Temperature-induced molecular orientation and mechanical properties of single electrospun polyimide nanofiber

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Abstract

Mechanical properties of polyimide (PI) electrospun nanofibers could be improved by increasing imidization temperatures. However, the intrinsic mechanism on this phenomenon is highly required, which is helpful to improve mechanical properties of electrospun nanofibers by external thermal treatment. In this work, single electrospun PI nanofibers (SNF-PI) with different imidization temperatures were prepared. The nanofiber morphology was studied by SEM and AFM and the mechanical properties were measured by single fiber micro-tensile test. Polarized Raman Spectroscopy was applied to determine the PI molecular orientation in SNF-PI. The molecular orientation factor provides directly explanation on the effect of imidization temperatures on the mechanical properties of SNF-PI.

1. Introduction

Polyimide (PI) nanofibers produced by electrospinning possess excellent mechanical properties and thermal stability [1]. They have been applied as battery separators [2,3], high flux and low fouling microfiltration [4], high temperature filtration [5], removal of PM2.5 [6], reinforcements [7,8], etc. One of the hot topic on electrospun PI nanofibers is their mechanical properties. Recently, our group found that the imidization temperatures could induce the enhancement of mechanical properties of aligned electrospun PI nanofiber belt [9]. The possible reason could be that the high imidization temperature provided more energy for the movement and re-orientation of PI molecules along the nanofiber axis.

Polarized FT-IR spectroscopy is widely used to investigate the molecule orientation in electrospun nanofibers [10,11]. However, this technique could only provide a static data on the molecule orientation in aligned electrospun nanofibers due to the limitation of sample size. As comparison, Polarized Raman Spectroscopy possesses much higher sensitivity, which can be applied on single electrospun nanofiber (SNF) [12]. Therefore, it could be considered an ideal technology to study the molecular orientation in electrospun nanofibers.

In this work, electrospun PI single nanofibers (SNF-PI) under different imidization temperatures were prepared and their mechanical properties were studied by single fiber micro-tensile test. Further Polarized Raman Spectroscopy was applied to show the relationship between the molecular orientation and mechanical properties of SNF-PI under different imidization temperatures.

2. Experimental

The electrospun SNF-PI was prepared according our previous reports [9,13,14]. In briefly, equimolar ratio of 3, 3'-4, 4'-biphenyl tetracarboxylic dianhydride (BPDA) and 4, 4'-diaminobiphenyl (BPA) were reacted in N,N'-dimethyl acetamide (DMAc) at 0 °C for 24 h. The obtained polyamic acid (PAA, 5.73 dL/g) solution was diluted to 3.5 wt% by DMAc for electrospinning. The electrospinning was performed under 100 kV/m electric field and 0.3 mL/h flow rate. The single PAA nanofiber (SNF-PAA) was collected by a rectangle steel frame (10 × 30 cm) and the useless fibers were picked out by tweezers. The SNF-PAA was imidized by first heating to 150 °C (5 °C/min, annealing 30 min) and then to the final temperatures of 250, 320, 370, 430 and 460 °C (2 °C/min, annealing 60 min). The corresponding samples were denoted as SNF-PI-250, SNF-PI-320, SNF-PI-370, SNF-PI-430 and SNF-PI-460, respectively.

https://doi.org/10.1016/j.matlet.2017.12.146
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Then the SNF-PI was fixed on a paper frame for morphology character-ization and single fiber micro-tensile test. To have an overview on the morphology of nanofibers, the randomly deposited PI-250 and PI-430 nanofiber mats were also prepared.

Fiber morphologies were characterized by atomic force microscopy (AFM, Shanghai Zhuolun MicroNano D5A) with tapping mode and scanning electron microscopy (SEM, TESCAN vega3). Polarized Raman Spectroscopy was performed on LabRAM HR-800 (Horiba Jobin Yvon; resolution: XY < 1 μm, Z < 2 μm; He-Ne laser light: 632.8 nm). During the measurement, the SNF-PI was perpendicular to the plane of light scattering. Mechanical properties of SNF-PI was measured by a micro-tensile tester (JSF10, Powereach, Shanghai) with a micro-load sensor (ULA-2GR, Minebea Co., Ltd). A tensile speed of 0.094 mm/min and a fiber gauge length of 4 mm were used for the micro-tensile test.

3. Results and discussion

Recently, Papkov et al. disclosed the size effect on mechanical properties of electrospun nanofibers that a dramatically increase of mechanical properties could be obtained when the fiber diameter is blow the critical size [15]. Therefore, it is really necessary to maintain all the PI fibers within similar diameter size. In this work, all the PI fibers were obtained from the same PAA solution and electrospinning conditions. Although the fibers experienced different final imidization temperatures, they still possessed similar fiber diameters due to the excellent thermal stability of PI nanofibers (Fig. 1). All the nanofibers showed very smooth surface without any beaded fibers. Thermal imidization temperature did not affect the fiber diameters too much. The PI-250 possessed an average fiber diameter of 215 ± 12 nm while PI-430 had an average fiber diameter of 220 ± 18 nm. Further study by AFM [16] showed that the diameter of single SNF-PI-430 nanofiber was 221 nm, which is nearly the same as measured by SEM. This dimensional stability guaranteed the comparability of the mechanical properties and molecular orientation of SNF-PI under different imidiza-tion temperatures.

Our previous work showed that BPDA-BPA based aligned PI nanofiber belts exhibited increased mechanical strength (σ) and modulus (E) as increasing the imidization temperatures [9]. However, the highest values were only 689 MPa and 13.2 GPa, respectively. These values only presented the mechanical properties of the belts and couldn’t exhibit the inherent mechanical properties of SNF-PI due to the porosity and the possible defects in the belts. Therefore, in this work, the measurement on the mechanical properties of SNF-PI was performed (Fig. 2 and Table 1). On the one hand, when comparing the mechanical properties of SNF-PI with the PI belts, it is obvious that SNF-PI possessed much higher σ and E, but much lower elongation at break (ε). The possible reason for the higher σ and E could be due to the less defect and higher molecular orientation in SNF-PI than belts. The much higher ε of belts than SNF-PI might be because the friction between the nanofibers delayed the fracture of the belts. On the other hand, as increasing the imidization temperatures, the σ and ε were first increased then decreased while the E was increased. The SNF-PI-430 showed the highest σ (2864 MPa), while SNF-PI-460 possessed the highest E (174 GPa), which were 12 and 6 times higher than those of SNF-PI-250. Recently, Chen et al. also found the same effect of imidization temperatures on the mechanical properties of pyrimidine contained SNF-PI [13]. However, proper explanations on the temperature-induced improvement on mechanical properties of SNF-PI are missing. The possible reason could be the high imidization temperature provided more energy for the re-orientation of PI molecules in the nanofibers.

Polarized Raman Spectroscopy have been extensively applied for the determination of molecular orientation in films, fibers and crystals [12,17]. Compared with polarized FT-IR spectroscopy, it has advantages of high resolution, small laser detecting point, tiny sample size even SNF, simple spectra curves without combined

<table>
<thead>
<tr>
<th>Sample</th>
<th>σ (MPa)</th>
<th>ε (%)</th>
<th>E (GPa)</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNF-PI-250</td>
<td>214 ± 21</td>
<td>1.00 ± 0.01</td>
<td>23.5 ± 2.6</td>
<td>0.69</td>
</tr>
<tr>
<td>SNF-PI-320</td>
<td>1328 ± 132</td>
<td>1.93 ± 0.02</td>
<td>68.1 ± 2.2</td>
<td>0.72</td>
</tr>
<tr>
<td>SNF-PI-370</td>
<td>1947 ± 118</td>
<td>2.34 ± 0.02</td>
<td>86.3 ± 6.5</td>
<td>0.79</td>
</tr>
<tr>
<td>SNF-PI-430</td>
<td>2865 ± 318</td>
<td>2.23 ± 0.01</td>
<td>129.8 ± 12.3</td>
<td>0.87</td>
</tr>
<tr>
<td>SNF-PI-460</td>
<td>2494 ± 144</td>
<td>1.43 ± 0.02</td>
<td>174.0 ± 10.5</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Fig. 1. Morphology of electrospun PI mats (a, b) and single nanofiber (c).

Fig. 2. Typical stress-strain curves of SNF-PI.
characteristic frequency bands and double frequency bands, etc. So it is very convenient to measure the molecular orientation in SNF. As shown in Fig. 3a, all SNF-PI were measured by Polarized Raman Spectroscopy in perpendicular directions designed as XX and YY directions. All the spectra showed the same characteristic peaks, indicating the same PI molecular structures under imidization temperatures from 250 to 460 °C. The strongest signal at 1612 cm⁻¹ could be attributed to the stretching of benzene rings in PI molecules. As the temperature increased, the intensity of 1612 cm⁻¹ in XX direction increased, suggesting the PI molecules re-oriented along the nanofiber axis. The molecular orientation factor (f) could be calculated by the equation: \( f = 1 - \frac{I_{YY}}{I_{XX}} \), where \( I_{XX} \) and \( I_{YY} \) are the absorption intensity of the Raman signal in XX and YY directions, respectively. When the imidization temperature was 250 °C, the f of SNF-PI-250 was only 0.69 (Table 1, Fig. 3b). When a small imidization temperature was applied, the PAA molecules can’t get enough energy for re-orientation, and imidized in insitu state, which led the PI molecules in curl state in the nanofibers. Therefore, the orientation factor was low. When higher imidization temperature was applied, the f of SNF-PI-460 could even increase to 0.91 (Table 1, Fig. 3b), which was 32% higher than that of SNF-PI-250. Under higher imidization temperatures, the PI molecules could get enough energy to improve the movement of PI molecular chains. Due to the very small diameter (220 nm), the PI molecules had to re-align along the nanofiber axis. The only exception is the sample SNF-PI-460. It had the highest f, but its σ and ε decreased compared to the sample SNF-PI-430. The possible reason could be the partial cleavage of the PI molecules due to the high imidization temperature. This phenomenon was also observed in previous work for pyrimidine-contained SNF-PI [13].

4. Conclusions

Imidization temperatures played an important role on the mechanical properties of SNF-PI. When the temperature increased, the tensile strength and modulus increased. Polarized Raman Spectroscopy was successfully applied to investigate the mechanism of the effect of temperature on the mechanical properties. The SNF-PI under higher imidization temperatures possessed higher molecular orientation factor in the nanofibers because the higher temperature could provide enough energy for the PI molecular movement and re-orientation along the fiber axis. These findings could be extended to other SNF to achieve better mechanical properties.

Acknowledgements

National Natural Science Foundation of China (Grants No.: 21574060 and 21374044); Major Special Projects of Jiangxi Provincial Department of Science and Technology (Grant No.: 20114ABG5100); Technology Plan Landing Project of Jiangxi Provincial Department of Education (GJC2011-24); Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References