Mechanically Strengthened Polyamide 66 Nanofibers Bundles via Compositing With Polyvinyl Alcohol

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Electrospun polyamide PA 66 nanofiber bundles were mechanically strengthened via compositing with polyvinyl alcohol (PVA). The highest tensile strength (126.4 MPa) was achieved for the bundles immersed in the solution with 5.0 wt% PVA, indicating sufficient PVA filling between nanofibers after drying the impregnated nanofiber bundles. The disappearance of voids for the bundles immersed in the PVA solution indicated a superb interface adhesion, which was responsible for the excellent mechanical properties of the composite bundles. Furthermore, the step-cycle and stress relaxation tests were carried out to shed light on the deformation evolution and the viscous stress of the bundles. The results further demonstrated the excellent mechanical properties of the composite bundles.

1. Introduction

The technique of electrospinning, a simple but versatile method, has attracted increasing attentions since it can fabricate fibers with diameters ranging from micrometers down to a few nanometers. [1,2] Generally, electrospun fibers are collected in the form of non-woven mats, exhibiting many promising applications in the fields of filtration, protective clothing, self-cleaning, drug delivery, electronic devices, and so on. [3,4] More interestingly, the non-woven mats containing electrospun fibers with high porosity and large specific surface area provide a potential to manufacture high-performance fiber-reinforced polymer composites through polymer solution impregnation. Recent experiments have demonstrated that the electrospun fibers are effective in reinforcing rubber films [5] and enhancing the strength and stiffness of the epoxy matrix. [6] The mechanical performance of the electrospun fiber-reinforced polymer composites is known critically depending on the interface adhesion between the fibers and the matrix. [7–9] As a result, the fabrication of electrospun fiber-reinforced polymer composites requires an effective impregnation of electrospun fibers with polymer matrix, and moreover an intimate contact between fibers and matrix phase is crucial. [9]

To date, although the applications of electrospun fibers for reinforcing purpose are still in its infancy, it is attracting more and more interests to prepare high-performance fiber-reinforced polymer composites. After the early work of Kim and Reneker [5] using polybenzimidazole nanofibers to reinforce epoxy and rubber matrix, many studies regarding various electrospun fibers have been carried out. Among these various electrospun fibers, electrospun nylon-6 (PA6) fibers are most commonly used as a reinforcement phase to improve the mechanical properties of the polymer matrix. [6–12] For example, Fong [8] manufactured the restorative composite resins through...
impregnating dental methacrylate into electrospun PA6 mats. Stachewicz et al.\textsuperscript{[9]} prepared void-free PA6/PVA composite mats with a large failure stress of approximately 750 MPa through solution impregnation. Jiang et al.\textsuperscript{[10–12]} adopted different methods to prepare electrospun PA6 nanofiber mats–reinforced polymer composites. Additionally, other polymeric electrospun nanofibers like cellulose, polyacrylonitrile (PAN), and polyamide 66 have also been used as reinforcement to prepare composites.\textsuperscript{[6,13,14]} Researchers have employed different methods to prepare macroscopically electrospun fiber bundles.\textsuperscript{[15–18]} In our previous study,\textsuperscript{[18]} employed different methods to prepare macroscopically electrospun fiber bundles rather than electrospun single fiber or its bundles containing numerous fibers.

As well documented, the non-woven fiber mats are randomly arranged and non-uniform. Such chaotic structure would restrict their further applications. The preparation of macroscopic structures based on the electrospun fibers is an important step toward practical applications. As another assembly of the electrospun fibers, the macroscopically electrospun fiber bundles are promising for a wide range of applications, including tissue scaffolds, reinforced composites, and ultrasensitive sensors.\textsuperscript{[15,16]} Unfortunately, the aforementioned studies concerning the reinforced polymer composites are based on electrospun fiber mats rather than electrospun single fiber or its bundles containing numerous fibers.

2.2. Electrospinning

The PA66 granules were completely dissolved in formic acid at 70 °C with stirring for 1 h to obtain a homogeneous solution with a concentration of 15 wt%.\textsuperscript{[18]} The modified electrospinning apparatus (see Figure 1a) consists of three components: a high-voltage supplier (DW-N503-4ACCD, Tianjin Dongwen High Voltage Power Supply Plant); a spinneret with a diameter of 0.5 mm; two electrode pins with a diameter of 0.5 mm serving as collector. The distance between the two pins is 3 cm. Electrospinning was carried out at an applied voltage of 25 kV over a distance of 25 cm from spinneret to collector. The environmental temperature and relative humidity were 25 ± 2 °C and 65 ± 5%, respectively.

2.3. Composites Bundles Preparation

PA66 was completely dissolved in formic acid at 70 °C with stirring for 1 h to obtain a homogeneous solution with different concentrations. Then, the PA66 nanofiber bundles were immersed in PVA solution (volume of this solution is 50 mL) for 10 min to prepare composite bundles. Furthermore, for comparison purpose, the PA66 nanofiber bundles were also immersed in distilled water and then dried in a vacuum drying chamber for 24 h at 70 °C before further characterization. This drying process can prevent the occurrence of air bubbles during drying process and further avoid the influence of air bubbles on the tensile properties of the composite bundles. For brevity, virgin electrospun nanofiber bundles, the bundles immersed in distilled water and PVA solution were labeled as PA66-virgin, PA66-H2O, and PA66-PVA, respectively. In the following, PA66-PVA represents the bundles immersed in the PVA solution with a concentration of 5 wt% if there is no special description.

2.4. Monotonic Tensile Test

The monotonic tensile test was conducted using a universal tensile testing machine (UTM2203, Sun Technology Stock Co., Ltd) at a...
crosshead rate of 0.1 mm·min⁻¹ with a gauge length of 10 mm. The test was performed at around 25 °C. To avoid inaccurate experimental data caused by personal stretching, two ends of the bundles were stuck on a self-made paper frame. For each condition, the average value reported was derived from at least 10 specimens.

2.5. SEM Microstructural Observation

The surface features of PA66-virgin, PA66-H2O, and PA66-PVA were characterized by SEM (JEOL JSM 7500F) operating with an accelerating voltage of 5 kV. With respect to the preparation of cross-section for the SEM observation, PA66-PVA was frozen in liquid nitrogen for 30 min, and then snipped perpendicular to the bundle axis by a pair of scissors. Before observation, the specimens were sputter coated with gold.

2.6. Step-Cycle Tests

The samples were deformed step by step with a constant strain rate. After each step, the sample’s strain rate was inverted till a stress of zero was reached. Thereafter, the samples were stretched again until it re-reached the predetermined strain.

2.7. Stress Relaxation Experiment

The stress relaxation measurement at a constant strain can provide a means to evaluate the viscous stress. The samples were first stretched to a predetermined strain at a constant strain rate. Subsequently, the strain was held constant and the force decay versus consumed time was recorded.

3. Results and Discussion

3.1. Mechanical Properties

The macroscopically electrospun PA66 nanofiber bundles (PA66-virgin), bundles immersed in distilled water (PA66-H2O), and PVA solution at different concentrations, with a length of approximately 3 cm, were successfully prepared. It should be noted that there is almost no difference in diameter for the bundles immersed in the PVA solution with different concentrations. Therefore, only the diameter of the bundles immersed in PVA solution with a concentration of 5 wt% is presented in Table 1 as a representative. For comparison purpose, the diameter of PA66-virgin and PA66-H2O is also included. Clearly, the diameter of the PA66-virgin is twice of that of the PA66-PVA, and the PA66-H2O is slightly larger than the PA66-PVA.

To investigate the influence of PVA impregnation on the mechanical properties, a monotonic tensile test was carried out. Figure 2 shows the typical stress–strain curves of PA66-virgin, PA66-H2O, and PA66-PVA. On the whole, it can be seen that PA66-PVA has the highest failure stress and the largest strain compared with PA66-H2O and PA66-virgin, that is, the impregnation of PVA solution synchronously increases the failure stress and strain. In order to quantitatively estimate the variations of the mechanical properties, Young’s modulus (E), failure stress (σ), failure strain (ε), and strain energy density at break (W_b) are obtained from the stress–strain curves and summarized in Table 2. As can be seen, the failure stress of PA66-PVA (126.4 MPa) has been increased by up to around 1100% compared with that of PA66-virgin (11.6 MPa) and up to 200% compared with PA66-H2O. In addition, the Young’s modulus, a manifestation of stiffness, increases from 110 MPa for PA66-virgin to 500 MPa for PA66-H2O and it reaches the largest value of 677 MPa for PA66-PVA. The simultaneous increase in the failure stress and Young’s modulus is therefore an indicative of the superb interface adhesion and effective stress transfer between the PA66 nanofibers and the PVA matrix, which will be verified in the following section. In addition, the largest ε and W_b of PA66-PVA suggest that electrospun PA66 nanofiber bundle obtained the optimal ductility and toughness once it was immersed in PVA solution.

To investigate the influence of PVA concentration on the mechanical properties of the composite bundles, a series of monotonic tensile tests were carried out. The failure stress and strain of the bundles immersed in the PVA solution with different concentrations can be obtained from these stress–strain curves, Figure 3. Obviously, at lower concentrations (<5 wt%), a sharp

| Table 1. Diameter distribution of PA66-virgin, PA66-H2O, and PA66-PVA. |
|-------------------------|------------------|------------------|
| Samples                 | PA66-virgin     | PA66-H2O        | PA66-PVA        |
| Diameter [um]           | 110 ± 10        | 58 ± 5          | 45 ± 5          |
increase in the failure stress with increasing the PVA concentration is observed, conforming to the fact that the voids within nanofiber bundle will be progressively filled with solid PVA with increasing the PVA concentration. However, a slight drop in the failure stress occurs once the concentration of PVA solution exceeds 5 wt%. This can be explained as follows: further increase in the concentration of PVA solution will result in a higher viscosity. As a result, the PVA solution with higher viscosity cannot effectively infiltrate in the space between the adjacent nanofibers in bundle. Thus, a lower failure stress is obtained. Furthermore, as shown in Figure 3b, the failure strain of the composite bundles generally has the same trend as the failure stress. That is, the failure strain increases with increasing the PVA concentration at lower concentration, and a slight decline occurs if the concentration of PVA solution exceeds 5 wt%. In other words, the supreme failure stress and strain, viz., balanced mechanical properties of such composite bundles were further investigated.

3.2. Morphology

To better understand the excellent mechanical properties of PA66-PVA, the surface morphologies of the PA66-virgin, PA66-H2O, and PA66-PVA are presented. As for the PA66-virgin (see Figure 4a–a’), apart from a small amount of randomly arranged fibers in bundle, most fibers align along the bundle’s longitudinal axis. The inset image in Figure 4a’ displays the diameter distribution of the electrospun PA66 fibers. Obviously, the diameter of these fibers is in the range of 60–230 nm and the mean diameter is about 140 nm, indicating that the diameter is indeed in nanoscale.[16] Moreover, compared with the PA66-virgin, the diameter of PA66-H2O and PA66-PVA significantly decreases, which is in consistent with the digital photo, Figure 1, and the statistical results presented in Table 1. Furthermore, as shown in Figure 4b–b’, the porosity of PA66-H2O is observed smaller than that of PA66-virgin. The explanations are as follows: PA66 nanofibers are easier to infiltrate in the polar solvents like water, so the nanofibers tend to stick together once water evaporated and a decreased porosity is expected. With respect to the PA66-PVA, it exhibits the smallest diameter, which can be explained by the following fact: PVA is easily dissolved in polar solvents (e.g., water) and it will fill in the spaces between PA66 nanofibers under the action of water, drawing nanofibers close and further sticking them together. Moreover, there are almost no voids at the interface between nanofibers and matrix (see Figure 4c–c’), indicating the superb interface adhesion between PA66 nanofibers and PVA matrix. Reasonably, effective stress transfer is realized. Therefore, the excellent mechanical properties of PA66-PVA should be ascribed to the combined action of PVA and H2O. On one hand, a better wettability between H2O and PA66 nanofibers allows PVA to easily fill in the spaces between nanofibers (Figure 4a’ and c’), drawing nanofibers close and sticking together; on the other hand, the superb interface adhesion improves the stress transfer efficiency and thereby enhances the mechanical properties of PA66-PVA.

To better understand the role of interface adhesion between the PA66 nanofibers and the PVA matrix on the mechanical properties, the cross-section of PA66-PVA was presented. As shown in Figure 5, there are almost no voids, suggesting the superb interface adhesion between nanofibers and matrix. This is in good agreement with the SEM images.

<table>
<thead>
<tr>
<th>Samples</th>
<th>E [MPa]</th>
<th>σ [MPa]</th>
<th>ε [%]</th>
<th>W_b [MJ m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66-virgin</td>
<td>110 ± 10</td>
<td>11.6 ± 2.4</td>
<td>16.4 ± 1.3</td>
<td>97.3 ± 8.5</td>
</tr>
<tr>
<td>PA66-H2O</td>
<td>500 ± 30</td>
<td>62.7 ± 5.8</td>
<td>17.7 ± 2.5</td>
<td>704.5 ± 23.5</td>
</tr>
<tr>
<td>PA66-PVA</td>
<td>677 ± 50</td>
<td>126.4 ± 10.5</td>
<td>36.3 ± 5.3</td>
<td>2644 ± 54.5</td>
</tr>
</tbody>
</table>

Figure 3. Plots of failure stress (a) and strain (b) of the composites prepared at different concentrations.
Figure 4c–c". More interestingly, the diameter of the nanofibers shown by the arrows in Figure 5b is larger than the statistical result, Figure 4a". This can be ascribed to the fact that the surface of PA66 nanofibers is covered with a thin layer of PVA matrix during the solution impregnation to yield the superb interface adhesion between the PA66 nanofibers and the PVA matrix.

As shown by the SEM images (see Figure 4a"–c"), the porosity of the PA66-virgin, PA66-H2O, and PA66-PVA decreases successively. In order to further illustrate the relationship between porosity and the excellent mechanical properties of PA66-PVA, the porosity was quantitatively evaluated. As documented in ref. [18], the porosity of bundles can be calculated by Equation (1):

$$P_c = 1 - \left( \frac{m_{nf}}{\rho_{nf}} \right) / V_c$$

(1)

$V_c$ is the total volume of bundles, $m_{nf}$ is the weight of bundles, and $\rho_{nf}$ is the density of PA66 nanofibers. Considering the fact that the bundles are generally in cylindric form, $V_c$ is therefore obtained by Equation (2)(see Figure 4a–c)

$$V_c = \pi d^2 l / 4$$

(2)

where $d$ and $l$ are respectively the diameter and length of bundles. According to Equation (1), the average porosity of PA66-virgin is 0.77 and that of PA66-H2O and PA66-PVA is 0.33 and 0.05, respectively. Therefore, it is understandable that the stress applied to break PA66-PVA will increase because the porosity is smaller.
compared with PA66-H2O and PA66-virgin, leading to a higher tensile strength of PA66-PVA.

3.3. Recovery Properties

The recovery frequency experiments were carried out to investigate the recovery properties of the PA66-virgin, PA66-H2O, and PA66-PVA. The procedures of the recovery frequency experiments are as follows. First, the nanofiber bundles were pulled by a pair of tweezers until two ends of the bundles were of the same vertical level; and then, the bundles were loosened and their vertical length at different times was recorded. The digital photos of PA66-virgin, PA66-H2O, and PA66-PVA during recovery are shown in Figure 6. The curves of the recovery frequency versus time are quantitatively calculated according to the Equation (3):

$$RF = \frac{(L_o - L_h)}{L_o} \times 100\%$$

where RF is the recovery frequency of bundles and $L_o$ is the original length of bundles (see Figure 6a1), $L_h$ is the length of bundles in horizontal direction, which has been marked in Figure 6b3.

The obtained recovery frequency is summarized in Figure 7. On the whole, all samples recover rapidly at first and then gradually reach a platform. More interestingly, PA66-PVA can recover nearly to its original shape (viz., recovery frequency is about 100%), indicating that PA66-PVA exhibits the strongest elastic recovery ability. With respect to PA66-H2O, its highest recovery frequency is about 80%, while that of PA66-virgin is as low as 30%. Because PA66-H2O and PA66-PVA have higher recovery frequency, they are therefore chosen for further step-cycle tests.

3.4. Step-Cycle Tests

In order to further shed light on the deformation evolution in PA66-H2O and PA66-PVA, the incremental cyclic loading tests were performed.[19,20] Figure 8a, b shows the typical curves monitored during such step-cycle tests. Generally, the stress grows with increasing the step-by-step strain and follows a hysteresis loop in each stress–strain cycle,
which means that there is energy loss in both samples.\textsuperscript{[19]} The observed energy loss per stress–strain cycle can be calculated by Equation (4).\textsuperscript{[21]}

$$EL = \frac{(E_l - E_u)}{E_l} \times 100\%$$  \hspace{1cm} (4)

where EL is the energy loss per cycle, $E_l$ and $E_u$ are the energy within the bundles when they were subjected to loading and unloading, respectively. As shown in Figure 8c, the EL calculated by Equation (4) is from 70 to 75\% for PA66-H$_2$O, while that of PA66-PVA ranges from 62 to 66\%. The less EL for PA66-PVA is therefore another evidence of the superb interface interaction between the nanofibers and the matrix.

In order to further clarify the recovery behavior of PA66-H$_2$O and PA66-PVA, 10 loading–unloading cycles were performed with a constant strain of 3\%. Figure 9a,b shows the stress evolution versus time. Obviously, the maximum stress is observed to exhibit a slight decrease with increasing the cycle number, which is the reflection of viscoelastic nature for both PA66-H$_2$O and PA66-PVA. Furthermore, the stress dissipation per stress–strain cycle can be calculated by Equation (5).

$$SD = \frac{(S_1 - S_n)}{S_1} \times 100\%$$  \hspace{1cm} (5)

where SD is the stress dissipation per cycle, $S_1$ and $S_n$ is the maximum stress when the bundles are respectively subjected to load at first cycle and $n$ cycle. The SD and consumed time at each cycle are respectively shown in Figure 9c, d. The highest SD calculated from Equation (5) is 33\% for PA66-PVA and 43\% for PA66-H$_2$O (see Figure 9c), respectively. Since the stress value cannot recover to its original level at any cycle, there must be structural changes at each step-cycle test. Smaller SD in PA66-PVA implies that PA66-PVA has more stable structures than that in PA66-H$_2$O, which is consistent with the results shown in Figure 8c. Furthermore, the consumed time for each cycle of PA66-H$_2$O and PA66-PVA was calculated from Figure 9a, b. Obviously, compared with PA66-H$_2$O, PA66-PVA consumes more time when stretched to a constant strain at each cycle (see Figure 9d). The longer consumed time means the superb interface interaction between the nanofibers and the matrix, which is in good agreement with the results shown in Figure 7.

### 3.5. Stress Relaxation Experiments

As shown in Figure 3, the fracture strain of PA66-H$_2$O and PA66-PVA exceeds 15\%, so the stress relaxation experiments were carried out when the strain reached 15\%. Figure 10 shows the typical stress relaxation curves for...
PA66-H2O and PA66-PVA. As can be seen, at the beginning of relaxation (viz., t = 0), the stress (σ0, viz., the initial stress) is the maximum value. Subsequently, it decreases sharply and then gradually decays to a plateau value, viz., the equilibrium stress (σt). As documented in ref. [21], the viscous stress was defined as the deviation between σ0 and σt. The viscous stress (σ) of PA66-H2O and PA66-PVA can be calculated by Equation (6).

$$\sigma = \sigma_0 - \sigma_t$$  \hspace{1cm} (6)

The σ calculated by Equation (6) is 21.3 MPa for PA66-H2O and 46.6 MPa for PA66-PVA, respectively. The σ of PA66-PVA originates from the interfacial interaction between PA66 nanofibers and PVA matrix and a stronger interfacial interaction will give birth to a larger σ.[21] In a word, it is understandable that composites with larger σ can result in excellent mechanical properties.

4. Conclusion

Mechanically enhanced composite bundles were successfully manufactured through solution impregnation. A series of monotonic tensile tests were carried out to investigate the influence of PVA concentrations on the mechanical properties. The results show that the supreme failure stress and strain, viz., balanced mechanical properties of the composite bundles can be achieved when the concentration of PVA solution is 5 wt%. This indicates that the effective removal of voids in the composites occurs at this concentration as well as better bonding between nanofibers and matrix. Furthermore, the step-cycle tests and stress relaxation experiments are another two methods to clarify the superb interface interaction between the nanofibers and the matrix.

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