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Novel multifunctional nanofibers based on thermoplastic polyurethane and ionic liquid: towards antibacterial, anti-electrostatic and hydrophilic nonwovens by electrospinning

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Received 7 November 2014, revised 26 December 2014
Accepted for publication 30 January 2015
Published 17 February 2015

Abstract
Novel antibacterial, anti-electrostatic, and hydrophilic nanofibers based on a blend containing thermoplastic polyurethane (TPU) and a room-temperature ionic liquid (IL), 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆], were fabricated by electrospinning. We investigated the effect of the IL on the morphology and the physical properties of the TPU nanofibers. Nanofibers with a ‘bead-on-string’ morphology were obtained by electrospinning from a neat TPU solution. The incorporation of the IL, at levels as low as 1 wt%, largely suppressed the formation of beads during electrospinning, and homogeneous nanofibers were obtained. The as-spun TPU/IL composite nanofibers showed significant activity against both Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus), with antibacterial activities of more than four and three, respectively. This means that the antibacterial efficiencies of TPU/IL composite nanofibers toward E. coli and S. aureus are 99.99% and 99.9%, respectively. Moreover, nonwoven fabrics derived from the electrospun TPU/IL composite nanofibers exhibit better stretchability, elasticity, and higher electrical conductivity compared to those made using neat TPU without an IL. Additionally, the incorporation of the IL leads to a hydrophilic surface for the TPU/IL composite nanofibers compared to hydrophobic neat TPU nanofibers. These multifunctional nanofibers with excellent antibacterial, anti-electrostatic, and mechanical properties and improved hydrophilicity are promising candidates for biomedical and wastewater treatment applications.

Keywords: nanofibers, electrospinning, ionic liquid, antibacterial, polyurethane

(Some figures may appear in colour only in the online journal)
1. Introduction

Thermoplastic polyurethanes (TPU) are linear diblock copolymers that consist of statistically alternating hard segments (HSs) and soft segments (SSs). From a structural point of view, the HSs are polyurethane blocks based on chain extenders that are frequently diols and diisocyanates. The SS blocks consist of macrodilns such as polyether, polyester, and even polycarbonate. Because of the thermodynamic incompatibility between the HSs and SSs, TPU often undergoes a noticeable phase separation at the microscale, which manifests as versatile physical properties. TPU has thus been studied extensively in the academic and industrial fields [1–5]. Additionally, the carbamate group (-NH-CO2-) in the TPU manifests as versatile physical properties. TPU has thus been studied extensively in the academic and industrial fields [1–5].

This is not favorable for water filtration, clinical, or biomedical applications. Many attempts have been made to enhance either the conductivity [12–16] or antimicrobial capability [17–21] of TPU nanofibers. However, it is still a challenge to fabricate high-performance electrospun TPU nanofibers with both anti-electrostatic and antimicrobial properties.

Room-temperature ionic liquids (ILs) are molten salts with a melting point below 100 °C. They have attracted much interest because of their many promising properties. ILs have an outstanding solvation ability toward a wide range of compounds. They have high chemical and thermal stability and an immeasurably low vapor pressure (commonly considered nonevaporable), a complete ionic structure, and a broad electrochemical potential window [22–24]. ILs have recently been used as effective plasticizers for polyvinyl chloride [25], poly(methyl methacrylate), [26–27] and poly (vinylidene fluoride) [28]. They are also used as compatibilizers to improve the interface between polymer matrices and some inorganic nanofillers typically involved with carbon nanotubes [29–35] and montmorillonite fillers [36]. Because of their pure ionic compound structures, ILs have favorable anti-electrostatic properties, and they act as antistatic agents when incorporated into polymer matrices. This enhances their ability to dissipate accumulated static charges [37–41]. Quaternary ammonium compounds (QAC) are a class of typical biocides that have been found to be effective against algae and bacteria under alkaline pH conditions because of their cationic surface activity [42]. ILs show antimicrobial activity against microorganisms, including bacteria as well as fungi [43–47]. This antimicrobial activity is independent of the type of anion, but it can be affected significantly by the length of the alkyl substituent. Therefore, ILs may provide both anti-electrostatic and antibacterial properties to TPU nanofibers upon the incorporation of the ILs into the TPU matrix.

We thus produced TPU/IL composite nanofibers by electrospinning, and the impacts of the IL on the structure and properties of the nanofibers were carefully evaluated. The as-spun composite nanofiber nonwovens are shown to be extremely effective against bacteria. The introduction of the IL into the TPU nanofibers decreased its surface resistivity, making them excellent anti-electrostatic materials. The resultant TPU/IL nanofiber mats have a good hydrophilic surface and can thus potentially be applied to biomedical and wastewater treatment applications.

2. Experimental section

2.1. Materials and sample preparation

TPU samples (trade name WHT-1295) were purchased from Wanhua Chemical Groups, Yantai, People’s Republic of China, and were used without further treatment. The TPU was formed by a reaction between toluene diisocyanates and polyester diols. The molecular weight and polydispersity of the TPU, as determined by gel permeation chromatography, were Mw = 99 700 and Mw/Mn = 1.867, respectively. The IL, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM] [PF6], was purchased from Sigma-Aldrich and used as received. Dimethyl formamide (DMF) was used as a solvent for the TPU.

TPU/IL composites with different IL content (0, 1, 2, 3, 4, 5, 10, and 15 wt%) were dissolved in DMF, and a fixed TPU/DMF weight ratio of 20% (w/w) was adopted. The mixtures were stirred into homogeneous and transparent polymer solutions at room temperature. They were then loaded into 5 mL plastic syringes equipped with metal needles that had an inner diameter of 0.25 mm. Typical electrospinning experiments were performed at 15 kV, with a polymer solution feed rate of 0.02 mL h−1. Aluminum foil was selected as a static and grounded collector, and its distance from the needle tip was 15 cm. Neat TPU and TPU/IL nonwoven mats were developed on the aluminum foil after electrospinning for 10 h. All the characterized samples were dried at 85 °C under vacuum, overnight.

2.2. Sample characterization

2.2.1. Morphology investigation. The microstructures of the fiber samples were obtained using field emission scanning electron microscopy (FESEM, SEM-JSM 6700). An
acceleration voltage of 3 kV was used for the fiber samples, which were coated with a thin layer of gold.

2.2.2. Antibacterial activity. The species of microorganism tested were *Escherichia coli* (*E. coli*, Gram-negative) and *Staphylococcus aureus* (*S. aureus*, Gram-positive). The antibacterial activity of the samples toward the two microorganisms was determined by TÜV SÜD PSB Products Testing Co., Ltd, Shanghai, People’s Republic of China, in accordance with the testing method for textile products recommended by JIS Z 2801. The antibacterial activity was determined according to the formula:

\[ R = \frac{\log(B/A) - \log(C/A)}{\log(B/C)} = \log(B/C) \]

where \( R \) is the antibacterial activity, \( A \) is the average number of viable bacteria cells immediately after inoculation on an untreated test piece (i.e., blank sample), \( B \) is the average number of viable bacteria cells on the untreated test piece (i.e., blank sample) after 24 h, and \( C \) is the average number of viable bacteria cells on the antimicrobial test piece (i.e., tested sample) after 24 h. The blank sample was a standard sample without any antibacterial ability. Each test area was 5 × 5 cm², and three repeat samples were used.

2.2.3. Electrical properties. The surface resistivity (\( R_s \)) and the volume resistivity (\( R_v \)) of each sample were examined using an ultrahigh-resistivity meter with a URS probe electrode (model MCP-HT450) at a direct-current voltage of 10 V. A URS ring electrode probe with an inner and outer
electrospun TPU and TPU/IL composite nano fibers reported as the contact angle. Measured at onto the sample and the contact angle values, which were varied from 2.13 to 4.03 μm (see figures 1(C)–(F)) and the beads disappear when the IL loading is higher than 10 wt% (see figures 1(G) and (H)).

Figure 2. Plot of mean fiber diameter versus IL loadings for electrospun TPU and TPU/IL composite nanofibers.

Beads have been known as defect structures, since they disturb the unique properties of electrospun fibers and largely decrease the surface-area-to-volume ratio, which can directly impair the mechanical properties of these fibers. Many polymer solution parameters are responsible for the formation of beads during electrospinning, such as a lower polymer concentration [48] or viscosity [49], higher surface tension [50], and poorer conductivity [49, 51–53]. In this work, the bead-on-string structure was significantly suppressed using even 1 wt% IL (0.2 wt% based on the electrospinning solution). Almost no viscosity change (about 1% decreasing measured by viscometer) was observed for the TPU/DMF solution with the incorporation of 1 wt% ILs. On the other hand, we found that the TPU/DMF electrospinning solution has almost the same contact angle on the silicon wafer as the solution incorporated with 1 wt% ILs, so the surface tension of the solution keeps almost constant (see figure S1). However, it was found that the electrical conductivity of the solution increased from 1.26 μs·cm⁻¹ for the solution of neat TPU to 0.17 ms·cm⁻¹ for the solution with the addition of 1 wt% ILs. It has been reported that the incorporation of salts as well as IL is able to enhance the conductivity of polymer solutions [54–56]. Therefore, we attributed the improved nanofiber morphology and the disappearance of the beads of TPU/IL composite nanofibers to the enhanced solution conductivity that stems from the IL. At 1–5 wt% IL, the increase in fiber diameters and distribution are the direct result of the stretching, thinning, and diminution of the beads, wherein a higher charge density is imposed by the addition of ion-conductive IL molecules. Similar morphological results were also obtained from atomic force microscopy (AFM) measurement, as seen in figures 1(a)–(h).

Figure 2 shows the fiber diameters as a function of the IL loadings. It shows that the fiber diameter increases with an increase in IL loading from 1–5 wt% IL. Note that the diameter value was only calculated for those thin fibers, not including the beads or spindle-like beads. The number of beads decreased gradually with the addition of the ILs, and therefore the average fiber diameter increased. Further increasing the IL loading led to a decrease in the viscosity, so the stretching of the fiber was further enhanced, resulting in a slightly decreased fiber diameter, as shown in figure 2.

Another important structural feature of the fibers is the surface roughness, which has a significant effect on the wettability of the fibers. A series of AFM images of the surface topography and the corresponding cross-sectional profiles of the TPU/IL composite fibers are shown in figure 3. As previously discussed, the incorporation of the IL into the TPU fibers significantly suppresses the formation of beads. These are usually considered defect structures, resulting in

3. Results and discussion

3.1. Morphology of the TPU and TPU/IL composite nanofibers

Figures 1(A)–(H) illustrate typical SEM morphology for electrospun neat TPU and TPU/IL, composite fibers. The fibers obtained from neat TPU were found to exhibit a ‘bead-on-string’ morphology, with large, irregular beads placed along the thin, uniform fibers. The diameters of these beads varied from 2.13 to 4.03 μm (see figure 1(A)). The mean fiber diameter was calculated to be approximately 320 ± 26 nm. The incorporation of the ILs leads to a significant change in fiber morphology. As shown in figure 1(B), a very small amount of the IL (i.e., 1 wt%) leads to a significant suppression of the beads and a slightly larger fiber diameter than that of neat TPU. The shape of the beads in the fibers changes from spherical to spindle-like. With an increase in IL loading, the number of these spindle-like beads along the fibers diminishes gradually (see figures 1(C)–(F)) and the beads disappear when the IL loading is higher than 10 wt% (see figures 1(G) and (H)).
Figure 3. AFM images of surface topography (150 × 150 nm²) and corresponding cross-sectional profiles of single electrospun TPU fiber with different IL contents: (A) 1 wt%; (B) 2 wt%; (C) 3 wt%; (D) 4 wt%; (E) 5 wt%; (F) 10 wt%; and (G) 15 wt%.
poor mechanical properties for the fibrous membranes. However, in terms of the hydrophobic behavior of the nonwoven fabrics, the beads are preferred because the degree of surface roughness is higher than that found in bead-free fibers (discussed in the next section). ILs increase the polymer solution’s conductivity, which results in fibers with very few beads. As shown in figures 3(A)–(G), the fluctuation of the surface of the single nanofiber is very low at less than 3 nm, indicating that the surface of the TPU/IL composite fibers is smooth.

Although the IL clearly affects the morphology of the final TPU/IL nanofibers, no significant difference was observed when they were compared with the neat TPU fiber mat in terms of the macroscopic appearance of the fiber mats, as shown in figure 4(A). Additionally, the deposition area on the aluminum foil for the TPU without the IL is relatively small, and the stripping of this sample was difficult. Therefore, the incorporation of the IL improved the spin ability of TPU fibers, as shown in figure 4(B). It is evident that the nonwoven fabrics are tough and elastic upon the addition of the IL, and this will be discussed in section 3.5.

3.2. Antibacterial properties

*E. coli* and *S. aureus* are typical bacteria and fall into the Gram-negative and Gram-positive categories, respectively. From table 1, the fiber produced from neat TPU shows favorable activity against both Gram-negative *E. coli* and Gram-positive *S. aureus*. The antibacterial activity values, *R*, of the two bacteria are 4.08 and 2.98, respectively, indicating that TPU is antibacterial toward both *E. coli* and *S. aureus*. A demand for antibacterial products exists in biomedical and wastewater treatment applications, especially for antibacterial activity against *S. aureus*, which has a complicated bacterial structure that can survive to some extent under harsh conditions. Although TPU fibrous mats without an IL exhibit good antibacterial performance, this is not sufficient for special applications. In this work, the IL, as an antibacterial agent, was integrated into TPU to improve its activity against microorganisms. As shown in table 1, the introduction of 5 wt% IL into the TPU/IL nanofiber mat reduced the colony-forming units (CFU) of the bacteria. The CFU values were 75 m⁻² for neat TPU, which decreased to 12 m⁻² for *E. coli* and from 66 m⁻² to 39 m⁻² for *S. aureus*. This resulted in improved *R* values of 4.89 and 3.20 for the TPU/IL mat toward *E. coli* and *S. aureus*, respectively. This means that the antibacterial efficiencies were 99.99% for *E. coli* and 99.9% for *S. aureus*. Figure 5 shows more photographs of the *E. coli* (figures 5(A) and (D)) and *S. aureus* (figure 5(B) and (C)) bacterial colonies after their elution from sheets of TPU and TPU/IL nanofibers containing 5 wt% IL. The two types of bacteria were nourished for 24 h. From the decrease in the visible *E. coli* and *S. aureus* cells, when the TPU mat is compared with the TPU/IL mat, the latter shows a more effective antibacterial ability. Additionally, the bulk TPU/IL blends prepared by melt-blending at 190 °C in a Haake mixer are also extremely effective against both *E. coli* and *S. aureus* (shown in figure S4).

This improved antibacterial activity against both types of bacteria for the TPU/IL composite fibers comes from the IL. We thus investigated the antibacterial properties of the pure IL. As shown in figure 6, clear and transparent inhibition rings for pure IL against *E. coli* (figure 6(A)) and *S. aureus* (figure 6(B)) were found after 24 h of bacterial incubation. This indicates that pure IL molecules are active against bacteria. Additionally, the larger area of the inhibition ring for the IL against *E. coli* compared with that of *S. aureus* suggests that the IL is far more effective or readily inhibits the growth of *E. coli* compared to *S. aureus*. The reason for this will be discussed in the following section. In contrast, the antibacterial activity of pure DMF was also determined, and no antibacterial activity against either *E. coli* or *S. aureus* was found, as shown in figure S5. This further confirms that the improved antibacterial activity for the TPU/IL composite fibers comes from the IL.

The cell wall is one of the most significant components of a bacterium because it plays an important role in maintaining the bacterium’s inherent shape. The cell wall protects the bacterium from a hypertonic condition and it participates in exchanging related nutrients, among other functions. For *S. aureus*, abundant peptidoglycans containing as many as 50 layers constitute the primary part of the cell wall, and the pentapeptide bridges that connect the tetrapeptide side chains cause the peptidoglycans to cross-link. This results in a strong

**Figure 4.** Photographs of (A) TPU nonwovens with and without IL. Note that TPU nonwovens incorporated by IL (B) are readily stripped from aluminum foil, showing a good spin ability for TPU fibers.
and compact cell wall, as shown in figure 7(C). In contrast, E. coli has a very weak cell wall because it lacks pentapeptide bridges, and the free state of the side chains of the peptidoglycans result in only 1 or 2 layers of peptidoglycans. This difference in their structures may be the main reason that E. coli is more readily eliminated by the IL than S. aureus.

The IL has a similar antibacterial property to QAC [42] because of its cationic ions interacting with the bacterium’s cell wall. As shown in figure 7(C), the cell wall of S. aureus is filled with teichoic acid and lipoteichoic acid, and many negatively charged sites are thus formed. When the negatively charged bacterial cell wall contacts cationic ions such as the limidazolium rings of the IL, an electrostatic interaction occurs. This neutralizes the accumulated negative charges and causes stress, leading to cell wall lysis and disintegration, as shown in figure 7(D). This type of deformed cell wall with poor permeability cannot supply the normal flow of critical nutrients to the cell, and the result is a cell death.

### 3.3. Anti-electrostatic properties

Accumulated static charges on insulation materials under dry conditions most often result in complicated problems such as skin irritation, the adsorption of pathogens and dust, and more seriously, explosions, as clearly shown in figure 7(A). These charged materials are considered undesirable for medical

<table>
<thead>
<tr>
<th>Samples</th>
<th>Species of test bacteria</th>
<th>Colony-forming units (CFU)/cm²</th>
<th>0 h</th>
<th>24 h</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat TPU</td>
<td>E. coli</td>
<td>Samples</td>
<td>/</td>
<td>7.5 × 10¹</td>
<td>4.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank sample</td>
<td>1.6 × 10⁴</td>
<td>9.4 × 10⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S. aureus</td>
<td>Samples</td>
<td>/</td>
<td>6.6 × 10¹</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank sample</td>
<td>7.5 × 10³</td>
<td>6.2 × 10⁴</td>
<td></td>
</tr>
<tr>
<td>TPU-5% IL</td>
<td>E. coli</td>
<td>Samples</td>
<td>/</td>
<td>1.2 × 10¹</td>
<td>4.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank sample</td>
<td>1.6 × 10⁴</td>
<td>9.4 × 10⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S. aureus</td>
<td>Samples</td>
<td>/</td>
<td>3.9 × 10¹</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank sample</td>
<td>7.5 × 10³</td>
<td>6.2 × 10⁴</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6. Photographic images of pure IL’s zones of inhibition against (A) *E. coli* and (B) *S. aureus* (B). Five filter papers with a 5-mm diameter were loaded with IL bulk liquid and placed on five different sites on petri plates. Clear and transparent inhibition rings of IL against the two different types of bacteria are shown in (A) and (B).

Figure 7. Schematic showing (A) the absorption of pathogen, dust, etc in a dry condition on the insulative TPU fibers accumulated by static charges (i.e. positive charges). (B) TPU fibers loaded with homogeneous IL molecules electrospun from TPU/IL composites. (C) Typical bacterial structure of a Gram-positive bacterium (*S. aureus* in this study). Note that the existence of teichoic acid and lipoteichoic acid make the bacterial cell walls negatively charged. (D) The lysis and disintegration of a cell wall through contact with the positively charged imidazolium ions of the ILs.
supplies and textile fabrics. Thus, anti-electrostatic properties of materials are important, especially in medical fabrics. We integrated an IL into TPU to produce anti-electrostatic fibers because the IL is an anti-electrostatic agent as a result of its high ionic conductivity and high ionic mobility. Table 2 and figure 8 show the electrical conductivity and anti-electrostatic effects of neat TPU and TPU/IL composite nanofibers with different IL loadings. The neat TPU nanofiber only exhibits a sufficient anti-electrostatic effect, with values of $4.31 \times 10^{11}$ $\Omega/\square$ and $4.25 \times 10^{10}$ $\Omega$ cm for surface resistivity and volume resistivity, respectively. The incorporation of the IL into the TPU nanofibers effectively decreases these two types of resistivity. The anti-electrostatic effects varied from 'sufficient' for TPU to 'very good' and 'excellent' for the TPU/IL composite nanofibers, with IL loadings of 5 and 10%, respectively. It is interesting to note that no bleeding phenomenon (i.e., migration of the IL on the sample’s surface) for the IL molecules was observed. This is very important for polymer/IL composites because the migration of the IL from the polymer matrix will impair both the anti-electrostatic property and the antibacterial property of the IL. Good compatibility between the TPU and the IL is evident from the depression of the glass transition temperature of the soft segment ($T_{g,ss}$) in the TPU, as shown in figure S6. More detailed information will be reported in a forthcoming article.

3.4. Wettability behavior

As the morphological results show, the morphology of the fibers produced using TPU/IL is distinct from that of neat TPU, so their wettability behavior is expected to be different from that of neat TPU. As shown in figure 9, the electrospun neat TPU fibers exhibit a WCA of $129.5^\circ$. The WCA of the TPU/IL composite nanofibers initially decreased with IL incorporation. The minimum WCA was about $81.5^\circ$ for the sample containing 4 wt% IL. This decrease in the WCA can be ascribed to a decrease in the degree of surface roughness because of the suppression of beads in the TPU/IL nanofibers, as shown in figure 1. The incorporation of an IL into TPU produces the TPU fiber's wettability from 'hydrophobic' to 'hydrophilic' states, which is of great importance for moisture regain, dye, and especially for wastewater filtration and biomedical applications. As the IL content was increased further, the WCA was found to increase slightly. This may be attributed to the intrinsic hydrophobic properties of the IL.

3.5. Mechanical properties

The mechanical property is one of the most important properties of nanofiber nonwoven fabrics. The effects of the IL on the tensile properties and the elasticity of nanofiber nonwoven fabrics were evaluated. Typical strain-stress curves of the neat TPU fiber sheet and the TPU/IL composite fiber sheet with an IL loading of 10 wt% are shown in figures 10(A) and (B). In figure 10(A), a neat TPU fiber sheet is shown to have poor elongation at the break point, with a value of only 73.6%. The tensile strength at the break

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Table 2. The surface resistivity ($R_s$) and volume resistivity ($R_v$) of neat TPU and the TPU/IL composite nanofiber with different IL loadings.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_s$ ($\Omega/\square$)</th>
<th>$R_v$ ($\Omega$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat TPU</td>
<td>$4.31 \times 10^{11}$</td>
<td>$4.25 \times 10^{10}$</td>
</tr>
<tr>
<td>TPU-1% IL</td>
<td>$3.44 \times 10^{10}$</td>
<td>$3.41 \times 10^{9}$</td>
</tr>
<tr>
<td>TPU-2% IL</td>
<td>$4.92 \times 10^{9}$</td>
<td>$4.88 \times 10^{8}$</td>
</tr>
<tr>
<td>TPU-3% IL</td>
<td>$2.80 \times 10^{8}$</td>
<td>$2.77 \times 10^{7}$</td>
</tr>
<tr>
<td>TPU-4% IL</td>
<td>$1.80 \times 10^{7}$</td>
<td>$1.76 \times 10^{6}$</td>
</tr>
<tr>
<td>TPU-5% IL</td>
<td>$1.49 \times 10^{6}$</td>
<td>$1.48 \times 10^{5}$</td>
</tr>
<tr>
<td>TPU-10% IL</td>
<td>$2.52 \times 10^{5}$</td>
<td>$2.49 \times 10^{4}$</td>
</tr>
<tr>
<td>TPU-15% IL</td>
<td>$2.92 \times 10^{4}$</td>
<td>$2.89 \times 10^{3}$</td>
</tr>
</tbody>
</table>

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Figure 8. Plot of surface resistivity ($R_s$) obtained from table 2 versus IL loading for electrospun TPU and TPU/IL composite nanofibers. The evaluation of antielectrostatic ability for each sample was judged from [40, 41].

Figure 9. WCA and the corresponding shapes of water droplets for the electrospun TPU and TPU/IL composite nanofibers, in which the average value of five measurements performed at different positions on the same samples was adopted as the WCA.
point was around 2.1 MPa. This can be attributed to its ‘bead-on-string’ morphology, as shown in figures 1(A) and (a), because the large amount of beads on the TPU fibers impairs the mechanical properties of the TPU. As expected, the TPU/IL fiber sheet with a 10 wt% loading and a bead-free morphology, because of the addition of the IL, showed a significant elongation at the break point with a value as high as 300%. It also had a higher tensile strength at the break point, with a value of 20.3 MPa. Additionally, this sample exhibited excellent elastic recovery, as shown in figure 10(B). The residual strain of the TPU/IL fiber sheet with a 10 wt% loading after one to six cycles with a 25% strain interval was found to be around 7.21%, 15.7%, 26.2%, 38.9%, 50.8%, and 63.3%, respectively. These results indicate the excellent elasticity of the TPU/IL composite mats. The good stretchability and excellent elasticity are indeed very important for the use of nonwoven fabrics in industrial and biomedical applications.

4. Conclusion

Novel multifunctional TPU/IL composite nanofibers were successfully produced from DMF solutions by electrospinning. The morphology and the physical properties of the as-obtained TPU fibers were carefully investigated. The incorporation of an IL resulted in an increase in solution conductivity and a significant suppression of TPU beads. An increase in the mean fiber diameter also occurred. The surface of the TPU/IL composite fiber was found to be smooth, and the corresponding fluctuation was less than 3 nm. Interestingly, the as-spun TPU/IL composite nanofiber has excellent antibacterial properties toward E. coli and S. aureus, and it has excellent anti-electrostatic properties. The as-prepared composite nanofiber mats show better stretchability, elasticity, and hydrophobicity compared to neat TPU nonwoven fabrics. Therefore, these antibacterial, anti-electrostatic, and hydrophilic nanofibers with excellent mechanical properties are promising candidates for biomedical and wastewater treatment applications.

Associated content

Supporting information

This content provides detailed information about the calculated values of CFU for bacteria (table S1), shapes of droplets for TPU and TPU/IL solutions (figure S1), antibacterial behaviors of a blank sample (figure S2), fiber mats of TPU and TPU/IL nanofibers (figure S3), TPU/IL blends (figure S4) and DMF (figure S5), and dynamic mechanical analysis for TPU and TPU/IL blends (figure S6).

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (51173036, 21374027) and the Program for New Century Excellent Talents in University (NCET-13-0762). This work was also supported by the Opening Project of the Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Chinese Academy of Sciences.

References


Rujitanaroj P, Pimpha N and Supaphol P 2008 Wound-dressing materials with antibacterial activity from electropun gelatin fiber mats containing silver nanoparticles Polymer 49 4723–32


Hagihara R and Ito Y 2000 Room temperature ionic liquids of alkylimidazolium cations and fluoroanions J. Fluorine. Chem. 105 221–7


Davis J H and Fox P A 2003 From curiosities to commodities: ionic liquids begin the transition Chem. Commun. 1209–12


Zhao L P, Li Y J, Cao X J and Dong W Y 2012 Multifunctional role of an ionic liquid in melt-blended poly (methyl methacrylate)/multi-walled carbon nanotube nanocomposites Nanotechnology 23 255702


methacrylate)/montmorillonite nanocomposites using imidazolium-based ionic liquids Polym. Int. 61 1382–8


[49] Fong H, Chun I and Reneker D H 1999 Beaded nanofibers formed during electrosprining Polymer 40 4585–92

[50] Doshi J and Reneker D H 1995 Electrosprining process and applications of electrosprun fibers J. Electrostatics 35 151–60

[51] Mazinani S, Ajji A and Dubois C 2009 Morphology, structure and properties of conductive PS/CNT nanocomposite electrosprun mat Polymer 50 3329–42

[52] Demir M M, Yilgor I, Yilgor E and Erman B 2002 Electrosprining of polyurethane fibers Polymer 43 3303–9


[56] Cengiz F and Jirsa O 2009 The effect of salt on the roller electrosprining of polyurethane nanofibers Fiber Polym. 10 177–84