The effect of graphene chain grafting on the mechanical properties of polymer/graphene nanocomposites

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Abstract— In the present article, the effect of graphene chain grafting on the mechanical properties of low density polyethylene (LDPE) nano-composites containing nanographite has been studied. Various graphite modified fillers was produced. Graphite oxide (GO) was produced by employing the modified Hummers method. Then amine functionalized graphite oxide (FGO) was prepared through amino-functionalization of GO by ethylene diamine. GO was reduced thermally to produce thermally expanded graphite oxide (TEGO) and was amine-functionalized to obtain amine functionalized nano-graphite (FNG). All the fillers were used to prepare LDPE nanocomposites by solution mixing in xylene. The mechanical properties of the nano-composites were measured and FTIR analysis was used to investigate the chemical changes in the fillers and the nanocomposites. The FTIR results showed that with the incorporation of amino-functionalized graphene sheets into polyethylene-grafted-maleic anhydride (PE-g-MA), the amine groups of graphene surface and maleic anhydride groups of PE-g-MA chains react and introduce covalent bonds between the sheets and polymer. The results of mechanical properties measurements showed significant improvement in elongation at break for the composites containing amine modified fillers. PE-g-MA/FGO(1wt%) showed a 155 percent enhancement in elongation at break when compared with PE-g-MA/GO(1wt%). The modulus and tensile strength of both nanocomposites increased in regards to those of the pure matrix. A ratio of 0.40 to 0.60 for PE-g-MA to LDPE resulted in the highest mechanical properties for LDPE/PE-g-MA/FGO(1wt%) nanocomposites.

Keywords— *Nano-composite, Grafting, Graphene, Graphite Oxide, Amino-functionalized, Polyethylene, Mechanical Properties*

I. INTRODUCTION

Low density polyethylene (LDPE) is known as a commercial polyolefin in the world since it is cost-effective and shows pristine properties such as toughness, flexibility, low density, etc [1]. Recently, graphene and its derivatives are considered as an interesting new class of reinforcing nano-scale carbon material with many unique and fascinating properties such as electrical conductivity of 7200 S/cm Young's modulus of 1 TPa [2-3]. However as a common challenge it is difficult to achieve good distribution and dispersion of nanofiller in polymer matrix and a good interface adhesion between matrix and nanofiller. The objective of this work is to deal with these challenges by grafting grapheme particles onto polymer chains and use it as a modified nanofiller in the matrix.

II. EXPERIMENTAL

The graphene layers in graphite have strong cohesive force; hence it is difficult to exfoliate these graphene sheets [4]. For exfoliation of graphite, graphite oxide (GO) was synthesized from graphite by using modified Hummers methods. In this approach, sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$) were used as oxidation agent to oxidize graphene surface and obtain graphite oxide (GO) [5]. Then, GO was exfoliated by rapid heating at 950 °C for 45 seconds [3] to prepare thermally expanded graphite oxide (TEGO). RGO was obtained through chemical reduction of GO with hydrazine.

Amino-functionalization of TEGO was carried out by using ethylene diamine and the product was named functionalized nanographite (FNG). In order to produce filler with more amine groups on its surface, amino-functionalization of graphite oxide was performed, directly. The obtained filler was named functionalized graphite oxide (FGO). Amine groups on the surface of FNG and FGO can react with functional groups such as maleic anhydride of PE-g-MA chains.

The obtained fillers were mixed with LDPE and PE-g-MA and their blend by solution mixing in xylene. The blend of LDPE and 10wt% LDPE-g-MA was named LDM and its nano-composites with TEGO and FNG was named LDMTEGO and LDMFNG. Also, MA indicates LDPE-g-MA. The numbers in front of the names show the content of the fillers.

III. RESULTS AND DISCUSSION

Fig. 1 shows FTIR spectra of GO and FGO. As shown in the figure peaks at 3185 cm^{-1} and 1543 cm^{-1} refer to N-H stretching and bending vibration, respectively. Also, peaks at 1458 cm^{-1} (C-N stretching) and 2924 cm^{-1} (C-H stretching in ethylene diamine on the FGO surface) confirm the reaction between ethylene diamine and carboxyl groups on the GO surface. The peak at 1641 cm^{-1} also indicates amide linkage.

The SEM images of the fillers are shown in Fig. 2. The thermal reduction and amino-functionalization of GO break down the size of graphite particles. However, their aspect ratio increases due to the exfoliation of graphite layers.
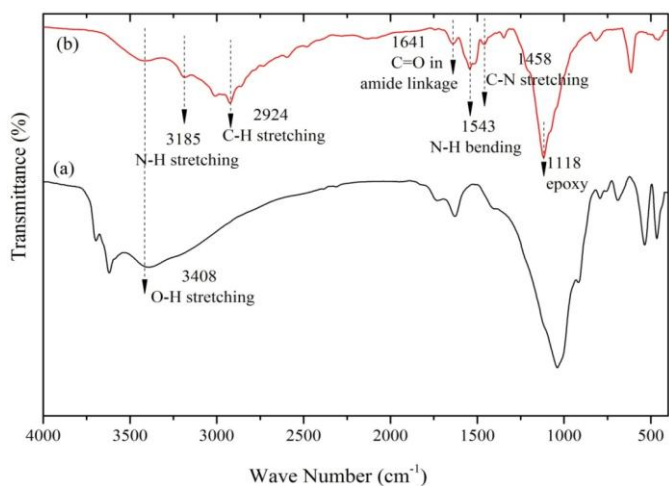
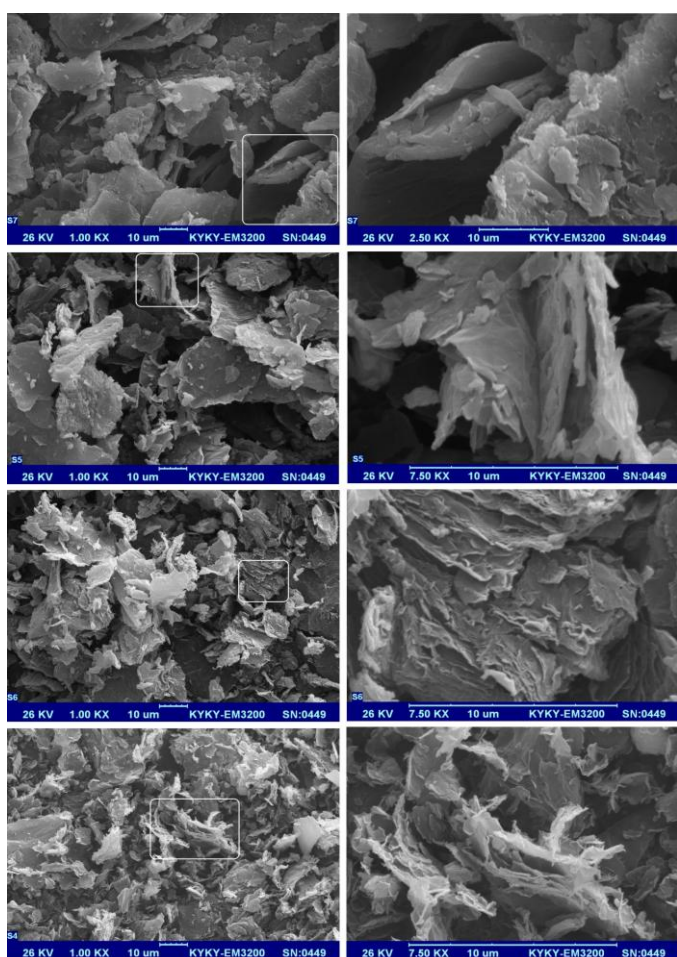Fig. 1. *FTIR spectra of (a)Graphite, (b)EG, (c)GO, (d)RGO, (e)TEGO and (f)FNG*

Fig. 2. *SEM images of (a,b) GO, (c,d) RGO, (e,f) TEGO and (g,h) FNG*

Tensile test was used in order to investigate the effect of grafting of graphene sheets to polyethylene. The tensile properties of LDMTEGO and LDMFNG nano-composites are compared in Fig. 3. It was found that elastic modulus of LDMTEGO nano-composites films increases by adding TEGO while its elongation at break decreases. Addition of 1 wt%

TEGO to LDM leads to an increase of 56% in elastic modulus and a decrease of 72% in elongation at break.

LDMFNG nano-composites exhibit the behavior similar to LDMTEGO nano-composites with the exception of elongation at break at 2 wt% as shown in Fig. 3. It is referred to a competition between filler agglomeration and filler-polymer interaction. FNG filler can create covalent bond with maleic anhydride groups on the polyethylene chains and make strong filler-polymer interaction, thus, to increase FNG loading, it is needed to increase the amount of filler-polymer linkages. On the other side, filler agglomeration occurs by increasing FNG content. At 2wt% FNG, filler-polymer interaction overcomes filler agglomeration. Conversely at 3wt% filler agglomeration is more affective.
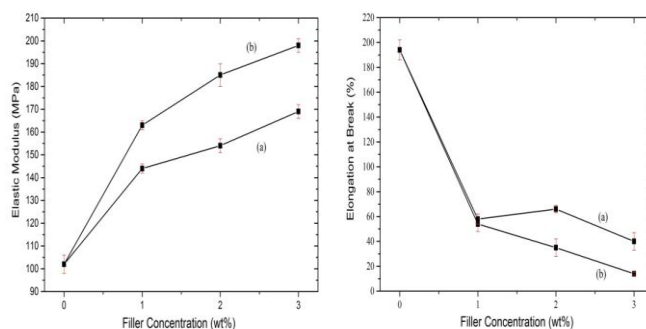

Fig. 3. *Comparing elastic modulus (left) and elongation at break (right) of (a) LDMTEGO and (b) LDMFNG nano-composites*

A new experiment was designed in order to highlight the effect of filler chain grafting on the mechanical properties. MATEGO-2 and MAFNG-2 were produced with the purpose of increasing covalent filler-polymer interaction and then their tensile properties were compared. Tab. 1 shows the tensile properties of neat LDPE-g-MA (MA) and its nano-composites with 2wt% TEGO and FNG. As shown in Tab. 1, elongation at break and tensile strength improved significantly due to improved filler-polymer interaction. It is very interesting to note that all the tensile properties are considerably greater than neat LDPE-g-MA. The elongation at break 100%, tensile strength 45% and elastic modulus about 30% were improved by creating the covalent bond between fillers and PE-g-MA matrix. These results indicate the important role of filler-polymer interaction on the mechanical properties of the nano-composites.

TABLE 1- *The tensile parameters of LDPE-g-MA and its nano-composites with TEGO and FNG*

	Elastic Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
LDPE-g-MA	74 ± 2	6.9 ± 0.5	88 ± 14
LDPE-g-MA+2%FNG	90 ± 1	9.9 ± 1.2	177 ± 12
LDPE-g-MA+2%TEGO	126 ± 6	7.6 ± 1.0	61 ± 7

The other method to increase the number of covalent bonds between filler and polymer is direct amino-functionalization of GO. GO was used without reduction to have access to many

oxygen-containing groups and carboxyl groups especially on the GO surface. Functionalize graphite oxide (FGO) was obtained by Amino-functionalization of GO. So, the number of ethylene diamine groups on the surface of FGO is much more than that of FNG. Hence, it is expected that FGO nano-composite benefit from much more covalent bonds between polymer chains and filler particles than FNG nano-composites. The maximum grafting occurs in PE-g-MA/FGO (MAFGO) nano-composites. Although the number of amine groups on the surface of FGO is more than FNG, but the degree of exfoliation in FGO is much less than FNG.

The results of tensile tests for MA, MAGO and MAFGO nano-composites containing of 1wt% filler have been shown in Fig. 4**Error! Reference source not found.**. MAFGO-1 shows higher elongation at break when compared with MAGO-1 which is equal to 155% increase in elongation at break by grafting filler to polymer chains.
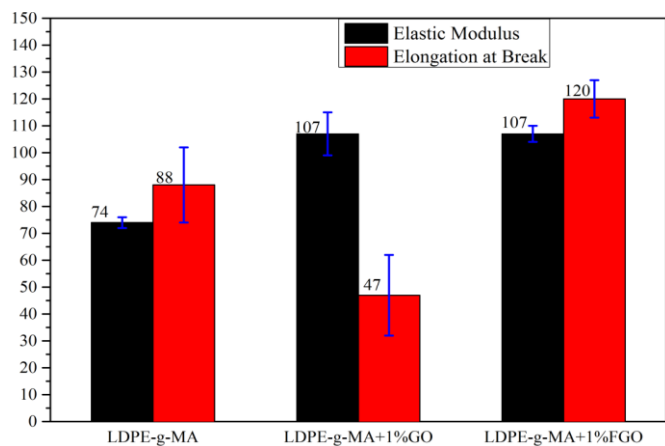

Fig. 4. *Elastic modulus and elongation at break of LDPE-g-MA and its nano-composites with GO and FGO*

Many articles have reported a decrease in elongation at break by addition of graphene derivative fillers to polymers. This has been reported for polycarbonate/graphene [6], polystyrene/graphene [7], LLDPE/graphene [8], EVA/functionalized-graphene [9] and etc. But present article shows an enhancement in elongation at break, tensile strength and elastic modulus simultaneously which is an outcome of improvement in polymer-filler interaction. In a similar work, Yadav et. al. indicated an increase in elongation at break in covalently bonded polyurethane-graphene nanocomposites as compared to the non-bonded nanocomposites however the elongation at break of the nanocomposites was lower than that of the neat matrix [10].

Finally, LDPE nano-composites with 1wt% FGO and varying amount of LDPE-g-MA were prepared to investigate the effect of LDPE-g-MA content on mechanical properties. As seen in Fig. 5 an optimum ratio of 0.4 to 0.6 for LDPE-g-MA to LDPE is suitable to reach the highest elongation at break for the nanocomposites.
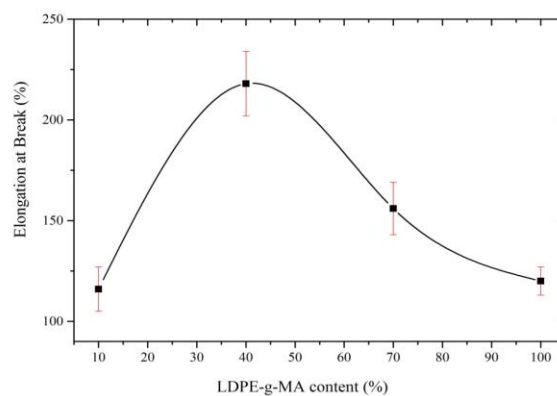

Fig. 5. *LDPE nano-composites with 1%wt FGO and 10, 40, 70, 100% LDPE-g-MA content*

IV. Conclusion

Polyethylene chains were grafted onto graphene surface to obtain modified nanographite filler. A significant improvement in mechanical properties of polyethylene/nanographite was observed by using the modified fillers. Elongation at break, tensile strength and elastic modulus of PE-g-MA/nanographite(1wt%) composites increased by 100%, 45% and 30% respectively by using chain grafted graphene sheets. Also PE-g-MA/FGO(1wt%) showed an increase of 155 percent in elongation at break when compared with PE-g-MA/GO(1wt%). The observed improvements are due to the presence of covalent bonds created between graphene surface and polymer chains. The modulus and tensile strength of both nano-composites increased as compared to those of the pure matrix. An optimum ratio of 0.40 to 0.60 for PE-g-MA to LDPE was found to reach the highest mechanical properties in LDPE/PE-g-MA/FGO(1wt%) nano-composites. The higher mechanical properties of polymer/nanographite composite than the original matrix is a unique and innovative outcome of this work.

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