Preparation of Polyester Resin/Graphene Oxide Nanocomposite with Improved Mechanical Strength

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ABSTRACT: Graphene oxide (GO) has attracted huge scientific interest due to its unique physical and chemical properties as well as its wide-scale applicability including facile synthesis and high yield. Here, we report preparation of nanocomposites based on GO and unsaturated polyester resin (PE). The synthesized samples were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and tensile strength measurements. A good dispersion of the GO sheets within the resin matrix was observed from the morphological analysis. A significant enhancement in mechanical properties of the PE/GO composites is obtained at low graphene loading. Around 76% improvement of tensile strength and 41% increase of Young's modulus of the composites are achieved at 3 wt % loading of GO. Thermal analysis of the composite showed a noticeable improvement in thermal stability in comparison to neat PE. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3432–3438, 2013

INTRODUCTION

Recently, most of the scientific researchers have focused on nanotechnology and nanomaterials. Nanomaterials exhibit some 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. Several GO-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.[4–7]

Polyester resin (PE) is a thermosetting polymer which is widely used in various industries such as coating, construction, transportation, storage tanks, and piping. Polyesters are also commonly used as matrix materials, 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 thermoset resins are that they polymerize at relatively higher temperatures and show significantly higher cure shrinkage, as compared to epoxy resins. Also, tensile strength and stiffness of the PE are lower than those of epoxy resin. So to get improved properties in the PE composites, different fillers like clay, layered silicates, carbon fiber, and CNTs have been used till date.[8–10] Bharadwaj et al.[11] prepared cross-linked polyester–clay nanocomposite by dispersing organically modified montmorillonite and cross-linked with methyl ethyl ketone peroxide (MEKP) catalyst. The composite showed good thermal, mechanical, and rheological behavior. Vilcakova et al.[12] investigated the electrical conductivity of composites of PE filled with short carbon fibers, and the composite showed a very low percolation threshold (0.7–0.8 vol % of the filler). Seyhan et al.[13] prepared CNT/unsaturated thermoset polyester nanocomposites using three-roll mill and sonication techniques. The CNT/polyester blend exhibited a shear thinning behavior, while PE 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.[14] developed electrically conductive nanocomposites based on multiwalled CNTs in an unsaturated polyester matrix. The nanocomposite showed a higher value of conductivity, with percolation threshold at 0.026 wt % loading of nanotubes.

GO is preferred over other expensive fillers like CNT due to its higher aspect ratio and extraordinary mechanical and thermal properties. It has a great potential to improve the properties of a low-cost resin like polyester at very low filler content. Wang et al.[15] 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 to 97°C. Yu et al.[16] prepared epoxy/GO composites and got improved thermal conductivity, elastic modulus, and tensile strength. Liu et al.[17] reported a novel route to fabricate polyester/reduced GO composites via thermoreduction 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 PE/GO composite. In this work, we have reported preparation of PE/GO composite by dispersing GO in PE and subsequently cross-linked using MEKP catalyst at different GO concentrations. Our work aims at obtaining a good dispersion of GO sheets within the polymer matrix as well as achieving good improvement in thermal and mechanical properties. The introduction of less amount of GO into PE is found to greatly enhance the properties of polyester.

EXPERIMENTAL

Materials
PE and hardener MEKP were of commercial grade and used as received. Graphite powder, concentrated sulfuric acid (98%), sodium nitrate, potassium permanganate, 30% H_2O_2 solution, hydrochloric acid, acetone, and N,N-dimethylformamide were of reagent grade and purchased from Merck (Mumbai, India). All the reagents were used without further purification.

Preparation of GO
GO dispersion was prepared from natural graphite using a modified Hummers method[18] where $KMnO_4$ and H_2SO_4 were used as oxidizing agents. For purification, the product was washed with 5% of HCl and then distilled water (DI H_2O) for several times. Finally, the product was exfoliated by ultrasonication for 1 h, and GO dispersion was obtained.

Preparation of PE/GO Nanocomposites
The required amount of GO was dispersed in minimum amount of tetrahydrofuran (THF) (solvent) by ultrasonication for 1 h. Then required amount of PE 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. Afterward, 4% of the hardener (MEKP) with respect to PE was added into the mixture, and the mixture

Table I. Composition of Nanocomposites

Sample particulars	PE (weight in g)	MEKP (wt %)	GO (wt %)
PE resin	3	4	0
PEGO1	3	4	1
PEGO2	3	4	2
PEGO3	3	4	3

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. Compositions of nanocomposites are given in Table I.

Characterization
Fourier transform infrared spectroscopy (FTIR) was used to record FTIR spectra by Nicolet FTIR (400 MHz) spectrometer at room temperature over a frequency range of 4000–500 cm^{-1}. The samples were crushed well and then examined in KBr pellets. The surface morphology of the composites was observed by scanning electron microscope (SEM) of model JSM-6390LV, JEOL, Japan. The surface of the sample was coated with platinum before SEM analysis. Transmission electron microscope (TEM) measurements were conducted on 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 TG 50, Simadzu Thermogravimetric Analyzer, Japan, from temperature range 298 to 973 K with a heating rate of 283 K min^{-1} under the nitrogen flow rate of 30 mL min^{-1}. 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^{-1} in the temperature range of 0–300°C. The X-ray diffraction (XRD) study was carried out at room temperature (ca. 298 K) using a Rigaku X-ray diffractometer with Cu-$K\alpha$ radiation ($\lambda = 0.15418$ nm) at 30 kV and 15 mA with a scanning rate of 0.05θ s^{-1} in the range of $2\theta = (10–70°)$. The tensile strength of the PE and its composites film were measured in a Zwick Z010 (Germany) Universal Testing Machine with a 10-kN load cell and at jaw separation speed of 50 mm min^{-1} under ambient conditions.

RESULTS AND DISCUSSION

PE/GO composite films at different GO concentrations were prepared by dispersing GO in PE and subsequently cross-linked using MEKP catalyst at different GO concentrations. A 3-mm-thick smooth, uniform, and flexible composite film containing 3 wt % GO is shown in Figure 1.

FTIR Study
FTIR spectra of pure PE, GO, and GO/PE resin composite are represented in Figure 2. In the FTIR spectrum of GO [Figure 2(a)], the broad peak at 3409 cm^{-1} and a peak at 1719 cm^{-1}
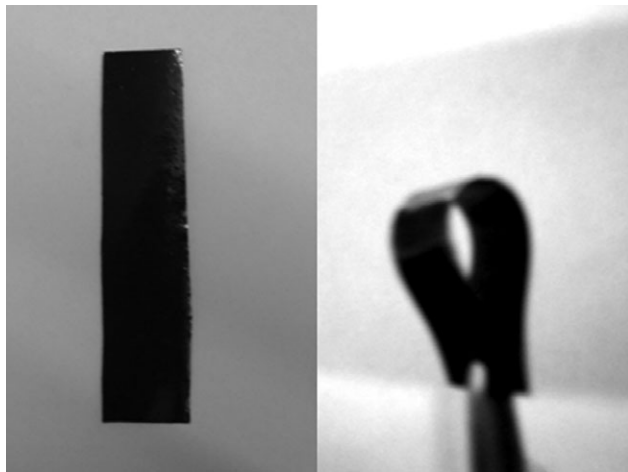
Figure 1. Photograph of a PE/GO (3%) composite film.

can be assigned to O–H stretching vibration and the carbonyl (C=O) stretching, respectively. The peaks at 1409 cm^{-1} and 1234 cm^{-1} represent the O–H deformation and C–OH stretching vibration.[19] The peak near 1065 cm^{-1} represents C–O stretching vibrations which confirm the presence of the epoxide group in the GO layers. The PE 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} appear for C–O–C stretching vibrations attached with aliphatic and aromatic moiety [Figure 2(c)]. From the FTIR spectrum of PE/GO resin composite [Figure 2(b)], it is seen 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 polyester segments (–COOH
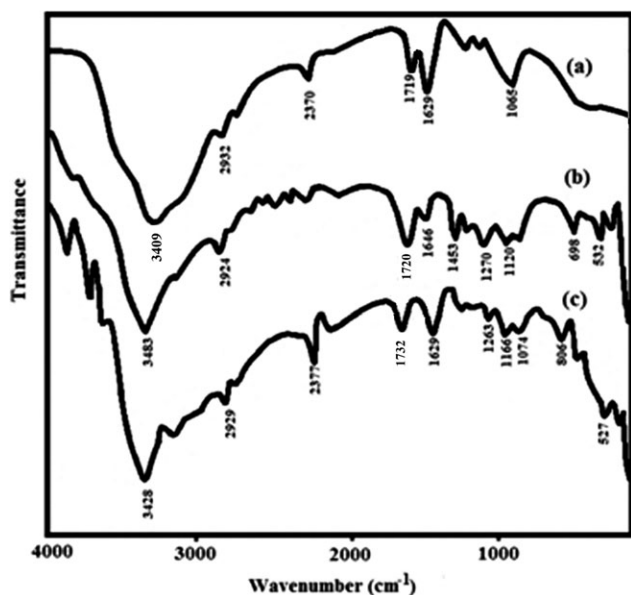
and –OH) with GO through H bonding or other polar–polar interactions. Thus, from the FTIR results, we can say that GO has been successfully incorporated in the polymer matrix.

XRD Analysis

The X-ray analysis was used to determine the structure and crystallinity of polymer matrices. The XRD patterns of GO, pristine PE, and its composite are given in Figure 3. The X-ray pattern of GO [Figure 3(a)] displays the presence of a strong peak at $2\theta = 11.45°$ that corresponds to (001) reflection peak.[3,20] From Figure 3(c), it can be seen that PE exhibits a weak and a broad diffraction peak at 25.5° which indicates that the resin is amorphous in nature. The XRD pattern of PE/GO composite (3 wt %) exhibits peak for both PE resin and GO in the angular range of this study. However, the reflection peak of GO becomes negligible in the nanocomposite which can be attributed to the exfoliation and homogeneous dispersion of GO in the polyester matrix. Similar results were observed for other GO-based polymer composites.[3]

Morphological Studies

The surface characteristics of PE resin and GO/PE resin composite were investigated using SEM. 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 [Figure 4(a,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 [Figure 5(a)]. Appearance of this layered structure in the composites results from the uniform dispersion of expanding GO layers in the polymer matrix. Figure 5(c) 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

Figure 2. FTIR spectroscopic analysis of (a) GO, (b) PE/GO composite, and (c) pure PE resin.
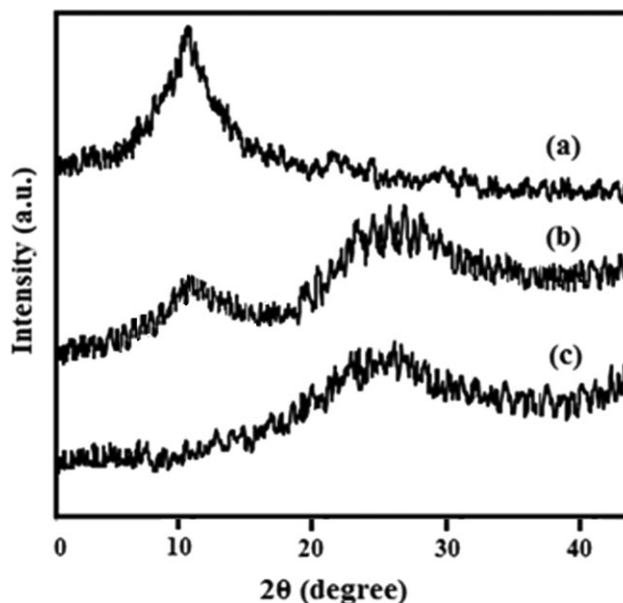
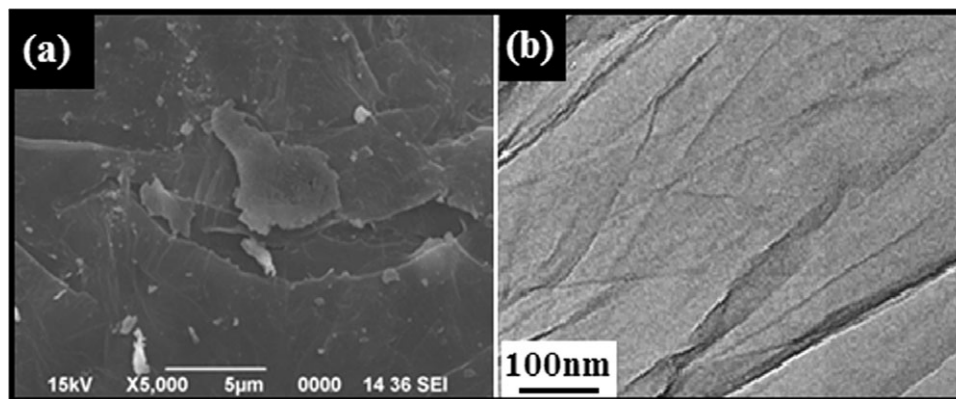**Figure 3.** XRD patterns of (a) GO, (b) PEGO3 composite, and (c) pure PE resin.

Figure 4. (a) SEM image of GO and (b) TEM image of GO.

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 matrix.

The dispersion of GO sheets in the matrix was also investigated by tapping mode AFM. Figure 6 shows the topology of surface of the pristine PE resin and PE/GO (3%) 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.

Thermal Properties

The effect of GO on the thermal degradation of PE and its composites was studied by TGA. TGA curves for PE resin,

PE/GO composite, and GO are shown in Figure 7 with respective data being summarized in Table II. From the TGA curve of PE resin, it is seen that initial weight loss occurs at temperature of 240°C [Figure 7(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 200–320°C is attributed to the removal of most of the oxygen-containing functional groups such as hydroxyl, epoxy, carbonyl, and carboxyl groups [Figure 7(e)]. The 60% residual weight of GO indicates that some functional groups existed on GO surface before the thermal treatment.[21] GO plays an important role in the thermostability of the composites. On incorporation of GO, the major degradation temperature of polyester was remarkably improved from 230 to 285°C [Figure 7(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
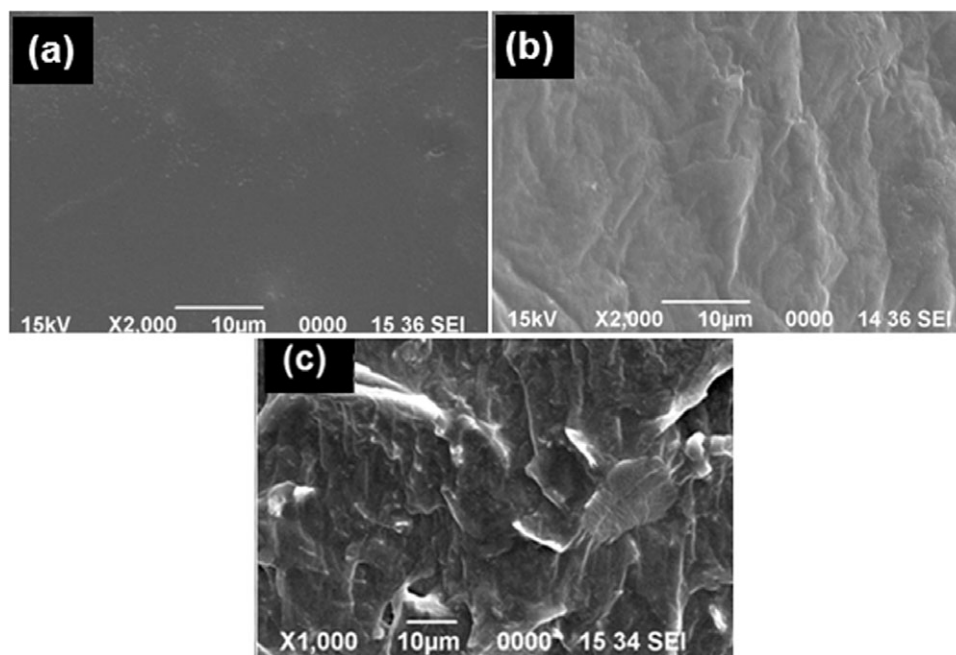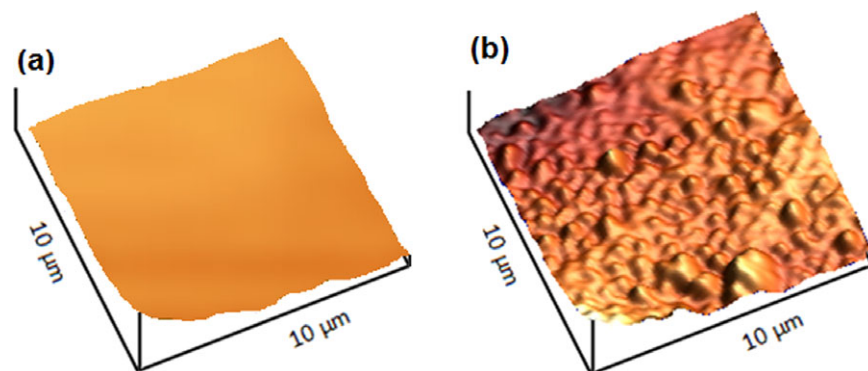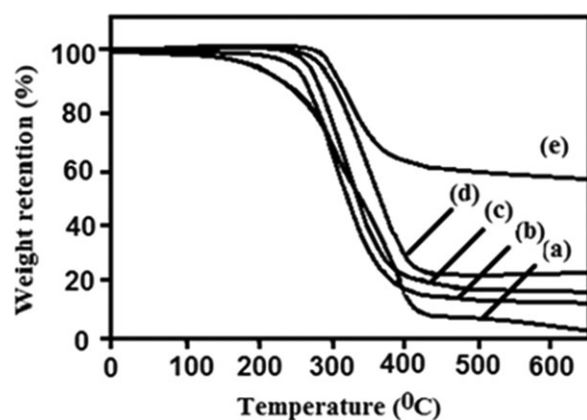

Figure 5. SEM image of (a) PE resin, (b) PE/GO composite (3 wt %) and (c) cross section of the composite.

Figure 6. AFM image of (a) PE resin and (b) PE/GO (3 wt %) composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between oxygen functionality on GO and polymer or some dipolar interactions between the two components. 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.[22] 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,[10,11] which showed only 30–40% improvement in major degradation temperature.

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 Figure 8. With increasing GO loading in the composites, the T_g of PE resin increases gradually from 54°C to 62°C. This increase in T_g indicates strong interaction between the PE and the GO sheets such as hydrogen bonding which reduces segmental motion of the polymer chain.

Mechanical Properties

The tensile strength of PE resin and PE/GO composite was 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. Figure 9 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 Figure 10. The figure shows an increasing trend of modulus with GO loading. 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.

The tensile properties of the PE/GO composite films are illustrated in Figure 11 and Table III. It is obvious that the addition of GO into the polymer matrix has a significant influence on the mechanical behavior of pure PE. 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 CNT-based PE

Figure 7. TGA curves of (a) PE resin, (b) PEGO1, (c) PEGO2, (d) PEGO3 composite, and (e) GO.
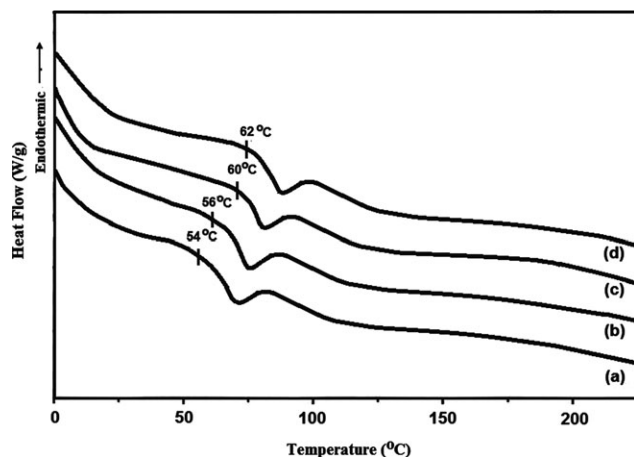
Table II. TGA Data of the Prepared Samples

| Sample particulars	Major degradation temperature (T_d) °C	Weight loss % at temperature				Weight retention (%) at 600°C
		200°C	300°C	400°C	500°C	
PE resin	245	8	30	80	90	5
PE/GO (1%)	260	6	35	80	82	15
PE/GO (2%)	270	5	25	75	80	20
PE/GO (3%)	285	3	15	65	70	25
GO	300	1	10	35	40	60

Figure 8. DSC curves of (a) PE resin, (b) PEGO1, (c) PEGO2, and (d) PEGO3 composite.

composites which showed only 17% increase in tensile strength.[13] 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.

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 graphene/GO-based polymer composites.[23–25] This mechanically
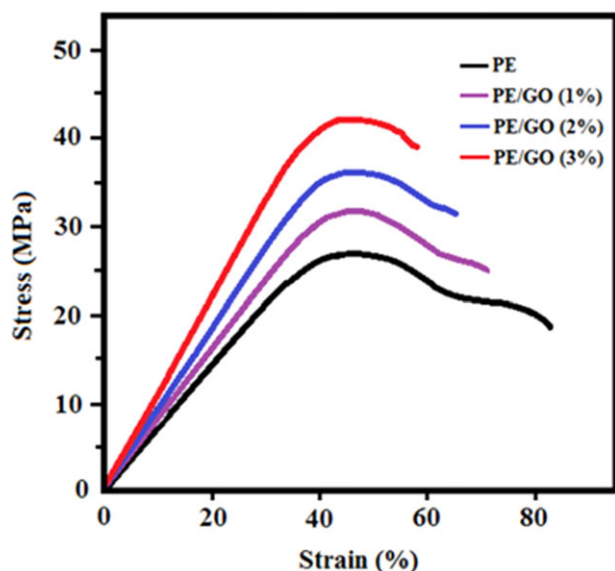
Figure 9. Representative stress–strain curves of the composites with various GO loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
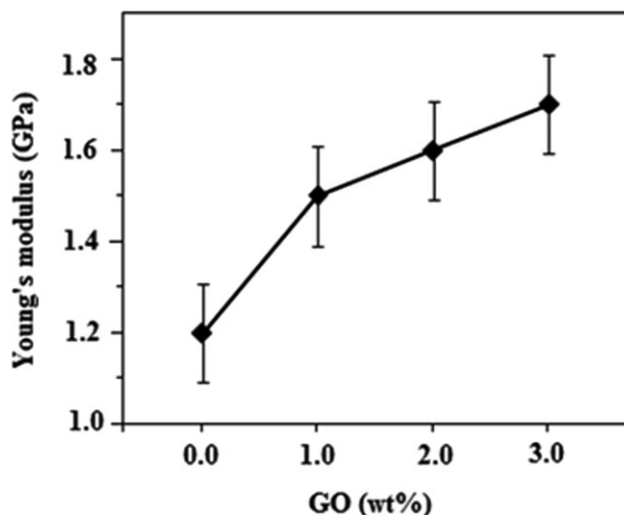

Figure 10. The calculated Young's modulus of the composites based on the slope of the elastic region.

strong composite system with improved thermal stability can be used in any high-tech structural applications, where high strength and stiffness are required.

CONCLUSIONS

This article demonstrates the successful preparation of GO-based PE composite with high thermal stability and mechanical strength. The FTIR and XRD results indicate successful incorporation of GO in the polymer matrix. Morphological analysis shows good dispersion of GO within the resin matrix. The composites show improved thermal stability compared to the pure PE. A significant improvement in major degradation temperature (260–285°C) and weight retention value (15–25%) is obtained on incorporation of GO in the polyester matrix. The 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
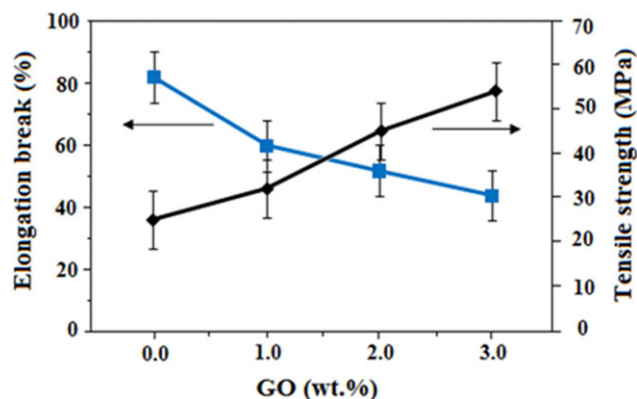
Figure 11. Mechanical properties of PE/GO nanocomposites with various GO loadings: tensile strength (right) and elongation at break (left) versus GO loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Mechanical Properties from the Tensile Test

Sample	Tensile strength (MPa)	Elongation (%)
PE resin	25	80
PE/GO (1%)	32	60
PE/GO (2%)	46	52
PE/GO (3%)	54	47

and the polymer matrix. These mechanically strong and ductile PE/GO composite films exhibit good potential in industrial applications.

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