristic bands of alkyl ether produced the broad peak around 1106 and 1079 cm\(^{-1}\) due to the C–O–C asymmetrical flexing vibration. These absorptions are also observed in figure 7 indicating the presence of PU polymer in the composite nanofibers; specifically the appearance of bands at 2937, 2854, 1730, 1702, 1479, 1109, and 1080 cm\(^{-1}\). Hence, it is concluded that the core–shell structure was formed as described.
3.3. Mechanical properties

The stress–strain data, which were converted from the measured loads versus the crosshead displacement are shown in figure 9 and table 2. From these results, an obvious difference is apparent in the mechanical performances of the pure polymer membrane and the composite fiber membranes. In general, the thinner the fibers in the non-woven fibrous membrane, then the better the mechanical performance [18]. However, this is true only when there are no defects such as beads on the fiber surface. The beads on the fiber surface effectively reduce the tensile property of a single nanofiber. Thus, the tensile properties of PU (shell)/Nylon-6 (core) membranes were lower than that of the PU alone. Since all of the PU/Nylon-6 membranes were prepared under identical electrospinning conditions (especially the same volume flow rates), the concentration of the Nylon-6 core in the composite nanofibers increased when the concentration of PU in the shell solution decreased from 10 to 6 wt.%. In comparing the individual mechanical properties of each component material, PU exhibited a higher modulus whereas Nylon-6 exhibited higher ultimate strength and ultimate strain. The beads (larger than nanofibers in diameter) have a much smaller surface area to volume ratio than that of the nanofibers, resulting in smaller contact areas between the beads and the nanofibers. Therefore the beads on the fiber surface may considerably reduce the cohesive force between the fibers of the non-woven membrane and result in reduced mechanical strength. The characteristics of the Nylon-6 in PU (6 wt.%)/Nylon-6 appeared to play a more important role than that of the morphology on the mechanical performance of the core–shell membrane. Hence, a better mechanical
Figure 9. Comparison for the tensile properties of the PU nanofiber mat and PU (shell)/Nylon-6 (core)
composite nanofibrous membranes with different core concentrations.

Table 2. Tensile properties of electrospun PU (shell)/Nylon-6 (core) composite fibers.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>PU/PA6 (6 wt.%/6 wt.%)</th>
<th>PU/PA6 (8 wt.%/6 wt.%)</th>
<th>PU/PA6 (10 wt.%/6 wt.%)</th>
<th>PU 8 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen thickness (mm)</td>
<td>0.080 (0.010)*</td>
<td>0.112 (0.017)</td>
<td>0.075 (0.009)</td>
<td>0.101 (0.021)</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td>4.15 (0.06)</td>
<td>3.00 (0.04)</td>
<td>2.75 (0.05)</td>
<td>9.29 (0.08)</td>
</tr>
<tr>
<td>Ultimate strength (MPa)</td>
<td>4.69 (0.10)</td>
<td>3.94 (0.16)</td>
<td>5.37 (0.12)</td>
<td>10.55 (0.09)</td>
</tr>
</tbody>
</table>

* Numbers in parenthesis are standard deviation = \( \sqrt{\frac{1}{n} \sum (x_i - \bar{x})^2} \), where \( \bar{x} \) is an averaged value.

performance than that of PU (8 wt.%)/Nylon-6 was seen although PU (6 wt.%)/Nylon-6
exhibited a poorer morphology. However, the beads on the fiber surface were the least
significant with the highest PU concentration, 10 wt.%, which gave rise to an enhanced
mechanical performance in comparison with the other composite fiber membranes. How-
ever, the mechanical performance of the PU (10 wt.%)/Nylon-6 system was still lower
than that of the PU membrane.
Table 3. Water vapor transmission rate (WVT) and pliability of the pure cotton fabric and the fabrics treated with different nanofiber membranes.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>PU/PA6 (8 wt.%/6 wt.%) WVT (g m(^{-2}) per 24 h)</th>
<th>PU/PA6 (6 wt.%/6 wt.%) WVT (g m(^{-2}) per 24 h)</th>
<th>PU 8 wt.% WVT (g m(^{-2}) per 24 h)</th>
<th>Pure cotton fabric WVT (g m(^{-2}) per 24 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pliability (cm)</td>
<td>9.8 ± 0.3</td>
<td>7.6 ± 0.8</td>
<td>10.2 ± 0.5</td>
<td>4.8 ± 0.2</td>
</tr>
</tbody>
</table>

3.4. Water vapor transmission rate and pliability

The difference of water vapor transmission rates (WVT) and pliabilities between the cotton fabrics affixed with PU (shell)/Nylon-6 (core) composite fiber membranes and the pure cotton fabric is presented in table 3. It can be seen that the membranes affected the fabric performance of the cotton fabric significantly. In terms of WVT and pliability the performances of the affixed fabrics decreased compared with the pure cotton fabric, but differences existed depending on the nanofiber system used. In figures 6(a) and (d), the nanofibers that were electrospun from pure PU and PU (shell, 8 wt.%)/Nylon-6 (core) were finer and more uniform than those from PU (shell, 6 wt.%)/Nylon-6 (core), and thus had higher porosity. Experiments showed that the fabrics coated with PU (shell, 8 wt.%)/Nylon-6 (core) or pure PU membrane exhibited higher water vapor transmission than with PU (shell, 6 wt.%)/Nylon-6 (core). Similarly, the nanofiber membrane of PU (shell, 6 wt.%)/Nylon-6 (core) possessed the largest average diameter, and thus the fabric treated with it gave the lowest WVT. As expected, the pure cotton fabric exhibited the highest water vapor transmission.

The pliability of a textile is dependent upon the polymer type and the diameter of the fibers, and the extent of fiber bonding. From table 3, the pliability of the fabrics covered by the PU electrospun membrane alone exhibited the worst pliability, presumably due to the significant bonding of the fibers. In the core–shell system, the Nylon-6 material contributed better pliability to the treated fabrics. However, in light of the key role of the bonding extent in the PU (shell, 8 wt.%)/Nylon-6 (core) membrane, the fabric coated with it showed poorer pliability than that treated with PU (shell, 6 wt.%)/Nylon-6 (core) membrane.

4. CONCLUSION

A method to coaxially electrospin PU (shell)/Nylon-6 (core) nanofibers was developed. The morphology and mechanical performance of the resulting nanofiber membranes were investigated. A preliminary trial indicated that it is feasible to attach core–shell compound nanofibers to a textile substrate. The core–shell nanofibers exhibited properties between those of the individual materials. Further investigation is underway to explore the possibility of functionalizing the shell material using various functional nanoparticles.

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NOTES

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