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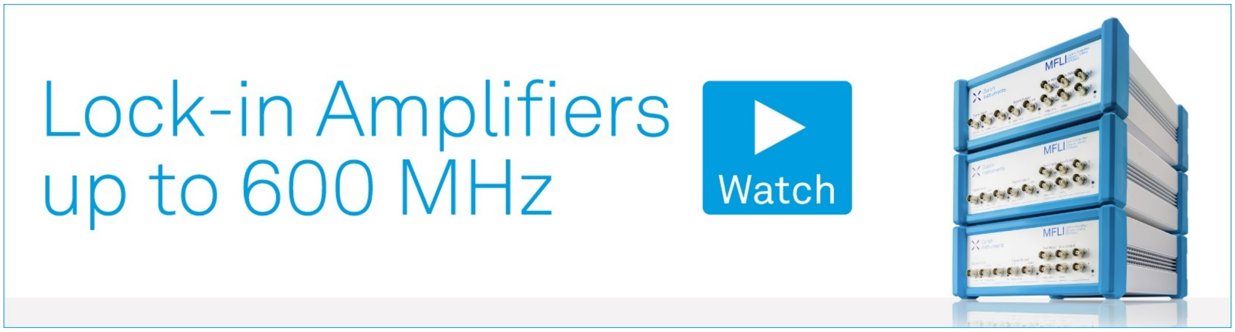

New Hybrid Nano Additives for Thermoplastic Compounding: CVD Grown Carbon Fiber on Graphene

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Abstract. Nano additives have unique characteristics widely used in high technology applications due to their ultrahigh mechanical and thermal properties. They are not preferred in price sensitive sectors especially in automotive applications because of their high cost. On the other hand, there is a growing interest to use graphene as a reinforcing agent in composite production. At this point, graphene platelet (GNP) produced from the recycle source was used as a template for carbon nanofiber production by using chemical vapor deposition (CVD) technique to overcome commercialization barrier. This bicomponent and novel structure is a good candidate to be used as a reinforcing agent in compound formulations. This produced hybrid additive was dispersed in thermoplastic resin by thermokinetic mixer to get homogeneous dispersion and provide strong interfacial interactions. In the current work, the outstanding properties of graphene with carbon fibers were combined into one type structure. With the further research, the number of graphene layer were adjusted in this hybrid structure to bring a new insight in graphene and its composite applications. After the fabrication of graphene and carbon fiber-based reinforcements with different graphene sources, mechanically and thermally improved Polyamide 6.6 were developed at very low loadings by a thermokinetic high shear mixer. This developed technology will utilize an innovation to produce advanced thermoplastic prepregs including graphene and its hybrid additives with high mechanical properties and increased recycling degree by decreasing manufacturing costs.

Keywords: Graphene, Hybrid structure, Mechanical properties, Thermal properties

INTRODUCTION

There is an increasing trend to use thermoplastic materials for composite part production due to their advantages such as high fracture toughness, high service temperature, shorter production time, and reusing and recycling potential [1][2][3]. Matrices of fiber based thermoplastic composites such as polypropylene and polyamide have already been used notably in automotive, industrial, sports and leisure industries owing to their cost saving and light weighting properties as well as being easy to process at the low processing temperature and pressure [4]. Polyamide 6.6 (PA6.6) as an engineering thermoplastic polymer which has high stiffness, toughness, and resistance to dynamic fatigue was selected in the current study [4][5]. In accordance with this purpose, several micro and nanoparticles have been investigated for the reinforcement of PA in fundamental research and industrial applications [5]. Graphene which has 2-dimentional structure and high surface area is a promising reinforcing agent in composites because of its high mechanical and thermal properties [6][7][8][9]. However, homogeneous dispersion of graphene sheets in the polymeric matrix is still a challenging issue [9][10]. Recently, many studies have focused on the improvement of mechanical and thermal properties of nanocomposites by integrating nanofillers such as graphene, carbon nanotubes

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(CNT) and nanofibers (CNF) by overcoming the agglomeration problem of nanoparticles. In addition, graphene and CNT have been used together in polymeric matrices to get the synergetic effect to attain an ideal composite structure.

In the current study, carbon nanofibers (CNF) were grown on three different graphene templates which were graphene nanoplatelets (GNP), multi-layer thermally exfoliated graphene oxide (TEGO) and single-layer graphene oxide (GO) by applying CVD technique. These graphene materials have differences in terms of carbon/oxygen ratio, layer number and production technique. In order to understand the performance of these produced hybrid nanoadditives, melt-compounding process were applied for nanocomposite production. These new design additives were used as reinforcing agents in PA6.6 for to understand their 3-dimensional structure on morphological, crystalline, thermal and mechanical properties of the nanocomposites.

EXPERIMENTAL

Synthesis of Hybrid Nanomaterials

Single graphene nanoplatelet (GNP) and thermally exfoliated graphene oxide (TEGO) having 25 graphene layers were purchased from NANOGRAFEN Co. Single layer graphene oxide (GO) was synthesized from graphite flakes by improved Hummers' technique [11,12]. Iron was used as a catalyst in CVD process to grow CNF on the surface of graphene based templates [13]. As-received graphene (GNP) contains 0.5 at% iron in its structure obtained from X-ray photoelectron spectroscopy (XPS). Iron oxide impregnation process was applied for GO and TEGO in different solvent systems of water and DMF, respectively. During CVD process, Fe impregnated graphene samples were exposed to 750ºC by purging gas mixtures of He and H_2 and then samples were kept about 10 min at this temperature for annealing. At the end of this stage, ethylene gas was purged to provide carbon source and grow CNF on graphene templates for 15 min at 750˚C.

Morphologies of hybrid additives and the length of fiber size were investigated by JEOL2100 Lab6 High Resolution Transmission Electron Microscope (TEM). X-ray diffraction (XRD) and Raman measurements were carried out by using Bruker D2 PHASER Desktop with a CuKα radiation source and Renishaw inVia Reflex Raman Microscopy System, respectively to understand the structural changes. Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer System (XPS) was used for quantitative elemental analysis of hybrid specimens.

Compounding by Thermokinetic Mixer

Hybrid reinforcements were compounded with PA6.6 matrix at 4700 rpm and 300 oC by using Thermokinetic Mixer. PA6.6 chip was supplied from Dupont. The content of hybrid additives were adjusted as 0.5 wt% to attain ideal dispersion and prevent agglomeration. For mechanical studies, test specimens were prepared by injection moulding. Crystallinity behaviour of PA6.6 based nanocomposites was examined by Differential Scanning Calorimeter (DSC) and the softening temperatures and glass transition temperatures (Tg) were examined by Thermomechanical Analysis (TMA) method using a 3 mm ball-point probe. The morphological structures of the nano additives were analyzed by JEOL2100 Lab6 High Resolution TEM.

RESULTS AND DICUSSIONS

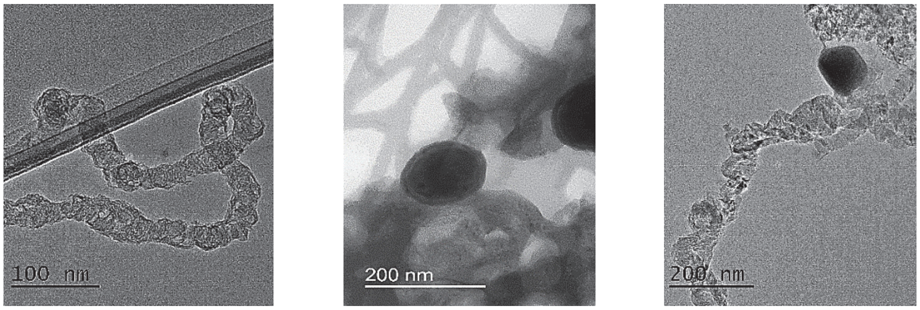
The Characteristic Properties of Hybrid Nano additives

TEM images of hybrid structures in Figure 1 indicates the formation of CNF on different graphene structures and are supported the formation of 3-dimensional structure having two different components. Iron particles with the average size of 100 nm were seen clearly in TEGO and GO based additives as seen in Figure 1(b) and 1(c) whereas the length of CNF in GNP is comparably shorter than TEGO and GO based additives. Table 1 summarizes the average diameter and length of CNF, C/O ratio obtained from XPS and intensity ratio of D and G (I_D/I_G) received from Raman spectroscopy of the produced nano additives in this study. CNF-TEGO has the highest C/O ratio as about 6.9 but GNP based hybrid has more oxygen functional groups on its surface.

The structural changes of hybrid structures of GNP, GO and TEGO were monitored by XRD analysis as seen in Figure 2(a). In all of the specimens, a diffraction peak at $2\Theta \approx 25°$ was corresponded to the (002) reflection of graphitic plane [14]. During CNF growth process, iron oxide catalyst was reduced to metallic Fe and Fe3C on all the graphene types labelled in Figure 2(a) [15]. XRD verified CNF growing process and addition of carbon atoms on metal catalysts deposited on graphene surface. Among three types of additives, TEGO based hybrid has the highest crystallinity.

TABLE (1). Summary of the characteristic properties of hybrid nano additives

Type of graphene in hybrid structure	**Production method of graphene**	**The of CNF length (µm)**	**The diameter of CNF (nm)**	**C (at%)**	**O (at%)**	**C/O ratio**	**I_D/I_G**
Graphene platelet (GNP)	Recycling and upcycling	1.0	40	91.7	5	6.6	0.98
Multi-layer graphene oxide (TEGO)	Thermal exfoliation	2.0	28	98.1	1.9	6.9	1.5
Single-layer graphene oxide (GO)	Improved Hummers' method [11] [12]	1.6	34	96.8	3.2	5.5	1.5



(a) (b) (c)

FIGURE 1. TEM images of **(a)** CNF-GNP, **(b)** CNF-TEGO and **(c)** CNF-GO

Raman characterization is an efficient technique to examine the changes in sp^2 and sp^3 degree of structure and the formation of additional carbon structure and defects. Graphene has three characteristic Raman peaks of D, G and 2D. In addition to these peaks, a second-order peak known as S3 at around 2929 cm^{-1} in the Raman spectra was appeared due to the interactions of intervalley and intravalley phonon scatterings between graphene and CNF [16]. As shown in Figure 2(b) and Table 1, a higher result in I_D/I_G of CNF-TEGO and CNF-GO compared to CNF-GNP showed the formation of more sp^3 bonds regarding the intensity of D band [17]. In conclusion, the differences in surface chemistry and crystalline structure of these fabricated nano hybrids can directly affect the performance of PA6.6 nanocomposites explained in the following sections.

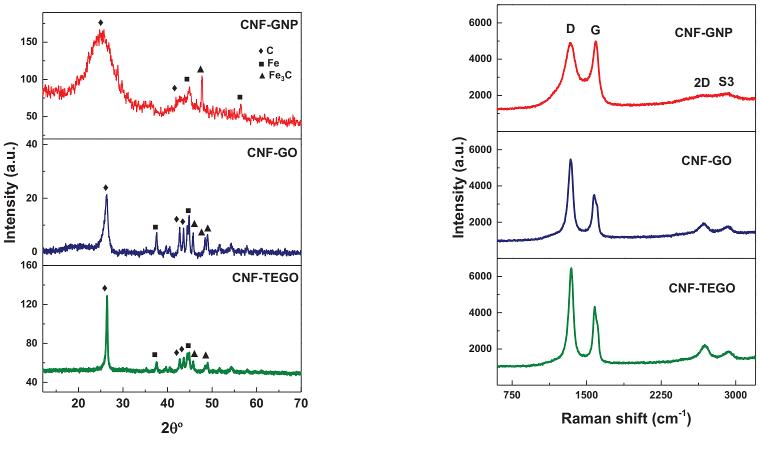


FIGURE 2. (a) XRD spectra and **(b)** Raman spectra of CNF-GNP, CNF-GO and CNF-TEGO

Crystalline and Thermal Behaviours of Nano Hybrid Reinforced Nanocomposites

The crystalline behaviour of nanocomposites were investigated by DSC technique. As seen in Table 2, there is no big difference in melting temperatures (T_m) of nanocomposites specimens in comparison of pristine PA6.6. The percent crystallinity degree is determined using *Eq. 1*:

$$X_c = (\Delta H_m / \Delta H_m^{100\%}) \times 100\% \quad (1)$$

where X_c is crystallinity degree, ΔH_m is melting enthalpy, and $\Delta Hm^{100\%}$ is purely crystalline PA6.6 enthalpy [18]. The significant increasing was observed in X_c values by the integration of each type of graphene hybrid additive which were acted as nucleating agents. In addition, an increase in X_c values of 0.5 wt% CNF-TEGO and CNF-GO-based PA66 nanocomposites is same compared to neat PA6.6 whereas X_c of CNF-GNP reinforced composites is slightly lower due to its production source which is recycled carbon and structural difference.

TABLE (2). DSC results of nano hybrid reinforced nanocomposites

Samples	T_m(^{0}C)	ΔH_m (J/gr)	X_c (%)
Pristine PA6.6	262	48.2	25.6
PA6.6+0.5 wt% CNF-GNP	261	68.7	36.5
PA6.6+0.5 wt% CNF-TEGO	262	74.2	39.4
PA6.6+0.5 wt% CNF-GO	262	74.2	39.4

Table 3 summarized the Tg received from TMA analysis and softening temperatures for pristine PA6.6 and hybrid nano additive reinforced PA6.6 based nanocomposites. No big difference was observed in Tg values of each composite specimens by integration of each nano additive. On the other hand, softening temperatures of CNF-TEGO and CNF-GO loaded nanocomposites were slightly decreased when compared to pristine PA6.6. In case of CNF-GNP reinforced nanocomposite, softening temperature was increased about 6 °C and this indicates an increase in resistance to thermal deformation and thus CNF-GNP can block the movement of polymer chains and improve its process conditions.

TABLE (3). TMA results of hybrid nano fillers loaded PA6.6 based nanocomposites

Samples	Tg (°C)	Softening Temperature (°C)
Pristine PA6.6	42.7	227.0
PA6.6 + 0.5 wt% CNF-GNP	42.4	233.3
PA6.6 + 0.5 wt% CNF-TEGO	43.8	225.0
PA6.6 + 0.5 wt% CNF-GO	43.9	226.0

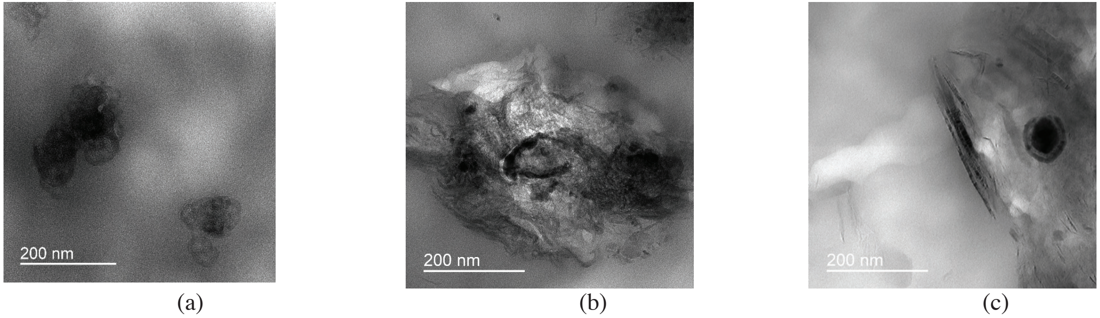
Mechanical Test Results

0.5 wt% hybrid reinforcements were compounded with PA6.6 polymer at high shear rates. Mechanical tests of the produced nanocomposites were performed with 2 mm/min speed by using Instron 5982 Static Test Machine for tensile (ISO 527-2) and flexural (ASTM D 790) tests. Table 4 summarizes mechanical characteristics of nanocomposite specimens. Tensile modulus calculated from the linear regions indicated that modulus of PA6.6 nanocomposite was enhanced up to 34% and 24% by the incorporation of 0.5 wt% CNF-GNP and multi-layer CNF-TEGO into the PA6.6, respectively. On the other hand, in the specimen reinforced by CNF-GO hybrid additive, the incorporation of 0.5 wt% reinforcement showed lower tensile modulus by 20%. This might come from the agglomeration of this type of hybrid additive and broken its fibers at high shear during compounding. This statement was also confirmed by microtomy study by TEM.

TABLE (4). Summary of mechanical properties of CNF-GNP, CNF-TEGO and CNF-GO loaded PA6.6 nanocomposites

Samples	Tensile Modulus (MPa)	Tensile Modulus Improvement (%)	Tensile Strength (MPa)	Tensile Strength Improvement (%)	Flexural Modulus (MPa)	Flexural Modulus Improvement (%)
Pristine PA6.6	2400	-	69.8	-	2570	-
PA6.6/0.5 wt% CNF-GNP	3225	34	73.4	8	3170	23
PA6.6/0.5 wt% CNF-TEGO	2971	24	80.6	15.5	2933	14
PA6.6/0.5 wt% CNF-GO	2868	20	71.7	2.7	2365	-8

Figure 3 represents TEM images of cross-sections of hybrid reinforced nanocomposites. CNF-GO based nanocomposite has agglomerated sheets in Figure 3(b) and in CNF-GNP based specimen, fibers are not aligned and aggregated as seen in Figure 3(a). In contrast, CNF-TEGO based nanocomposite has separated graphene, fibers and also iron metal catalyst. Tensile strength showed improvement in all cases of nanocomposites compared to neat PA6.6 specimen but exhibited different behaviour regarding the type of reinforcement. In case of only CNF-TEGO reinforced nanocomposites, the highest tensile strength was achieved at the loading of 0.5 wt%. The flexural modulus of all types of hybrid additives loaded PA6.6 nanocomposites are shown in Table 4. The best flexural property was achieved by using 0.5 wt% CNF-GNP providing 23% improvement in flexural modulus. On the other hand, CNF grown on TEGO at 0.5 wt% loading showed better performance in both tensile and flexural tests since the diameter of fibers on TEGO was smaller than the one grown on single-layer GO and this hybrid might reduce stress concentration of nanocomposites.



(a) (b) (c)

FIGURE 3. TEM images of **(a)** CNF-GNP, **(b)** CNF-GO and **(c)** CNF-TEGO reinforced nanocomposites at 0.5 wt% loadings

CONCLUSIONS

To conclude, CNF were successfully grown on Fe loaded three different graphene templates by CVD method and the structural formation of each sample was confirmed by spectroscopic and macroscopic techniques. CVD grown CNF on graphene acted as a reinforcing and nucleating agent in thermoplastic resins. Stronger interfacial interactions were achieved by CNF-TEGO nanoadditive and thus its nanocomposite showed better mechanical performance. Further improvement in graphene structure will influence the performance of structural composites especially used for load bearing applications in a positive manner.

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