

## Influence of Aminized Graphite Nanosheets on the Physical Properties of PMMA-based Nanocomposites

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In this work, poly(methyl methacrylate) (PMMA) was grafted onto amine treated graphite nanosheets (NH<sub>2</sub>-GNs) and the surface characteristics and physical properties of the NH<sub>2</sub>-GNs-g-PMMA films were investigated. The graft reaction of NH<sub>2</sub>-GNs and PMMA was confirmed from the shift of the N<sub>1S</sub> peak, including amine oxygen and amide oxygen, by X-ray photoelectron spectroscopy (XPS). The surface characteristics of the NH<sub>2</sub>-GNs-g-PMMA films were measured as a function of the NH<sub>2</sub>-GN content using the contact angle method. It was revealed that the specific component of the surface free energy ( $\gamma_s$ ) of the films was slightly increased as the NH<sub>2</sub>-GN content increased. Also, the thermal and mechanical properties of the NH<sub>2</sub>-GNs-g-PMMA films were enhanced with the addition of NH<sub>2</sub>-GNs. This can be attributed to the chemical bonding caused by the graft reaction between the NH<sub>2</sub>-GNs and the PMMA matrix.

**Key Words:** Composites, Interfaces, Surface properties, Electrical properties, Mechanical properties

### Introduction

Polymer nanocomposites based on carbon materials are expected to replace the traditional materials used in the electronics industry. A considerable amount of research has been conducted that centers on this technology owing to the superior thermal, mechanical, and electrical properties it offers. It is also inexpensive and lightweight and is known for its flexible features and simple processing techniques.<sup>1,2</sup>

Among the many carbon materials, graphites are naturally abundant. They are widely used as conductive filler to obtain conductive polymer composites as they have an excellent conductivity rating of 10<sup>4</sup> S/cm.<sup>3</sup> Graphites are composed of carbon nanolayers which are bound by weaker van der Waals force. These characteristics of graphites result in the formation of the graphite intercalation compound (GIC), also known as graphite oxide (GO). Exploiting the rapid heating of GO has led to what is known as expanded graphites (EGs), which are characterized by their high aspect ratio and low density. Polymer nanocomposites based on EGs show higher thermal, mechanical, and electrical properties with a low EG content compared to conventional carbon fillers.<sup>4-6</sup>

More recently, in an effort to improve the properties of the polymer nanocomposites with less filler content, graphite nanosheets (GNs) have received much attention as a type of nanoscale filler. GNs are easily prepared by exfoliation of EGs *via* ultrasonic treatment. They have a high dispersity rating and a high aspect ratio, leading to nanocomposites with superior thermal, physical, and electrical properties.<sup>7,8</sup> However, these properties are strongly dependent on the dispersity and interaction of the carbon fillers in the polymer matrix, as these carbon fillers are non-uniformly dispersed in the polymer matrix due to the van der Waals interaction between them. Therefore, in an effort to alleviate this non-uniformity, various methods have been utilized with these nanocomposites, including surface functionalization, *in-situ* polymerization, and ultrasonication, *etc.*<sup>9-11</sup>

Among the various polymers, poly(methylmethacrylate)

(PMMA) is one of the most widely used thermoplastic due to its many excellent physical and optical properties. It can be simply prepared in many forms, such as fibers, films, and moldings with various fillers. This makes it viable for use in a range of applications, including glazing, lighting, architecture, transportation, and bio materials.<sup>12-14</sup>

Therefore, in this work, GNs as conductive fillers are functionalized by ethylenediamine, and poly(methylmethacrylate) (PMMA) is then grafted onto amine-treated GNs (NH<sub>2</sub>-GNs). NH<sub>2</sub>-GNs-g-PMMA films are prepared in a solution casting method after a graft reaction. The surface characteristics and physical properties of the NH<sub>2</sub>-GNs-g-PMMA films are investigated.

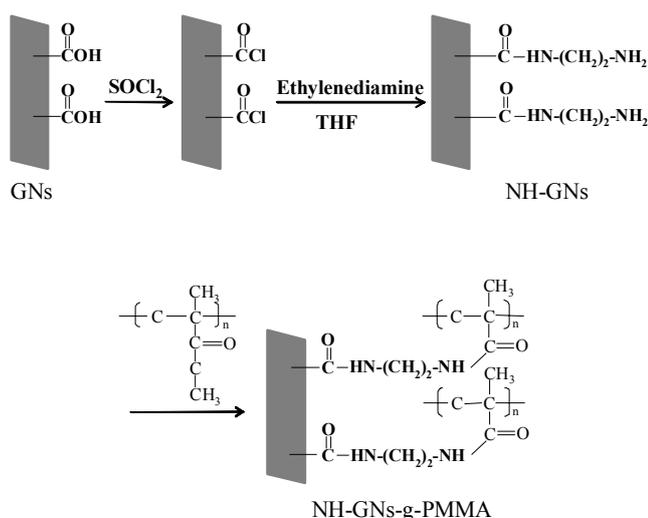
### Experimental

**Materials.** PMMA was obtained from LG MMA. The natural graphites (N-GP) were supplied from Aldrich. Thionyl chloride, tetrahydrofuran (THF), chloroform, and ethylenediamine (EDA) were supplied from Aldrich.

**Preparation of Amine Treated GNs.** EGs were produced by chemical oxidation using a sulfuric and nitric acid solution in conjunction with a rapid heat treatment at a temperature of 1000 °C for 90 s. GNs were obtained by exfoliation of the EGs *via* an ultrasonic treatment for 6 h in acetone.

For the surface treatment of the GNs, they were further acid-reacted with a sulfuric acid and nitric acid (3:1) mixture that was stirred for 3 h. They were then washed and dried at 80 °C. In the next step, the dried GNs were put in an excess amount of thionyl chloride and the mixture was stirred at 70 °C for 24 h. The excess thionyl chloride was decanted and the acyl-derived GNs (GNs-COCl) were washed by THF and dried under a vacuum at room temperature. Finally, the GNs-COCl was reacted with excess EDA at 100 °C for 12 h and then washed by THF and dried at 80 °C. It was termed NH<sub>2</sub>-GNs.

**Preparation of NH<sub>2</sub>-GNs-g-PMMA Films.** The NH<sub>2</sub>-GNs-g-PMMA films were prepared with different NH<sub>2</sub>-GN contents



**Figure 1.** Schematic diagram showing the preparation of the  $\text{NH}_2$ -GNs and  $\text{NH}_2$ -GNs-g-PMMA.

using a solution blending method. The  $\text{NH}_2$ -GNs concentrations were 1, 2, 3, and 4 wt % of the total PMMA weight. In this process, PMMA was dissolved in chloroform and  $\text{NH}_2$ -GNs were then dispersed in PMMA solution with sonication for 3 h. Finally, the  $\text{NH}_2$ -GNs and PMMA were reacted for 12 h at  $70^\circ\text{C}$  while stirring.  $\text{NH}_2$ -GNs-g-PMMA films were prepared in a solution casting method and were then dried in an oven at  $80^\circ\text{C}$ . The product was then dried in a vacuum oven at  $80^\circ\text{C}$  for 2 days. The preparation procedure of the  $\text{NH}_2$ -GNs and  $\text{NH}_2$ -GNs-g-PMMA is presented in Fig. 1.

**Measurements.** The surface morphologies of  $\text{NH}_2$ -GNs and  $\text{NH}_2$ -GNs-g-PMMA films were observed by scanning electron microscopy (SEM, S-4200, Hitachi) and transmission electron microscopy (TEM, Jeol FE-TEM 2006).

The structures of the pure PMMA and  $\text{NH}_2$ -GNs-g-PMMA film were determined by X-ray diffraction (XRD, Rigaku D/Max 2200 V) at 40 kv and 40 mA using  $\text{Cu K}\alpha$  radiation. The XRD patterns were obtained in  $2\theta$  ranges between  $2^\circ$  and  $70^\circ$  at a scanning rate of  $2^\circ/\text{min}$ .

$\text{NH}_2$ -GNs and  $\text{NH}_2$ -GNs-g-PMMA films were characterized by X-ray photoelectron spectroscopy (XPS, K-Alpha) using a VG Scientific ESCALAB MK-II spectrometer equipped with an  $\text{Mg K}\alpha$  (1253.6 eV) X-ray source, a high-performance multi-channel detector that was operated at 200 W.

Contact angles were measured using the sessile drop method on a Rame-Hart goniometer. Approximately 5  $\mu\text{L}$  of wetting liquid was used for each measurement at a temperature of  $20^\circ\text{C}$ . A reading within 5 s of the formation of a drop was taken for the critical surface tension measure. The testing liquids used

**Table 1.** Surface free energy and related components of the liquids, measured at  $20^\circ\text{C}$  ( $\text{mJ}/\text{m}^2$ )

	$\gamma_L$	$\gamma_L^d$	$\gamma_L^{SP}$	$\gamma_L^+$	$\gamma_L^-$
Water	72.8	21.8	51.0	25.5	25.5
Diiodomethane	50.8	50.42	0.38	0	0
Ethylene glycol	47.7	31.0	16.7	1.92	47.0

were deionized water, diiodomethane, and ethylene glycol. The basic characteristics of the surface free energy of the liquids are given in Table 1.

The electrical conductivity of the  $\text{NH}_2$ -GNs-g-PMMA films was measured at room temperature using a four-probe digital multimeter (MCP-T610, Mitsubishi Chem.).

The thermal stability of the  $\text{NH}_2$ -GNs-g-PMMA films was measured by means of thermogravimetric analyses (TGA, DuPont TGA-2950 analyzer) from  $30$  to  $850^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in a nitrogen atmosphere.

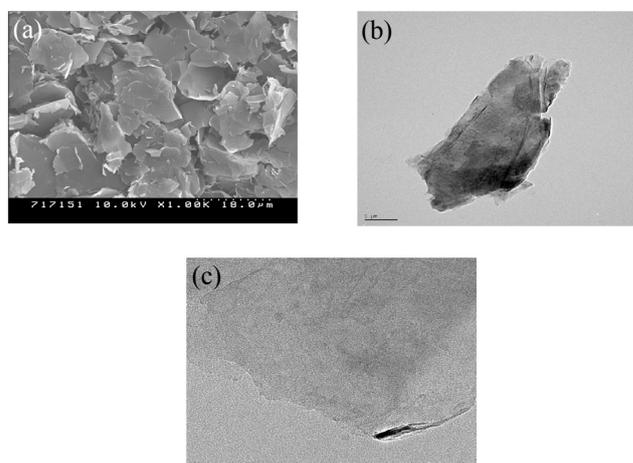
The mechanical properties of the  $\text{NH}_2$ -GNs-g-PMMA films were measured using the tensile strength method on a universal testing machine (UTM, Lloyd, LR5K). Each sample was tested at a crosshead speed of  $2\text{ mm}/\text{min}$  at room temperature.

## Results and Discussion

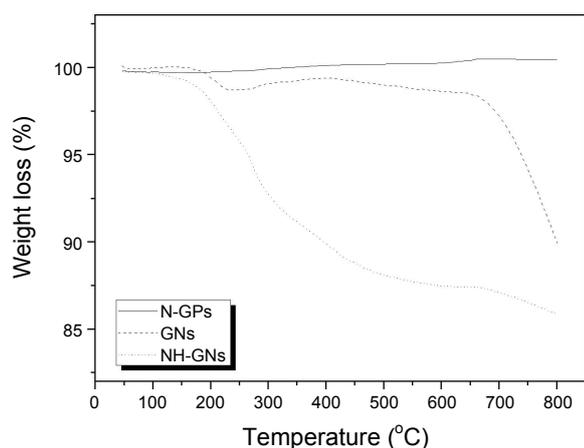
**Characterization of  $\text{NH}_2$ -GNs.** Fig. 2 shows  $\text{NH}_2$ -GNs images after the ultrasonic and surface treatment. After powdering the EGs, the worm-like EGs were exfoliated by the ultrasonic treatment, producing a thin plate form with a dimension from a few  $\mu\text{m}$  to nearly  $18\ \mu\text{m}$  and a nano-size thickness. It was clear that the  $\text{NH}_2$ -GNs had a high aspect ratio. The thin-plate-type  $\text{NH}_2$ -GNs were further observed *via* TEM, as shown in Figs. 2 (b) and (c).

Fig. 3 presents TGA thermograms of the N-GP, GNs, and  $\text{NH}_2$ -GNs. As shown in Fig. 3, N-GP shows high thermal stability up to  $800^\circ\text{C}$ . However, the GNs and  $\text{NH}_2$ -GNs show the two weight loss intervals. GNs show a low weight loss from  $180$  to  $660^\circ\text{C}$  due to the decomposition of the organic functional groups of the carboxyl and hydroxyl groups which formed during the preparation of GNs. They also show a sharp inflection peak at  $660^\circ\text{C}$ , which can be attributed to the thermal decomposition of GNs. The  $\text{NH}_2$ -GNs show additional weight loss from  $130$  to  $660^\circ\text{C}$  compared to the GNs. The greater weight loss at a low temperature most likely resulted from the increased thermal decomposition of organic functional groups containing carboxyl, hydroxyl, and amine groups on the GNs due to the additional chemical treatment.

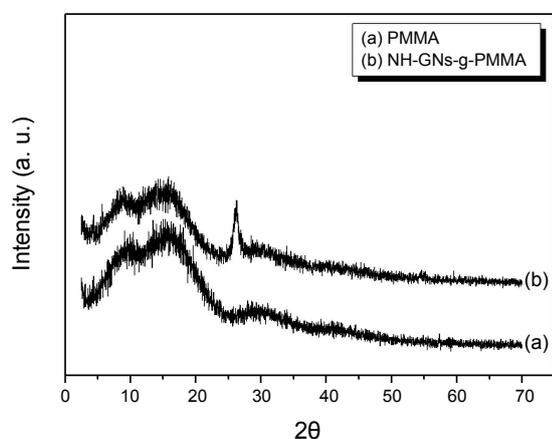
**Grafting of PMMA onto  $\text{NH}_2$ -GNs.** Fig. 4 shows XRD pa-



**Figure 2.** SEM (a) and TEM (b, c) images of  $\text{NH}_2$ -GNs.



**Figure 3.** TGA thermograms of N-GPs, GNs, and NH<sub>2</sub>-GNs.

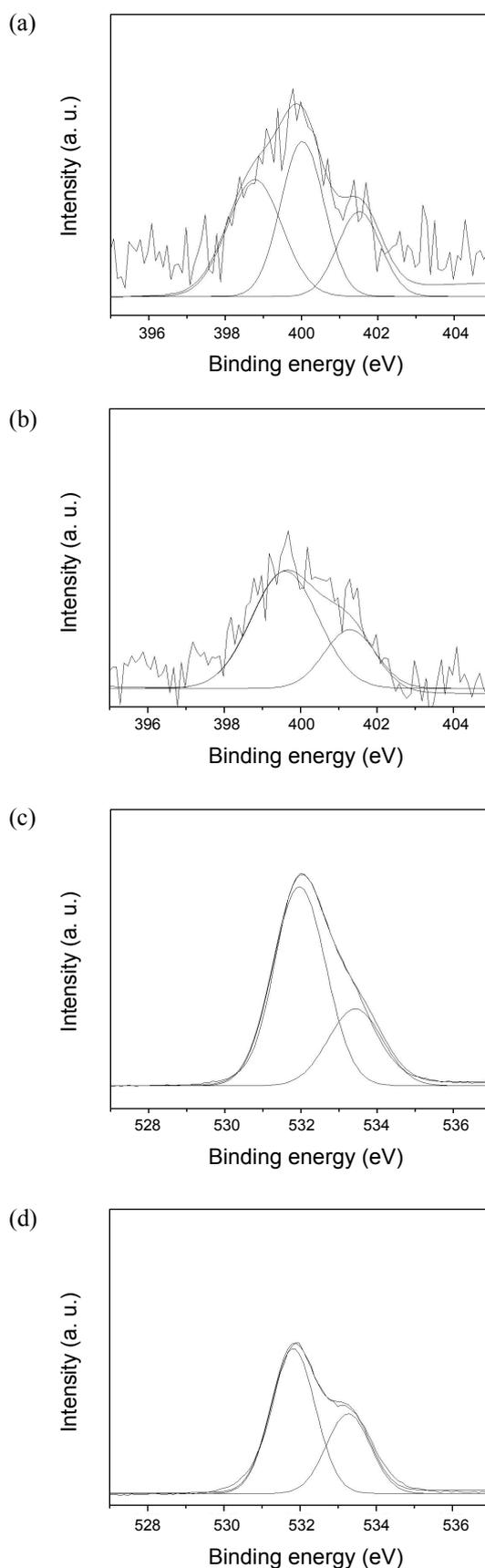


**Figure 4.** XRD patterns of pure PMMA and NH<sub>2</sub>-GNs-g-PMMA films.

tterns of the pure PMMA and NH<sub>2</sub>-GNs-g-PMMA films. As expected, the NH<sub>2</sub>-GNs-g-PMMA film shows a weak graphite diffraction (002) peak at approximately  $2\theta = 26^\circ$ , whereas the pure PMMA film is amorphous. This indicates that the NH<sub>2</sub>-GNs are randomly oriented in the PMMA matrix, resulting in a decrease in the number of regular planes that satisfy the Bragg's equation at  $2\theta = 26^\circ$ .

The grafting of PMMA onto the NH<sub>2</sub>-GNs is confirmed by XPS analysis, as shown in Fig. 5. The N<sub>1s</sub> peak of the NH<sub>2</sub>-GNs can be curve-fitted with three component peaks, as shown in Fig. 5 (a). The lower binding energy peak at 398.7 eV is attributed to the amine nitrogen. The higher binding energy peaks at 400.0 and 401.5 eV are attributed to the amide nitrogen by the electron-withdrawing carbonyl group. Fig. 5 (b) shows the N<sub>1s</sub> spectrum of the NH<sub>2</sub>-GNs-g-PMMA films after the graft reaction. The N<sub>1s</sub> peak can also be curve-fitted with two component peaks, one at 400.0 eV and one at 401.5 eV. The absence of the amine nitrogen peak at 398.7 eV reveals that all of the amine groups of the NH<sub>2</sub>-GNs have reacted with the PMMA.

In Fig. 5 (c), the O<sub>1s</sub> peak of pure PMMA can be curve-fitted with two component peaks. The peaks at 532.7 eV and 533.8 eV arise from carbonyl oxygen and ether oxygen, respectively. The O<sub>1s</sub> peak of the NH<sub>2</sub>-GNs-g-PMMA films can be also curve-fitted with two component peaks (amide oxygen and ether



**Figure 5.** XPS N<sub>1s</sub> spectra of NH<sub>2</sub>-GNs (a), NH<sub>2</sub>-GNs-g-PMMA films (b) and O<sub>1s</sub> spectra of pure PMMA (c), NH<sub>2</sub>-GNs-g-PMMA films (d).

oxygen); is the peaks are broader and the intensity of the amide oxygen peak is lower as compared with the pure PMMA. This is clearly attributable to the decrease of the amide oxygen due to the grafting reaction of the NH<sub>2</sub>-GNs and PMMA.

**Surface Energetics of the Films.** The measurement of the contact angle is a well known as useful technique to investigate the characteristics of a surface using polar liquids and nonpolar liquids, the hydrophilic-hydrophobic property, acid-base interactions, and the van der Waals force. The London dispersive and specific components, including the electron acceptor and donor parameters of the surface free energy of the films, were determined by measuring the contact angles of three testing liquids with known London dispersive and specific components. The surface free energy of the films was calculated according to the following equation, as proposed by Owens and Wendt<sup>15</sup> and Kaelble,<sup>16</sup> using the geometric mean:

$$\gamma_L(1 + \cos \theta) = 2(\gamma_L^L \gamma_S^L)^{1/2} + 2(\gamma_L^{SP} \gamma_S^{SP})^{1/2} \quad (1)$$

Here, the subscripts *L* and *S* represent the liquid and solid states, and  $\gamma^L$  and  $\gamma^{SP}$  are the London dispersive (superscript: *L*) and specific (superscript: *SP*, Debye, Keesom of the van der Waals force, H-bonding,  $\pi$ -bonding, and other small polar effects) components of the surface free energy of the constitutive elements, respectively.

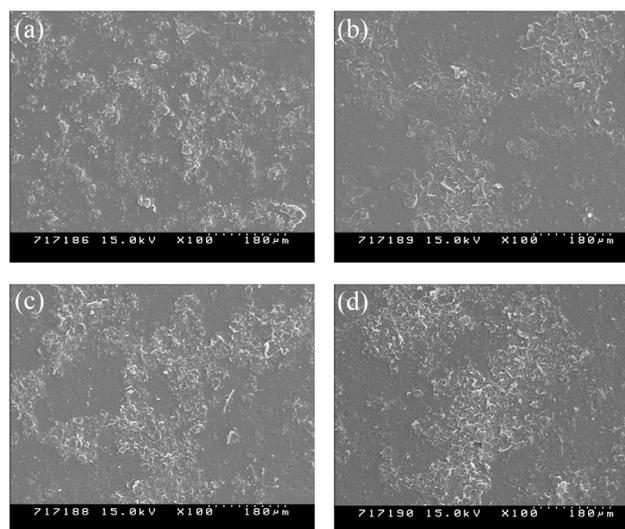
Table 2 summarizes the calculated results of the surface free energy and their components for the pure PMMA and NH<sub>2</sub>-GNs-g-PMMA films investigated in terms of their contact angles. The surface free energy of the films decreased as the NH<sub>2</sub>-GN content increased, mainly due to the decrease of the London dispersive component. In contrast, the specific component increased slightly, resulting from the polar group increase of the GNs caused by the chemical treatment. These results suggest that the NH<sub>2</sub>-GNs do not significantly affect the surface characteristics of the films due to an addition of a relatively low NH<sub>2</sub>-GN content.

**Electrical Properties of the Films.** The electrical conductivity of the NH<sub>2</sub>-GNs-g-PMMA films was measured using a four-probe method. The electrical conductivity of the films was examined as a function of the NH<sub>2</sub>-GN content. This is listed in Table 3. Generally, graphite nanoplate filler provide higher improvement of the thermal and electrical conductivity compared with carbon nanotubes, which is attributed to the strong interaction between graphite nanoplate of flate type and polymer matrix and high aspect ratio of graphite nanoplates.<sup>17</sup> The findings show that the electrical conductivity of the pure PMMA

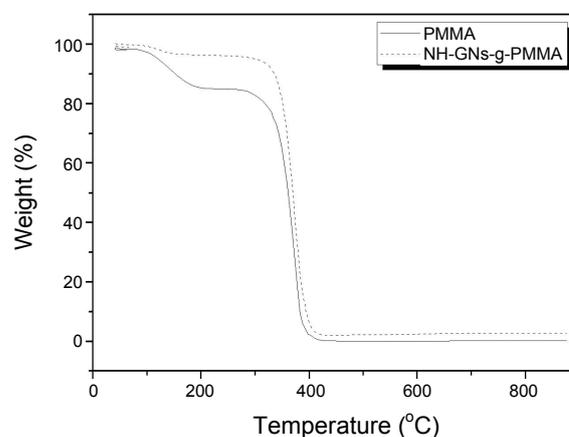
film is not detectable (over the limit of the equipment). However, the electrical conductivity of the films increases remarkably with an increase of the NH<sub>2</sub>-GN content. It was found that the increase in the NH<sub>2</sub>-GN content causes the formation of a conductive network, resulting in additional conductive pathways.<sup>18</sup>

Fig. 6 shows the surface of the NH<sub>2</sub>-GNs-g-PMMA film as a function of the NH<sub>2</sub>-GN content. In PMMA films containing 1 wt % NH<sub>2</sub>-GNs, the NH<sub>2</sub>-GNs are well dispersed in the PMMA matrix, whereas NH<sub>2</sub>-GNs become aggregated as the NH<sub>2</sub>-GN content increases. This suggests that aggregation between NH<sub>2</sub>-GNs, resulting in multiple conductive networks, can improve the electrical conductivity as compared to well-dispersed NH<sub>2</sub>-GNs.

**Thermal Properties of the Films.** The thermal stabilities of pure PMMA and PMMA films containing 4 wt % NH<sub>2</sub>-GNs are shown in Fig. 7. The initial decomposed temperature (IDT) of the NH<sub>2</sub>-GNs-g-PMMA film is higher (299.8 °C) than that of the pure PMMA film (120.4 °C). The NH<sub>2</sub>-GNs-g-PMMA films become degraded near 312 °C, which is higher compared to the degradation temperature of pure PMMA (270 °C). This



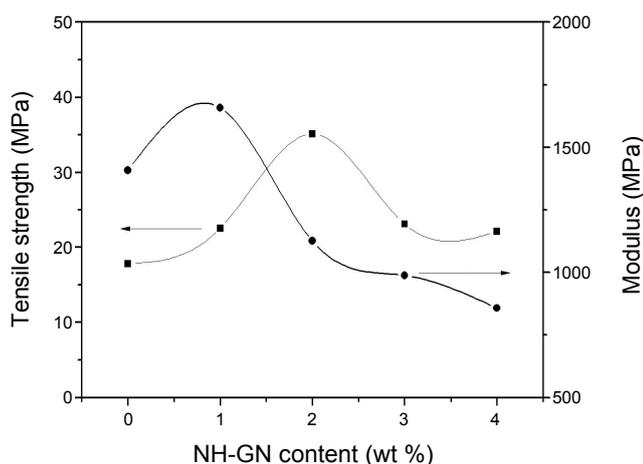
**Figure 6.** SEM images of NH<sub>2</sub>-GNs-g-PMMA films as a function of the NH<sub>2</sub>-GN content.



**Figure 7.** TGA thermogram of pure PMMA and 4 wt % NH<sub>2</sub>-GNs-g-PMMA films.

**Table 2.** Surface free energy and related components for pure PMMA and NH<sub>2</sub>-GNs-g-PMMA films as a function of the NH<sub>2</sub>-GN content, measured at 20 °C (mJ/m<sup>2</sup>)

Sample	$\gamma_s$	$\gamma_s^L$	$\gamma_s^{SP}$
PMMA	40.66	40.45	0.21
NH <sub>2</sub> -GNs-1	40.63	40.42	0.21
NH <sub>2</sub> -GNs-2	40.49	40.19	0.30
NH <sub>2</sub> -GNs-3	39.15	38.72	0.43
NH <sub>2</sub> -GNs-4	38.76	38.21	0.55



**Figure 8.** Tensile strengths and moduli of NH<sub>2</sub>-GNs-g-PMMA films as a function of the NH<sub>2</sub>-GN content.

**Table 3.** Electrical conductivity of NH<sub>2</sub>-GNs-g-PMMA films as a function of the NH<sub>2</sub>-GN content

NH <sub>2</sub> -GNs (wt %)	Electrical conductivity (S/cm)
0	-
1.0	$3.90 \times 10^{-4}$
2.0	$2.01 \times 10^{-2}$
3.0	$2.76 \times 10^{-1}$
4.0	$5.20 \times 10^{-1}$

is attributed to the grafting between the NH<sub>2</sub>-GNs and PMMA, which causes a trammel effect of the movement of the PMMA chains. In addition, no significant weight change was observed at temperatures in excess of approximately 450 °C; moreover, the residual weight percent is higher (2.8%) than that of the pure PMMA (0.3%). These results indicate that the difference in the total weight loss is most likely due to the excellent thermal stability of the NH<sub>2</sub>-GNs dispersed in the PMMA matrix.<sup>19,20</sup>

**Mechanical Properties of the Films.** Fig. 8 shows the tensile strength and moduli of NH<sub>2</sub>-GNs-g-PMMA films as a function of the NH<sub>2</sub>-GN content. The tensile strength of the films is improved by the addition of NH<sub>2</sub>-GNs. The maximum value is shown at 2 wt % NH<sub>2</sub>-GNs, showing a value that exceeds approximately 97% as compared with the pure PMMA film. This is attributed to the chemical bonding caused by the graft reaction of the NH<sub>2</sub>-GNs and the PMMA matrix. However, above 2 wt % NH<sub>2</sub>-GN content, the tensile strength is decreased upon the accumulation of NH<sub>2</sub>-GNs that occurs during the processing stage. The aggregates of NH<sub>2</sub>-GNs result in weak interaction between the NH<sub>2</sub>-GNs and the PMMA matrix. The moduli of the NH<sub>2</sub>-GNs-g-PMMA films is also improved with the by nearly 17% compared with the pure PMMA film due to the better dispersion of NH<sub>2</sub>-GNs in the PMMA matrix, leading to the strong interaction between the NH<sub>2</sub>-GNs and the PMMA matrix.<sup>21-24</sup>

### Conclusions

Amine-treated GNs-g-PMMA films were prepared by solu-

tion casting after a graft reaction. The grafting of PMMA onto the NH<sub>2</sub>-GNs was confirmed by means of XPS, showing that it resulted from the shift of the N<sub>1s</sub> peaks. The surface free energy of the film measured according to the contact angle was slightly decreased as the NH<sub>2</sub>-GN content increased due to the decrease of the London dispersive component. The electrical conductivity of the NH<sub>2</sub>-GNs-g-PMMA films increased as the NH<sub>2</sub>-GN content increased due to the increase in the number of electron conductive pathways. Additionally, the thermal and mechanical properties of the NH<sub>2</sub>-GNs-g-PMMA films were improved with the addition of NH<sub>2</sub>-GNs. It was found that the NH<sub>2</sub>-GNs were well dispersed in the PMMA matrix and that the grafting of NH<sub>2</sub>-GNs and the PMMA matrix led to an effective reinforcement effect for the NH<sub>2</sub>-GNs.

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### References

1. Yasmin, A.; Luo, J. J.; Daniel, I. M. *Compos. Sci. Tech.* **2006**, *66*, 1182.
2. Kim, S.; Park, S. J. *Anal. Chim. Acta* **2008**, *619*, 43.
3. Freris, I.; Cristofori, D.; Riello, P.; Benedetti, A. *J. Colloid Interface Sci.* **2009**, *331*, 351.
4. Toyoda, M.; Inagaki, M. *Carbon* **2000**, *38*, 199.
5. Hartono, T.; Wang, S.; Mab, Q.; Zhu, Z. *J. Colloid Interface Sci.* **2009**, *334*, 50.
6. Fawn, M. U.; Charles, A. W. *Polym. Degrad. Stab.* **2002**, *76*, 111.
7. Li, J.; Wong, P. S.; Kim, J. K. *Mater. Sci. Eng. A* **2008**, *483-484*, 660.
8. Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. *Compos. Sci. Tech.* **2007**, *67*, 2045.
9. Chen, G.; Wu, C.; Weng, W.; Wu, D.; Yan, W. *Polymer* **2003**, *44*, 1781.
10. Choi, H. J.; Lim, J. Y.; Zhang, K. *Diamond Relate. Mater.* **2008**, *17*, 1498.
11. Yang, B. X.; Shi, J. H.; Pramoda, K. P.; Goh, S. H. *Compos. Sci. Tech.* **2008**, *68*, 2490.
12. Li, S.; Toprak, M. S.; Jo, Y. S.; Dobson, J.; Kim, D. K. *Adv. Mater.* **2007**, *19*, 4347.
13. Gross, S.; Camozzo, D.; Noto, V. D.; Armelao, L.; Tondello, E. *Euro. Polym. J.* **2007**, *43*, 4593.
14. Seo, M. K.; Park, S. J. *Mater. Sci. Eng. A* **2009**, *508*, 28.
15. Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.
16. Kaelble, D. H.; Uy, K. C. *J. Adhesion* **1970**, *2*, 50.
17. Yu, A.; Ramesh, P.; Itkis, M. E.; Bekyarova, E.; Haddon, R. C. *J. Phys. Chem. C* **2007**, *111*, 7565.
18. Martin, C. A.; Sandler, J. K. W.; Shaffer, M. S. P.; Schwarz, M. K.; Bauhofer, W.; Schulte, K.; Windle, A. H. *Compos. Sci. Tech.* **2004**, *64*, 2309.
19. Xiao, M.; Lu, Y.; Wang, S. J.; Zhao, Y. F.; Meng, Y. Z. *J. Power Sources* **2006**, *160*, 165.
20. Mo, Z.; Sun, Y.; Chen, H.; Zhang, P.; Zuo, D.; Liu, Y.; Li, H. *Polymer* **2005**, *46*, 12670.
21. Debelak, B.; Lafdi, K. *Carbon* **2007**, *45*, 1727.
22. Seo, M. K.; Lee, J. R.; Park, S. J. *Mater. Sci. Eng. A* **2005**, *404*, 79.
23. Kim, K. S.; Rhee, K. Y.; Lee, K. H.; Byun, J. H.; Park, S. J. *J. Ind. Eng. Chem.* **2010**, *16*, 572.
24. Zheming, G.; Chunzhong, L.; Gengchao, W.; Ling, Z.; Qilin, C.; Xiaohui, Li.; Windong, W.; Shilei, J. *J. Ind. Eng. Chem.* **2010**, *16*, 10.