graphite nanosheets as low shrinkage additive and conductive filler for unsaturated polyester resin

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Abstract—Graphite nanosheets (GNSs) are considered as highly prospective filler materials for future polymer composites due to their high aspect ratio and superior electrical and thermal conductivity. We investigated the effect of GNSs on electrical properties and polymerization shrinkage of unsaturated polyester (UP) resin. A solution of polystyrene (PS) in styrene was used as low profile/shrinkage additive (LPA). The results of X-Ray diffraction analysis (XRD) and transmission electron micrographs (TEM), clearly showed a well distribution and delamination of GNS particles in the matrix. The high aspect ratio and surface area of the nanoparticles were confirmed by scanning electron microscopy (SEM) images. Accordingly a low percolation threshold of 0.7 wt.% was obtained for the nanocomposites. Differential scanning calorimetry (DSC) analysis revealed an accelerating effect of GNS on the curing of polyester compounds curing and showed an increase in the glass transition of the cured resin. The presence of 2.5 phr GNS in UP/LPA compounds helped to reduce polymerization shrinkage by 16%. In this regard, it has been shown that GNSs increase the rate of curing of UP/LPA resin.

Keywords—unsaturated polyester resin; graphite nanosheets; polymerization shrinkage; electrical properties; curing behaviour

I. INTRODUCTION

The discovery of polymer nanocomposites by Toyota research group opened a new dimension in the field of materials science. In particular, the use of nanomaterials as fillers in the preparation of polymer composites has attracted increasing interest owing to their unique properties and numerous potential applications in automotive, aerospace, construction and electronic industries [1]. Graphite flakes have been known as host materials for intercalated compounds. By applying rapid heating, some of the graphite-intercalated compounds (GICs) expand and a significant increase in volume takes place. This worm-like accordions with low density and high temperature resistance is known as exfoliated or expanded graphite (EG). EG is composed of stacks of nanosheets that may vary from 100 to 400 nm. Ultrasonication of EG in solvents is usually adopted to obtain thinner GNSs (30–80 nm), which can be dispersed further by high speed shearing in the presence of a polymer matrix [2].

Unsaturated polyester resin is one of the most successful materials used to fabricate polymer composites. The major problem of unsaturated polyester resin is its high polymerization shrinkage of approximately 7-10 vol.%. The high degree of shrinkage causes problems such as poor surface appearance, poor dimension accuracy for molded parts, internal cracks and voids in thick sections. One approach to solve this problem is to use 7 to 20 wt.% of certain types of thermoplastics such as polystyrene [3], the so-called low profile/shrinkage additives, in the resin formulation. The objective of this work is to use GNS as conductive filler in UP resin and investigate its effect on mechanical properties, glass transition temperature, shrinkage and curing rate.

II. MATERIALS AND EXPERIMENTS

A. Materials

A graphite intercalated compound with an average size of 500 µm, supplied by Superior Graphite, China, was used to prepare expanded graphite. GNS was prepared by sonication of expanded graphite in ultrasonic bath. Unsaturated polyester resin was supplied by Fiber Shargh company (Iran). Methyl ethyl ketone peroxide (MEKP) and cobalt octoate were used as hardener and accelerator, respectively. A solution of polystyrene (40 w% PS in styrene monomer (MERK)) was used as LPA. Polystyrene (GPPS 1540/1) was supplied by Tabriz Petrochemical company (Iran).

B. Preparation

1) Preparation of GNS

GICs were heat treated at 900 °C for 15 s to obtain expanded graphite particles with bulk density of 0.0037g/cm³. Expanded graphite was immersed in methyl acetate liquid in an ultrasonic bath. The dispersion was sonicated for 5 hr, and then was filtered and dried to produce GNS.

2) Fabrication of UP Nanocomposites

In situ polymerization is an efficient method to improve the dispersion of the graphic fillers in polymer matrices. Composites fabricated by in situ polymerization technique exhibit better mechanical properties and lower percolation
threshold than those made by solution compounding or melt blending techniques [2]. Thus, UP/GNS composites were prepared by in-situ polymerization. Preweighed UP resin and GNSs were mixed for several minutes to obtain a homogeneous dispersion of GNSs within the matrix. Then, initiator (MEKP) and promoter (cobalt octoate) were added into the mixture. The mixture was cast in a silicon rubber mold to prepare samples for analysis. After 24h, the specimens were placed in an oven and post-cured at 80 °C for 3 hr.

C. Measurements and Analysis

1) Electron Microscopy

The fracture surface of nanocomposites was studied by a KYKY EM3200 scanning electron microscope (China). Transmission electron micrographs were obtained with a Philips CM10 0 apparatus using an accelerator voltage of 100 kV.

2) X-Ray Scattering Analysis

XRD analysis was performed by a Siemens D5000 diffractometer using Cu Ka radiation (wavelength, 1.936 Å) at room temperature with a scanning rate of 1.2 °/min over 20°=5-40° .

3) Fourier Transform Infrared Spectroscopy (FTIR)

The study of the chemical functional groups on the nanographites was conducted on a BRUKER Tensor 27 (Germany).

4) Differential Scanning Calorimetry

The differential scanning calorimeter was carried out in NETZSCH DSC 200F3 (Germany), which calculates the heat flow to and from the specimen with respect to the temperature and time, sample weight of 20-30 mg at heating rate of 10 °/min under nitrogen atmosphere from 25°C to 250°C, in aluminium pan.

5) Electrical Measurements

A two-probe technique was used for the through-plane electrical conductivity measurements across the sample thickness. And a four-probe technique was used for the in-plane electrical conductivity measurements. Electrical measurements were conducted using a BK PRECISION multimeter and an Itche source meter, or a Keithley Electrometer, depending on the conductivity level of the samples. To ensure good electrical contact, the surfaces of the specimens were polished with 1500 grit sand paper. The size of the specimens was 12.7 mm × 4 mm × 100 mm. At least three samples were tested for each concentration.

6) Shrinkage Measurement

Density of the cured samples was measured by buoyancy method to calculate the volume shrinkage of the resin system. The density of the cured sample (d_e) and the volume shrinkage can be calculated by using the following equations [4]:

\[ d_e = \frac{m_i}{(m_i - m_s)} \times d_{\text{methanol}} \]  

\[ d_0 = \frac{1}{\sum \frac{m_i}{d_i}} \]  

\[ \text{volume shrinkage(%) = } \left( 1 - \left( \frac{d_e}{d_0} \right) \right) \times 100 \]  

in which \( d_e \) is density of the cured sample, \( m_i \) and \( m_s \) are the sample weights when measured in air and in methanol, respectively. \( d_0 \) is the density of the resin mixture before cure, \( W_i \) and \( d_i \) are weight fraction and density of each component of the mixture, respectively.

Linear shrinkage of UP resins containing GNS was calculated by measuring the length of mold and the length of cured sample. The linear shrinkage was changed to the volume shrinkage according to the following equation [5]:

\[ \text{volume shrinkage(VS)(%) = } (1 + LS)^2 - 1 \]  

In which \( L_0 \) is the length of mold at temperature room and \( L_1 \) is the length of cured sample after 24hr at temperature room and then 3hr post-cure at 80°C.

III. RESULTS AND DISCUSSION

A. Characterization of Graphite Nanosheets

1) Scanning Electron Microscopy

Thermal shock of intercalated graphite flakes caused rapid vaporization of intercalated species. The force caused by the exhaust of gaseous products exfoliated the graphite layers. The loose and porous structure of expanded graphite was produced as shown by SEM image in Fig. 1. Fig. 2 shows the SEM image of sonicated expanded graphite. Ultrasonic radiation produced GNS particles. SEM images revealed that the three-dimensional structure of EG turned to two-dimensional and sheet-like structure of GNS with a thickness of about 20 nm and a diameter of about of 10 µm. Estimated aspect ratio and surface area of GNS were calculated to be 500 and 45 m²/g, respectively. Chen et al. [6] also treated expanded graphite with sonication and produced nanosheets with a thickness of 30 –80 nm and diameter of 0.5 – 20 µm.
2) **FTIR Analysis**

Fig. 3 exhibits FTIR spectra of EG and GNS. The band at 3433 cm$^{-1}$ can be attributed to O–H stretching vibrations of phenolic or alcoholic functional groups present on EG and GNS particles. The presence of carboxyl functional groups can also be detected at around 1650 cm$^{-1}$ [7]. A strong absorption band, especially in the spectra of GNS, appeared at 2357 cm$^{-1}$ which can be attributed to C≡C and C=C=C bonds. Ultrasonic waves can cause more breakdown of sp2 carbon atoms on EG surface by creating very hot and high pressure spots in the liquid. The band at around 1030 cm$^{-1}$ indicates the presence of oxygen-containing functional groups. These results confirmed previous studies [8-10].

3) **X-ray Diffraction**

The XRD patterns of natural graphite, GIC, EG and GNS are shown in Fig. 4. The diffraction peak at (d=3.34 Å) corresponds to the (002) panel and satisfies Bragg’s equation.

$$2d \sin \theta = n\lambda \quad (5)$$

After acid treatment and thermal shock, the sizes of the natural graphite reduced in three directions. Accordingly, the intensity of the diffraction (002) peak also changed. The sharp decreased intensity of the peak corresponded to exfoliate of graphite layers in EG and GNS. It caused extremely higher aspect ratio than natural graphite.

As shown in Fig. 4 the different treatments couldn't change angle of basal peak. Therefore, the distance between graphene layers didn't increase by even thermal shock and sonication.

4) **Electrical Conductivity of Nanographite Powder**

According S. Rattanaweeranon et al. work [11], higher density of bulk graphite leads to higher electrical conductivity because there is more chance for the electrons to move across them. So, natural graphite and graphite nanosheets powders were compressed inside a tube into bulk graphites with same density. The density was calculated by measurement of mass and volume of the compact sample. The through-plane conductivity of the samples at room temperature was measured by four probe technique. The top and the bottom of the samples were attached to wire electrodes. They were connected to the Multimeter. The measurements were repeated for 3 times.

The electrical conductivity of compact GNS was lower than the electrical conductivity of compact natural graphite flakes (-18%) as shown in Table 1. Thus, it can be said the chemical and thermal treatment of graphite and sonication of...
EG particles reduced insignificantly the conductivity.

### B. Characterization of Nanocomposites

1) **X-ray Diffraction**

Fig. 5 presented the XRD patterns of UP/GNS nanocomposites. The patterns of UP/1.5phr GNS sample and UP/2.5phr GNS sample did not show the any basal peak. It can be attributed to low concentration of nanographite in nanocomposites. Disappearance of the peak in XRD pattern of nanocomposites with low concentration of nanoclay has also reported [12].

the presence of a (002) sharp peak in XRD pattern confirmed not only the presence of pure graphite based on stacks of parallel graphene sheets, but also the statement that the process technique applied is not able to exfoliate or completely separate the graphite layers and some graphite sheets still exist in the aggregate form [13]. So, the appearance of the (002) peak with very low intensity in the pattern of UP/5phr GNS sample (Fig. 5) can illustrate good homogeneity of nanosheets in UP matrix. In addition, UP/5phr GNS nanocomposite did not show signs of intercalation of UP between graphene sheets, likely due to the insufficient interlayer distance between graphene layers.

2) **Electron Microscopy**

SEM micrograph in Fig. 6 illustrated the microscopic structure of fracture surface of UP/2.5phr GNS nanocomposite. The presence of GNS particles with layer and sheet-like structure in UP matrix was clear. And the resin could wet the nanofillers very well.

TEM observation of the nanocomposites mentioned a high distribution and dispersion level of the graphite nanosheets in the polymer matrix (Fig. 7a, b). Dispersed exfoliated layers and thin sheets of graphite were visible into the UP matrix.

3) **Electrical Conductivity**

Fig. 8 represented the variation of the in-plane electrical conductivity of the nanocomposites as a function of GNS content. The nanocomposites exhibited a sharp transition from an electrical insulator to an electrical semiconductor at a very low GNS content of about 0.5 vol. %. Percolation theory defines an insulator-conductor transition and its corresponding threshold of the conducting filler concentration $P_c$, via the following equation,

$$\sigma = \sigma_0 (P - P_c)^t \quad \text{For} \quad P > P_c$$

(7)

Where $\sigma_0$ is a constant, $\sigma$ the electrical conductivity of composite, $P$ the volume fraction of graphite, and $t$ the critical exponent. The exponent $t$ depends on filler dimensionality and its values are $t \approx 1.33$ and $t \approx 2.00$ for two and three dimensions, respectively [9]. In here, best-fitted values based on the scaling law were 0.0045 for $P_c$ and 1.6 for the $t$ as shown in Fig. 9. The low value of $t=1.6$ suggested that charge transported through a two-dimensional structure; therefore the value of the resulted critical exponent for graphite nanosheets is reasonable. The very low value of $P_c$ (0.4 vol. % equal to 0.72 wt. %) was excellent when compared with the data reported [14-17]. For example, the lowest percolation threshold of the UP/GNS composites was 1.2 wt. % [18] and this value for UP/milled EG was reported 2phr [19]. This is due to the sheet-like structure of the GNS particle having a very high aspect ratio and a large specific surface that were estimated from electron microscopy micrographs (Fig. 1, Fig. 7a and Fig. 7b). The appropriate dispersion and distribution of nanofiller in UP resin made a conductive network at lower content of GNS. This result is similar to the published percolation threshold for epoxy/graphene composites with 0.52 vol. % [20]. The percolation threshold about 0.1 vol. % may expect if the disc-like particles with aspect ratio about 1000 disperse randomly in matrix [21].

For comparison, the through-plane and in-plane electrical conductivity of nanocomposites were listed in Table 2. In

<table>
<thead>
<tr>
<th>No.</th>
<th>samples</th>
<th>Density(g/cm³)</th>
<th>Through-plane conductivity(S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Compact NG</td>
<td>2.14±0.12</td>
<td>14.8±0.4</td>
</tr>
<tr>
<td>2</td>
<td>Compact GNS</td>
<td>2.14±0.12</td>
<td>12.1±0.6</td>
</tr>
</tbody>
</table>

**Table 1.** Through-plane electrical conductivity of graphite powders at 298 K (25 °C).

Fig. 5. The XRD patterns of the UP/GNS nanocomposites.

Fig. 6. The SEM micrograph of the UP/2.5phr GNS nanocomposite.
through-plane measurements by 2-probe technique, it is impossible to remove the contact resistant. So, it is expected the value of through-plane conductivity will be even lower in composites with random dispersion--lower than in-plane conductivity as shown in Table 2. Higher contents of nanofiller caused to form the denser and wider conducting filler network. Therefore, the difference between through-plane and in-plane conductivity decreased in higher concentrations of GNS. In addition, through-plane conductivity of UP/5phr GNS composite was measured about 35 times of through-plane conductivity of UP/5phr natural graphite composite. This result reemphasized that the graphite nanosheet with high aspect ratio is more effective in forming conducting network. And the higher electrical conductivity of natural graphite flakes (Table 1) was not enough to reach the composite with more conductivity.

4) Thermal Analysis

The effect of the graphite nanosheets on curing of polyester resin is investigated by DSC analysis. Fig. 1 showed the dynamic DSC thermograms of the polyester mixtures over the 25-250 °C range. The thermal properties derived from the dynamic DSC thermograms were summarized in Table 3 in terms of the total heat of reaction (ΔH_{dyn}, referred to the unit mass of mixture), the glass transition and the reaction peak temperatures (T_g and T_{peak}) for all samples. An increase in T_g of UP resin by addition of expanded graphite was reported [19]. M. Chieruzzi et al. [22] showed T_g also increased with nanoclay content. The glass transition process is related to molecular motion at a structural level. The increase in T_g of the nanocomposites with respect to the neat UP resin (as shown in Table 3) can be attributed to an improved adhesion between the resin and nanofiller surfaces that restricts the motion of molecular segments. It was also obvious from Table 3 that the presence of GNS in matrix increased ΔH_{dyn} of mixtures with respect to the neat UP resin. Since the released heat during the cure reaction of thermosetting resin is an indicator of curing, it can be said the more total heat of reaction (ΔH_{dyn}) correspond to the higher degree of curing [23]. Qiu et al. [24] illustrated that GO has an accelerating effect on the curing process of epoxy nanocomposites with a trend of cure reaction peaks towards lower temperatures. It was observed (in Table 3) that T_{peak} decreased with the presence of GNS, indicating that the GNSs act as catalysts to accelerate the curing reaction of UP resin. Therefore, it may be concluded that the different types of oxygen functionalities (which agreed with the result of FTIR discussed above) on the surface of GNS are considered as catalysts to accelerate the cure reaction of UP resin.

In addition, because of the thermal conductivity of graphite sheets, the heat generated by the exothermic curing reaction...
transfers faster and more uniformly in the whole mixture that improves the curing rate of UP resin. However, in the higher concentrations the presence of GNSs prevents from crosslinking of resin and acts against two factors discussed above. That is why it was observed that no linear relationship of \( \Delta H_{\text{dyn}} \) and \( T_{\text{peak}} \) between different contents of GNS.

5) **The effect of GNS on shrinkage control of UP resin**

In the UP/styrene (St)/LPA system, a reaction-induced phase separation occurs during curing, resulting in the UP-rich phase and the LPA-rich phase are formed. If microvoids can form in the LPA-rich phase or at the interface of the two phases, polymerization shrinkage can be reduced or eliminated without any thermal effect. It was found that the reaction rate of the LPA-rich phase is much lower than that of the UP-rich phase because of the high St/UP ratio (i.e. the St–St reaction is much slower than the St–UP copolymerization) and the low cobalt promoter level in the LPA-rich phase (i.e. the cobalt promoter has a higher solubility in the UP-rich phase during partitioning). Since a liquid LPA phase can release stresses resulting from polymerization shrinkage of the UP-rich phase, the stress-induced local cracking in the LPA-rich phase or at the interface of the two phases will not occur until after the gelation of the LPA-rich phase. This local cracking leads to volume expansion of the curing system, thereby compensating some of the polymerization shrinkage. It has been suggested that increasing the reaction rate in the LPA-rich phase could result in an earlier microvoid formation/volume expansion in the system for better shrinkage control [4]. Accordingly, Xu et al. [4] showed the positive effect of nano clay on shrinkage control of the UP/St/polyvinyl acetate systems. Therefore, we were going to investigate the effect of GNS on the UP/LPA(polystyrene) systems. The content of LPA was constant (equal to 7phr) in all samples. Table 4 presented density and volume shrinkage results of the cured samples. It showed the presence of GNS in matrix reduced significantly the volume shrinkage of pure resin and UP/LPA mixture. Also, the linear shrinkage of cured samples was calculated by measuring of the length. Then, the values of linear shrinkage converted to the values of volume shrinkage (as shown in Table 5). The results of Table 5 confirmed the control effect of GNS on UP resin shrinkage. Both results (in Table 4 and Table 5) showed a similar trend with the different concentrations of GNS. After these observations, the study on morphology of UP/LPA/GNS nanocomposites and curing rate of UP/LPA/GNS mixtures were conducted.

a) **Morphology of UP/LPA/GNS Nanocomposites**

To study the effect of GNS on the shrinkage control of the UP/St/LPA system, the final morphology of the cured samples was observed under SEM. Fig. 1 shows the fracture surface

![Fig. 1](image.png)

**Table 2.** Comparison of through-plane and in-plane conductivity of nanocomposites.

<table>
<thead>
<tr>
<th>No.</th>
<th>Nanocomposites</th>
<th>In-plane conductivity (S/cm)</th>
<th>Through-plane conductivity (S/cm)</th>
<th>Ratio of in-plane conductivity to through-plane conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UP/1phr GNS</td>
<td>0.001±0.0002</td>
<td>0.000046±0.000003</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>UP/2.5phr GNS</td>
<td>0.029±0.0025</td>
<td>0.003±0.0006</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>UP/5phr GNS</td>
<td>0.127±0.0377</td>
<td>0.012±0.002</td>
<td>11</td>
</tr>
</tbody>
</table>

![Fig. 10](image.png)

**Fig. 10.** DSC thermograms of UP/GNS mixtures at different concentration of GNS with a heating rate of 10°C/min.

**Table 3.** The results of dynamic tests on UP/GNS mixtures.

<table>
<thead>
<tr>
<th>No.</th>
<th>Samples</th>
<th>( \Delta H_{\text{dy}} ) (J/g)</th>
<th>( T_{\text{peak}} ) (°C)</th>
<th>( T_{\delta} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UP/0phr GNS</td>
<td>206.1</td>
<td>118.6</td>
<td>205.8</td>
</tr>
<tr>
<td>2</td>
<td>UP/1.5phr GNS</td>
<td>270.1</td>
<td>90.3</td>
<td>207.9</td>
</tr>
<tr>
<td>3</td>
<td>UP/2.5phr GNS</td>
<td>222.3</td>
<td>113.3</td>
<td>214.8</td>
</tr>
</tbody>
</table>

**Table 4.** Density and volume shrinkage of cured samples (7phr LPA, 0.4phr cobalt octoate, 1.2phr MEKP).

<table>
<thead>
<tr>
<th>No.</th>
<th>Samples</th>
<th>( d_{l} ) (g/cm³)</th>
<th>( d_{v} ) (g/cm³)</th>
<th>Volume shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UP/0phr GNS</td>
<td>1.256±0.0034</td>
<td>1.150</td>
<td>8.4</td>
</tr>
<tr>
<td>2</td>
<td>UP/1.5phr GNS</td>
<td>1.239±0.0197</td>
<td>1.157</td>
<td>6.7</td>
</tr>
<tr>
<td>3</td>
<td>UP/LPA/0phr GNS</td>
<td>1.190±0.0013</td>
<td>1.113</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>UP/LPA/1.5phr GNS</td>
<td>1.171±0.0084</td>
<td>1.119</td>
<td>4.4</td>
</tr>
<tr>
<td>5</td>
<td>UP/LPA/2.5phr GNS</td>
<td>1.166±0.01</td>
<td>1.123</td>
<td>3.6</td>
</tr>
</tbody>
</table>
of the sample containing 7phr LPA with different amounts of GNS. For all three samples, a two-phase structure was found. The flake-like structure corresponds to a highly concentrated UP region. The particulate region is formed by UP and LPA (LPA-rich phase) [25]. The particulate region (LPA-rich phase) was small and formed the dispersed phase with domain diameter less than 10µm to 40µm. The flake-like region (UP-rich) formed the continuous phase. The Fig. 12 showed the LPA-rich phase has tiny pores. As expected, the formation of microvoids at the interface of the two phases was clear that caused the better volume shrinkage in samples containing of LPA. But, these voids reduce the strength of interfacial in two phases and cause a decreasing in mechanical properties of samples containing of LPA. As seen in Fig. 11(b, c), the presence of GNS has not changed the morphology of nanocomposites. There is a significant observation, GNS particles have influenced on the interface of the two phases and improved the interaction between the two phases (LPA-rich and UP-rich phases) that suggested nanographite is more compatible to the LPA-rich phase (where has higher concentration of polystyrene).

IV. CONCLUSIONS

Unsaturated polyester/graphite nanosheet nanocomposites were prepared through in-situ polymerization method. The very low value of percolation threshold (0.4 vol. %) was excellent when compared with the other data reported. This result is similar to the published percolation threshold for epoxy/graphene composites with 0.52 vol. % [20].

It was observed (in DSC results) that $T_{\text{peak}}$ decreased with the presence of GNS in matrix, indicating that the GNSs acted as facilitate the curing reaction of UP resin.

The results confirmed the control effect of GNSs on UP resin shrinkage. There was a significant observation, GNS particles have influenced on the interface of the two phases and improved the interaction between the two phases.

GNSs introduced as a new curing facilitator and low shrinkage additive of unsaturated polyester resin.
References