Special Issue Paper

Enhanced Mechanical Properties of Functionalized Graphene Oxide/linear Low Density Polyethylene Composites Prepared by Melt Mixing

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ABSTRACT: Graphene oxide (GO) was concurrently reduced and functionalized using long alkyl chain dodecyl amine (DA). The DA functionalized GO (DA-G) was assumed to disperse homogenously in linear low density polyethylene (LLDPE). Subsequently, DA-G was used to fabricate DA-G/LLDPE composites by melt mixing technique. Fourier transform infrared spectra analysis was performed to ascertain the simultaneous reduction and functionlization of GO. Field emission scanning electron microscopy analysis was performed to ensure the homogenous distribution and dispersion of DA-G in LLDPE matrix. The enhanced storage modulus value of the composites validates the homogenous dispersion of DA-G and its good interfacial interaction with LLDPE matrix. An increased in tensile strength value by ~ 64% also confirms the generation of good interface between the two constituents, through which efficient load transfer is possible. However, no significant improvement in glass transition temperature was observed. This simple technique of fabricating LLDPE composites following industrially viable melt mixing procedure could be realizable to developed mechanically strong graphene based LLDPE composites for future applications.

Key Words: Functionalization, Composites, Melt mixing, Mechanical properties

1. INTRODUCTION

The intriguing properties of graphene have led to the development of light weight, yet strong polymer composites materials. The idea of integrating graphene or its derivatives with polymer matrix has been appealing from various perspectives. Graphene, as reinforcing filler have outperformed the performance of other widely used nanofiller such as CNT or MWCNT [1]. The physical properties of polymer composites were found to depend upon dispersion of filler and its interaction with the polymer system. The improvement in the mechanical properties of the composites is basically the function of degree of adhesion of filer to the polymer matrix and efficient stress transfer. Various technique such as solution processing [2], melt mixing [3], in-situ polymerization [4], have been utilized to combine the graphene with polymer and

to maximize the dispersion and homogenous distribution of graphene or functionalized graphene.

Graphene oxide (GO), precursor of graphene being hydrophilic in nature has less compatibility with most of the organic polymer. Moreover, strong π-π interaction and van der Waal's force between the graphene sheets restrain its complete exfoliation in polymer matrix. Thus, transfer of fundamental properties of graphene into polymer system necessitates homogenous distribution of filler, good dispersion and strong interaction at the graphene-matrix interface and junction cohesion. As GO surface is crowded with several chemically vulnerable groups, upon which various chemical entities can be introduced through chemical reaction. By introducing organic moieties, the surface of GO can be subtly tuned to enhance the compatibility of graphene with polymer matrix and junction cohesion can also be improved.

Myriad of works are reported on the chemical functionlization of GO, in an attempt to exploit most of its properties for instance, isocyanate modification, amination esterification [5-9]. Nucleophilic addition of various organic groups to GO surface is more viable way to the production of bulk amount of surface modified graphene [10]. Kuila *et al.* modified surface of GO by dodecyl amine and fabricated linear low-density polyethylene (LLDPE) composite and reported 46% enhancement in tensile strength at 3% weight of DA-G [6]. Jang *et al.* modified surface of GO by different alkyl chain length alkyl amine, prepared composite with polystyrene and reported enhancement in storage modulus and thermal stability [11]. Kim et al used ethylenediamine for the simultaneous functionalization, reduction and stitching of GO and investigated its effect on the mechanical properties of the LLDPE composites [12]. It is assumed that the introduction of alkyl chain amine on GO enhance the compatibility, dispersion and junction cohesion, which is crucial for stress transfer at the junction and in some cases it also reduced GO without using additional hazardous reducing agents [9]. However, in most of the cases, the composites were prepared by solution mixing, where chemically hazardous solvent was used to finely disperse graphene.

Herein, we used dodecyl amine to concurrently functionalized and reduced GO, and its impact on mechanical properties of the LLDPE composites was studied. We choose to study LLDPE polymer as it is one of the most widely used thermoplastic polymers, having enormous applications, mainly for plastic films, tubes etc. due to its excellent tear and impact strength, large elongation, and superb puncture resistance. Nevertheless, pure LLDPE has low mechanical properties, which impairs its applicability in different area. Melt mixing technique was employed to fabricate the DA-functionalized GO/LLDPE composites. Melt mixing can be considered more viable than solution mixing technique, as this process does not require hazardous solvent.

2. EXPERIMENTAL

2.1 Materials

Natural graphite flakes were purchased from Sigma-Aldrich., hydrochloric acid, sulphuric acid, potassium permanganate and hydrogen peroxide were purchased from E-Mark, Mumbai; India. DA was procured from Sisco research Laboratories, Mumbai, India. LLDPE polymer pellets were supplied by Reliance industries Limited, Gujarat, India. All the reagents were of analytical grade and used as received without further purification.

2.2 Preparation of DA modified GO (DA-G)

Graphite oxide was prepared through modified Hummer's method as reported earlier by our group [13]. DA-G was prepared following the method as reported from our previous
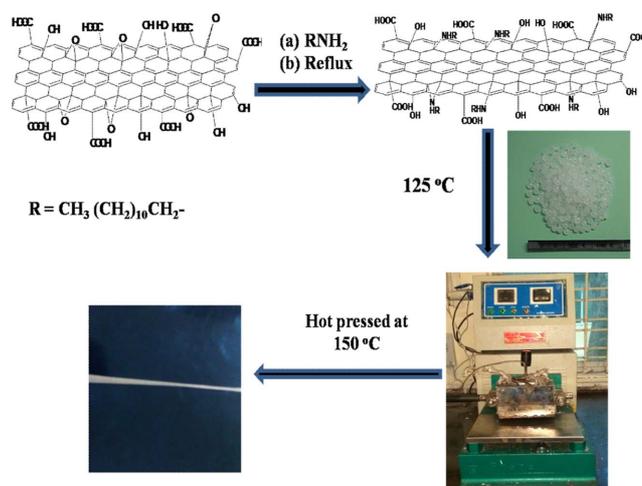
Fig. 1. Schematic for the functionlization of graphene oxide by DA and preparation of LLDPE composites by melt mixing

publication [2]. In brief, ~1 g of graphite oxide was dispersed in 100 ml of DI water by continuous water-bath sonication (Emmi20, Germany) with applied frequency of 45 kHz for about 30 min. The un-exfoliated graphite oxide was removed via centrifugation at 3000 rpm for about 15-20 min. About 3 g of DA was dissolved in 100 ml of ethanol. The mixture was stirred at room temperature for ~24 h and another ~16 h under refluxing condition. The conversion of brown to black colour aggregates confirmed the simultaneous surface functionlization and partial reduction of GO [9]. The black precipitate was vacuum filtered by washing repeatedly with water-ethanol mixture and dried under vacuum at 60ºC for ~72 h to achieve black dry powder of DA-G.

2.3 DA-G/LLDPE composite preparation

LLDPE composites using different weight fraction of DA-G were prepared by melt compounding using sigma melt mixture, at a processing temperature of 125ºC, screw speed of 60 rpm and the mixing time of 15 min. The melt mixing was carried out by slowly adding the LLDPE pellets into the mixing site. DA-G was added to the melt polymer. The materials obtained after melt mixing were cooled to room temperature and collected as a lump. It was then hot pressed into sheet of thickness of 2 mm using an electrically heated hydraulic press for ~15 min at 150ºC. After cooling to room temperature, the samples were cut from the sheet for various testing. Fig. 1 shows the schematic of the functionlization of GO with DA and preparation of its composites with LLDPE matrix by melt mixing.
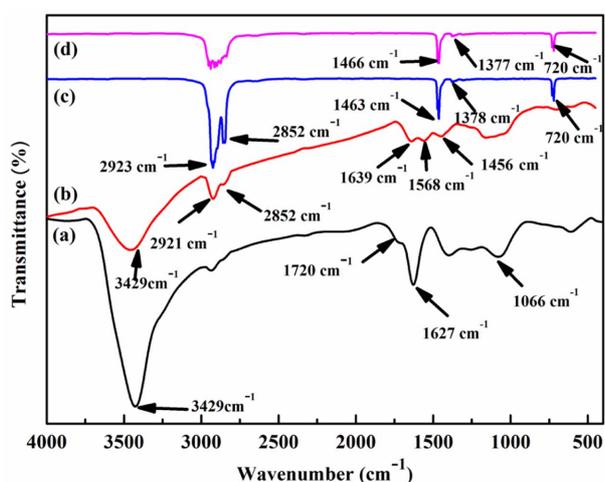
2.4 Characterizations

Fourier transform infrared (FT-IR) spectra were recorded with PerkinElmer RXI FT-IR in the frequency range of 4000-400 cm^{-1}. Field emission scanning electron microscopy (FE-SEM) was carried out with Σigma HD, Carl Zeiss, Germany.

The tensile measurements were carried out according to ASTMD-638 standard using a Tinius Olsen h10KS universal testing machine at 25°C with a crosshead speed of 2 mm min⁻¹. The dimension of the tensile sample was 77 mm length (working length of sample was 31 mm), 1 mm width and 1.5-2 mm thickness. Five specimens of each composite were tested to obtain the standard deviation. Dynamic mechanical analysis (DMA) was carried out with DMA 8000 Perkin Elmer in the temperature range of -90 to 90°C with a heating rate of 3°C min⁻¹ at a constant frequency of 1 Hz at a load strain of 0.010 mm. Rectangular specimens of dimension $10 \times 9 \times 2.5$ mm³ were prepared for DMA measurements.

3. RESULTS AND DISCUSSION

3.1 FT-IR Spectra analysis

Fig. 2 shows the FT-IR spectra of GO, DA-G, pure LLDPE and DA-G/LLDPE composites at 0.25 wt%. The peaks at 1720 and 1066 cm⁻¹ of GO are assigned to the -C=O stretching vibration and -C-O-C- in epoxide group of GO, respectively. The bands at 1627 and 3429 cm⁻¹ can be attributed to the graphitic sp² C and hydroxyl group. The appearance of the peak at 1639 cm⁻¹ in DA-G corresponding to the C-O stretching vibration established amide bonds formation. The reaction between the epoxide group of graphene oxide and amine group of DA can be confirmed by peaks at 1568 and 1456 cm⁻¹, which could be accounted for N-H and C-N stretching vibration. The appearance of peaks at 2852 and 2921 cm⁻¹, which is due to the C-H stretching vibration of -CH₂ and -CH confirms the grafting of DA on the surface of GO. Pure LLDPE and its composites with DA-G exhibited bands at 2923 and 2852 cm⁻¹, which is assigned to the -C-H bond symmetric and asymmetric stretching respectively. The spectrum of neat LLDPE showed peak at 1463 and 1378 cm⁻¹ which is due to the defor-

mation of -CH₂ and -CH₃ groups were shifted slightly to 1466 and 1377 cm⁻¹ in DA-G/LLDPE composites, which could be due to the possible interaction between the LLDPE matrix and DA-G. The peak of the DA-G/LLDPE composites at the region of 2800~3000 cm⁻¹ is quite different from that of the pure LLDPE. The appearance of not distinct but fused multiple peak may be assigned to the -C-H bond symmetric and asymmetric stretching of DA entity and LLDPE polymer matrix. Small interaction of DA-G with LLDPE matrix may be responsible for the multiple nature of the peak. Though the shift is very small (just 1~3 cm⁻¹), possible interaction between the LLDPE matrix and DA-G cannot be rule out. The observed small shift may be due to the little amount of DA-G (0.25 wt%) relative to the polymer matrix. The broad band that appeared in spectrum (a & b) at 3429 cm⁻¹ may be due to the -O-H stretching in both graphene oxide and DA-G spectra indicating incomplete reduction of graphene oxide [14].

3.2 Stress-Strain properties

Fig. 3 represents the typical stress-strain curve of melt processed DA-G/LLDPE composites. The DA-G incorporated LLDPE composites exhibit enhanced tensile properties, the maximum tensile strength enhancement of 60.62% was observed at 0.5 wt % of DA-G against neat LLDPE. The improvement in tensile strength may be accounted to the fine dispersion of high surface area DA-G and its strong interfacial adhesion with the LLDPE matrix, thereby, facilitating the efficient transfer of stress across interface. The addition of 3 wt% DA-G, decreased the tensile strength but it was found higher than the neat LLDPE. The decreased at higher loading may be due the agglomeration of the DA-G sheets. However, the elongation at the break of the DA-G/LLDPE composites was found to decrease, which may be attributed to the constrained movement of the polymer matrix due to the addition of filler particles.

Fig. 2. FT-IR spectra of (a) graphene oxide, (b) DA-G, (c) LLDPE and (d) 0.25 wt% DA-G/LLDPE composites
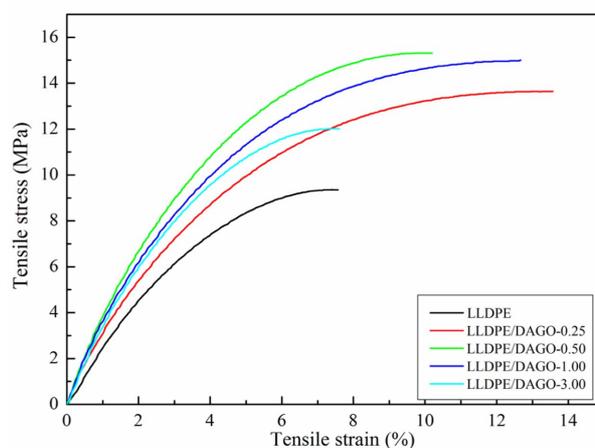
**Fig. 3.** Stress- strain curve of neat LLDPE and its composites with DA-G at various loadings
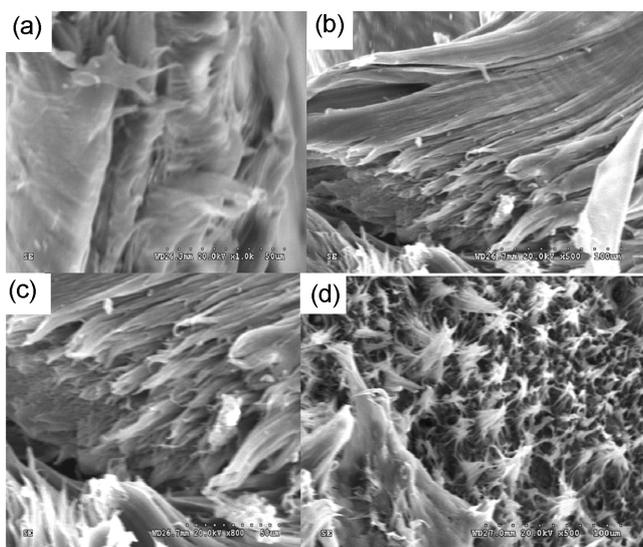
Fig. 4. FE-SEM images of the tensile fractured surface of (a) at LLDPE (b) (0.25 wt%) and (c&d) (0.5 wt%) DA-G/LLDPE composites

Fig. 5. Variations of the storage modulus of DA-G/LLDPE composites at different weight fraction

3.3 FE-SEM analysis of the composites

To examine the differences in the tensile fracture morphology of pure LLDPE and its composites with DA-G, FE-SEM images were analyzed in detail. Fig. 4(a-d) represents the overview of the fracture morphology of the LLDPE and DA-G/LLDPE composites. The fracture surface morphology of the pure LLDPE was smooth plain which suggest the failure of the material take placed at lower stress. In contrary to pure LLDPE, DA-G/LLDPE composites revealed comparatively rough fracture surface, which accounts for the improved mechanical properties. As can be seen from the Fig. 4c&d the sheets of the carbon layered of the polymer matrix are protrude which manifest the strong interfacial interaction between the DA-G and LLDPE polymer matrix and validate the improvement in storage modulus, strength value, which was improved by ~64% against neat LLDPE polymer. This simple strategy to produce functionalized GO/LLDPE composites by industrially viable technique could be promising in the direction of developing mechanically strong graphene based composites.

3.4 Dynamic mechanical properties

The storage modulus (E'), loss modulus (E''), and tan δ (loss factor) of the DA-G/LLDPE composites are presented in Fig. 5-7 as a function of temperature. E' measures the capability of material to store energy under cyclic load, and it also accounts the stiffness of the materials, whereas, E'' quantifies the amount of unrecoverable energy dissipation per cycle. Tan δ or damping is the ratio of the E'' to E' and is associated with the segmental motion of the polymer chains. DMA values of the DA-G/LLDPE composites are shown in Table 1. The storage modulus of the composites was found to increase with the
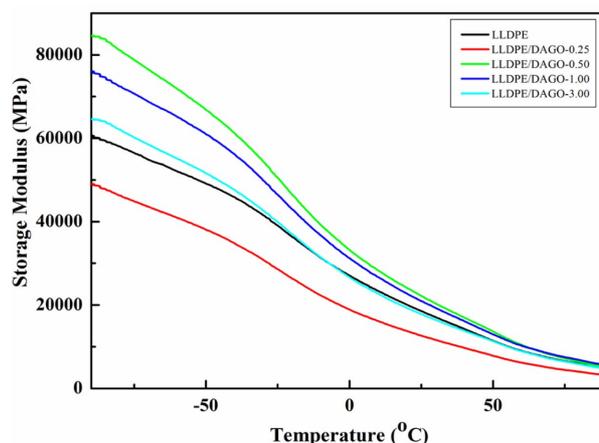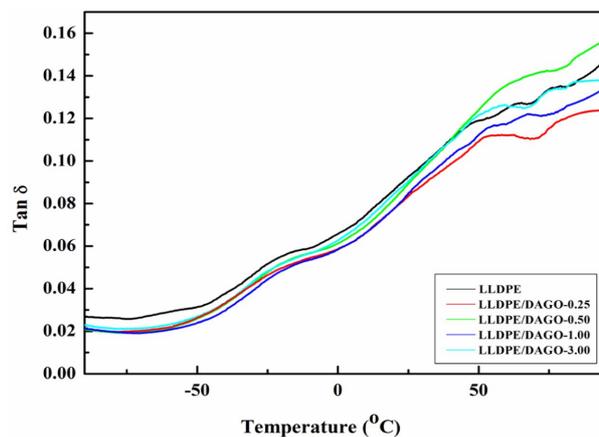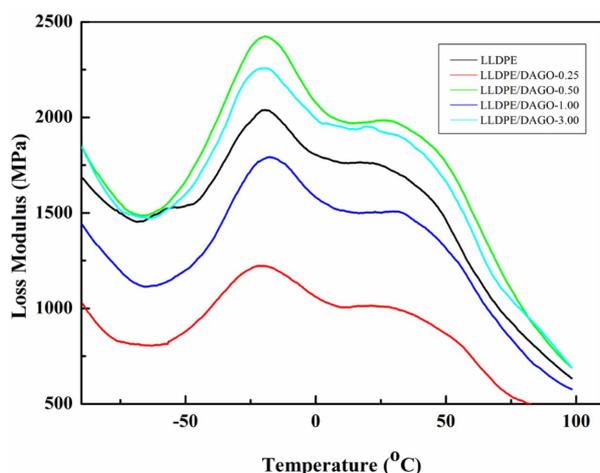

Fig. 6. Variation of tan δ of DA-G/LLDPE composites against temperature

content of DA-G, except for 0.25 wt% DA-G. The highest improvement in the E' was recorded at 0.5 wt% of DA-G, which may be due to the maximum degree of dispersion at this weight fraction and good degree of interfacial interaction. The good interfacial interaction generates strong junction cohesion, which helps in efficient load transfers and also inhibits the segmental mobility of the polymer chain. The intrinsic stiffness characteristics of the graphene contributes to improve the E' of the LLDPE composites. Thus, incorporation of DA-G endows the stiffness to the LLDPE composites. The decrease in E' at 0.25 wt% of DA-G, may be due to the low content of DA-G, which might not generate good interface with the matrix and thus, could not produce enough lamellar barrier effect sufficient to inhibit the segmental motion of LLDPE polymer matrix.

The tan δ curve of the neat LLDPE and its composites is shown in Fig. 6. As can be observe from the figure, neat LLDPE and its composites showed two relaxation one one at -24 to -20ºC (β-relaxation) and another in the range of 79-

Fig. 7. Variation of loss modulus of DA-G/LLDPE composites against temperature

Table 1. DMA values of neat LLDPE and DA-G/LLDPE composites

Sample	E' MPa (-90°C)	E'' MPa (-90°C)	Tan $\delta_{\alpha\text{-max}}$ At 80°C
LLDPE	60316.06	1677.05	0.134
LLDPE-0.25	48884.98	1027.36	0.1195
LLDPE-0.5	84521.51	1846.76	0.1446
LLDPE-1	75724.31	1841.15	0.1244
LLDPE-3	64503.95	1440.00	0.1344

90 °C (α-relaxation). The tan δ peak which is very sensitive to structural transformation can be used to derive T_g from its peak position. However, the tan δ peak in the study as evident from the figure is not completely discernible. There was very little change in the and β value for both LLDPE and its composites with DA-G. The decreased height of the tan δ peak suggests decreased damping property of the DA-G/LLDPE composites.

The peak position of E'' curve is also helpful to determine the T_g value in instances when tan δ peak fails to provide. Fig. 7 shows the E'' curve, which also shows marginal changes in relaxation.

4. CONCLUSIONS

Long alkyl chain DA functionalized GO was used to fabricate LLDPE composites via economically viable and environmentally friendly melt mixing technique. FT-IR spectra analysis was performed to substantive the functionlization and partial reduction of GO. FE-SEM micrograph was analyzed to study the fracture surface morphology of pure LLDPE and its composites. The presence of alky chain on DA helped to generate good interfacial interaction with the LLDPE matrix, which reflected in the enhanced storage modulus of the com-

posites. The reinforcing capability of the DA-G endows stiffness to the LLDPE matrix. The efficient junction cohesion was also reflected in the improved tensile strength value, which was improved by ~ 64% against neat LLDPE polymer. The fabrication of LLDPE/graphene composites with enhanced mechanical properties through industrially viable and environmentally friendly technique could be promising in the direction of developing high performance composites.

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