High performance polyimide composite films prepared by homogeneity reinforcement of electrospun nanofibers

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A. Introduction

In the past two decades, polymer nanocomposites have received significant attention in both industry and academia for their enhanced mechanical and other physical properties [1–10]. Fibrous fillers such as carbon nanofibers have been utilized for improving the strength and rigidity of polymers due to their high aspect ratio and unique properties [1,5,7,8]. One of the key issues to successfully develop nanofiber-filled polymer nanocomposites is fine dispersion and high orientation of nanofibers in polymer matrices. However, on the one hand, it is not easy to achieve homogeneous dispersion of nanofibers in polymer matrices because of their high surface area. A poorly dispersed nanomaterial may degrade the mechanical properties because of poor adhesion at the fiber–matrix interfaces [10–12]. On the other hand, nanofibers usually cannot be effectively aligned in the matrix, which prevents the nanofillers from being efficiently used as the ideal reinforcing agents [5,8,11–15].

Polyimide (PI) is particularly attractive for their outstanding thermal stability and good mechanical properties and usually used as high-performance engineering plastics [6,14,16,17]. Polyimide nanocomposites containing fibrous nanoparticles are considered to be promising for many applications, especially as light-weight high-performance materials [13,14,18–20]. Fu and Zheng synthesized polyimide/silica tubes nanocomposites with improved tensile strength and ductility by using γ-aminopropyltriethoxysilane as the coupling agent [14]. Li found that the nitric acid oxidized carbon fibers can improve the mechanical and tribological properties of the polyimide [19]. However, nearly all the nanofiber reinforced composites need the modification of nanofibers or the use of coupling agents, which may seriously affect the properties of the as-prepared nanocomposites. Besides that, it is difficult to obtain nanocomposites with good nanofibers alignment because the nanofibers tend to be randomly distributed in the nanocomposites. That is why the mechanical properties of the nanofibers reinforced nanocomposites cannot be remarkably improved.

Electrospinning is a low-cost but effective method to continuously produce polymer nanofibers [13,21–25]. As the electrospun nanofibers shows extraordinary properties such as excellent mechanical strength, high aspect ratio and surface-to-volume ratios, they are ideal candidates for reinforcing polymer materials [13,21–26]. Herein, we fabricate polyimide films by using the highly aligned homogeneous PI nanofibers as reinforcing fillers. The good compatibility between the electrospun nanofibers and the matrix can be obtained easily without chemical modification of the PI nanofibers or adding any coupling agents, and the highly aligned PI fibers can be efficient for the load transfer from the PI
matrix to the PI nanofibers. Thus, the mechanical properties of PI films are remarkable improved by incorporating the highly aligned neat PI and CNT/PI nanofibers. Interestingly, the electrospun nanofibers can improve not only the tensile strength but also the tensile strain at break of polyimide films. The as-prepared high-performance PI composite films maintain good transparency after the incorporation of nanofibers and the density of the reinforced films is lower than that of neat PI. The as-prepared PI films may have potential applications in microelectronics, optical and light-weight aerospace materials.

2. Experimental section

2.1. Materials

Pyromellitic dianhydride (PMDA), 4,4’-oxydianiline (ODA), N,N-dimethylacetamide (DMAc) were commercially obtained from China Medicine Co. Pristine multiwalled carbon nanotubes were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, and the outer diameters of the CNTs are about 5–10 nm. The pristine CNTs were refluxed in concentrated HNO₃ for 12 h with a weight ratio of the acid to the CNTs of 50:1 and the acid functionalized CNTs can be stably dispersed in DMAc upon sonication.

2.2. Preparation of electrospinning solutions

The precursor of polyimide, poly(amic acid) (PAA) was synthesized from PMDA and ODA with an equivalent molar ratio. The polycondensation was performed in DMAc at a temperature of about 0 °C, and the solid content of the pristine PAA solution was 25 wt.%. For the preparation of neat PAA solution used for electrospinning, the pristine PAA solution was diluted by DMAc; and for CNT/PAA solutions, the pristine PAA solution was diluted by CNT/DMAc solution. Prior to solution mixing, the CNT/DMAc solutions were sonicated for 2 h to uniformly disperse the carbon nanotubes and the solid content of all the solutions for electrospinning was fixed at about 16.7 wt.%.

2.3. Electrospinning and imidization of nanofiber membranes

Electrospinning was carried out using a syringe with a spinneret having a diameter of 0.5 mm at an applied voltage of 18–25 kV at ambient temperature. The feeding rate was about 0.25 mL per hour and the spinneret-collector distance was set to be 20 cm. The PAA nanofibers were collected using a rotating disk collector with a diameter of 0.30 m and a width of 10 mm. During electrospinning, the linear speed of the rotating collector was about 20 m s⁻¹ because lower rotation speed cannot efficiently align the nanofibers and higher speed may leads to the breakage of the nanofibers. All the electrospun nanofiber membranes were dried at 60 °C for 4 h to remove the residual solvent and then thermally imidized using the following program to complete the imidization process: heating up at a rate of 3 °C min⁻¹ to 100, 200 and 300 °C, followed by an annealing at each temperature stage for 30 min.

2.4. Preparation of nanofibers reinforced PI films

The as-prepared electrospun (neat PI and CNT/PI nanofibers) membranes were soaked or immersed in the dilute solution of PAA (with a solid content of 5 wt.%) for 120 s, and then experienced the same imidization process as mentioned above to obtain the nanofibers reinforced PI composite films. The soaking process should be taken carefully as small air bubbles in the reinforced films may lead to the deterioration of film properties.

2.5. Characterization

A scanning electron microscope (SEM, Tescan) performed at an acceleration voltage of 20 kV was used to observe the surface morphology of the electrospun nanofiber membranes and the fractured surfaces of PI films. Transmission electron microscopy (TEM) observations of nanofibers were performed under an acceleration voltage of 200 kV with a Philips CM 300 FEG TEM. TEM specimens were prepared by directly collecting the electrospun nanofibers onto copper grids during the fabrication of membranes. Tensile tests of the film samples were carried out using an Instron universal material testing system, and the samples were directly mounted to the sample clamps and stretched at a speed of 5 mm min⁻¹. The loading direction of the tensile tests for the PI films reinforced with nanofibers is along the fiber alignment direction and parallel to the fiber axis. Tensile property values reported here represent an average of the results for tests run on at least five samples. Thermogravimetric analysis (Pyris 1 TGA) was performed under nitrogen flow from 100 to 800 °C at a heating rate of 20 °C min⁻¹. Dynamic mechanical analysis (DMA, Netzsch) of the nanocomposite films were carried out under tensile membrane mode from 50 to 450 °C at a frequency of 1 Hz and heating rate of 3 °C min⁻¹.

3. Results and discussion

Electrospinning, which utilizes an external electrostatic field to generate nanofibers, is widely used as an effective method to continuously produce polymer nanofibers with anisotropic physical properties. By changing the experimental parameters, such as the polymer solution properties (e.g., viscosity, surface tension) and electrospinning conditions (e.g., voltage, spinneret-collector distance), nanofibers with diameters between 200 and 300 nm can be obtained. As shown in Fig. 1a by SEM, neat PI nanofibers collected by a high speed rotating method were highly aligned. Fig. 1b is the SEM image of neat PI nanofibers at a higher magnification. It can be seen that the diameter of the as-prepared nanofibers is uniform, and the surfaces of the electrospun nanofibers are smooth and almost free of defects such as beads. As we know, the diameter uniformity and absence of beads in the electrospun nanofibers are of vital importance for achieving high strength and toughness. Polyimide nanofibers containing different CNT loadings were also prepared by electrospinning. By electrospinning of the CNT/PAA solution and subsequent thermal imidization, PI nanofibers with various CNT contents were prepared. Fig. 1c and d shows the SEM micrographs under different magnifications for the electrospun 3.5 wt.% CNT/PI nanofibers. It can be seen that the diameter of the nanofibers containing 3.5 wt.% CNTs was not as uniform as that of neat PI nanofibers and the incorporation of CNTs leads to the widening of the diameter distribution.

During the electrospinning process, some nanofibers were collected on copper grids for TEM observations. Fig. 2a–c shows the TEM micrographs of the electrospun PAA nanofibers containing 2, 3.5 and 5 wt.% CNTs, respectively. After the acid functionalization of CNTs, the PAA chains might form a coating layer around each individual CNT rope due to hydrogen bonding and keep the nanotubes from aggregating or bundling together and thus the CNTs can be well dispersed in the electrospun nanofibers at a low CNT loading (Fig. 2a). The finely dispersed CNTs were aligned parallel along the axis of the electrospun fibers easily, which is mainly ascribed to the large electrostatic field and elongation forces applied to the liquid jet during electrospinning. It can be seen that the surface of 2 wt.% CNT/PAA nanofiber was smooth, and no beads or other defects were observed in the nanofiber. Further increase of the CNT contents, especially for the nanofibers with 5 wt.% CNTs, may lead to the agglomeration of CNTs within the nanofibers. As shown in
As ideal reproduction and strong interfacial interactions can usually be achieved by using homogeneity self-reinforcement strategy for making high performance polymer composites, here we attempted to fabricate the self-reinforced PI films by using their own electrospun nanofibers. Fig. 3a–c shows the photographs of solution cast PI film, the nanofiber reinforced PI film and the electrospun PI nanofiber membranes, respectively. Excellent transparency of the yellow PI film prepared by conventional solution casting can be observed (Fig. 3a). The PI membrane consisting of electrospun PI nanofibers was totally opaque because of light scattering (Fig. 3c). It is interesting to find that the nanofiber reinforced PI film (Fig. 3b) showed considerable transparency because most of the voids between the electrospun nanofibers were filled by the PI matrix during the infiltration and subsequent imidization process. The density of the reinforced films was estimated to be about 70% of the cast bulk PI film (1.47 g/cm³), which means that about 30% of the reinforced PI film was not filled by the nanofibers. That is why the transparency of the reinforced film (Fig. 3b) was not as good as that of the cast PI film (Fig. 3a).

Fig. 4 shows the typical stress–strain curves of neat cast PI film and highly aligned nanofiber reinforced PI films. The tensile properties such as tensile strength, tensile modulus and elongation at break were averaged and listed in Table 1. The tensile strength and elongation at break of electrospun nanofiber reinforced film are much higher than those of the cast film, due to the high orientation of the electrospun nanofibers in the film. It is known that electrosprinng is a facile method for obtaining high orientation of polymer chains in the nanofibers. Therefore, the significant improvement of tensile properties of the neat PI nanofiber reinforced PI film can be ascribed to twofold orientations: (1) high orientation of electrospun PI nanofibers in the PI films (due to high-speed rotation collecting method), and (2) high orientation of PI chains in the electrospun PI nanofibers. As shown in Fig. 3b, the nanofiber reinforced PI film was nearly transparent because of the good compatibility between the nanofibers and PI matrix. By the incorporation of highly aligned PI nanofibers as reinforcing agents, the tensile strength and elongation at break of neat PI films were remarkably improved by about 97% and 46%, respectively. The significant improvement in overall mechanical properties of PI films can be ascribed to the good compatibility and thus strong interfacial interaction between PI nanofibers and PI matrix as well as the dual high-orientation factors mentioned above.

It can be seen from Fig. 4 and Table 1 that, the tensile modulus of neat PI nanofiber reinforced film is slightly higher than those of 1 wt.% and 2 wt.% CNT/PI nanofibers reinforced films, because of better compatibility between neat PI fibers and the matrix. With the increase of CNT content, the moduli of the reinforced PI films were gradually increased and the 5 wt.% CNT/PI membrane possessed the highest tensile modulus. The elongation at break for the PI films was greatly improved by incorporating 1 wt.% and 2 wt.% CNTs into the PI nanofibers. And the optimal tensile properties were achieved for the PI film reinforced with 2 wt.% CNT/PI nanofibers. Compared with the solution cast PI films, the tensile strength and elongation at break for the PI film reinforced with 2 wt.% CNT/PI nanofibers were significantly increased by 138%...
and 104%, respectively. As we know, polyimide usually possesses low toughness. Here, high-performance homogeneity reinforced polyimide nanocomposites were successfully prepared with high toughness and enhanced overall mechanical properties by incorporation of 2 wt.% CNT/PI nanofibers as reinforcing agents. For the 3.5 wt.% and 5 wt.% CNT/PI nanofibers reinforced PI films, the tensile properties were moderately decreased (in comparison with those of the 2 wt.% CNT/PI nanofibers reinforced one), probably because the CNTs may form bundles or aggregates in the electrospun nanofibers with the increase of CNT contents. As shown in Fig. 2b and c, the entangled nanotubes were prone to aggregate close to the nanofiber surface rather than being dispersed and aligned well in the nanofibers, thus leading to the coarseness of surfaces and the un-uniformity of the diameters of the electrospun nanofibers. These will greatly deteriorate the quality or mechanical performance of the electrospun nanofibers, thus partially sacrificing their reinforcement effect. In addition, for the nanofibers reinforced PI films, good interfacial adhesion between the nanofibers and the matrix is crucial for achieving excellent mechanical properties. When the CNTs form aggregates close to the nanofiber surface, good interfaces cannot be formed between the nanofibers and PI matrix, thus the concept of homogeneity self-reinforcement will not play a full role.

Table 1
Summary of mechanical properties of solution cast neat PI film, electrospun neat PI and CNT/PI nanofibers reinforced PI films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Elongation at break (%)</th>
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<tbody>
<tr>
<td>Solution cast neat PI film</td>
<td>88.4 ± 17.6</td>
<td>1.29 ± 0.15</td>
<td>39.3 ± 9.2</td>
</tr>
<tr>
<td>Neat PI nanofiber reinforced film</td>
<td>174.1 ± 10.4</td>
<td>1.31 ± 0.12</td>
<td>57.2 ± 9.6</td>
</tr>
<tr>
<td>1 wt.% CNT/PI reinforced film</td>
<td>176.5 ± 10.2</td>
<td>1.23 ± 0.13</td>
<td>79.3 ± 8.6</td>
</tr>
<tr>
<td>2 wt.% CNT/PI reinforced film</td>
<td>210.4 ± 14.6</td>
<td>1.26 ± 0.13</td>
<td>80.8 ± 9.4</td>
</tr>
<tr>
<td>3.5 wt.% CNT/PI reinforced film</td>
<td>169.2 ± 15.1</td>
<td>1.34 ± 0.15</td>
<td>56.4 ± 10.3</td>
</tr>
<tr>
<td>5 wt.% CNT/PI reinforced film</td>
<td>171.5 ± 14.3</td>
<td>1.47 ± 0.12</td>
<td>57.3 ± 11.4</td>
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</table>
Fig. 5a and b shows the fractured surfaces of cast PI film and neat PI nanofibers reinforced PI film, respectively. It can be seen that the fractured surface of the cast PI film is smooth and homogeneous, while that of the PI film reinforced by the electrospun PI nanofibers is very rough. As shown in Fig. 5b, the neat PI nanofibers were intimately surrounded by the PI matrix, which can be ascribed to the excellent compatibility and strong interfacial bonding between them. The highly aligned PI nanofibers embedded in the matrix tended to be broken (as indicated by red arrows) instead of being simply pulled out from the matrix. That is why the mechanical strength of the nanofibers reinforced films is significantly improved compared with the cast PI films. A steady increase or hardening of the stress was observed after the yield point for the nanofiber reinforced film (Fig. 4). However, this was not seen for the solution cast film. This is probably because at early stage of the tensile tests, only part of the aligned nanofibers within the films may work and bear the load. During the tensile testing, more and more nanofibers in the film are extended and suffered the load, thus leading to a steady increase of tensile strength and an enhanced toughness. As electrospinning can be an efficient method to realize the orientation of polymer chains along the nanofiber axis direction, the increased orientation of PI chains in the electrospun nanofibers may also lead to an increase or improvement of both tensile toughness and strength. Moreover, the nanofibers may serve as connecting bridges to prevent the matrix from fracturing upon mechanical deformation, thus also enhancing the mechanical properties of PI films.

Fig. 5c and d shows the SEM images of fractured surfaces of 2 wt.% and 3.5 wt.% CNT/PI nanofiber reinforced PI films, respectively. The CNTs (i.e., the bright dots or lines as indicated by the blue arrows) embedded in the electrospun nanofibers can be clearly observed because of their relatively high electrical conductivity. It can be occasionally seen that the electrospun CNT/PI nanofibers are individually protruded out of the fractured surfaces, as indicated by the red arrows in Fig. 5c and d. And, some cavities (as indicated by white arrows) are left behind and clearly observed after the nanofibers are pulled out from the matrix due to debonding; whereas the neat PI nanofibers were closely surrounded by the matrix.
matrix (Fig. 5b). This is probably because the interfacial bonding between the high CNT loading nanofibers and PI matrix is not as strong as that of the neat PI nanofibers. It was observed that the agglomerated CNTs tended to be protruded out of the electrospun nanofiber surfaces because of their high surface energies (Fig. 3). Here, with the increase of CNT contents in the electrospun nanofibers, the CNTs are inclined to form agglomerates close to the nanofiber surfaces. The nanofibers with CNT agglomerates on their surfaces possess relatively poor interfacial interaction with the PI matrix.

Fig. 6 shows the TGA curves under nitrogen atmosphere for solution cast neat PI and different nanofibers reinforced PI films. It can be seen that all the PI films reinforced by electrospun nanofibers possess excellent thermal stability. Although the nanofibers experienced twice high temperatureimidization processes, the thermal stability of the reinforced PI films was no worse than that of solution cast neat PI film.

Fig. 7a and b depict the DMA results showing storage modulus ($G'$) and tan($\delta$) versus temperature curves for neat PI and its CNT nanofiber reinforced films. The steady increased modulus can be attributed to the strengthening effect of high oriented electrospun nanofibers in the matrix and the combined good dispersion and stiffening effect of CNTs. The glass transition temperatures for all the films were higher than 350 °C, indicating excellent thermal properties of PI composite films. The solution cast PI film possesses the highest tan($\delta$) value probably because the free volume in neat PI film is very small, thus more energy is required for chain mobility. The tan($\delta$) value of PI was decreased by addition of electrospun nanofibers. The reduction of tan($\delta$) may result from the increase of $G'$ by adding nanofillers, indicating strong bonding between the nanofibers and PI matrix. Generally, the incorporation of CNTs may lead to the increase of glass transition temperature of polymer. The nanofibers containing 2 wt.% CNTs reinforced PI film possesses the lowest tan($\delta$) and glass transition temperature, indicating that the 2 wt.% CNT/PI fiber reinforced film possesses the highest toughness, which is consistent with the tensile tests. Thus, this homogeneity reinforcing method is very successful for fabricating high mechanical performance polyimide nanocomposites with low cost.

4. Conclusions

In this study, light-weight and high-performance polyimide nanocomposite films with good transparency were fabricated by a homogeneity self-reinforcing method. By using electrospinning and the subsequent high-speed rotation collecting methods, highly aligned PI nanofibers with different CNT loadings were prepared. TEM micrographs indicated that the functionalized CNTs were homogeneously dispersed and well oriented in the nanofibers. It was found that the as-prepared aligned electrospun nanofibers are ideal and efficient self-reinforcing agents to prepare high-performance PI nanocomposite films because of good compatibility between the electrospun nanofibers and the matrix. Compared with solution cast neat PI film, the tensile strength and elongation at break for the PI composite film reinforced with 2 wt.% CNT/PI nanofibers were increased by 138% and 104%, respectively. Such a homogeneity self-reinforcement approach to fabricate high-performance PI/CNT nanofiber films is a good attempt toward utilizing CNTs in polymer matrices to achieve ultrastrong, tough, and light-weight nanocomposites that can be used in defense or aerospace areas.

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References


