Processable Conductive Graphene/Polyethylene Nanocomposites: Effects of graphene dispersion and polyethylene blending with oxidized polyethylene on rheology and microstructure

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Abstract

Poor dispersion of graphene in non-polar polymer matrices creates composites with limited applications. A method to improve the dispersion of graphene in polyethylene (PE) via blending PE with oxidized PE (OPE) is examined. Graphene was produced by simultaneous thermal exfoliation and reduction of graphite oxide. Nanocomposites of graphene with PE as well as graphene with PE/OPE-blends were prepared by solvent blending. Improved dispersion of graphene in PE/OPE blends substantially decreases percolation from both rheological (0.3 vol%) and electrical (0.13 vol%) measurements compared to neat PE nanocomposites (1 and 0.29 vol%), respectively. A universal Brownian dispersion of graphene in polymers was concluded similar to that of nanotubes, following the Doi-Edwards theory. Micromechanical models, such as Mori-Tanaka and Halpin-Tsai models, modeled the mechanical properties of the nanocomposites. The nanocomposites microstructure, studied by small angle x-ray scattering, confirmed better dispersion of graphene at lower loadings and the formation of surface fractals in the blend/graphene nanocomposites; whereas only mass fractals were observed in neat PE/graphene nanocomposites.

Keywords: graphene, polyethylene, nanocomposites, SAXS, rheology, micromechanical models

1.0. Introduction

Due to the widespread interest in nanotechnology and its applications, polymer nanocomposites, which are polymers with nano-scale fillers, have shown enormous potential. For example, carbon nanotubes (CNTs) and graphene [1-4] are promising, conductive nano-fillers used for reinforcement of polymers as well as inducing electrical and thermal conductivity in the nanocomposites.

Graphene is a 1-atom thick layer of sp^2 -hybridized carbon atoms, consisting of honeycomb-like assembly of C-atoms. Outstanding properties of graphene/polymer nanocomposites include mechanical enhancement [5], improved electrical conductivity [3, 4, 6], thermal conductivity [7-9], gas barrier [4], and flame retardancy [10, 11]. To achieve combinations of practical properties in graphene/polymer nanocomposites, a homogenous dispersion of graphene in polymer matrix is essential. In order to obtain good graphene dispersion, graphene agglomerates must be broken down to single layers during processing (e.g., solvent, melt blending, or *in-situ* polymerization), or by surface functionalization of graphene, or altering chemistry of the polymer matrix. Regarding the microstructure of graphene in polymer matrices, two open questions need to be addressed: 1) Does graphene dispersion follow traditional theories, such as the Brownian diffusion; 2) What is the structure of the graphene network inside polymer matrix?

Single layer graphene has exceptionally high modulus of ~1,000 GPa in tension compared to ~1 to 10 GPa for polymers, and 10 to 800 GPa for other fillers [1, 12]. Such high strength of graphene enables graphene/polymer nanocomposites to carry the applied load. Because of its high surface area and sheet structure, graphene can, in principle, significantly alter the properties of the polymer matrix, e.g. polymer crystalline morphology [13], chain conformation [14], and dynamics through confinement effects [15]. Thus, many factors are responsible for the property changes offered by graphene, and better understanding of the property improvements requires additional studies of the behavior of graphene inside the polymer matrix.

Translating graphene's unique properties to nanocomposites is difficult, since graphene is known to poorly disperse in polyolefins, including polyethylene [6] and polypropylene [16, 17], due to the non-polar nature of polyolefins. Several groups are attempting to develop strategies to homogeneously disperse graphene in polyethylene, since polyethylene is one of the most widely

used commodity thermoplastics. For example, Kim et al. reported high electrical percolation threshold of graphene (12-15 wt%) nanoplatelets in polyethylene [18], which is significantly higher than many polar polymers [1]. High percolation is directly associated with poor dispersion and larger graphene aggregates in polyolefins [6, 19]. Improved dispersion of graphene in polyethylene was reported using amine functionalized graphene [20]. About 150% increase in elastic modulus was achieved at 3 wt% loading using functionalized graphene, compared to graphene oxide.

Introducing functional groups onto the polymer can improve dispersion of the nano-fillers in polyolefins. Maleic anhydride-grafted polyethylene [21], and chlorinated-polyethylene [22, 23] were reported as compatibilizers for graphene/polyethylene nanocomposites. However, transmission electron microscopy showed that chlorinated polyethylene did not reduce graphene stacking in the nanocomposites. Functionalized polyethylene containing cyano- and amino-functional groups, showed improved mechanical properties, but the electrical conductivity of functionalized polyethylene/graphene nanocomposites was lower than that of neat polyethylene/graphene nanocomposites [6].

Also, poor dispersion was reported when polyethylene chains were *in-situ* polymerized on graphene surface [24]. Despite the goals of attaining better dispersion and high conductivity, nanocomposites with 10 vol% graphene loading exhibited electrical conductivity of 10^{-4} S/cm, which is a strikingly low conductivity at such high loading. However, using such high loading of graphene in a non-polar polymer also increases the viscosity by several orders of magnitude [16, 25], which limits processing operations. In a report, Pang et al. [26] reported a very low electrical percolation threshold (0.07 vol%) for graphene/polyethylene nanocomposites via formation of a segregated structure, but other thermo-mechanical properties were not provided. Therefore, polyolefin nanocomposites having reduced graphene stacks, and with controlled processing properties is highly desirable.

Commonly used as a processing aid [27, 28] or biodegradable polyethylene [29], oxidized polyethylene (OPE) also improved the barrier properties of polyethylene/clay nanocomposites [30]. Leveraging our earlier work on blending OPE with PE to produce high modulus materials with controlled processing properties [31], we combined blends of polyethylene and OPE with

graphene as a nano-filler to create conductive nanocomposites. Overall, the purpose of this study is to better understand the origin of the reinforcement observed in PE/OPE/graphene nanocomposites with improved dispersion. Graphene loading was varied to understand the filler microstructure. Linking the thermo-mechanical properties of nanocomposites with their microstructure using scattering will also be detailed. In addition, graphene nanocomposites will be compared with carbon black composites.

2.0. Experimental Details

2.1. Materials

Natural flake graphite (-10 mesh, 99.9% Alfa Aesar), carbon black(CB) (99.9%, bulk density = 170-230 g/L, surface area = 75 m²/g, Alfa Aesar), linear low density polyethylene (LLDPE) with molecular weight 3.6 x 10⁶ g/mol (determined via gel permeation chromatography) and bulk density 0.97 g/cm³ (428078, lot#07730MEV, Aldrich), p-xylene (99%, Sigma Aldrich), potassium permanganate (Fisher Scientific), sulfuric acid (95-97%, J.T. Bakers), phosphoric acid (>99%, Aldrich), hydrogen peroxide (30% solution, BDH), HCl (37%, Reidel-deHaen), were used as received. Oxidized polyethylene with an acid number of 7 and density of 0.94 g/cm³ was supplied by Marcus Oil and Chemicals (Texas, USA).

2.2. Synthesis of TRG

TRG has been prepared by thermal exfoliation and reduction of graphite oxide (GO) [32-34]. For synthesis of GO, Tour's method [35] was employed. Typically, 5 g of natural flake graphite was dispersed in a mixture of H₂SO₄ (272 mL) and H₃PO₄ (33 mL), and stirred for 30 minutes. About 27.8 g KMNO₄ was gradually added into the mixture over the course of one hour to minimize the potential for explosion. The mixture was stirred continuously using an overhead stirrer for three days at room temperature. After the completion of reaction, H₂O₂ (30%, 17.5 mL) and deionized water (137.5 mL) were added to the reaction mixture, and stirred until the color of the mixture turned from dark brown to bright yellowish, indicating high oxidation level of graphite. GO was washed three times with 1M HCl aqueous solution, and further repeatedly washed with deionized water until a pH of 4-5 was obtained. The separation of the washed GO was carried out by a centrifuge with a force of 10000 g followed by dialysis. The washed GO was dried under vacuum for two days to remove any traces of water. The dried GO was thermally exfoliated and reduced by heating rapidly at 1000°C for 30 s under nitrogen flow in a tube furnace to produce thermally reduced graphene (TRG). The produced TRG was dried overnight under vacuum before using in the nanocomposites.

2.3. Preparation of Composites

Low density polyethylene (PE) and OPE were dispersed in p-xylene at 120°C for one hour under reflux. Meanwhile, TRG (or CB) was sonicated in p-xylene for one hour at room temperature in a sonication bath. TRG dispersion was added into PE/OPE mixture, and solution was further stirred for another hour to form a homogenous solution at 120°C. After the formation of homogenous solution, the solution was drop cast on a heated glass plate at 80°C, and the solvent was allowed to evaporate for two hours. The complete solvent removal was achieved by drying in a fume hood at ambient conditions for 24 h followed by drying in convection oven at 80°C for 5 h. The complete solvent removal was confirmed by running thermal scans in a differential scanning calorimeter, where no solvent peak was observed. The dried samples were chopped into pieces 3-5 mm wide, heated at 160°C for 10 min and hot pressed for 3 min under 5000 kPa pressure to prepare circular discs (thickness 1-1.3 mm and diameter ~ 25 mm) for rheological testing. Similarly, thin films (100-200 µm) for mechanical and scattering testing were prepared by the same method using more dilute solutions of PE/OPE and TRG (or CB) in p-xylene, and drop casting in a petri dish at 80°C, and following the same drying procedures.

For pure PE/OPE blends, the same procedure was used without TRG or CB. The PE/OPE solution was stirred for 2 hours at 120°C under reflux before drop casting on a glass plate or in a petri dish.

2.4. *Characterization*

Wide angle x-ray diffraction (XRD) was performed on a Phillips PW 3040/60 with CuK α radiation at a scanning rate of 0.02°/s to study exfoliation of graphite. Transmission electron microscope (TEM) images of nanoparticles were obtained using a FEI Phillips C200 at 200 kV to confirm the production of TRG nanosheets. For TEM measurements, a dilute dispersion of TRG (0.1 mg/20 mL acetone) was prepared by bath sonication for 10 minutes, and one drop of solution was deposited on a 300-mesh Cu grid with holey carbon. The TEM morphology of nanocomposites was obtained by cutting thin slices of nanocomposite films using a diamond knife. The micro-images of blends and composites were obtained using JEOL-JSM-7000F field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 3 kV. The blends and composites were cryo-fractured in liquid nitrogen, and sputter coated with gold for 120 seconds. Functional groups on TRG surface were analyzed by Fourier transform infra red

spectrometer (FTIR) (NicoletTM iSTM 10, Thermo scientific FTIR) with 32 scan at a resolution of 4 cm⁻¹ (TRG in KBr). Very dilute dispersions of CB (0.1 mg/mL) and TRG (0.025 mg/mL) were dispersed in acetone via bath sonication at room temperature, and dynamic light scattering (DLS) was performed using particle size analyzer (NanoBrook 90Plus, Brookhaven) at 25°C.

Rheological measurements of blends and composites were performed at 160°C using TA Instrument AR-G2 rheometer equipped with 20 mm parallel plate. Tests were conducted in air while samples were covered with an aluminum solvent trap to avoid temperature fluctuations during the run. Linear viscoelastic (LVE) region was determined by conducting strain sweep in 0.01-100% strain range at 1 Hz frequency. The frequency sweep experiments were performed in the frequency range of 0.01-100 Hz at fixed strain within LVE region.

Mechanical properties of thin films were determined following ASTM D882, using ARES-G2 (TA Instruments) rheometer with Film & Fiber tool. Measurements were carried out at room temperature at a stretching speed of 0.0167 mm/s using thin rectangular samples ~10 mm long and ~5 mm wide.

The in-plane electrical conductivity was calculated using electrochemical impedance spectroscopy (EIS) using the following equation:

$$\text{Conductivity} = \frac{L}{R.w.t}$$

Where, R is the film resistance, L is the distance between the sense electrodes, w is the width of film, and t is the sample thickness. The impedance spectra were obtained over a frequency range of 0.3 Hz to 100 kHz using a four-electrode test cell connected to a multi-channel potentiostat (Biologic VMP3, Knoxville, TN). All measurements were carried in an environmental chamber to control sample temperature and humidity (TestEquity Model 1007H, Moorpark, CA). The samples were polished using a 100-mesh grit paper before conductivity measurements in order to remove thin polymer layer transported to the surface during the film formation and drying process. Due to polishing, TRG and CB composites exhibited static current build up, which was removed by conditioning the samples at 95% relative humidity and 50°C for one hour. The results reported are averaged over 3 samples at 25°C temperature and 95% relative humidity.

Small angle X-ray scattering (SAXS) experiments were performed using beamline 12-ID-C at the Advanced Photon Source at Argonne National Laboratory. Data were collected at 60°C under dry conditions, and averaged over three exposures times. Details of the procedure and temperature/humidity control can be found elsewhere [36, 37].

3.0. Result and Discussion

3.1. Characterization of TRG and CB

Rapid heating of GO produced a substantial increase in volume, and GO was exfoliated into TRG. Typically, GO has a bulk density of 0.5 g/cm^3 (1 g with a bulk volume of $\sim 2 \text{ cm}^3$), while the TRG product has a bulk density of $\sim 10 \text{ mg/cm}^3$ (1 g TRG with a bulk volume of 100 cm^3). An exfoliated sheet-like structure was observed when TRG was deposited on a TEM grid from a very dilute solution (Fig. 1a). A paper-like morphology of graphene nano-sheets was observed where the graphene sheets were overlapping, extended to a few hundred nanometers. The actual graphene sheets are extremely transparent to the electron beam, however, the folded edges appeared dark, as observed by others [34]. The CB particles are clusters of almost spherical particles, forming fractal structures extending over $2 \text{ }\mu\text{m}$ (Fig. 1b). The size of the individual CB particles was $\sim 60\text{-}80 \text{ nm}$. Although the TEM images were taken from extremely dilute suspension of CB in acetone, the particles still formed large aggregates. The size of these aggregates might increase at higher CB concentrations in polymers. Complete characterization of TRG, and CB particles by XRD, TEM, FTIR, and DLS is provided in the supporting information.

Fig. 1. TEM image of TRG (a), and CB (b)

3.2. Melt Rheological Analysis

3.2.1. Rheology of Blends and TRG-Nanocomposites

Melt rheology of polymers and polymer nanocomposites is essential for understanding their processing and developing structure-property relationships. Viscoelastic (VE) response can be connected to the intrinsic behavior of polymers, inter-particle, and polymer-particle interaction. In general, rheological properties depend on the input strain, whether in the linear or non-linear VE region. The dynamic strain sweep determines the strain dependent viscoelastic response and the linear viscoelastic (LVE) region. The addition of OPE in PE led to the formation of miscible blends, where OPE mainly resided within the amorphous region of the long period domains of PE [31]. Due to miscibility and plasticization, OPE decreased the complex viscosity of PE (complex viscosity at 0.01 Hz, Fig. 2). An approximately 7-fold decrease in viscosity was observed for 60/40 blend compared to neat PE. This lower viscosity can be very advantageous when processing polyolefin nanocomposites that require high filler loadings. The complete rheological, thermal, mechanical, and structural properties of PE/OPE blends can be found in our previous work [31].

Fig. 2. Processing control by PE/OPE blends

TRG-filled PE, PE/OPE 80/20, and 60/40 blends exhibited different rheological responses at various TRG loadings (Fig. 3). Adding TRG to PE increased G' at all TRG loadings (Fig. 3a). With increasing TRG, an exponential increase in G' was observed. Also, the low frequency slope of G' decreased, leading to asymptotic behavior that is nearly independent of frequency. This asymptotic behavior indicates the development of a concentrated, percolating network [38]. A similar trend was observed for 80/20/TRG nanocomposites (Fig. 3b). Increasing TRG loading

increased G' of 80/20/TRG nanocomposites, leading to exponential growth in G' with increased loading.

A peculiar rheological behavior was observed for 60/40/TRG nanocomposites at low TRG loadings (Fig. 3c). For $\text{TRG} < 1 \text{ wt\%}$, G' decreased with TRG addition compared to the unfilled blend. At higher TRG loadings, an exponential increase in G' was observed, similar to the PE/TRG and 80/20/TRG nanocomposites. For 60/40 blends, the decrease in G' for dilute TRG loadings might be attributed to the slipperiness between TRG and polymer interface layers due to a low surface friction, and possible exfoliation of TRG sheets [25]. Exfoliation of TRG into smaller stacks might lead to sheet alignment, which could decrease the VE response from the nanocomposites. Further details of this slippery behavior will be discussed in conjunction with scattering results later.

The viscosity of nanocomposites plays a vital role in practical processing for mass production and product formation. PE showed a typical non-Newtonian shear thinning viscosity profile with increasing frequency (Fig. 3d), which increased with TRG addition. Increasing frequency (or correspondingly the shear rate according to Cox-Merz rule [39]) produced a similar shear thinning profile, attributed to the alignment of graphene sheets in the shearing direction. At higher TRG loadings (5 wt%), a rheological response typical of a highly filled percolated network ($\eta^* \sim f^{-1}$) was observed. Similar trends were observed for 80/20/TRG nanocomposites (Fig. 3e). The 60/40/TRG nanocomposites exhibited similar peculiar behavior for the η^* as was observed for $G' \sim f$ data (Fig. 3f). The viscosity decreased at low TRG loading, and a continuous increase in viscosity was observed with increasing TRG loading above 1 wt%. The three matrices (PE, 80/20 and 60/40) showed similar asymptotic behavior $\eta^* \sim f^{-1}$ at higher TRG loading (5 wt%). However, due to the plasticization effect of OPE, the low frequency viscosity for 60/40/TRG nanocomposites was even lower than that of 80/20/TRG composites, which was lower than PE/TRG nanocomposite viscosity. The reduced viscosity of blend nanocomposites provides ease of processing for PE nanocomposites. Furthermore, reduction in viscosity is also an indication of reduced melt strength in polymers. However, a relationship between viscosity measured from a rotational rheometer and the melt strength is outside the scope of the current study.

Mackay [40] reported the non-Einstein viscosity behavior in nanocomposites with nanoparticles smaller than the radius of gyration of the polymer. The TRG used in this study, have approximately 5-6 nm thickness and 0.6-1 μm length. Due to highly non-polar nature of polyolefins leading to insufficient filler/polymer interactions, TRG sheets tend to agglomerate into a few hundred nanometer thick particles, becoming larger than the radius of gyration of polyolefins, which do not exhibit slipperiness (Fig. 3a). However, in 60/40/TRG nanocomposites, OPE might be wetting the graphene surface, breaking down TRG agglomerates to a few nanometer thin particles, leading to slipperiness. Therefore, we hypothesize that particles with one dimension smaller than the radius of gyration of polymer might also exhibit Mackay's non-Einstein behavior. However, detailed investigation of this behavior is beyond the scope of this study. The microstructure developed in nanocomposites at lower TRG loading will be discussed in detail in the scattering section.

The rheological properties of CB-filled composites showed similar trends as observed for TRG-filled nanocomposites (see supporting information). However, higher loading of CB (5-10 wt%) was required to reach the percolation in the CB-composites. At dilute loadings, the complex viscosity of 60/40/CB composites was lower than that of neat 60/40 blends, exhibiting a similar slipperiness as was observed in 60/40/TRG nanocomposites. However, the slippery behavior was less prominent in CB-composites, which might be due to the highly fractal forming nature of CB. Details on microstructure of CB-filled composites will be discussed in scattering section.

Fig. 3. Representative shear modulus and complex viscosity vs. frequency curves for PE/TRG (a, d), PE/OPE 80/20/TRG (b, e) and 60/40/TRG (c, f), respectively. Solid lines represent the polymer matrix in each box and numbers next to each curve correspond to weight % of TRG

3.2.2. Percolation and Scaling Analysis

The amount of filler needed to create an interconnected network within a polymer matrix, called percolation threshold, is associated with polymer-particle interactions and particle dispersion in the polymer matrix. In order to determine percolating volume fraction (Φ_p), we analyzed the increase in G' in the terminal region (at 0.01 Hz, $G'_{0.01}$), which is presented in Fig. 4. With increasing TRG loading, an exponential increase in $G'_{0.01}$ corresponds to the transition to solid-like behavior, which indicates Φ_p . Above Φ_p , the $G'_{0.01}$ exhibited a power law dependence on TRG volume fraction as follows:

$$G'_{0.01} \sim (\phi - \phi_p)^\alpha$$

where α is the power law exponent. **Similar percolation analyses were observed in many previous reports [4, 41-43].** The measured Φ_p values were 1, 0.7, and 0.3% for PE/TRG, 80/20/TRG, and 60/40/TRG nanocomposites, respectively. The corresponding percolation in weight% are 2.3%, 1.6%, and 0.7 wt%, respectively. The substantial decrease in Φ_p for 60/40 blends indicated highly improved dispersion of TRG, likely due to the increased graphene/matrix

chain interactions. Lowering percolation in polymer nanocomposites further increases the potential for applications of nanocomposites. Reducing percolation helps in designing conductive nanocomposites at lower cost using low amount of the conductive fillers [44]. The cost of both OPE (www.jbaux.com) and PE (2015 pricing report on PE www.spendmatters.com) is ~\$1500-1700/metric ton. The equal price of PE and OPE shows that replacing PE with OPE in the polymer blend matrix does not induce any effects on the overall cost of the nanocomposites, which essentially remains the same. However, inclusion of OPE does help in lowering the percolation limits and increasing mechanical properties of the nanocomposites which are the added advantages of OPE mixed in PE.

Fitting to percolation power law yielded the α values of 2.9, 2.5, and 2.7 for PE/TRG, 80/20/TRG, and 60/40/TRG nanocomposites, respectively (inset in Fig. 4). Typically, a stress-bearing network produces α ranging from 2.1 to 3.75. Here, $\alpha > 2.1$ may indicate the establishment of graphene-graphene bridging network, which could derive from π - π interactions in graphene sheets at higher loadings. Generally, an $\alpha < 2.1$ shows a network of particles bridged with polymer chains is formed, whereas a direct particle-particle network is established for $\alpha > 3.75$ [45-47]. However, a three dimensional network exhibits $\alpha \geq 3$, to form a rigid percolating network [43, 48, 49].

Furthermore, the aspect ratio of graphene in these matrices (A_f) can be determined from Φ_p . A_f is the ratio of width to the thickness of the filler (l/d), and is considered as an indicative parameter for exfoliation and dispersion. A_f is equal to 1 for perfectly spherical filler. In case of TRG/polymer nanocomposites, A_f is maximum for completely exfoliated structures depending on the lateral size of graphene layers. Ren et al.[50] proposed a formula to determine the relationship between the number of clay layers in each tactoid above percolation and clay concentration. This expression was further simplified to calculate the average aspect ratio of TRG [3] as follows:

$$A_f = \frac{3\phi_{pR}}{2\phi_p}$$

where Φ_{pR} is the percolation threshold volume fraction for randomly packed spheres, and Φ_p is the experimentally determined percolating volume fraction. Combining $\Phi_{pR} \sim 0.3$, a constant for

the randomly packed spheres [3], and measured Φ_p values (from Fig. 4), the aspect ratio was calculated for each nanocomposite. A more exfoliated structure exhibits higher A_f values. In TRG-filled systems, A_f increased from 41 to 60 as the polymer matrix changed from neat PE to PE/OPE 80/20 blend. However, an A_f of 155 was obtained for PE/OPE 60/40 matrix, indicating better exfoliation and improved dispersion of TRG in the 60/40 blend (Table 1).

Fig. 4. Percolation analysis of TRG filled PE, PE/OPE 80/20 and 60/40 blends. Solid lines are linear fit to experimental data. The point of intersection of two lines indicates the percolation threshold, Φ_p . Inset shows power law fit to percolation law for PE, 80/20 and 60/40 blends-filled with TRG, and the numbers next to each line are the power law exponents. Color schemes are same in both panels.

By determining the power law dependences of $G'_{0.01}$ and critical strain (γ_c %) on TRG volume fraction (Φ), LVE properties of nanocomposites can quantify the microstructure of fillers in polymer nanocomposites. Critical strain (γ_c %) is defined as the strain (γ %) at which G' decreases to 90 % of its initial value in a strain sweep experiment. Shih et al. [51] proposed a scaling model for the elastic properties of fractal networks built up by filler aggregates above Φ_p . In nanocomposites, the fractal network is considered as elastically linked filler aggregates. A decrease in γ_c % behavior with increasing filler volume fraction above Φ_p (a representative decrease in linearity with increase TRG Φ is provided in supporting information) can be explained by the physical links between the aggregates, called the strong-link regime. In the

percolation region, the power law dependence of γ_c and $G'_{0.01}$ can be described by the following equations:

$$\gamma_c \sim \phi^{-(1+x)/(3-d_f)}$$

$$G'_{0.01} \sim \phi^{(3+x)/(3-d_f)}$$

where, d_f is the fractal dimension of the filler aggregates, and x is an exponent related to filler Φ , and aggregate size by giving dimension of aggregate backbone, which is responsible for elasticity. The γ_c and $G'_{0.01}$ (above percolation threshold) were plotted as a function of TRG Φ (Fig. 5), and exponents of Φ were evaluated. Both PE/TRG and 80/20/TRG nanocomposites exhibited similar exponent of γ_c , whereas the exponent decreased for 60/40/TRG nanocomposites. The scaling exponent of G' was lower for PE/TRG system (3.8), than for 80/20/TRG and 60/40/TRG nanocomposites (4.3). The higher value of G' exponent further indicates the formation of elastic network [43], which is more efficient in storing elastic energy in blend/TRG nanocomposites compared with PE/TRG nanocomposites. In addition, G' scaling exponents (3.8 and 4.3) in this study are higher than that reported for CNTs/polypropylene nanocomposites (2.8) [52]. This difference in scaling exponents implies that the scaling can depend on the fillers dimensionality, and the two-dimensional platelets, such as TRG nanosheets might be more effective in enhancing the elastic contribution in polymers compared to the one-dimensional nanotubes.

The exponents scaling for γ_c and $G'_{0.01}$ above percolation can be expressed as:

$$\gamma_c \sim \phi^{m_\gamma}$$

$$G'_{0.01} \sim \phi^{m_G}$$

Combining the scaling equations, the power law exponents become:

$$d_f = 3 - \frac{2}{m_\gamma + m_G}$$

$$x = \frac{2m_G}{m_\gamma + m_G} - 3$$

The calculated values for d_f and x were 0.6 and 6.3 for PE/TRG, 1.4 and 3.7 for 80/20-TRG, and 1.8 and 2.2 for 60/40-TRG nanocomposites, respectively. Surprisingly, d_f increased with increasing OPE loading, which is different from other reports [42, 43]. Usually, d_f decreases with increasing A_f , which is exhibited by various clay [41] and graphene filled polymers [43]. A relatively high value of x for PE/TRG system indicates that most sheets in TRG fractals (flocs) contribute to network elasticity, and the structural defects are elastically inactive such as dangling ends which rarely exist [43, 45]. The value of x decreased with increasing OPE loading in nanocomposites. However, all three values of x are still large enough to confirm that the flocs are elastically active in the three nanocomposites [43].

Fig. 5. Scaling behavior of critical strain (a), and G' (b) above percolation threshold

3.2.3. Mechanism of TRG Dispersion

The dispersion mechanism of nanoscale, hard, and rigid disks in a polymer matrix is governed by either Brownian motion of particles or non-Brownian interactions. According to the Stokes-Einstein equation [53] for disk-shaped particles (of length L), particle rotary diffusion coefficient (D_r , s^{-1}) in dilute concentration regime in a suspending medium of viscosity (η_o) is given as:

$$D_r = \frac{3k_B T}{4\eta_o L^3}$$

Where, k_B is the Boltzmann constant, and T is the temperature in absolute scale. Considering $L \sim 600$ nm (longest dimension in Fig. 1), the D_r calculated for PE/TRG, 80/20-TRG, and 60/40-TRG at 160° C were 5×10^{-9} , 1×10^{-8} , and $1 \times 10^{-7} s^{-1}$, respectively. Conversely, the diffusion time,

$\tau \sim 1/D_r$ was 10^8 , 10^8 , and 10^7 s, respectively, which represents the time needed for nanosheets to travel a distance equal to their radii (300 nm) at the processing temperature (160°C). The diffusion time, however, seems unrealistic, since a polymeric material would degrade if kept at that high temperatures (160°C) for long times (e.g., >10 hours). Thus, the diffusion coefficient or diffusion time alone cannot answer whether the diffusion of graphene inside a polymer matrix follows the Brownian or non-Brownian dynamics. Therefore, the concept of D_r is further extended to describe the dynamics of disk-shaped particles via the universal Doi-Edwards theory, originally developed for CNTs.

The Doi-Edwards theory [54] describes the dispersion of nanorods of length L , and diameter d , in liquid suspension in dilute and semi-dilute regimes. For nanorods, ν is the number of nanorods per unit volume, which is related to volume fraction of nanorods as $\Phi = d^2 L \nu \pi / 4$. Considering d as the thickness of graphene nanosheets ($d = 5$ nm for TRG, since Raman analysis indicated that our TRG was comprised of about four 1-atomic thick sheets [34]). According to Doi and Edwards, the concentration dependence of the zero shear viscosity, η_0 for dilute regime obeys the following scaling law:

$$\frac{\eta_c}{\eta_M} \sim (\nu L^3)^1$$

Here, η_C , η_M are viscosity of composites, and that of matrix, respectively. The rotary diffusion of particles is hindered by neighboring particles in semi-dilute regime, and D_r is predicted to follow the power law $D_r \sim (\nu L^3)^{-2}$. Consequently, the viscosity scales in the semi-dilute regime as follows:

$$\frac{\eta_c}{\eta_M} \sim (\nu L^3)^3$$

However, in the concentrated regime, the factors such as sheet flexibility, Brownian motion, and van der Waals interactions are strongly affected by the viscosity of the matrix [55]. The Doi-Edwards theory can be applied to any nanorods (or nano-sheets, in this case), provided these particles behave as solid Brownian entities in the suspending medium on the nanometer scale. Thus, from the equations derived by Doi and Edwards, the variation of the reduced viscosity

(η_c/η_M) with νL^3 should follow a master curve. The Brownian motion of nanosheets (similar to nanorods) should be universal and independent of their nature. Recently, Cassagnaue [56] reported the universal master curve of CNTs, cellulose whiskers, and polymer nanofibers in different polymer matrices, which indicates that the rotary motion of these fillers was dominated by the Brownian motion. It is worth mentioning that even extremely dilute suspensions of nanorods were not able to produce $\eta_c/\eta_m \sim \Phi^1$ behavior [55, 56].

Following the Doi-Edward theory, a universal curve of $\log (\eta_c/\eta_M)$ versus the particle concentration (νL^3) was created for TRG-based nanocomposites (Fig. 6). The successful building of the universal curve indicates that TRG dispersion in these matrices is dominated by the Brownian forces [55, 56]. The TRG nanocomposites showed $\eta_c/\eta_M \sim (\nu L^3)^3$ behavior in the concentrated regime. A downshift in the master curve was observed for 60/40/TRG nanocomposites, attributed to the extremely low viscosity of 60/40 blends. Thus, the diffusion of graphene sheets in polymers follows the Brownian diffusion. However, further investigations in the low viscosity polymers filled with graphene nanosheets should be carried out to claim the universality of this behavior.

Fig. 6. Universal behavior for TRG-filled matrices

3.3. SAXS-based Microstructure

The microstructural parameters, such as d_f and x , extracted from melt rheology scaling are averaged over the entire composite. However, each composition has its own microstructure, which can be analyzed using scattering methods, including small angle x-ray scattering (SAXS).

SAXS measures the shape and size of polymers between 5 and 25 nm of the repeat distances [57]. The scattering vector (q) probes different structural features at various length scales (length scale $\sim 2\pi/q$) in polymers and polymer nanocomposites.

Increase in power law decaying exponent ($\log(I) \sim \log(q)^{-\alpha}$) at lower q values indicates a larger size of scattering objects. For clay minerals, Malekani et al. [58] proposed that the decaying exponent α was directly related to the fractal dimensions, d_f . For $\alpha \leq 3$, the particles form mass fractals (a substance whose surface and mass are both characterized by the fractal properties). In this case, α directly corresponds to mass fractal dimensions, d_m . If $3 \leq \alpha \leq 4$, surface fractals are formed where the scattering is observed from a smooth surface. The surface fractal dimensions, d_s , is calculated from α as follows: $\alpha \equiv 6 - d_s$ where $3 < 6 - d_s \leq 4$ [58, 59]. Thus, d_s varies from 3 to 2, where $d_s \sim 2$ indicates a smooth surface approaching Porod's scattering ($\alpha = 4$) [60], and $d_s \sim 3$ indicates uneven concentration of scattering objects at the scattering surface [61].

Pure PE exhibited $\alpha = 2.3$, typical for randomly oriented polymer chains [60] (Fig. 7a). Inclusion of OPE in PE increased α to 2.9 for PE/OPE 60/40 blends (Fig. 7b). In the absence of any filler, higher α indicates increased mass fractal concentration in blends, which is attributed to immiscibility of OPE at higher loadings [31]. Addition of TRG in PE showed smaller α values (1.5 to 2.1) until a loading of 1 wt% (Fig. 7a). The small α values at low TRG concentration indicate the exfoliation of TRG sheets inside PE matrix, **whereas α increased with increasing TRG loading to 5 wt%. Also, $\alpha < 3$ in PE/TRG nanocomposites further indicates the formation of mass fractals.** The 80/20/TRG nanocomposites exhibited a similar pattern of α increasing, and only the mass fractals being observed (supporting information). However, 60/40/TRG nanocomposites showed a different behavior when $\text{TRG} \geq 3$ wt%; $\alpha > 3$ was observed. The increased α showed the formation of surface fractals [58], which was attributed to the better exfoliation, and high A_f in 60/40/TRG nanocomposites, which verifies the finding from rheology discussed earlier.

Scattering from the nanocomposites changes above the percolation threshold. The PE/TRG nanocomposites exhibited the rheological percolation at ~ 1.0 vol% (2.2 wt%), whereas the percolation for 60/40/TRG nanocomposites was observed at 0.3 vol% (0.7 wt%). Below percolation, low α values were measured at 1 wt% for 60/40/TRG system (1.9) and PE/TRG

nanocomposites (2.1), which indicated better dispersion of TRG. Also, the slippery behavior observed in the rheological data for 60/40/TRG nanocomposites below percolation can be associated with this small α values. Since, we did not observe the slipperiness in PE/TRG nanocomposites, it might also be associated with relatively low viscosity of 60/40 blends, and shear alignment of TRG sheets upon exfoliation.

Above the percolation threshold (TRG > 3 wt%), the TRG formed surface fractals ($\alpha = 3.5$) in the 60/40 blend, whereas only mass fractals were observed for PE/TRG nanocomposites ($\alpha = 2.7$). The large difference in α values further indicates markedly improved exfoliation and dispersion of TRG in 60/40 blends.

Fig. 7. $I(q) \sim q$ log-log plots of PE/TRG (a), and 60/40/TRG nanocomposites (b). Note: The lines in all panels are stacked in the same order with Y-offset for clarity.

Due to the fractal forming nature of CB particles, a relatively large $\alpha = 2.1$ was observed at 0.5 wt% CB loading in 60/40/CB composites (Fig. 8). A consistent increase in α was observed with increasing CB loading. The arrangement of CB particles to form surface fractals was observed at 10 wt%, which indicates the buildup of strong network and a good dispersion of CB in 60/40 blend. However, the surface fractals ($\alpha > 3$) were observed only in 60/40/CB composites, showing better dispersion of CB in 60/40 blends. The PE/CB, and 80/20/CB composites showed similar increase in α with increasing CB concentrations, but no surface fractals were observed (see supporting information). In addition, secondary structure was observed in all CB-filled

composites, which could be seen as a shoulder appearing at low q values. With increasing CB concentration, the shoulder shifted to higher q (smaller length scales). The calculated length scales associated with this shoulder are shown later in this section.

Fig. 8. $I(q) \sim q$ log-log SAXS data for PE/OPE 60/40 Blends-CB composites. Note: The lines in all panels are stacked in the same order with Y-offset for clarity.

The SAXS-knee in the range of 0.02 to 0.08 $\text{\AA}^{-1}$ corresponds to the lamellar thickness in polymers (Fig. 7). The lamellar thickness (L_p) or interparticle spacing can be extracted from the maxima in the Kratky plots [62, 63], also called Lorentzian corrected plots, where $I(q)q^2$ is plotted versus the scattering vector (q). The maxima is converted into length scales by $L_p \sim 2\pi/q$. The L_p is the sum of amorphous and crystalline fractions in polymers [31].

The L_p was calculated for the TRG-filled nanocomposites, and CB-filled composites (see supporting information for a representative Kratky plot). Inclusion of OPE in PE has already been shown to decrease L_p from 180 $\text{\AA}$ for neat PE to 161 $\text{\AA}$ for 80/20 blends, which further reduced to 147 $\text{\AA}$ for 60/40 blends [31]. Substantial decrease in L_p was observed with increasing TRG in PE/TRG, and 60/40/TRG nanocomposites (Fig. 9a). Similarly, the nanofillers (TRG or CB) do not affect the WAXS patterns of the matrices (supporting information). Therefore, it is reasonable to believe that the fillers reside inside the amorphous portion of the matrix, and overall L_p decreased due to the packing of fillers inside lamellae. The decrease in L_p has been reported to have a direct effect on the macroscopic mechanical properties of polymers. Specifically, the Young's modulus of polymers increases with decreasing L_p (see mechanical

properties section) [31, 64, 65]. A constant L_p with $TRG \geq 3$ wt% clearly indicated the percolation behavior in TRG-filled nanocomposites.

For CB-filled composites, the L_p also decreased with increasing CB loading in PE and PE/OPE blends (Fig. 9b). However, the decrease in L_p was not as significant as it was in TRG-filled nanocomposites. The scattering also corroborates that high CB loading leads to lower mechanical and rheological properties than TRG-filled nanocomposites. A constant L_p was not observed for CB-filled composites at higher CB loading, which also indicates that these composites do not achieve percolation.

Fig. 9. Kratky analysis of TRG-filled nanocomposites (a), and CB-filled composites (b). Color schemes in (a) show percolation of each matrix.

3.4. Thermal properties

Neat PE is thermally stable for a polymer, completely decomposing around 500°C. The PE/OPE 60/40 blend showed lower thermal stability compared with neat PE, which is attributed to miscibility and plasticization effects of PE and OPE, and oxygen contents of OPE [31]. On the one hand, addition of 5 wt% TRG in PE (Fig. 10) did not affect the stability of the nanocomposite (decomposition temperature ~ 474°C) compared to that of neat PE (473°C). The unaffected thermal stability of PE/TRG nanocomposites indicates the absence of any favorable

interactions between graphene and PE [66, 67]. On the other hand, thermal stability of 60/40 blends at 5 wt% TRG was enhanced as the decomposition temperature increased from 472° C for neat 60/40 blend to 477° C for the nanocomposite, attributed to improved graphene-matrix interactions in these nanocomposites. Similar patterns of thermal stability were observed for CB-filled composites (see supporting information). The lack of interactions between CB and PE reduced the thermal stability of PE/CB composites at 10 wt% loading. However, due the presence of OPE, and interactions in blends, the stability of blend-CB composites was also improved.

Fig. 10. Thermograms for PE, PE+TRG 5 wt%, PE/OPE 60/40, and 60/40+TRG 5 wt%. Inset shows derivative of TGA versus the temperature.

3.5. Mechanical Properties

One of the advantages of adding nanofiller to a polymer matrix is improving the mechanical properties. Mechanically robust nanocomposites can be used for a large number of practical applications. Young's modulus of PE decreased from 1.6 MPa to ~1 MPa for 80/20 blends, and increased to 1.8 MPa for 60/40 blends. The increase in Young's moduli of blends was directly associated with the decreased L_p [31, 64, 65]. The superiority of TRG over CB as filler for polymers is evident by the comparatively improved Young's modulus of filled matrices (Fig. 11). The PE/TRG and PE/CB exhibited similar Young's moduli, showing the poor dispersion of these fillers in PE in the absence of any filler/polymer interactions. However, approximately ~3-fold increase in modulus was observed for 60/40/TRG nanocomposites compared to PE/TRG nanocomposites due to the increased filler/matrix interactions. The melt viscosity of 60/40

blends is ~7-fold lower than that of neat PE, whereas the increase in the Young's modulus was 3-fold higher for 60/40/TRG nanocomposites compared to that of PE/TRG nanocomposites. This significantly lower processing viscosity and increased mechanical property indicates the formation of processable and mechanically robust nanocomposites, which is very remarkable to achieve as most nanocomposite that yield enhanced mechanical properties suffer from significant increase in viscosity.

Fig. 11. Comparison of the Young's moduli of TRG and CB filled composites

The elastic properties of fiber/flake polymer nanocomposites can also be predicted by numerous micromechanical models [68]. Generally, the elastic properties in micromechanical models depend on particle/matrix stiffness ratio (E_p/E_m), particle volume fraction (Φ_p), particle aspect ratio (A_f), and orientation of particles in the matrix [69]. In this study, both TRG and the matrices are assumed to be linearly elastic, either of which can be taken as isotropic or transversely isotropic. Two widely-used models are the Halpin-Tsai and Mori-Tanaka models [69]. The Halpin-Tsai (H-T) [70] equation gives reasonable estimate for effective stiffness in nanocomposites, but the Mori-Tanaka model (M-T) [71] is considered more accurate for high aspect ratio fillers. Considering longitudinal stiffness (E_{11}) of nanocomposites (obtained from tensile testing), the H-T equation is given as:

$$\frac{E_{11}^{(H-T)}}{E_m} = \frac{1 + 2A_f\eta\phi_p}{1 - \phi_p\eta}$$

$$\eta = \frac{(E_p / E_m) - 1}{(E_p / E_m) + 2A_f}$$

and Mori-Tanaka (M-T) model is represented as:

$$\frac{E_{11}^{(M-T)}}{E_m} = \frac{1}{1 + \frac{\phi_f \left[-2\nu_m A_3 + (1 - \nu_m) A_4 + (1 + \nu_m) A_5 A \right]}{2A}}$$

Here, ν_m , and ν_p are the matrix and particle Poisson ratios, and constants A , A_3 , A_4 , A_5 are calculated from matrix/particle properties and components of the Eshelby tensor [72, 73], which depend on the particle A_f , and dimensionless elastic constants of the matrix. For modeling, we used E_p as 250 GPa for TRG sheets [74, 75], ν_p as 0.0006 [76], ν_m as 0.48 for PE [77], whereas the experimentally determined E_m values are used throughout. The only variable fitting parameter in the two models is the particle aspect ratio (A_f).

The tensile moduli of nanocomposites normalized by the moduli are compared to the loading to examine the model fits (Fig. 12). PE filled with TRG at 2.14 vol% was approximately 50% stiffer than neat PE. On the other hand, 80/20/TRG nanocomposites showed ~150% more stiffness compared to the neat 80/20 blend, and the 60/40/TRG nanocomposites exhibited ~500% increased stiffness compared with the neat blend. Fitting based on the effective medium models (H-T and M-T) were applied to moduli increase versus TRG concentration (wt%), and the effective aspect ratio (A_f) of the dispersed TRG sheets were estimated. Both the H-T and M-T models produced similar A_f of TRG for PE and 80/20 blends (Fig. 12). However, M-T model exhibited insensitivity for the 60/40/TRG nanocomposites due to large increase in modulus. Only, H-T model was able to capture the A_f for 60/40/TRG system, which was ~460. A very large E_p/E_m ($\sim 10^5$) might be the reason for M-T model's insensitivity above $A_f > 200$. However, for small E_p/E_m ($\sim 10^2$), H-T model overestimates E_{11}/E_m compared with that obtained from M-T model [69].

Fig. 12. Mechanical properties of TRG-filled nanocomposites. Solid lines are fit to Halpin-Tsai model, and dashed lines represent Mori-Tanaka micromechanical model. Inset shows estimated aspect ratio (A_f) of TRG for nanocomposites from the best fit.

3.6. Electrical Properties

The electrical properties of graphene/polymer nanocomposites are strongly dependent on effective dispersion of graphene and its aspect ratio, whereas the dispersion is directly connected to graphene-polymer and inter-graphene interactions. The electrical conductivity (σ) of PE/TRG, 80/20/TRG and 60/40/TRG nanocomposites (measured at 0.01 Hz) showed significant improvement as the concentration of graphene was increased from 0 to 5 wt%. PE/OPE 60/40 blends exhibited a low rheological percolation threshold, and a similar transition was observed for the electrical conductivity (Fig. 13). **The electrical conductivity of neat PE, 80/20, and 60/40 blends were 7.4×10^{-14} , 7.6×10^{-14} , and 7.4×10^{-14} S/cm, respectively.** At almost same TRG loading, 60/40/TRG nanocomposites exhibited more than 1 order of magnitude improvement in the electrical conductivity compared with PE/TRG and 80/20/TRG nanocomposites. The increase in σ is attributed to enhanced TRG-matrix interactions, and large A_f in blend-nanocomposites due to OPE. Also, at similar loadings, the TRG nanocomposites exhibited better electrical conductivities compared to CB composites. The electrical conductivity of TRG nanocomposites was ~ 2 orders of magnitude higher than that for CB composites (Fig. 13).

Fig. 13. Comparison of electrical conductivities of TRG-filled and CB-filled composites

A low electrical percolation threshold also signifies the improved interactions in nanocomposites. The σ increased from 7.4×10^{-14} to 3.6×10^{-4} S/cm for PE/TRG as TRG concentration was increased from 0 to 5 wt% (Fig. 14). Similarly, the σ for 80/20 blends increased from 7.6×10^{-14} to 1.1×10^{-4} S/cm, and from 7.4×10^{-14} to 9.6×10^{-4} S/cm for 60/40 blends for the same TRG concentration range. The electrical percolation threshold values ($W_{p\sigma}$) were 0.67, 0.45, and 0.3 wt% for PE/TRG, 80/20/TRG, and 60/40/TRG nanocomposites, respectively. The rheological percolation thresholds were higher than the electrical percolation for all composites. Similar to the rheological percolation, the 60/40/TRG nanocomposites exhibited the lowest percolation, which further signifies the increased graphene-matrix interactions, and high A_f of TRG in the nanocomposites. Moreover, the CB filled nanocomposites exhibited similar increase in electrical conductivity with increasing CB loading. Expectedly, the electrical percolation thresholds for CB-filled composites were higher than those obtained for TRG-filled nanocomposites. Higher percolation threshold in CB-filled composites is attributed to highly fractal, and agglomerate-forming nature of CB. The complete electrical conductivity data of CB-composites is provided in the supporting information.

Again, a power law scaling relationship can be applied to the electrical conductivity data as follows:

$$\sigma \propto (W - W_{p\sigma})^t$$

A log-log plot between σ and $W-W_c$ should give a straight line with exponent t . The inset in Fig. 14 shows the power law fitting, and the power law exponents (t) are shown next to each set of data (also see Table 1). The exponent, t , reflects the dimensionality of the system. Typically, $1.6 < t < 2.0$ is for three dimensional network, and $1 < t < 1.3$ is exhibited by the two dimensional network in nanocomposites [78-80]. In this study, $t > 1.3$, which showed a three dimensional network was formed by TRG in all composites. Interestingly, the t -values for CB composites were even higher than that for TRG nanocomposites, which can be attributed to the fractal network forming nature of CB to construct a three dimensional network in composites (suppl information). However, the electrical conductivity of CB composites are lower than that TRG, which might be due to structural imperfections in the networks formed by the CB particles.

Fig. 14. Electrical conductivity of TRG-filled nanocomposites. Solid lines are to guide the eye only. Inset shows the power law fit, the numbers indicate the power law exponents.

Table 1 Electrical and rheological percolation threshold and power law exponents for TRG-based nanocomposites

	<i>Rheological</i>				<i>Electrical</i>		
	$W_{pR}\%$	$\Phi_{pR}\%$	α	A_f	$W_{p\sigma}\%$	$\Phi_{p\sigma}\%$	t
PE/TRG	2.3	1	2.9	41	0.7	0.3	2.6
80/20/TRG	1.7	0.7	2.5	60	0.5	0.2	1.5
60/40/TRG	0.7	0.3	2.7	155	0.3	0.1	1.7

3.7. Morphology

The dispersion of TRG in the nanocomposites was studied with TEM images (Fig. 15). The dispersion is in agreement with the rheological and scattering results discussed earlier. Substantial aggregation of graphene was observed in PE/TRG nanocomposites (Fig. 15a). Similar aggregation was observed in 80/20/TRG nanocomposites (Fig. 15b). However, majority of graphene was dispersed in 80/20 blends, consistent with increased aspect ratio of the dispersed TRG compared to that in PE/TRG nanocomposites. Furthermore, TRG was well dispersed throughout the 60/40 blend matrix (Fig. 15c). The well-dispersed TRG in 60/40 blend confirms our hypothesis that blending OPE with PE increases TRG dispersion, leading to lower percolation in nanocomposites.

Fig. 15. TEM images of nanocomposites at 5 wt% TRG loading: (a) PE/TRG, (b) 80/20/TRG, and (c) 60/40/TRG.

Also, the cryogenically fractured nanocomposites at 5 wt% loadings were used to study the morphology via FE-SEM (Fig. 16). The SEM images were taken at two different magnifications. The PE/TRG nanocomposites (Fig. 16 a, b) showed graphene being pulled out during cryo-fracturing. The graphene stacks were more visible in the high resolution image (Fig. 16b). Similar morphology was exhibited by 80/20/TRG nanocomposites. High A_f of TRG in these nanocomposites compared to PE/TRG system was evident in the high-resolution image (Fig. 16d) as smaller graphene stacks are seen in these nanocomposites. The 60/40/TRG nanocomposites exhibited morphology similar to PE/TRG in low-resolution images. However, under high-resolution, 60/40/TRG nanocomposites showed very different, exfoliated morphology. The TRG stacks in these nanocomposites were either very small (seen at a few locations across the sample), or not seen at all. These results are in agreement with the

rheological, mechanical, and scattering analysis, that better exfoliation was observed in 60/40/TRG nanocomposites compared with the other two composite systems.

Fig. 16. SEM images of PE/TRG (a, b), 80/20/TRG (c, d), 60/40/TRG (e, f) at 5 wt% loading. The arrows indicate TRG sheets located in these composites

Conclusions

Dispersion of thermally reduced graphene (TRG) in PE, and PE/OPE blends was investigated by thermo-mechanical, electrical, and scattering techniques. Reduced rheological and electrical

percolation thresholds in PE/OPE blends showed better dispersion, and exfoliation of graphene sheets in the blends compared to neat PE. The universal behavior of TRG diffusion in polymers followed the classical Doi-Edwards theory for CNTs dispersion, showing that TRG follows the Brownian diffusion. The microstructure developed in TRG-filled nanocomposites by SAXS showed the formation of mass and surface fractals in nanocomposites. At lower TRG loadings, TRG showed better dispersion as indicated by smaller slopes in $I \sim q$ log-log plots. The dispersion of TRG was fairly inconsistently similar at low TRG concentrations. However, a more detailed study of SAXS with carefully synthesized nanocomposites is highly desirable to understand this discrepancy in dispersion. A decrease in long period order (L_p) was linked with the mechanical properties, where substantial decrease in L_p in blend nanocomposites correlated with remarkable improvement in elastic moduli. micromechanical modeling of mechanical properties showed higher exfoliation of graphene sheets in nanocomposites. A ~3-fold increase in elastic properties of TRG-filled blends with a ~7-fold lower melt viscosity indicates the formation of processable blend nanocomposites with improved filler/matrix interactions. Higher electrical conductivity of blend-TRG nanocomposites than that of PE/TRG nanocomposites is another indication of better dispersion and exfoliation of TRG in the blends. These novel nanocomposites can offer an alternative to graphene/PE nanocomposites for various applications.

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