The Effect of Nonwoven Electrospun PAN Nanofiber Mat on Mechanical and Thermal Properties of Epoxy Composites

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Electrospinning, Nanofiber, PAN, Composite, TGA, DSC

Abstract: In this study mechanical and thermal properties of epoxy resin reinforced with different numbers of nanofiber layers which produced with electrospinning method was investigated. Solution of 10 wt% of polyacrylonitrile (PAN) in N,N-dimethylformamide (DMF) was used for electrospinning. The diameters of the obtained nanofibers were in the range of 380-420 nm. The average thickness of the produced nanofiber layer was about 200 µm. The special molds were prepared to produce the laminated composite plates. The tensile tests show that the using of nanofiber PAN layers increase the tensile force 34.54% and decrease the elongation 8.87% in comparison with neat epoxy. The fracture surfaces of the specimens were inspected by using optical and scanning electron microscopy (SEM). The thermal properties of the nanofiber layered composites were determined by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis. It was observed that the glass transition temperature increased parallel to this as the number of PAN layers increased and rose up to 86°C, while the thermal stability did not show much effect of PAN layers.

Örgülü Olmayan Elektrospin PAN Nanofiber Malzemenin Epoksi Kompozitlerinin Mekanik ve Termal Özelliklerine Etkisi

Anahtar Kelimeler
Elektrospin, Nanofiber, PAN, Kompozit, TGA, DSC

Özet: Bu çalışmada elektrospin metodu ile üretilmiş farklı sayıldıkları nanofiber takviyeli tabakalı epoksi kompozitlerin mekanik ve termal özellikleri araştırılmıştır. Elektrospin işleminin sonrası %10 oranında poliakrilonitril (PAN) ve N,N-dimetilformamid (DMF) çözeltisi kullanılmıştır. Elde edilen nanofiber çapları 380-420 nm aralığında. Üretilen nanofiber tabaka kalınlığı ortalamada 200 µm'dir. Tabakalı kompozit plakaları elde etmek için özel kalıplar hazırlanmıştır. Çekme deney sonuçları nanofiber tabaka kullanımın çekme kuvvetini sıfı epoksiye oranla % 34.54 artırdı ancak uzamași sıfı epoksiye oranla % 8.87 azaldığı belirlenmiştir. Numunelerin kırılma yüzeyleri optik ve taramali elektron mikroskopu (SEM) ile incelenmiştir. Üretilen nanofiber tabakalı kompozitlerin termal özellikleri termal gravimetrik analiz (TGA) ve diferansiyel taramali kalorimetre (DSC) analizleri ile belirlenmiştir. Camsı geçiş sıcaklığının PAN tabaka sayısı arttıkça buna paralel olarak arttığı ve 86 °C ye kadar çıktığı, termal kararlılıktı ise PAN tabakalarının etkisinin çok fazla olmadığını görülmüştür.

1. Introduction

The epoxy resins are generally used as a matrix in composites materials and for their adhesive, chemical resistance, electrical insulation, low density and strong bond properties [1–3]. For achieving required mechanical and thermal properties, the approach of adding micro or nanofillers to polymer materials was applied [4,5]. The fibers which have diameters in nanometers show many good properties such as flexibility, large surface area and high mechanical performance [6].

The nanofiber reinforced composite laminates are expected to have an improved strength, interlaminar fracture toughness, and delamination resistance towards static, impact and fatigue loadings. Especially, the nanofibrous reinforcement could be useful to prevent delamination from any source such as matrix cracks, notches, holes, bolted joints, etc. The
aim of nanofibers is to bond adjacent plies and to reduce the stress concentration without reduction of in-plane properties. The matrix between adjacent plies of the laminate can be reinforced with nanofibers [7,8]. There are several techniques to produce the nanofibers like jet blowing, melt blowing, co-extrusion, interfacial polymerization, electrospinning and others [9–14]. The electrospinning method has been widely used, among these techniques, to produce nanofibers of polymer and to produce also nanofibers filled with various nanoparticles [15–22].

Many researches have been carried out on the use of nanofibers in laminated composites to enhance the mechanical performance. But, there are a few papers in the literature [23–27] and additional researches are required to be carried out on the benefits of electrospun nanofibers in composite materials.

This study presents an investigation of the use of polymeric nanofibrous layers to increase mechanical performance of the composite materials. The electrospun nanofibers of PAN layers are produced by electrospinning and placed in an epoxy. Three different layers were used to reinforce the epoxy. The fracture surface characterization is performed after the tensile test and the fiber breakage are investigated by using scanning electron microscopy (SEM).

2. Materials and Methods

2.1. Polymeric nanofibrous mats

Polyacrylonitrile (PAN) and pure N,N-dimethylformamide (DMF) were provided from Sigma–Aldrich. PAN granules were dissolved at 10 wt% in DMF. PAN solution was stirred at room temperature and stirred with magnetic stirrer to ensure its dissolution. A horizontal setup was used for electrospinning processes. A syringe was used as injector. The electrospinning setup consisted of a high voltage power supply, a syringe pump, a syringe and a grounded electrode connected with rotating drum.

The parameters for electrospinning processes were chosen as 20 kV voltage, the distance between the collector and the tip of the spinneret 15 cm and the feed rate 2 mL/h. The electrospinning setup is shown in Figure 1. The nanofibers were collected on a rotating drum. The fiber diameter and its alignment mainly depend on the applied voltage, flow rate and distance between needle and collector [28].

2.2. Thermal properties

The curing behavior of the neat epoxy, 1, 2 and 3 layer reinforced epoxy is investigated using DSC (METTLERTOLEDO DSC 1 STAR System) in a temperature range 20–350 °C. The thermal decomposition behavior of the composite specimens was carried out using TGA (METTLER TOLEDO TGA/DSC 2 STAR System) in the range 30–800 °C.

2.3. FTIR

Fourier transform infrared (FTIR) spectrum measurements were performed by means of a BRUKER-Vertex 70 spectrophotometer. All analyses were made in the range between 400 and 4000 cm⁻¹ with a resolution of 2 cm⁻¹ at room temperature.

2.4. Specimen fabrication

The composite laminate production is summarized in Figure 2. In composite materials Momentive MGS L285 (diglycidyl ether of bisphenol A) was used as a resin and Momentive MGS H285 was used as a hardener. The PAN nanofibrous layers were placed in a special prepared mold then epoxy resin added. The mold is left for 24 hours at room temperature before it is placed into the oven for 80 °C temperature post cure for 15 hours.

3. Results and Discussion

3.1. Characterization of nanofibers

The morphology and structure of the PAN nanofibers were analyzed by SEM. Electrospun non-woven mats
were found to be 200 ± 10 µm thick and kept at room temperature for 24 h. The SEM image of electrospun fabric is shown in Figure 3. Fibers diameter (400 ± 20 nm) was measured by using image acquisition software.

3.2. DSC and TGA studies on the composites

As shown in Figure 4(a), DSC was used to analyze the neat epoxy and three different PAN layers/epoxy composites. The glass transition heat of epoxy resin $T_g$ shows an endothermic peak at 64.33 °C. The glass transition temperature ($T_g$), reaction enthalpy ($\Delta H$) and heat capacity ($C_p$) temperature for each composite are shown in Table 1. Figure 4(b) shows TGA results of neat epoxy and reinforced epoxy with various layers of PAN. The higher mass loss rate occurs at temperatures between 297 °C and 309 °C.

Table 1. The glass transition temperature ($T_g$), reaction enthalpy ($\Delta H$) and heat capacity ($C_p$) temperature of samples.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$T_g$ (°C)</th>
<th>$\Delta H$ (J/g)</th>
<th>$C_p$ (J/g°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>64</td>
<td>382</td>
<td>0.278</td>
</tr>
<tr>
<td>1 Layer PAN</td>
<td>80</td>
<td>285</td>
<td>0.142</td>
</tr>
<tr>
<td>2 Layer PAN</td>
<td>75</td>
<td>294</td>
<td>0.246</td>
</tr>
<tr>
<td>3 Layer PAN</td>
<td>86</td>
<td>290</td>
<td>0.201</td>
</tr>
</tbody>
</table>

The results show that $T_g$ values increase with the increasing of PAN layers compared to neat epoxy. The PAN layers show the catalytic effect in epoxy, they reduce the free space between macromolecular structures in the interface of PAN-epoxy. They increase also the crosslink intensity and decrease the unsaturated bonds. Similarly, by increasing the PAN layers the values of $\Delta H$ and $C_p$ decrease. This means that the PAN layers in the composite absorb heat and act as a heat sink in the structure [31,32]. $C_p$ generally related with the molecular mobility, the increase in molecular mobility gives higher $\Delta C_p$ values. Eventually increasing in $T_g$ values cause decreasing in molecular mobility and $C_p$ values.

3.3. FTIR spectra

The FTIR spectrum of nanofiber layers of PAN reinforced resin are depicted in Figure 5. and FTIR results for pure resin is given also for comparison. FTIR spectra of the resin with PAN layers prepared
was used to clarify the possible interaction between the epoxy resin and PAN layers. In the FTIR spectrum of the resin with PAN layers and without layers the characteristic absorption of the nanofibers based PAN layers was superposed over the pure epoxy resin structure.

![FTIR spectra of neat epoxy and nanofiber PAN layers](image)

**Figure 5.** FTIR spectra of neat epoxy and nanofiber PAN layers

Chemical structure of epoxy resin based on bisphenol A, amino curing agent and PAN are given in Figure 6. Stretching vibration of different chemical groups of the neat epoxy and nanofiber PAN layers are given in Table 3 [33,34].

Two characteristic peaks at 2239 and 1447 cm\(^{-1}\) attributed to the \(-\text{C}==\text{N}\) stretching vibration and \(-\text{CH}_2\) scissoring vibration of PAN polymer structure are not observed. No shifts can be detected in the fundamental vibration frequencies resulting from composite formation. Furthermore, the spectrum of nanofibers based PAN did not show any appearance or disappearance of bond formation between resin and PAN layers, which indicates that no new chemical bonds are formed in the interaction.

This situation supports the possible intermolecular interactions such as hydrogen binding, van der walls attractions and weak or strong dipol-dipol interactions between resin and PAN materials.

### 3.4. Tensile properties

The typical load-displacement diagram of the pure epoxy and three nanocomposites with the reinforcement content of one, two and three-layered plates are illustrated in Figure 7. The presented results show obvious changes in the mechanical behavior of the epoxy under tensile loading. The curves of reinforced epoxy show increasing of the value of load with a decrease in the plastic region comparing to the neat epoxy (Figure 8 (a-d)).

![Chemical structure of a) epoxy resin based on bisphenol A, b) amino curing agent and c) PAN](image)

**Figure 6.** Chemical structure of a) epoxy resin based on bisphenol A, b) amino curing agent and c) PAN

**Table 3.** Stretching vibration of different chemical groups of the neat epoxy and nanofiber PAN layers

<table>
<thead>
<tr>
<th>Bands (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3340-3500</td>
<td>Hydroxyl ((-\text{OH})) stretching</td>
</tr>
<tr>
<td>3060</td>
<td>Symmetric stretching of C–H of the oxirane ring</td>
</tr>
<tr>
<td>2960-2870</td>
<td>Alkyl units ((-\text{C–H}) and (-\text{CH}_2)) stretching</td>
</tr>
<tr>
<td>2349</td>
<td>(-\text{CO}_2)</td>
</tr>
<tr>
<td>1607</td>
<td>C=C stretching of aromatic ring</td>
</tr>
<tr>
<td>1509</td>
<td>C=C stretching of aromatic ring</td>
</tr>
<tr>
<td>1236</td>
<td>(-\text{C–C–O–C}) stretching</td>
</tr>
<tr>
<td>1036</td>
<td>C–O–C stretching of ethers</td>
</tr>
<tr>
<td>828</td>
<td>Aromatic absorbance</td>
</tr>
</tbody>
</table>

![Tensile graphs of the composites with different layer numbers](image)

**Figure 7.** Tensile graphs of the composites with different layer numbers

The tensile test results of epoxy and composites are given in Figure 9. The highest improvements of these four graphs were achieved for two-layered PAN composite with enhancement of 34.54% in tensile strength while elongation decreases 8.87% compared with neat epoxy.
Figure 8. The yield points and plastic deformation regions of neat epoxy and composites in the tensile graphs.

3.5. Structural and morphological characterization after tensile tests

Figure 10. shows cross-sectioning and optical microscope study after tensile tests. The Figures 10(b-d) show that PAN layers are straight, tight and bonded perfectly with epoxy.

Figure 9. Tensile tests results
SEM fractographs were taken after failure of the specimens at various points. The matrix cracks inclined towards the direction of crack propagation Figure 11(a-b).

Figure 11. SEM pictures of fractured surfaces of neat epoxy (a) X21 (b) X500 magnification.

Figure 12. SEM images of tensile fracture surface of 1 layer PAN-epoxy (a) X20 (b) X1000 (c) X5000 (d) X10000 magnification; where A-debonding, B-pullout, C-breakage.

4. Conclusions

The nanoﬁber PAN layers were produced using electrospinning by dissolving PAN in DMF solution. PAN layers are placed in epoxy using special mold. Thermal and mechanical properties of neat epoxy, one-layer PAN, two-layer PAN and three-layer PAN reinforced composites plates were investigated.

DSC results show that the PAN layers/epoxy composites have slight higher temperature range comparing to neat epoxy. TGA thermograms show that there is no remarkable effect on thermal stability of epoxy with increasing the PAN layers. As a result of tensile tests, PAN layers increase the tensile stress but they decrease the elongation. Two-layered composite gives the highest tensile load value.

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