CHAPTER 3

Graphene oxide (GO) and graphene (GR) based polyester (PE) resin composites with improved mechanical strength
Graphene oxide (GO) and graphene (GR) based polyester (PE) resin composites with improved mechanical strength

3.1 Introduction

Recently, most of the scientific researchers have focused on nanotechnology and nanomaterials. Nanomaterials exhibit superior properties, as compared to other conventional micro or macro sized analogues. To get improved properties in nanocomposites, layered materials of natural origin like montmorillonite type of layered silicate compounds or synthetic clay have been widely used for decades. But the electrical and thermal conductivity of clay minerals are quite poor. To overcome these drawbacks, carbon-based nanofillers such as carbon black, expanded graphite and carbon nanotube (CNT) have been introduced in the preparation of polymer nanocomposites.1

Graphene oxide (GO), a single sheet of graphite oxide bearing oxygen functional groups on their basal planes and edges is found to be a promising filler in polymer matrices.2,3 GO sheets consisting of covalently attached oxygen-containing groups such as hydroxyl, epoxy, carbonyl and carboxyl groups can alter the van der Waals interactions significantly and facilitate its dispersion in solvent as well as in the polymeric matrix. GO can be prepared in large scales from low-cost natural graphite which is an easily available material. The oxygen-containing groups of GO impart strong interaction with polar molecules or polymers to form GO intercalated or exfoliated composites. Similarly, graphene (GR) is considered as promising versatile nanofiller due to its extraordinarily high electrical and thermal conductivities, great mechanical strength and low manufacturing cost. GO/GR based nanocomposites have attracted enormous interest due to its wide variety of applications in the areas of materials science and engineering.4-6 Several GO and GR based polymer composites have been developed till date and the mechanical, thermal and electrical properties of these composites are found to be improved as reported.7-10

This part of the thesis is published in
Polyester (PE) resin is a thermosetting polymer which is widely used in various industries such as coating, construction, transportation, storage tanks and piping. PE is also commonly used as matrix material, particularly with glass fiber reinforcement. It is an economic and chemically resistant material which has high dimensional stability and low moisture absorption. The disadvantages of these thermosetting resins are that they show significantly higher cure shrinkage, as compared to epoxy resins. Also tensile strength and stiffness of the polyester resin are lower than those of epoxy resin. To get improved properties in the PE resin composites, different fillers like clay, layered silicates, carbon fiber and CNTs have been used till date. Bharadwaj et al. prepared crosslinked polyester-clay nanocomposite by dispersing organically modified montmorillonite. The composite showed good thermal, mechanical and rheological behavior. Vilcakova et al. investigated the electrical conductivity of composites of PE resin filled with short carbon fibers and the composites showed a very low percolation threshold (at 0.7-0.8 vol.% of the filler). Seyhan et al. prepared CNT/unsaturated thermoset PE nanocomposites using 3-roll mill and sonication techniques. The CNT/PE blend exhibited a shear thinning behavior, while PE resin blends act as a Newtonian fluid. Nanotubes with amine functional groups showed superior tensile strength, as compared to those with untreated CNTs. Battisti et al. developed electrically conductive nanocomposites based on MWCNT in an unsaturated PE matrix. The nanocomposite showed a higher value of conductivity, with percolation threshold at 0.026 wt.% loading of nanotubes.

GO and GR are preferred over other expensive fillers like CNT due to their higher aspect ratio, extraordinary mechanical and thermal properties. They have great potential to improve the properties of low cost resins at very low filler content. Wang et al. studied the curing dynamics and network formation of cyanate ester resin/GO nanocomposites by means of differential scanning calorimetry (DSC). The incorporation of GO into the resin showed a strong catalytic effect on the cure of the resin and addition of 4 wt.% GO resulted in the decrease of curing temperature significantly at about 97°C. Yu et al. prepared epoxy/GO composites and got improved thermal conductivity, elastic modulus and tensile strength. Liu et al. reported a novel route to fabricate PE/GR composites via simultaneous dispersion and
thermo-reduction of GO during in-situ melt polycondensation. The composite showed a significant improvement in tensile strength and elongation at break.

However, to the best of our knowledge only few works have been reported in the literature based on GO and GR filled PE resin composite. Therefore in our present investigation we have used GO and GR as fillers in the PE resin matrix to improve mechanical strength, thermal stability as well as to introduce new characteristic like electrical conductivity of the resin at very low filler content. In this work we have reported preparation of GO and GR based PE resin composite by dispersing GO/GR in PE resin and subsequently crosslinked using methyl ethyl ketone peroxide (MEKP) catalyst at different GO concentration. Our work aims at obtaining a good dispersion of GO/GR sheets within the polymer matrix as well as achieving good improvement in thermal and mechanical properties. GR has been found to have good antibacterial activity towards microorganisms. Hu et al.\textsuperscript{21} reported the antibacterial activity of water dispersible GO and GR nanosheets. They found that such GR-based nanomaterials can effectively inhibit the growth of \textit{Escherichia coli} bacteria while showing minimal cytotoxicity. The antibacterial activity of the PE/GR nanocomposite was also evaluated against a number of bacterial strains.

3.2 Experimental

3.2.1 Materials

PE resin and hardener MEKP were of commercial grade and used as received. Graphite powder, concentrated sulfuric acid (98\%), sodium nitrate, potassium permanganate, 30\% H\textsubscript{2}O\textsubscript{2} solution, hydrochloric acid, acetone, N,N-dimethylformamide (DMF) and hydrazine monohydrate were of reagent grade and purchased from Merck. All the reagents were used without further purification. GO and GR is prepared from natural graphite using modified Hummers method as described in Chapter 2.
3.2.2 Preparation of PE/GO nanocomposites

The required amount of GO was dispersed in minimum amount of THF (solvent) by ultrasonication for 1 hr. Then required amount of PE resin was introduced into the above dispersion and mixed under vigorous mechanical stirring followed by ultrasonication for 30 min. The mixture was then degassed for about 20 min under vacuum until it was completely bubble free. Afterwards, 4% of the hardener (MEKP) with respect to PE resin was added into the mixture and the mixture was cast on teflon plates and dried under vacuum in desiccators for overnight at room temperature. Then they were allowed to cure at 120°C for further study.

3.2.3 Preparation of PE/GR nanocomposites

PE/GR composites of different weight percentage of GR to PE resin (1-3 wt.%) were prepared as follows: The required amount of GR was dispersed in a minimum amount of THF (solvent) by ultrasonication for 1 h. Then required amount of PE resin was introduced into the above dispersion and mixed under vigorous mechanical stirring followed by ultrasonication for 30 min. The mixture was then degassed for about 20 min under vacuum until it was completely bubble free. Afterwards, 4% of the hardener (MEKP) with respect to PE resin was added into the mixture and the mixture was cast on teflon plates and dried under vacuum in desiccators for overnight at room temperature. After that the composite films were cured at 120 °C. Compositions of nanocomposites are given in Table 3.1.

### Table 3.1: Composition of PE resin/GO and PE resin/GR nanocomposites

<table>
<thead>
<tr>
<th>Sample particulars</th>
<th>PE resin (wt. in gm)</th>
<th>MEKP (wt.%</th>
<th>GR (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>3</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>PE/GO1</td>
<td>3</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>PE/GO2</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>PE/GO3</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>PE/GR1</td>
<td>3</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>PE/GR2</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>PE/GR3</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

*PE: polyester resin; PE/GO1: 1 wt.% of GO w.r. to PE; PE/GO2: 2 wt.% of GO w.r. to PE; GR: graphene; PE/GR1: 1 wt.% of GR w.r. to PE resin and so on.
3.3 Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Impact 410 spectrophotometer at room temperature, over a frequency range of 500-4000 cm$^{-1}$. The samples were crushed well and then examined in KBr pellets. The X-ray diffraction (XRD) study was carried out at room temperature (25 °C) using a Rigaku X-ray diffractometer (Miniflex, UK) with Cu Ka radiation (k = 0.15418 nm) at 30 kV and 15 mA with a scanning rate of 0.05 h/s in the range of 2θ = (10°-70°). The surface morphology of the composites was observed by scanning electron microscope (SEM) of model JSM-6390LV, JEOL, Japan at an accelerating voltage of 5-15 kV. The surface of the sample was coated with platinum before SEM analysis. Transmission electron microscope (TEM) measurement was carried out by a PHILIPS CM 200 microscope at 200 kV. The TEM sample was prepared by dispensing a small amount of dry powder in ethanol. Then, one drop of the suspension was dropped on 300 mesh copper TEM grids covered with thin amorphous carbon films. Atomic force microscopy (AFM) observation was performed on the DI Multimode V in tapping-mode. To study the thermal degradation of the samples, thermogravimetric analysis (TGA) was performed using Shimazu TGA 50 thermal analyzer, Japan from temperature range 25-700 °C with a heating rate of 10 °C min$^{-1}$ under the nitrogen flow rate of 30 mL min$^{-1}$. Differential scanning calorimetric (DSC) analysis of the samples was done using Shimadzu DSC-60. The analysis was run in the presence of nitrogen gas at a scanning speed 10 °C/min in the temperature range of 0-300 °C. For measurement of the mechanical properties, the composite films were cut to a width of 10 mm and a thickness of 3 mm. The tensile strength measurements were conducted with a Zwick Z010 (Germany) universal testing machine (UTM) with a 10-kN load cell and at jaw separation speed of 50 mm/min at room temperature (25 °C). Measurements of electrical conductivities of the samples were performed using Keithley 2000 (Keithley Instruments Inc., USA) instrument. The resistivity of the samples was measured in a four-point probe unit using the following equation:

\[
\text{Resistivity (} \rho, \text{ ohm-cm} ) = (V/I) \frac{2\pi d}{2} \\
\text{Conductivity (} \sigma, \text{ S cm}^{-1} ) = \frac{1}{\rho}
\]
where \( V \) is the applied voltage, \( I \) is the measured current through the sample and \( d \) is the distance between the probes.

### 3.4 Antimicrobial activity test

The well diffusion technique was used in the present investigation. 200µl of the log phase culture of the test microbes (\(10^7-10^8\) cell as per McFarland standard) which includes *Staphylococcus aureus* (ATCC 11632), *Bacillus subtilis* (ATCC 11774), *Escherichia coli* (MTCC 40), *Pseudomonas aeruginosa* (MTCC 7812) and *Klebsilla pneumoniae* (ATCC10031) were seeded on the surface of the Muller Hinton agar medium, using a micropipette and spread over the medium uniformly using a sterile glass spreader. Further, with the help of a sterile cork borer three wells, each with a diameter of 6 mm were made on Muller Hinton agar (MHA) plate. Samples were dissolved in sterilized dimethyl sulfoxide (DMSO) (10%, v/v) and introduced into each of the wells. Streptomycin sulfate (1mg/mL) was taken as a positive control. The culture plates were incubated at 37±2 °C for 24 h. The observed zones of inhibition were measured using transparent metric ruler. The experiment was done thrice and the mean values were determined.

### 3.5 Results and discussion

GO and GR based PE resin composite films at different GO/GR concentration were prepared by dispersing the nanofillers in polyester resin and subsequently crosslinked using MEKP catalyst at different GO/GR concentration. A 3 mm-thick smooth, uniform and flexible composite film containing 3 wt.% GO is shown in Figure 3.1. The synthetic process of PE/GR composite is illustrated in Fig. 3.2.
3.5.1 FTIR study

FTIR spectra of pure PE resin, GO, GR and PE/GR composite are represented in Fig. 3.3 (a). In the FTIR spectrum of GO, the broad peak at 3409 cm\(^{-1}\) and a peak at 1719 cm\(^{-1}\) can be assigned to O-H stretching vibration and the carbonyl (C=O) stretching respectively. The peaks at 1370 and 1250 cm\(^{-1}\) represent the C-O-C and C-OH stretching vibration. The peak near 1065 cm\(^{-1}\) represents C-O stretching vibrations which confirm the presence of the epoxide groups in the GO layers. In the FTIR spectrum of GR (3.3 (b)), a broad peak appears at 3426 cm\(^{-1}\) corresponding to O-H stretching vibration which is due to the absorption of moisture by the GR sheets. The peaks at 2850 and 2915 cm\(^{-1}\) corresponds to aromatic C-H stretching vibration.
Upon reduction of GO, the absorption bands at 1719, 1370, 1250 and 1060 cm\(^{-1}\) decreased indicating successful reduction of GO into GR. The PE resin film shows important characteristic absorption bands at 1732 cm\(^{-1}\) for carbonyl group (C=O), 3428 cm\(^{-1}\) for O-H stretching and 1629 cm\(^{-1}\) for aromatic C=C stretching. The peaks at 1166 cm\(^{-1}\) and 1263 cm\(^{-1}\) band appears for C-O-C stretching vibrations attached with aliphatic and aromatic moiety. From the FTIR spectrum of PE/GO composite (Fig. 3.3 (c)), it is observed that the absorption peaks are almost similar to pure PE resin except that the carbonyl stretching vibration is shifted to lower frequencies (1720 cm\(^{-1}\)) than the pristine polyester. The shifting of the peaks indicates the interactions of the PE segments (–COOH and –OH) with GO through H-bonding or other polar-polar interactions. FTIR spectrum of PE/GR composite shows similar absorption peaks to pure PE resin. However some peaks have shifted to lower frequencies than the pristine PE. The shifting of the peaks indicates the interactions of the PE segments (–COOH and –OH) with the remaining oxygen functional groups of GR through H-bonding or other polar-polar interactions. Thus from the FTIR results we can say that both GO and GR have been successfully incorporated in the polymer matrix.
3.5.2 XRD analysis

The X-ray analysis was used to determine the structure and crystallinity of polymer matrices. The XRD patterns of GO, GR, pristine PE resin and its composites are given in Figure 3.4. The X-ray pattern of GO (Fig. 3.4 (a)) displays the presence of a strong peak at $2\theta = 11.45^\circ$ corresponds to (001) reflection peak.\textsuperscript{3,22} In GR, the peak at 11.45$^\circ$ disappears and a broader diffraction peak at $2\theta = 24^\circ$ is observed which can be correlated to an interlayer spacing of 0.36 nm in the graphene sample (Fig. 3.4 (b)). This indicates the successful reduction of GO to GR. From the Fig. 3.4 (e) it can be seen that polyester resin exhibits a weak and a broad diffraction peak at 25.5$^\circ$ which indicates that the resin is amorphous in nature. The XRD pattern of PE/GO
Chapter 3: Graphene oxide and graphene based polyester resin composites

Composite (3 wt.%), exhibits peak for both PE resin and GO in the angular range of the study (Fig. 3.4 (c)). However, the diffraction peak of GO becomes negligible in the nanocomposite which can be attributed to the exfoliation and homogeneous dispersion of GO in the polyester matrix. The PE/GR composite (3 wt.%) exhibits a weaker diffraction peak compared to the neat resin indicating strong interaction between the polymer chains and the filler (Fig. 3.4 (d)). The diffraction peak of GR disappears in the nanocomposite indicating exfoliation and homogeneous dispersion of GR in the PE matrix. 

Fig. 3.4 XRD spectra of (a) GO, (b) GR, (c) PE/GO composite, (d) PE/GR composite and (e) PE resin.

3.5.3 Morphological studies

The surface characteristic of the composites was investigated using scanning electron microscope. A layered, wrinkled structure of individual GO sheets with a lateral dimension of few micrometers is observed in the SEM and TEM images of GO (Fig. 3.5 (a) and (b)). In the SEM image of PE resin a smooth surface appears. SEM image of the composite shows a rough, layered surface which is totally different from that of pure PE resin (Fig. 3.5 (d)). Appearance of this layered structure in the composites results from the uniform dispersion of expanding GO layers in the
polymer matrix. Figure 3.5 (e) shows a SEM image of the cross-section of the PE/GO with a loading of 3 wt.% GO. The image shows well dispersion of GO within the polymer matrix. It also demonstrates the random dispersion of GO in the polymer matrix with a few restacks which might affect the improvement in mechanical property. Thus from the morphological study of the surfaces it can be concluded that GO has been successfully incorporated in the PE resin matrix.

In the SEM of GR a layered, wrinkle-like structure is observed (Fig. 3.6 (a)). The TEM image of GR (Fig. 3.6 (e)) shows a crumpled and agglomerated sheet like structure with hundreds of nanometers. The wrinkled structure observed in the TEM image of GR sheets is due to the rapid removal of intercalated functional groups in graphitic oxide during exfoliation. SEM image of the composite (Fig. 3.6 (c)) displays a rough, layered structure compared to the smooth surface of the neat PE resin (Fig. 3.6 (b)). Appearance of this layered structure in the composites results from the uniform dispersion of GR sheets in the polymer matrix and the strong interaction between remaining oxygen functional groups. Fig. 3.6 (d) shows a fractured surface of the PE/GR (3 wt.%) composite film. The image reveals the random dispersion of GR sheets in the polymer matrix with a few restacking which may affect the mechanical and other properties of the composite. Fig. 3.7 shows the Energy-dispersive X-ray (EDX) spectra of GO and GR. GO exhibits oxygen content of 45 atom%. The atomic ratio of carbon to oxygen in GO was found to be 1.25. After reduction, the atomic ratio of carbon to oxygen was 9, as shown in the EDX spectra of GR. Only 15% oxygen content remained in the GR which indicates successful reduction of the GO.

The dispersion of GO sheets in the matrix was investigated by tapping mode AFM. Fig. 3.8 shows topology of surface of the pristine PE resin and PE/GO (3 wt.%) composite. The surface of neat resin appears very smooth which is similar to the SEM analysis. The average roughness of the surface was found to be around 0.01 µm. On the other hand, the composite shows a rough surface which is consistent with SEM observations. The average roughness of the composite surface was increased to 0.1 µm. Moreover, no significant thickness variations were observed in the PE/GO composite film which indicates the uniform distribution of GO in the polyester matrix.
Chapter 3: Graphene oxide and graphene based polyester resin composites

Fig. 3.5 (a) SEM image of GO, (b) TEM image of GO; SEM images of (c) PE resin, (d) PE/GO composite (3 wt.%), and (e) cross section of the composite.

Fig. 3.6 SEM images of (a) GR, (b) PE resin and (c) PE/GR composite (3 wt.%), (d) SEM image of cross section of the composite, (e) TEM image of GR.
Chapter 3: Graphene oxide and graphene based polyester resin composites

Fig. 3.7 EDX spectra of GO and GR

The dispersion of GO sheets in the matrix was investigated by tapping mode AFM. Fig. 3.8 shows topology of surface of the pristine PE resin and PE/GO (3 wt.% composite. The surface of neat resin appears very smooth which is similar to the SEM analysis. The average roughness of the surface was found to be around 0.01 µm. On the other hand, the composite shows a rough surface which is consistent with SEM observations. The average roughness of the composite surface was increased to 0.1 µm. Moreover, no significant thickness variations were observed in the PE/GO composite film which indicates the uniform distribution of GO in the polyester matrix.

Fig. 3.8 Tapping mode AFM images of (a) PE resin (b) PE/GO (3 wt. %) composite and (c) GR.
AFM is also used to measure the thickness of the GR sheets. Fig. 3.8 (c) shows a typical tapping-mode AFM image of GR sheets deposited onto a mica substrate. It revealed that the average thickness of the GR sheets was around 4 nm, indicating well exfoliated nanosheets.

3.5.4 Thermal properties

The effect of GO on the thermal degradation of polyester resin and its composites were studied by TGA. TGA curve for PE resin, PE/GO composite and GO are shown in Fig. 3.9 with respective data are being summarized in Table 2. From the TGA curve of PE resin, it is seen that the initial weight loss occurs at temperature of 240 °C (Fig. 3.9 (a)). The weight loss after 300 °C corresponds to the complete degradation of the polymer. In case of GO major weight loss at the temperature range of 200 °C to 320 °C is attributed to the removal of most of the oxygen-containing functional groups such as hydroxyl, epoxy, carbonyl and carboxyl groups (Fig. 3.9 (e)). The 60% residual weight of GO indicates that some functional groups existed on GO surface before the thermal treatment. GO plays an important role in the thermostability of the composites. On incorporation of GO, the major degradation temperature of PE resin was remarkably improved from 230 to 285 °C (Fig. 3.9 (b)-(d)). This improvement in thermal stability is attributed to the strong interaction between GO and PE resin which restricts the mobility of the polymer segments at the interfaces of PE and GO. The interaction is may be due to the formation of hydrogen bonding between oxygen functionality on GO and polymer or some dipolar interactions between the two component. Further it is seen that the weight retention value increases with the incorporation of GO with PE resin matrix. The PE/ GO composites show almost 15-25% weight retention values at 600 °C which is probably due to the existence of a carbon net structure in the composite. Also, the incorporation of GO into the matrix acts as a mass transport barrier to the volatile products generated during decomposition which may enhance the overall thermal stability of the composite. The values obtained here are better than other PE resin composites which showed only 30-40% improvement in major degradation temperature.
Fig. 3.9 TGA curves of (a) PE resin, (b) PEGO1, (c) PEGO2, (d) PEGO3 composite and (e) GO.

Table 3.2 TGA data of PE and PE/GO composites

<table>
<thead>
<tr>
<th>Sample particulars</th>
<th>Major degradation temperature (Td) °C</th>
<th>Weight loss % at temperature</th>
<th>Weight retention (%) at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 °C</td>
<td>300 °C</td>
<td>400 °C</td>
</tr>
<tr>
<td>PE resin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEGO1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEGO2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEGO3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TGA curve for PE resin, PE/GR composite and GR are shown in Fig. 3.10 with respective data are being summarized in Table 3.3. GR showed around 20% weight loss at the temperature range of 250 to 500 °C, which is due to the removal of most of the oxygen-containing functional groups during the chemical reduction process. About 70% residual weight of GR at 600 °C indicated its higher thermal stability compared to GO. In the TGA curve of PE resin, initial weight loss occurs at a temperature of 240 °C. The weight loss after 300 °C is due to the complete degradation of the polymer. The major degradation temperature of polyester was found to be improved from 245 to 289 °C on incorporation of the GR. This
improvement in thermal stability is ascribed to the strong interaction between GR and PE resin which restricts the mobility of the polymer chains. The interaction is may be due to the formation of hydrogen bonding between residual oxygen functionality on GR and polymer or some dipolar interactions between the two components. Also the weight retention value increases with the incorporation of GR with PE resin matrix. Almost 25-30% weight retention values were observed in the TGA curves of the composites at 600 °C which is much higher than the 15-25% weight retention value of the PE/GO composite at the same temperature. Thus GR based PE resin composites have shown better thermal stability compared to GO and other nanofillers based PE resin composites.\textsuperscript{15,16}

![Fig. 3.10 TGA curves of (a) PE resin, (b) PE/GR1, (c) PE/GR2, (d) PE/GR3 composite and (e) GR.](image)

<table>
<thead>
<tr>
<th>Sample particulars</th>
<th>Major degradation temperature (Td) °C</th>
<th>Weight loss % at temperature</th>
<th>Weight retention (%) at 600 °C</th>
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<tr>
<td></td>
<td>200 °C</td>
<td>300 °C</td>
<td>400 °C</td>
</tr>
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<td>PE resin</td>
<td>245</td>
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<td>30</td>
</tr>
<tr>
<td>PEGR1</td>
<td>265</td>
<td>7</td>
<td>32</td>
</tr>
<tr>
<td>PEGR2</td>
<td>274</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>PEGR3</td>
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<td>15</td>
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<tr>
<td>GR</td>
<td>310</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3.3 TGA data of PE resin and PE/GR composites
Chapter 3: Graphene oxide and graphene based polyester resin composites

The glass transition behavior of PE/GO composites was also investigated by using DSC. PE resin exhibits glass-transition temperature ($T_g$) at around 54 °C as shown in Fig. 3.11. With increasing GO loading in the composites, the $T_g$ of PE resin increases gradually from 54 °C to 62 °C. Similarly, in PE/GR composite (Fig. 3.12.), the $T_g$ of PE resin increases from 55 °C to 63 °C with an increase in the GR content. The increase in $T_g$ in both the composites can be attributed to the reinforcing effects of GO and GR which reduces the segmental motion of the polymer chain.

**Fig. 3.11** DSC curves of (a) PE resin, (b) PEGO1, (c) PEGO2 and (d) PEGO3 composite.

**Fig. 3.12** DSC curves of (a) PE resin, (b) PEGR1, (c) PEGR2 and (d) PEGR3 composite.
3.5.5 Mechanical properties

The tensile strength of PE resin and PE/GO composite were measured with a UTM. GO is expected to have good reinforcement effect for tensile properties due to its large aspect ratio and excellent mechanical strength. The mechanical properties of the composite films were found to be increased significantly compared to pure PE resin. Fig. 3.13 represents the stress-strain curves of PE/GO composites with various GO loadings. The slope of the curves increases with increasing GO content. The corresponding Young’s modulus values are shown in Table 4. For the composite film with 3 wt.% of GO loading, Young’s modulus increased to 1.7 GPa, corresponding to an increase of 41% compared to pure PE resin.

![Stress-strain curves of PE/GO composites](image)

**Fig. 3.13** Representative stress-strain curves of the composites with various GO loadings.

The tensile properties of the PE/GO composite films are illustrated in Fig. 3.14 and Table 3.4. It is obvious that the addition of GO into the polymer matrix has a significant influence on the mechanical behavior of pure PE resin. The composites showed a maximum of 76% increase in tensile strength for 3 wt.% of GO loading i.e. 54 MPa compared to neat resin (25 MPa). The value is higher than that of carbon nanotube based PE resin composites which showed only 17% increase in tensile strength.\(^{16}\) Also the tensile strength values are found to be increased with increasing
GO loading. The enhanced tensile properties can be ascribed to the homogeneous dispersion of GO in resin matrix and the stronger interfacial interactions such as hydrogen bonding or some possible ionic interactions between both the components.

![Graph showing mechanical properties of PE/GO composites](image)

**Fig. 3.14** Mechanical properties of PE/GO composites with various GO loadings: tensile strength (right) and elongation at break (left) versus GO loadings.

**Table 3.4** Mechanical properties from the tensile test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE resin</td>
<td>25</td>
<td>80</td>
<td>1.2</td>
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<tr>
<td>PEGO1</td>
<td>32</td>
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<td>1.4</td>
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<tr>
<td>PEGO2</td>
<td>46</td>
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<td>1.5</td>
</tr>
<tr>
<td>PEGO3</td>
<td>54</td>
<td>47</td>
<td>1.7</td>
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</table>

On the other hand, the elongation at break of the composites gradually decreases with increasing GO content. The average value of elongation at break decreases to 47% for the 3 wt.% GO loading from 80% for the pure sample. The reason may be attributed to a large aspect ratio and the interaction between GO and the polymer matrix, which confines the movement of the polymer chains. Similar results were observed for other GO based polymer composites.28,29 The incorporation of GR into
the polymer matrix has a significant influence on the mechanical behavior of the composite due to its large aspect ratio and excellent mechanical strength. The representative stress-strain curves of neat PE resin and its composites at various GR loadings are shown in Fig. 3.15. The mechanical properties of the composite films were found to be increased significantly compared to pure PE resin. The slope of the curves increases with the increasing GR content. Based on the slope of the elastic region, the Young’s modulus values are calculated and are shown in Table 3.5. On introduction of GR sheets the Young’s modulus values are found to be increased. For the composite film with 3 wt.% of GR loading, Young’s modulus increased to 3 GPa, corresponding to an increase of 87% compared to pure PE resin.

![Stress-strain curves](image)

**Fig. 3.15** Representative stress-strain curves of the composites with various GR loadings.

The tensile strength and the percentage elongation at break of the PE/GR films are represented in Fig. 3.16 and Table 3.5. The average tensile strength for pure PE resin is 26 MPa. The tensile strength values are found to be increased with increasing GR loading. PE/GR composite with 3 wt.% of GR loading showed the tensile strength value of 58 MPa, corresponding to an improvement of 123% compared to neat resin. The value is higher than the above mentioned PE/GO composite as well as other carbon nanofiber and carbon nanotube based PE resin composites.\textsuperscript{16,30}
Fig. 3.16 Mechanical properties of PE/GR composites with various GR loadings: tensile strength (right) and elongation at break (left) versus GR loadings.

This enhanced tensile property can be attributed to the well dispersion of GR in the polymer matrix and strong interfacial interactions between both the components. On the other hand, a gradual decrease in the elongation at break of the composites was observed with increasing GR content. For the 3 wt.% GR loading, the elongation at break decreased to 45% from 81% for the pure polymer. It could be due to the large aspect ratio and the interaction between GR and the polymer matrix, which restricts the movement of the polymer chains. The results were similar to that of other GR based polymer composites. These mechanically strong composite systems with improved thermal stability can be used in any high-tech structural applications, where high strength, stiffness are required.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength/MPa</th>
<th>Elongation (%)</th>
<th>Young’s modulus/GPa</th>
<th>Conductivity (σ, S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE resin</td>
<td>26</td>
<td>81</td>
<td>1.4</td>
<td>3.09×10⁻¹²</td>
</tr>
<tr>
<td>PEGR1</td>
<td>35</td>
<td>58</td>
<td>1.9</td>
<td>1.10×10⁻⁵</td>
</tr>
<tr>
<td>PEGR2</td>
<td>47</td>
<td>50</td>
<td>2.3</td>
<td>7.50×10⁻⁵</td>
</tr>
<tr>
<td>PEGR3</td>
<td>58</td>
<td>45</td>
<td>3.07</td>
<td>3.70×10⁻⁴</td>
</tr>
</tbody>
</table>
3.5.6 Electrical properties

The electrical conductivities of pure PE resin and PE/GR composites at different GR content were determined using a fourpoint probe resistivity measurement system (Table 3.5). The conductivity of pristine PE resin is around $3.09 \times 10^{-12}$ S cm$^{-1}$. On incorporation of GR the conductivity of the composites increases rapidly and the highest conductivity of $3.7 \times 10^{-4}$ S cm$^{-1}$ is achieved for composite containing 3 wt.% GR. Such an improvement in conductivity can be explained by the large specific surface area and excellent homogeneous dispersion of GR sheets which form a conducting network in the insulating resin matrix. The conductivity obtained here is higher than that of carbon fiber and CNT based PE resin composite.$^{15,17}$ However, PE/GO composites showed negligible value of conductivity which may be due to the insulating nature of GO.

3.5.7 Antibacterial Activity

An organized glimpse of data for the antibacterial property of the synthesized composites is illustrated in Table 3.6, which shows a highly significant and pronounced antibacterial behavior of the tested samples against five different bacterial growths of *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Klebsilla pneumonia*. Samples were dissolved and tested for corresponding antimicrobial activities in 10% DMSO (v/v) aqueous solution. It was found from literature that 10% DMSO (v/v) has been used for antimicrobial and other biological activities as it is highly miscible with water, highly polar and stable.$^{32,33}$ In the presence of 10% DMSO (v/v) both the gram positive and gram negative bacteria showed no detectable effect on bacterial growth. Both gram positive and gram negative bacteria were found sensitive to the composites; predominantly the composites were appeared to be more effective towards the gram negative. It is clear from the above set of tests that *Pseudomonas aeruginosa* bacteria is very sensitive toward the PE/GR composites and *Escherichia coli* shows the lowest degree of inhibition. The antibacterial effect of composites increases with the GR content. The composite containing 3 wt.% of GR has showed the highest degree of inhibition.
against all the five kinds of bacterial strains for which the diameter of the zone of inhibition is more (Fig. 3.17).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.17.png}
\caption{Antibacterial test against \textit{Escherichia coli}, (a) Pure PE resin, (b) PE/GR1, PE/GR2 and PE/GR3 composite.}
\end{figure}

The reason for the growth inhibitory property of the nanocomposites might be due to the cellular damages of the bacterial cells. Such cellular damages are caused due to the effect of either oxidative stress or physical disorder caused by GR. Similar observation was also reported in other carbon nanomaterials like CNTs and fullerene.\textsuperscript{34,35}

\begin{table}[h]
\centering
\caption{Antibacterial activities of synthesized compounds against different bacterial strains}
\begin{tabular}{llllll}
\hline
Test sample & \textit{Staphylococcus aureus} (ATCC11632) & \textit{Bacillus subtilis} (ATCC11774) & \textit{Escherichia coli} (MTCC40) & \textit{Pseudomonas aeruginosa} (MTCC7812) & \textit{Klebsilla pneumoniae} (ATCC10031) \\
\hline
10\% DMSO (v/v) & 0 & 0 & 0 & 0 & 0 \\
PE resin & 10 & 10 & 10 & 11 & 10 \\
PEGR1 & 11 & 11 & 10 & 12 & 12 \\
PEGR2 & 12 & 11 & 11 & 13 & 13 \\
PEGR3 & 13 & 12 & 12 & 15 & 14 \\
\hline
\end{tabular}
\end{table}
3.6 Conclusion

- This work demonstrates the successful preparation of GO and GR based PE resin composite with high thermal stability and mechanical strength. The FTIR and XRD results indicate successful incorporation of GO and GR in the polymer matrix. Morphological analysis shows good dispersion of GO and GR within the resin matrix.

- The PE/GO composites show improved thermal stability compared to the pure PE resin. A significant improvement in major degradation temperature (260-285 °C) and weight retention value (15-25%) is obtained on incorporation of GO in the resin matrix. A much enhancement in thermal stability of the PE/GR composites was obtained compared to PE/GO composites. The major degradation temperature of the composite started at relatively higher temperature (260-285 °C) than that of PE/GO composites. Also, the PE/GR composites showed a higher weight retention value (25-30%) compared to PE/GO composites.

- The PE/GO composite films exhibited a significant improvement in the mechanical properties. A 76% increase of tensile strength and 41% increase in Young’s modulus are obtained with 3 wt.% of GO loading, which reveals the efficient load transfer between GO and the polymer matrix. The PE/GR composite demonstrated superior mechanical properties compared to PE/GO composites at very low GR loading. Around 123% increase of tensile strength and 87% increase in Young’s modulus are obtained with 3 wt.% of GR loading.

- The PE/GR composite film (with 3 wt.% GR loading) was found to possess a higher value of conductivity (3.7 $10^{-4}$ S cm$^{-1}$) compared to pure resin due to the incorporation of highly conducting GR sheets which forms a conducting network in the insulating resin matrix.
Chapter 3: Graphene oxide and graphene based polyester resin composites

- The PE/GR composites imply proficient antibacterial activity towards the five different kinds of bacterial strains and the antibacterial activity was found to be increased with increasing GR content. Among all the bacterial strains, *Pseudomonas aeruginosa* was much more sensitive towards the PE/GR composites.

- These mechanically strong and ductile PE/GO and PE/GR composite films exhibit good potential in industrial applications. The GR based PE resin composites with improved antibacterial activity could offer new opportunities for the development of a new range of environmental friendly and high strength structural material.
Chapter 3: Graphene oxide and graphene based polyester resin composites

REFERENCES


