6. PREPARATION AND CHARACTERIZATION OF POLYIMIDE - GRAPHENE OXIDE NANOFIBER COMPOSITES

6.1 INTRODUCTION

Aromatic polyimides (PI) are one of the most important high performance materials in microelectronics and aircraft industries because of their superior mechanical properties, excellent thermal stability, high glass transition temperature, and good resistance to solvents. Electrospun nanofibers possess many unique properties including a large specific surface area and superior mechanical properties, and they have potential use as nanoscale building blocks. Nanofibers have been successfully prepared for many applications such as filters, nano electronics, optical and chemical sensors, catalyst systems, scaffolds for tissue regeneration and immobilized enzymes. The main advantage of electrostatic spinning is the ability to produce ultra-fine fibers ranging from nanometer to sub-micron diameters [124].

Wu et al. reported polyimide-based composite films containing carbon black (CB), carbon nanotube (CNT) and carbon nanofiber (CNF), respectively [125]. They were prepared using low-molecular-weight poly (amic acid) (PAA), a precursor of PI, as an impurity-free dispersant. A significant improvement in the Young’s modulus of the composites was observed compared to neat PI and the CNT-loaded composites showed a higher Young’s modulus than the CB or CNF-loaded composite. Si et al. synthesized non-woven polyimide and silica nanofiber composites combining electrospinning and controlled in-situ sol-gel techniques [32]. This composite with a 6.58 % w/w of SiO₂ content showed an increase of 133 °C in the decomposition temperature and a four-fold increase in the ultimate tensile strength, compared to a neat PI fabric.
Graphene and related materials, make attractive materials for electric, optoelectronic, and photonic devices, due to their fascinating electrical and mechanical properties such as superior Hall mobilities, thermal conductivity, current-carrying capabilities, and room temperature ballistic transport. However, pristine graphene is unsuitable for intercalation in polymer chains, because graphene tends to agglomerate in the polymer matrix during processing. Graphene converted to graphene oxide shows improved dispersability in polymer matrices and organic systems.

Wang et al. investigated the synthesis and properties of graphene oxide reinforced polyimide nano composite films with low dielectric constant and high strength [126]. Longun, et al. reported composites of polyimide with nanoscale graphene synthesized via in situ condensation polymerization [127]. They reported that the presence of graphene significantly influenced the storage modulus, the damping ability and the glass transition temperature of the composite. Graphene contents (≥ 18 vol. %), were found to hinder polymer chain flexibility and chain motion due to the 2D geometry of graphene.

The present study deals with the synthesis and characterization of GO and PI nanofiber composites for potential electronic applications. GO was synthesized from graphite (<20 µm; Sigma Aldrich) by Hummer’s method and dispersed in N, N dimethyl formamide (DMF) [91]. The polymerization of poly (amic acid) (PAA) was carried out in the GO-DMF dispersion. The GO content tried for PI composites are 0.1 %, 1 % and 2 % by weight. The experimental details are described in chapter 3 (section 3.4 and 3.5). The resulting nanofiber composites were characterized by Fourier transform infrared spectroscopy (FTIR), high resolution scanning electron microscopy (HRSEM), x-ray diffraction (XRD) Raman analysis and Dynamic mechanical analysis (DMA).
6.2 RESULTS AND DISCUSSION

6.2.1 Structural and morphological studies

The FTIR spectra of graphite and GO are shown in Figure. 6.1 (a) & (b). Among the salient features observed are the bands at 1617 cm\(^{-1}\) and 3171 cm\(^{-1}\) corresponding to the stretching modes of \(-C=C\) and \(-OH\) groups. The bands at 1060 cm\(^{-1}\) and 1378 cm\(^{-1}\) are attributed to bending modes of \(-C-O\) and \(-C-H\) groups in GO respectively. Figure. 6.2 depicts the FTIR spectra of GO-PAA and Figure. 6.3 shows the GO-PI nanofiber composites. The GO-PAA composites electrospun on Al foil, showed the carboxylic \(-OH\) stretching (3500 cm\(^{-1}\)), the \(-C=O\) stretching (1719 cm\(^{-1}\)) and amide group vibration modes (1660 cm\(^{-1}\) and 1544 cm\(^{-1}\)), consistent with the presence of PAA. After heat treatment, which led to amidation of PAA between 50 – 125 ℃ and imidization at around 350°C, the carboxylic \(-OH\) stretching band was found to be absent, indicating the conversion of PAA to PI. The other characteristic peaks of polyimide such as \(C=O\) asymmetric stretch (1775 cm\(^{-1}\) and 725 cm\(^{-1}\)), \(C-N\) stretch (1377 cm\(^{-1}\)) and \(C=O\) bending (725 cm\(^{-1}\)) were also observed. The absence of the \(C-N-H\) stretch (1544 cm\(^{-1}\)) indicated complete imidization in the sample.

![Figure 6.1: FTIR spectra of (a) Graphite, and (b) Graphene oxide.](image)
Figure. 6.2: FTIR spectra of PAA/GO with GO contents of 0 % (neat PAA), 0.1 %, 1.0 %, and 2.0 % (by weight).

Figure. 6.3: FTIR spectra of PI/GO with GO contents of 0 % (neat PI), 0.1 %, 1.0 %, and 2.0 % (by weight).
The Raman spectra of graphite and graphene oxide are shown in Figure 6.4 (a) & (b). The samples were characterized by two prominent features: a G-band at 1578 cm\(^{-1}\) arising due to the first order Raman scattering of the E\(_{2G}\) phonon at the Brillouin zone center of sp\(^2\) carbon atoms and a D-band arising from the breathing mode of the k-point phonons of A1G symmetry at 1321 cm\(^{-1}\). The D-band requires a defect for its activation and hence, it is an indicator of defects. The Raman spectrum of GO shows an intense D-band at 1321 cm\(^{-1}\) as expected, and a broad G-band at 1578 cm\(^{-1}\). The ratio of the intensities of the D-band and G-band is 0.85 and it indicates the presence of defects introduced in graphene layers during the oxidation process of graphite.

![Figure 6.4: Raman spectra of (a) Graphite and (b) Graphene oxide.](image)

Raman spectroscopy has been widely used for characterizing polymers and graphene. Figure 6.5 shows the Raman spectra of neat PI and its nanofiber composites with different GO content. The peak at 1390 cm\(^{-1}\) in neat PI indicates the C–N stretching of the imide ring. The characteristic Raman features of graphene namely the D band (~1321 cm\(^{-1}\)) and the G band (~1578 cm\(^{-1}\)) can also be observed in the composite samples. However, in the composite samples, the band of PI at 1390 cm\(^{-1}\) and the D band of GO at 1321 cm\(^{-1}\) were found to overlap and could not be distinguished as they were broad and close to each
other. With increasing GO content in the nanofiber composites, the peaks in the vicinity of 1320 cm\(^{-1}\) (predominantly due to the graphene D-band) and 1575 cm\(^{-1}\) (graphene G-band) were both found to increase as expected.

Figure. 6.5: Raman spectra of PI/GO with GO contents of 0% (neat PI), 0.1 %, 1.0 % and 2.0 % (by weight).

Figure. 6.6: X-ray diffraction pattern of (a) Graphite and (b) Graphene oxide.

Figure. 6.6: X-ray diffraction pattern of (a) Graphite and (b) Graphene oxide.
The distinctive powder X-ray diffractogram features of graphite and the synthesized GO are presented in Figure. 6.6 (a) & (b). For the graphite sample, the characteristic peak of hexagonal graphite corresponding to a d-spacing of 0.334 nm was found at 26.35°. Upon conversion of the graphite into GO, the peak position is shifted to 10.26° corresponding to an interlayer spacing to 0.878 nm. This increase in d-spacing is due to the intercalation of –OH and other functional groups in between the graphene layer.

Figure. 6.7: AFM micrograph of graphene oxide.

Figure. 6.8: The height profile of the graphene oxide in AFM micrograph.
Figure 6.7 shows the AFM image of GO deposited on a freshly cleaved mica slide, which confirms the HRSEM observations. The GO sheets appear to be folded, wrinkled and stacked above one another in places. A line scan was conducted on this sample as shown in Figure 6.7. The height profile of the line scan is shown in Figure 6.8. The thickness of this layer from the mica surface is roughly 7 nm. Assuming the thickness of each layer of GO to be about 0.878 nm, it can be inferred that this is 8-layer sheet of GO.

![Figure 6.7: AFM image of GO deposited on a freshly cleaved mica slide.](image)

Figure 6.9: SEM micrographs of (a) and (b) graphite, (c), and (d) graphene oxide.

The morphology of graphite and graphene oxide was studied by scanning electron microscope. Figure 6.9 (a) & (b) show the SEM micrographs of graphite
and Figure. 6.9 (c) & (d) attribute to graphene oxide. It is observed that the exfoliation of graphene layers due to oxidation process which involves the intercalation of functional groups such as –OH, –COOH, and –O– between the layers. Figure. 6.10 (a) shows HRSEM image of neat PAA and Figure. 6.8 (b–d) show the HRSEM images of PAA nanofibers with GO content of 0.1, 1, and 2 % w/w. Bead or spindle-like structures were observed in the nanofibers in the GO-PAA nanofiber composites.

Figure. 6.10: Scanning electron micrographs of PAA/GO with GO content of (a) 0 % (neat PAA), (b) 0.1 % (GO), (c) 1 % (GO), and (d) 2 % (GO) by weight.

The size of the nanofibers in the PAA/GO composites was calculated in Figure. 6.10 (a-d) using ImageJ software. The diameter of the nanofibers was in the range of 94–143 nm and the size of the beads were in the range of 0.65–0.77
µm (Table 6.1). Figure 6.11 (a-d) shows the HRSEM image of PI nanofibers with GO content of 0, 0.1, 1, and 2 % w/w. After thermal imidization, the PI/GO nanofiber composites (Figure 6.11 (a–d)) did not show a significant change in either the nanofiber diameters (84–143 nm) or the bead sizes (0.79–0.91 μm). This is due to the large variability in the nanofiber diameters and bead sizes relative to the change in mass (volume) of PAA upon conversion to PI. The density of these beads (numbers over an area of 11×11 μm) as observed in the SEM images was found to increase with increasing content of GO (35, 100 and 110 beads respectively for PI/GO (0.1 %), PI/GO (1 %) and PI/GO (2 %) by weight).

Figure 6.11: Scanning electron micrographs of PI/GO with GO content of (a) 0% (neat PI), (b) 0.1 % (GO), (c) 1 % (GO), and (d) 2 % (GO) by weight.
Figure 6.10 (a) shows PAA nanofibers with few tens of micrometer lengths and an average diameter of 94 ±18 nm. Figure 6.11 (a) shows the presence of PI nanofiber with few tens micrometer length and an average diameter of 84 ± 16. Thus, shrinkage in the average fiber diameter from 94 nm in PAA to 84 nm in PI was observed after thermal imidization. The similar type of shrinkage was also observed in diameter of PAA and PI nanofibers with f-SWCNTs. This can be attributed to the elimination of water molecules during imidization. Table 6.1 indicates the diameters of the nanofibers in composites containing 0 %, 0.1 %, 1 % and 2 % of GO (by weight).

Table 6.1: Diameter of the PAA and PI nanofiber composites with GO contents of 0 % (neat PAA/PI), 0.1 %, 1.0 % and 2.0 % (by weight).

<table>
<thead>
<tr>
<th>Sample</th>
<th>GO-PAA</th>
<th>GO-PI diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO content</td>
<td>Fiber (nm)</td>
<td>Bead (µm)</td>
</tr>
<tr>
<td>Neat (0%)</td>
<td>94 ±18</td>
<td>-</td>
</tr>
<tr>
<td>(0.1%)</td>
<td>120 ± 25</td>
<td>0.67±0.14</td>
</tr>
<tr>
<td>(1.0%)</td>
<td>125 ± 23</td>
<td>0.77±0.22</td>
</tr>
<tr>
<td>(2.0%)</td>
<td>143± 25</td>
<td>0.65±0.11</td>
</tr>
</tbody>
</table>

The TEM images of PAA/GO (1 % w/w) are shown in Figure 6.12. It is clearly observed from these images that the bead-like structures (0.50–1.20 µm) are nanofibers that have bulged due to the GO present inside them. Rolled GO sheets can also be seen extending from the bulged areas into the nanofibers.

We propose that during the electrospinning process as the GO-polymer solution is squeezed through the syringe needle, the GO gets deformed under shear. As the jet of the polymer solution exits the needle in its flight towards the collecting drum, the GO in the jet relaxes and gets bunched up before the solidification of the jet into a nanofiber. H. Fong et al. have reported similar bead and spindle-like structures in electrospun nanofibers of poly (ethylene oxide) with NaCl [128].
Figure. 6.12: High resolution transmission electron micrographs of PAA/GO 1 % w/w nanofiber.

Since the sizes of the GO sheets are in the order of a few microns and the nanofiber diameters are in the order of a 100nm, the bulging of the nanofibers due to the inclusion of the GO sheets is highly probable. The formation of the beads are indicative of low interfacial interaction between GO and the polymer matrix, which encourages GO to bunch up rather than conform to the shape of the matrix. It is possible to avoid bead formation only at very low content of GO (~0.07 % w/w) and by specific functionalization of the GO so as to improve its compatibility with the polymer matrix. However, since the GO used for this study was not specifically functionalized, an increasing GO content is likely to lead to a higher number of beads per unit area.
6.2.2 Thermal properties

Thermal stability is an important property for PI-based nanocomposites since they are often used as high-performance engineering plastics. The presence of inert nanofillers in PI can improve the thermal and mechanical properties. Figure 6.13 shows the TGA curves of neat PAA, PI, GO and PI/GO nanofiber composites. The TGA curve of GO indicates weight losses of 17 %, 33 % and 50 % at 150 °C, 200 °C and 350 °C respectively. These have been respectively attributed to evaporation of absorbed water, the decomposition of labile oxygen functional groups such as hydroxyl, epoxy and carbonyl and the removal of the more stable oxygen functionalities (such as phenol, carbonyl, quinone).

Figure 6.13: TGA curves of PI/GO nanofiber webs with GO contents of 0 % (neat PI), 0.1 %, 1.0 %, and 2.0 % (by weight) at nitrogen atm.

In TGA curve of neat PAA nanofiber web, there was a significant weight loss (10.7 %) at 250 °C. This is due to the loss of H₂O molecules during the formation of the imide linkage from amic acid. In the case of the neat PI nanofiber
mat, there was a weight loss of only about 3% up to 300°C. These results are indicative of the conversion PAA to PI. Further, all the PI composite samples showed a significant increase in thermal stability with increasing GO content, compared to neat PI. The temperatures for a 10% weight loss in GO-PI samples containing 0%, 0.1%, 1% and 2% GO (by weight) were found to be 503 °C, 527 °C, 543 °C, and 603 °C respectively.

6.2.3 Dynamic mechanical properties

The DMA studies of the electrospun PI nanofiber webs with different GO contents (0 – 2% w/w) are shown in Figure. 6.14. The glass transition temperature (Tg) of the samples as measured from the peaks in the tan δ vs. temperature curves, increased from 317 °C to 323 °C as the GO content increased from 0 to 2% w/w.

Figure. 6.14: DMA curves of PI/GO nanofiber webs with GO contents of 0% (neat PI), 0.1%, 1.0% and 2.0% (by weight).
The storage modulus ($E'$) values also increased from $1.4 \times 10^8$ to $3.8 \times 10^8$ Pa for the same samples. This is indicative of some interaction between the PI matrix and the GO filler. This interaction might be the result of carrying out the polymerization of the samples in the presence of GO leading to possible hydrogen bonding between the PI matrix and the functional groups on GO. Moreover, the beads in the nanofiber mat are likely to provide better interlocking between the fibers, leading to an overall stiffer material (higher $E'$).

The tan δ values of the composites with different contents of GO are shown in Table 6.2. The tan δ values of the composites showed a decrease at 0.1% GO content followed by an increase at 1% and 2% GO content. Similar trends have been found in the literature as well. The decrease in tan δ at 0.1% GO can be explained by the increased value of $E'$ upon addition of the GO. The increase in tan δ at higher GO contents could be the consequence of GO interrupting the connectivity of the polymer chains and facilitating chain slippage, leading to a higher loss modulus ($E''$).

Table 6.2 DMA analysis of PI/GO with GO contents of 0 % (neat PI), 0.1 %, 1.0 % and 2.0 % (by weight).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Storage Modulus x $10^8$ Pa</th>
<th>Tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PI</td>
<td>317±3</td>
<td>1.4 ±0.23</td>
<td>0.428±0.05</td>
</tr>
<tr>
<td>PI-GO (0.1%)</td>
<td>319±2</td>
<td>2.5±0.21</td>
<td>0.395±0.03</td>
</tr>
<tr>
<td>PI-GO (1.0%)</td>
<td>320±2</td>
<td>2.8±0.18</td>
<td>0.533±0.06</td>
</tr>
<tr>
<td>PI-GO (2.0%)</td>
<td>323±3</td>
<td>3.8±0.24</td>
<td>0.510±0.07</td>
</tr>
</tbody>
</table>

6.2.4 Electrical properties

Electrical resistance was measured with a two point probe setup which consists of two silver probes in voltage range of 0–30 V DC. The electrical resistance, volume resistivity, and conductivity of PI nanofibers with GO up to 2 % w/w are given in Table 6.3. In spite of the higher conductivity of graphene
oxide as compared to PI, the composites with GO content of up to 2 % w/w did not show a drastic increase in the electrical conductivity as compared to neat PI since, the GO remains bunched up in the form of beads and isolated from other beads in the insulating PI nanofibers.

Table 6.3 Electrical properties of PI/GO nanofiber webs with GO contents of 0 % (neat PI), 0.1 %, 1.0 % and 2.0 % (by weight).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistance (Ω)</th>
<th>Volume resistivity (Ω-m)</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PI</td>
<td>1.96±0.023×10^9</td>
<td>1.29±0.01×10^{12}</td>
<td>7.74±0.03×10^{18}</td>
</tr>
<tr>
<td>PI-GO (0.1%)</td>
<td>1.91±0.15×10^9</td>
<td>9.75±0.80×10^{11}</td>
<td>1.23±0.01×10^{12}</td>
</tr>
<tr>
<td>PI-GO (1.0%)</td>
<td>1.90±0.13×10^9</td>
<td>9.72±0.91×10^{11}</td>
<td>1.021±0.15×10^{12}</td>
</tr>
<tr>
<td>PI-GO (2.0%)</td>
<td>1.86±0.37×10^9</td>
<td>1.90±0.31×10^{12}</td>
<td>6.26±0.95×10^{13}</td>
</tr>
</tbody>
</table>

6.3 CONCLUSION

Polyimide-Graphene oxide (PI-GO) nanofiber composite mats with up to 2 wt% of GO were made by electrospinning of polyamic acid followed by thermal imidization. The presence of graphene oxide in the composites and the complete conversion of poly(amic acid) to polyimide were confirmed by Raman spectroscopy, XRD and FTIR. The graphene oxide formed bead or spindle-shaped structures in the nanofibers as observed by HRSEM and TEM. The composites showed a significant improvement in the storage modulus, glass transition temperatures and thermal stability with increasing graphene oxide content. The electrical resistance of the composites was found to be largely unaltered by the addition of GO up to 2 % w/w in PI.