# Graphene Nanoplates Filled Nylon 6,6 Nanocomposites, Morphological, Thermal, Mechanical and Solvent Uptake Study

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**Summary:** Effect of graphene nanoplates (GNPs) on the properties of Nylon 6,6 (Nyl 6,6) is investigated in present study. The morphological studies presented that the GNPs were dispersed inside the Nyl 6,6 matrix. The thermo gravimetric analysis (TGA) illustrated that the thermal degradation of nanocomposites samples were started at the range of 350-393 °C, which was appreciably higher than neat Nyl 6,6 (360 °C). The differential scanning calorimetry (DSC) analyses revealed that the crystallization temperature (Tc) of GNPs/Nyl 6,6 increased as increased the addition of GNPs, which might be due to the nucleation effect of GNPs. The mechanical properties of Nyl 6,6 was enhanced by incorporation of GNPs upto the addition of an optimal quantity of filler (5%wt GNPs) into the polymer matrix. The stress yield and Young's modulus of 5%wt GNPs/Nyl 6,6 was 96.79 and 1.54, N/nm$^2$, respectively. Both Nyl 6,6 and nanocomposites samples were also used for the adsorption of Neutral red chloride (NRC) dye, which significantly remove the dye from the aqueous solution. The neat nylon 6,6 and GNPs (5 and 10 wt%)/Nyl 6,6 adsorbed about 88.49, 93.15, and 93.60% within 2 h, respectively.

**Keywords**: Nylon 6,6; Graphene nanoplates; Neutral red chloride dye; Adsorption.

## Introduction

Graphene is two-dimensional carbon nanofiller with one atomic thick planar sheet of sp$^2$ covalently bonded carbon atoms densely packed in honeycomb crystal lattice [1]. Graphene has attracted tremendous interest in recent years due to their unique properties. Graphene has high mechanical, electrical and thermal properties. The surface area and electrical conductivity of graphene is 2630 m$^2$/g and 1738 siemens/m, respectively [2, 3]. Its mechanical strength is about 1100 GPa [4], and ease of functionalization [5]. Due to these extraordinary properties, researchers have focused on utilizing these remarkable properties for engineering applications. For example, it use in nanocomposites, sollar cells, flexible electrodes for displays, electronic circuits, sensors [6]. It also has superficial impact in energy technology [7-9], catalysis [10], bioscience /biotechnologies [10-13], and as adsorbent [14, 15].

Polymers based nanocomposites composed organic/inorganic fillers and polymers, where at least one material is in nanometer range [16]. Majority of the polymeric materials have low optical, electrical, thermal, and mechanical properties, which may be increased by addition of minute quantity of fillers like carbon nanotubes, clays, graphene sheets etc. Recently, graphene as a filler in polymeric materials paid great attention due to exceptional properties [17]. Rath and Li [18] prepared Exfoliated graphite nanoplates/polystyrene-b-poly(ethylene-r-butylene)-b-polystyrene by the simple melt-compounding method. It was found that the mechanical properties of the nanocomposite were higher than the neat polymer matrix (Tensile modulus of the unfilled elastomer is 9.22 MPa, while the composite modulus is 81.7 MPa). Wang *et al.* [19] prepared a novel poly(arylene ether nitrile)/graphene composites and reported that the electrical properties of polymeric material were drastically enhanced by adding graphene. Zhao *et al.* [20] prepared a novel polyvinyl chloride membrane and then modified with graphene oxide via phase inversion method. They were found that the graphene oxide/polyvinyl chloride hybrid membranes displayed appreciably high hydrophilicity, water flux, and mechanical properties. Milani *et al.* [16] synthesized polypropylene/GNs nanocomposites by *in situ* polymerization, where the graphene nanosheets were homogeneously dispersed within the polymeric matrix. They found that the Young's modulus of the nylon 6,6 films was increased more than two times while the electrical conductivity reached to 10$^{-2}$ S/cm by addition of 20 wt.% graphene nanoplatelets. Haggenmueller *et al.* [21] prepared SWNTS/nylon 6,6 by interfacial polymerization. They reported that the electrical and mechanical properties of the SWNTS/nylon 6,6 were higher than the neat nylon 6,6. Chavarria and Paul [22] prepared organoclay/nylon 6 and organoclay/nylon 6,6 nanocomposites by melt processing using a twin screw extruder. They studied

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the effects of polyamide type and processing temperature on the mechanical properties and the morphology of the nanocomposites. Liu and Wu [23] prepared by nylon 6,6/clay nanocomposites via melt compounding method. They found that the mechanical properties and heat distortion temperature of nylon 6,6 increased dramatically.

In present study, GNPs were used as fillers in Nyl 6,6 matrix. The GNPs was first functionalize with nitric acid in order to introduce carboxylic group, which might be chemical interact with Nyl 6,6. The pure Nyl 6,6 and its nanocomposites were characterized by SEM, TGA, DSC and a universal testing instrument. The water uptake study and adsorption behavior of both neat and GNPs filled Nyl 6,6 was also performed.

## Experimental

### *Materials*

Nyl 6,6, formic acid and nitric acid were purchased from Sigma Aldrich Company. GNPs were obtained from Chengdu Organic Chemicals Co. Ltd., (Chinese Academy of Sciences). The thickness and diameter of GNPs were 4-20 nm and 5-10 µm, respectively. Neutral red chloride dye was purchased from British drug house Ltd, London.

### *Purification of Graphene Nanoplates*

GNPs were purified/functionalized by the using acid treatment method. 3 grams GNPs and concentrated (8M) nitric acid were taken in flask and then refluxed for about 10 h at 120 °C. The GNPs were then washed with water for the elimination of any attached impurities from GNPs and then dried.

### *Preparation of GNPs/Nyl 6,6 nanocomposites*

By using weight/weight (%) measuring unit of neat Nyl 6,6 and nanocomposite sheets prepared via solution casting method. To prepare GNPs/ Nyl 6,6 nanocomposite, the known amount of GNPs and formic acid (5 mL) were taken in beaker and stirred for 10 min. The dispersed GNPs and dissolved Nyl 6,6 were mixed and sonicated for 20 min in order to get a homogenous solution. The GNPs(3 wt%) polymer solution was spread on glass plate and then dip into distilled water. After removal of solvent, smooth thin films of nanocomposite were obtained at room temperature. Similar practice was employ for 5 and 10 wt% GNPs/Nyl 6,6 nanocomposite films.

### *Adsorption of NRC dye*

The adsorption of NRC dye on prepared neat polymer and GNPs/Nyl 6,6 nanocomposites was studied at room temperature. Known volume (10 mL) of dye solution was taken in a vial with fixed weight of samples (0.025 g) and then stirred for 2 h. The following equation is used for determination of percent adsorption of NRC dye.

$$\text{Adsorption rate (\%)} = \left(\frac{C_0 - C}{C_0}\right) \times 100$$

$$\text{Degradation rate (\%)} = \left(\frac{A_0 - A}{A_0}\right) \times 100$$

where $C_o$ and C stands for initial dye concentration and dye concentration after specific adsorption time. $A_o$ shows initial dye absorbance and A present dye absorbance after specific time.

## Results and Discussion

### *Morphology of GNPs/Nyl 6,6 nanocomposites*

The morphological analysis was performed in order to verify the dispersion of GNPs inside the Nyl 6,6. The better filler dispersion inside the polymeric materials appreciably affects the properties like thermal, crystallization and mechanical properties of the polymer matrix. Fig. 1 shows the SEM images of broken surface of GNPs (15 wt%)/Nylon6-6 nanocomposite. The SEM images presented that the GNPs were well dispersed within the Nyl 6,6. This dispersion of GNPs in the GNPs/Nyl 6,6 is due to their chemical modification during nitric acid treatment, which enables the GNPs to be more compatible with polymer matrix.

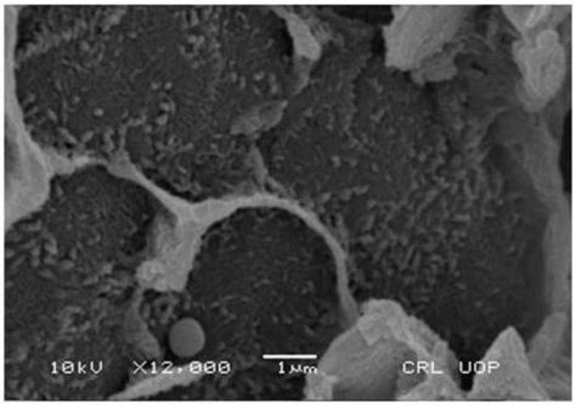

Fig. 1: SEM image of (15% wt) of GNPs/Nyl 6,6 nanocomposites.

*Thermal study*

The thermal studies of Nyl 6,6 and nanocomposites were performed by TGA and DSC. Fig. 2 shows the TGA thermograms of Nyl 6,6 and the nanocomposites, which illustrated that the weight of neat Nyl 6,6 remain unchanged upto 360 °C and then the curve suddenly dipping down. The thermograms also showed that the neat Nyl 6,6 completely degraded at about to 440 °C. The thermograms of GNPs/N 6-6 nanocomposites showed that the thermal degradation of nanocomposite started from 350-393 °C and then degraded completed at about 500 °C. The results presented that the addition of GNPs into polymer matrix significantly enhance the thermal stability of the Nyl 6,6. It was also found that the degradation temperature of each GNPs/Nyl 6,6 nanocomposites samples was gradually shifted towards higher temperature as the quantity of GNPs increased in nanocomposites.

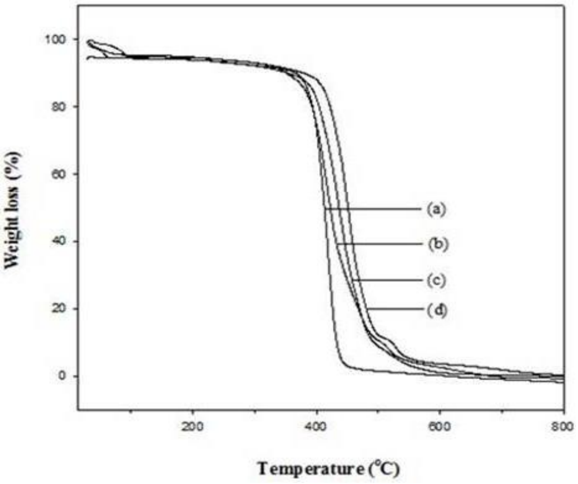

Fig. 2: TGA thermograms of (a) neat Nyl 6,6, (b) GNPs(3wt%)/Nyl 6-6, (c) GNPs(5wt%) /Nyl 6-6, and (d) GNPs(10 wt %)/Nyl 6-6.

Fig. 3 and 4 show the crystallization and melting temperature of Nyl 6,6 and nanocomposites. DSC thermogram shows that the crystallization temperature ($T_c$) of neat Nyl 6,6 is about 233 °C. Whereas the Tc of GNPs/Nyl 6,6 were gradually increases as increasing the quantity of GNPs (Fig. 3). The thermograms presented that the Tc of 5 and 10 wt% GNPs/Nyl 6,6 were about 235 and 237 °C, respectively. The increase in Tc presented that GNPs network imposed a confinement effect on crystal growth and chain diffusion polymer, which led to higher temperature for nanocomposites.

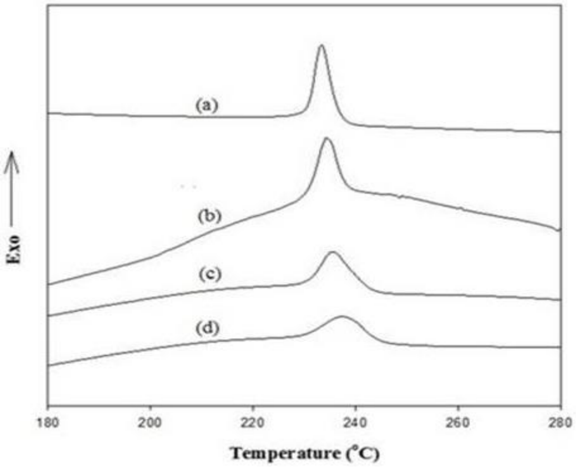

Fig. 3: DSC Tc thermograms of; (a) Neat Nyl 6-6, (b) GNPs(3wt%)/Nyl 6-6, (c) GNPs(5wt%) /Nyl 6-6, and (d) GNPs(10 wt %)/Nyl 6-6.

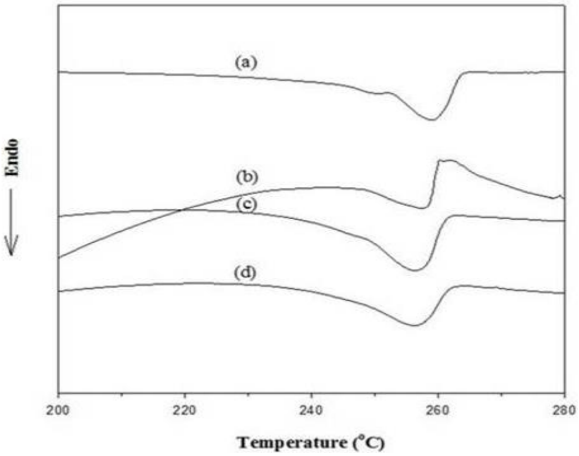

Fig. 4: DSC Tm thermograms of; (a) neat Nyl 6-6, (b) GNPs(3wt%)/Nyl 6-6, (c) GNPs(5wt%) /Nyl 6-6, and (d) GNPs(10 wt %)/Nyl 6-6.

Fig. 4 shows melting temperature (Tm) of both neat polymer and GNPs/Nylon 6-6. The thermogram of neat Nyl 6,6 shows that the Tm of neat polymer was about 259 °C while the Tm of GNPs/Nyl 6,6 were decreased up to 253 °C. The decrease in Tm in the case of GNPs/Nyl 6,6 is might be due to the nanoscale interactions between the GNPs surface and polymer matrix and that result the development of less stable crystals from the melting state during the crystallization.

*Mechanical Properties*

The mechanical properties of polymer based composites depend upon the better dispersion of fillers within the polymeric materials. Table-1 shows the mechanical properties of the Nyl 6,6 and the GNPs/Nyl 6,6 nanocomposites. Young’s modulus of neat Nyl 6,6 and GNPs/Nyl 6,6 (3, 5, 10 wt%) nanocomposites were 52.8, 58.47, 96.79 and 54.76 N/mm$^2$ and stress yield were 1.10, 1.15, 1.54, and 1.04 N/nm$^2$, respectively. The Young’s modulus and stress yield of Nyl 6,6 was enhanced by incorporation of an optimal quantity of filler (5 wt% GNPs) into the polymer matrix. Enhancing the properties might be the better dispersion of GNPs into the nylon. However, the Young’s modulus and stress yield of the nanocomposites was decreased by the addition of high amount of GNPs (10 wt%). The decrease in mechanical properties by the addition of high quantity of filler is might be due to the agglomeration of GNPs within the polymer matrix. The elongation at break which indicates flexibility of the material was increased by incorporation of 3 wt% but after that the elongation at break was decreased gradually by the addition of 5 and 10 wt% GNPs into the Nyl 6,6. It presented that the GNPs made Nyl 6,6 less flexible but stronger. The increase in Young’s modulus and stress yield and lower elongation at break was also report by Saeed et al. [24] for CNTs/Nyl 6,6 nanocomposites.

### *Water uptake by Nyl 6,6 and GNPs/Nyl 6,6 nanocomposites*

Table 2 shows water uptake results of pure Nyl 6,6 and its nanocomposites. The results showed that the neat Nyl 6,6 absorb high percentage of water content as compared to nanocomposite samples. The neat Nyl 6,6 absorb about 56% of distilled water. While the absortivity of water gradually decreased as increased the amount of GNPs in Nyl 6,6 matrix. The GNPs (3 wt%/Nyl 6,6 and GNPs (10 wt%/nylon) 6,6 absorb 52 and 41% of distilled water within 6 h, respectively. The lower %absorption of water by GNPs/Nyl 6,6 nanocomposite is might be because of hydrophobic nature of GNPs.

### *Adsorption Study of NRC by Nyl 6,6 and GNPs/Nyl 6,6 Nanocomposites*

Adsorption has been used widely in industrial process for many purposes of purification and separation. Adsorption is considered effective method for removal of colored and colorless organic pollutants from industrial waste water [25], Negh *et al*. [26] used chitson composites for adsorption of catinonic and anionic dyes. Gang and Wang [27] prepared multiwalled carbon nanotubes as adsorbent for adsorption of dyes. In the present study we used neat Nyl 6,6 and GNPs/Nyl 6,6 nanocomposites as adsorbent for the adsorption of NRC dye. The adsorption of NRC in aqueous media were studied on neat Nyl 6,6 and GNPs/Nyl 6,6 nanocomposites in concentration range of 50 ppm. Fig. 5 shows the UV-VIS spectra of NRC in aqueous solution before and after adsorption. The adsorption of NRC was measured via relative intensity of UV/VIS spectra, which present maximum absorbance peak at 521 nm. The spectra presented that the adsorption of NRC by Nyl 6,6 and GNPs/Nyl 6,6 nanocomposites is increased as increased the amount of GNPs. Fig. 6 shows neat Nyl 6,6 adsorbed 88.49% within 2 h, while the GNPs/Nyl 6,6 nanocomposites of (3,5,10 wt%) adsorbed NRC dye 88.60, 93.15, and 93.60% within 2 h, respectively. The high adsorption of GNPs/Nyl 6,6 nanocomposites might be due to the surface roughness of GNPs/Nyl 6,6 nanocomposites.

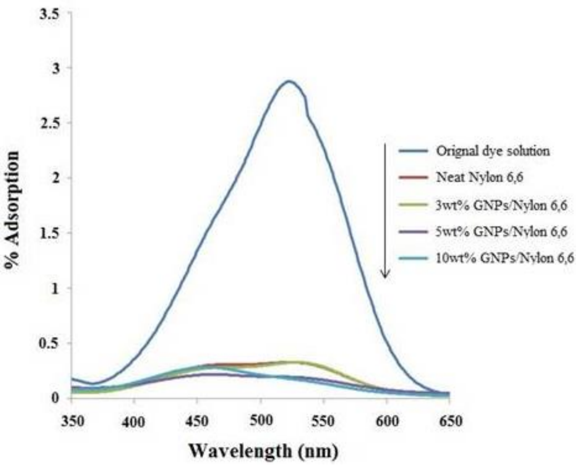

Fig. 5: UV/VIS absorbance spectra of NRC dye adsorbed by neat Nyl 6,6 and GNPs/Nyl 6,6 nanocomposites for specific time.

Table-1: Mechanical properties of neat Nyl 6,6 and GNPs/Nyl 6,6 nanocomposites.

| Sample | Stress Yield (N/mm$^2$) | Young Modulus (N/mm$^2$) | Elongation at Break (%) |
|---|---|---|---|
| Nyl 6,6 | 1.10 | 52.8 | 21.12 |
| GNPs(3wt%)/Nyl 6,6 | 1.15 | 58.47 | 27.59 |
| GNPs(5wt%)/Nyl 6,6 | 1.54 | 96.79 | 24.90 |
| GNPs(10wt%)/Nyl 6,6 | 1.04 | 54.76 | 21.47 |

Table-2: Water uptake via Neat nylon and GNPs/Nyl 6,6.

| Time (h) | Neat nylon (g) | GNPs (3 wt %) /Nyl 6,6 (g) | GNPs (10wt %)/Nyl 6,6 (g) |
|---|---|---|---|
| 0.16 | 41.6 | 36.3 | 35.5 |
| 0.33 | 50.0 | 66.6 | 33.3 |
| 1 | 53.3 | 48.2 | 44.4 |
| 2 | 56.2 | 68.7 | 48.3 |
| 6 | 56.2 | 52.2 | 41.1 |

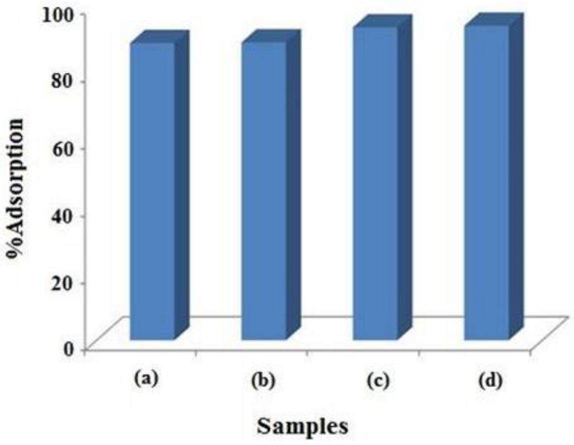

Fig. 6: Percent adsorption of NRC dye by (a) neat Nyl 6-6, (b) GNPs(3wt%)/Nyl 6-6, (c) GNPs(5wt%) /Nyl 6-6, and (d) GNPs(10 wt %)/Nyl 6-6.

## Conclusion

The morphological study presented that the GNPs were well dispersed within Nyl 6,6 polymer. The thermal stability of Nyl 6,6 (360 °C) was improved gradually by the ddition of GNPs, which reached to 393 °C by addition of 10 wt% GNPs. It was also found that the Tc of Nyl 6,6 was about 5 °C increased by addition of GNPs. The mechanical properties of Nyl 6,6 was improved by incorporation of GNPs up to an optimal quantity of filler (5 %wt GNPs) into the polymer matrix. The water uptake of nanocomposites was lower than neat Nyl 6,6, which might be due to hydrophobic nature of GNPs. The adsorption study presented that Nyl 6,6 and GNPs/Nyl 6,6 nanocomposites removed 88.49 and 93.6% of NRC dye from aqueous solution, respectively. It means that both are best adsorbents for the removal of toxic materials.

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