Transparent nano-composites by Nylon 66 and PAN nanofiber layers

Farnaz Memarian a, Hamid Reza Pakravan b,* , Masoud Latifi a

a Textile Engineering Department, Textile Research and Excellent Center, Amirkabir University of Technology, Tehran, Iran
b Young Researchers and Elite club, Central Tehran Branch, Islamic Azad University, Tehran, Iran

* Corresponding author. Tel.: +98-2164542684;
E-mail address: hamid.pakravan@gmail.com

Abstract

Keywords: Nanofiber, Electrospinning, Transparent, Composite, Tensile Strength.

In this work nanofiber layers reinforced composites with nylon 66 and PAN have been prepared and compared in terms of tensile properties and light transparency. Nylon 66 and PAN nanofiber layers are fabricated using electrospinning method with the approximately same size of nanofiber's diameter. The nanocomposites prepared with nylon 66 nanofibers shown better transparency compared to the PAN nanofibers. Results indicated that nylon 66 and PAN nanofiber layers significantly enhanced the tensile stress (increased by 80% and 102%, respectively) and the Young’s modulus of the composite (increased by 15% and 54%, respectively). The contact angle analysis indicated that the nanofibers with hydrophobic nature have better wettability by epoxy resin, leading to the better mechanical performance of the composite. The priority of this work to others is in the use of two polymers with different chemical properties and considering their effect on the properties of nanofiber reinforced composites.

1. Introduction

Fiber/matrix adhesion in composites materials plays crucial role on composite mechanical properties [1]. Nanometer sized fibers have the high surface-to-volume ratio which may produce a high adhesion with the matrix subsequently improving the mechanical and physical properties of composites [2]. Electrospinning is a versatile method which is used widely for producing fibers from different polymers [3]. Generally, materials developed at nanoscale usually have some superior properties as compared with bulk materials [4-5].

There is currently strong interest in development of nanofiber reinforced polymer composites, not only because of their potential for high mechanical properties but also for their electrical and thermal properties [6]. So far, Fibers in nano scale have been used as composite reinforcement [7, 8]. Among them, Bhatnagar [9] used cellulose nanofibers to improve mechanical properties of PVA matrixes for
applications in medical devices, aerospace and automotive sectors. They obtained nanofibers using natural resources such as flax bast fibers and kraft pulp by chemical treatment. Xu [10] investigated the effect of graphite carbon nanofiber produced chemically for the improvement of shear strength of adhesive layers which can be applied for metal/composite joints.

Since electrospinning technique can produce nanofibers with diameters ranging from several to hundreds of nanometer, their diameter are usually less than wavelength of visible light and expected to give transparent composites [11]. A lightweight, optically transparent composite with excellent mechanical properties will have appealing future [12].

Epoxy resins are well established thermosetting matrices due to their significant applications in advanced composites and ease of processing [13]. They have exhibited dimensional stability at elevated temperatures, excellent thermal and chemical resistances, good stiffness and high mechanical strength [13, 14]. Because of its brittle nature and poor resistance to crack propagation, strengthening with microscale and nanoscale materials such as micro-fibers and nanofibers has been considered [7, 15-17]. In this study two different types of electrospun polymers, PAN and nylon 66 nanofibers are used to prepare a tough epoxy composite which preserves its transparency (after the addition of the nanofiber layer to the epoxy). The mechanical properties of the composite including the tensile modulus, tensile stress and work of fracture are also measured. To do this, nonwoven layer with approximately similar nanofiber diameter were electrospun, reinforced epoxy composites were fabricated and their tensile properties and light transparency were investigated.

2. Experimental procedures

2.1. Materials

Polyacrylonitrile (PAN) having molecular Weight 10,000 g/mole was purchased from Iran Polyacryl and dimethylformamide (DMF) with molar mass 73.1 g/mole was obtained from Merck as the polymer and solvent. Pure polyamide (nylon 66) with molecular weight 30,500 g/mole and its solvent formic acid was taken from Sigma Aldrich.

Because of its’ widely used in composite fabrication, epoxy resin was chosen as the matrix in this experiment. The resin used in this study was the epoxy polymer bisphenol A.

2.2. Experimental test

- Electrospinning of Nanolayers

The electrospinning apparatus consists of a syringe pump, syringe needle, high voltage power supply and an Al sheet as the collector. The electrospinning set up used is indicated in figure 1. Each solution was loaded into a syringe and positive electrode was clipped onto the syringe needle. The flow rate of the polymer solution to the needle tip was maintained so that a pendant drop remains during
electrospinning. Solutions were electrospun horizontally onto the target. To obtain layers with the same nanofiber diameter for nylon 66 and PAN polymer many experimental procedures were carried out. The parameters influencing the nanofiber diameter were adjusted to achieve an optimized setting for electrospinning. Electrospinning of PAN was performed at a distance of 8 cm between the nozzle and the collector with the rate of 2 ml/hr and the applied voltage of 20 kV to obtain Nanofibers with diameter range of approximately 200 nm. For nylon 66, the flow rate was set to 0.1 ml/hr for the distance between the nozzle and the collector of 8 cm and the electric field applied was 14 kV to electrospun nanofibers with the same diameter range as PAN nanofibers.

- Composite preparation:
The nanofiber layer/epoxy laminate with 5.5 wt% of nanofibers have been prepared under the same circumstances. Polyethylene mold because of its low surface free energy and minimum adhesion to resins was used to produce 40 mm × 20 mm size composite specimens. The composite samples were laminated into matrix as schematically shown in Figure 2. Firstly, the resin and hardener were poured into the mold, and then nanolayer was carefully laid up into the mold. Afterwards, another layer of resin and hardener were poured on to nanolayer surface. Finally, to achieve uniform thickness and fiber content, a weight was employed to press and to remove additional resin and trapped air bubbles for 24h at room temperature. The composite samples were demoulded after 24 h and cured for 1 h at 60°C. Before tensile test, the final dimension of specimens especially their thickness were precisely measured.
- **Characterization**

The tensile strength, strain at breakage and work of fracture of resin and nanolayer reinforced composites were determined using a tensile test. The size of the specimens was 40 mm × 20 mm. A span length of 20 mm with the crosshead speed of 1.0 mm/min was adjusted for testing. The work of fracture was calculated from the area under the tensile behavior curve of specimens. Three to five specimens were tested and the average of the results was reported.

Wettability of the nanofiber layers is calculated by measuring the contact angle of a drop set on to the sample. A digital microscope pro (Dino-lite) was used to capture a picture of the liquid on the surface of the sample.

The morphology of the nanofiber layers were studied with a scanning electron microscope (Philips XL30) at an accelerating voltage of 25 kV. For diameter analysis, three samples from different parts of nanofiber layers were obtained. Imagej software was used to measure the diameter of fibers for at least 70 randomly selected points to generate an average value for the nanofiber diameter.

**3. Results and discussion**

The SEM micrographs of electrospun nanolayers are presented in Figure 3. As it is shown in the figure the diameter of PAN nanofibers and nylon 66 nanofibers were in the range of 150 nm-250 nm.
3.1. Transparency

The light transparency of nanolayer reinforced composite prepared from PAN and nylon 66 nanofibers were shown in Figure 4. The prepared composites’ films are visualized by putting them on letters. The dried nanolayer as shown in Figure 4b was white and no letter could be observed. The lack of transparency was due to the surface light scattering caused by nanofibers random orientation. Whereas, the nanolayer reinforced composites prepared with PAN nanofibers and nylon 66 nanofibers became semi-transparent, as shown in Figure 4c and Figure 4d, respectively. The transparency of nanocomposite prepared with nylon 66 nanofibers was higher than PAN nanofibers. This appearance of the composites is attributed to the nearly the same refractive index of the nanolayers and epoxy resin. The nanometer diameters of electrospun nanofibers decreases the refractive index difference between the resin and reinforcing nanolayer, which is a significant advantage in producing transparent composites [18].

![Fig. 4: Transparency observation of (a) Control, (b) pure Nanolayer, (c) PAN reinforced composite, and (d) Nylon 66 reinforced composite.](image)

3.2. Tensile properties

The tensile stress-strain behavior of pure resin without nanofibers, PAN nanolayer reinforced composite and nylon 66 nanolayer reinforced composite are shown in Figure 5. The nanolayer reinforced composites show higher tensile stress value than the neat resin. The details of tensile properties in terms of tensile strength and ultimate strain are shown in Table 1.
Comparison of the mechanical properties of pure resin and PAN nanolayer reinforced composite reveals that the ultimate tensile stress, Young’s modulus and break strain of the composite increased by 102.54%, 54.44% and 39.29%, respectively. The tensile strength and break strain of nylon 66 nanolayer reinforced composite increased by 80.27% and 153.57%, respectively, while an increment up to 15% was observed for Young’s modulus.

Table 1: Details of tensile test results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Strain (%)</th>
<th>Young’s modulus (GPa)</th>
<th>Nanofiber weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure resin</td>
<td>11.21±2.79</td>
<td>1.22±0.16</td>
<td>0.90±0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>PAN- composite</td>
<td>22.28±0.27</td>
<td>2.04±0.25</td>
<td>1.39±0.05</td>
<td>5.64%</td>
</tr>
<tr>
<td>Nylon66- composite</td>
<td>19.83±0.54</td>
<td>2.98±0.31</td>
<td>1.04±0.08</td>
<td>5.50%</td>
</tr>
</tbody>
</table>

The increase in tensile properties of pure resin and composite samples is presented in Figure 6. The results showed that the work of fracture of nano composites with PAN nanolayer and nylon nanolayer considerably increased by 1705% and 853.85%, respectively, compared to neat resin.
3.3. Wettability

When a liquid drop is brought onto the planar solid surface, the contact of liquid/solid reaches an equilibrium condition. The liquid makes an angle at the three-phase contact point with the solid surface known as the contact angle (θ) which is schematically shown in Figure 7. Contact angle is generally used to characterize the wettability of a liquid on a solid surface and provide a source of adhesive strength. The interatomic and intermolecular forces between the liquid and solid surface are responsible for this phenomena. Therefore, the contact angle is directly related to the surface energies of the contact surfaces. Since the contact angle ranges from 0° to 180°, if contact angle is higher than 90°, it means poor wetting and poor adhesiveness reflecting a hydrophobic surface. Whereas the contact angle lower than 90° is attributed to the hydrophilic surface which reflects better wetting and better adhesiveness.

![Fig. 7: Contact angle θ for a liquid drop on a solid surface](image)

For nanolayers, the contact angles with water are presented in Figure 8. The contact angle of water on the PAN nanofiber layer was shown in Figure 8 (a) which is higher than 90°, revealing the hydrophobic behavior of this layer. The hydrophobic behavior of PAN nanofibers were also reported in some previous studies [19, 20].
The contact angle of water on the nylon 66 layer is inferior to 90°, so the wetting of the liquid is in a hydrophilic situation. The water liquid was completely spread on the nylon layer after 10 s.

The wettability of nanofiber layers with epoxy resin was also examined. The contact angle of a resin drop on the nanofiber layer surface is presented in Figure 9. The contact angle of resin on the PAN nanofiber layer is inferior to 90°, so the resin perfectly wetted the layer. For the nylon 66 layer, a contact angle higher than 90° was obtained as shown in Figure 9 (b). During the test spontaneously wetting of PAN layer with epoxy resin was observed, whereas an external acting was needed for spreading the resin on the nylon 66 layers.

The previous research on the surface free energy of epoxy resins exhibited that the contribution of the dispersion component is the main part of the total surface energy [21, 22]. It can be concluded that the affinity of epoxy resin with the hydrophobic PAN nanofiber is higher than nylon 66 nanofiber. The higher affinity causes the higher adhesion between the reinforcement and surrounding matrix and consequently better performance in the mechanical properties. Proper wetting of fiber network surfaces by the resin is a key to creating good adhesion at the fiber network-matrix interface which causes infiltration of the resin into the fiber network during the fabrication process [23].

4. Conclusions

In this work the tensile behavior and transparency of nanofiber layer composites based on two different polymer including nylon 66 and PAN has been investigated. The nano composites have been prepared by hand lamination followed by pressing using epoxy resin as the matrix. The nanofiber
layers with approximately the same range of nanofiber diameters were electrospun by experimental procedures. The embedded nanofiber layers significantly increased the strength and stiffness of the composite. The following conclusions can be drawn from the present work:

i. The nanocomposite reinforced with both nanofiber layers shown a remarkable improvement in the mechanical properties compared to the un-reinforced pure resin. The nylon 66 and PAN nanofiber layer improved the tensile stress up to 80% and 102%, respectively.

ii. The PAN nanofiber layer showed better mechanical properties compared to the nylon 66 layer.

iii. The nanocomposite prepared with nylon 66 layer presented better transparency compared to that of PAN layer.

iv. The wettability of layers was investigated with water and resin. The PAN nanofiber layer indicated hydrophobic properties but its wettability with epoxy resin was better than the nylon 66 layer.

References


