

# Graphene and polymer composite using easy soluble expanded graphite

Jong Hak Lee<sup>1</sup>, Xianhui Meng<sup>2</sup>, Dong-Wook Shin<sup>1</sup>, and Ji-Beom Yoo<sup>1,2\*</sup>

<sup>1</sup> Department of Sungkyunkwan Advanced Instituted of Nanotechnology (SAINT),  
Sungkyunkwan University, 300, Chunchun-dong, Jangan-gu, Suwon, 440-746, Korea

<sup>2</sup> Advanced Materials Science and Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon 440746, Republic of Korea

## ABSTRACT

Easy soluble expanded graphite (ESEG) was prepared from a fluorinated graphite intercalation compound (FGIC) -  $C_2F_nClF_3$  containing inorganic volatile intercalating agent  $ClF_3$ . The interlayer distance of ESEG was approximately 17 % higher than that of ordinary graphite. This severe expanded state, together with high specific surface area of the ESEG can give us essential material properties for dispersing easily the ESEG in the solution. ESEG suspension prepared in several organic solvents and water with common surfactants using sonication process was subjected to electron microscopy techniques. This one step exfoliation process of ESEG can allow the low cost mass production of graphene because of the very simple and short process time. In addition, well-dispersed graphene in water and organic solutions have potential use in high-performance, scalable graphene-based applications. We demonstrated that ESEG could be considered as the preferable reinforcing filler in polymer matrices.

**Keywords:** easily soluble expanded graphite, dispersion, mass production, graphene-polymer composite

## 1 INTRODUCTION

Recently, graphene have attracted enormous scientific attention on account of its extraordinary electronic and mechanical properties resulting from one-atom-thick layers and hexagonally arrayed  $sp^2$ -hybridized carbon atom structure<sup>1,2</sup>. There are several examples of graphene layers being used in devices and composites<sup>3,4</sup>. However, graphene suffers from several problems, such as the difficulty in depositing a uniform film onto a substrate. Therefore, a great deal of effort has been made to form a uniform graphene film. Thus far, graphene films have been prepared by a variety of techniques, including “mechanical exfoliation”<sup>5,6</sup>, “graphene in solution”<sup>7,8</sup> and “epitaxial growth”<sup>9,10</sup> methods. “Mechanical exfoliation” produces the highest quality graphene, which is suitable for fundamental studies. “Epitaxial growth” provides the shortest path to graphene-based electronic circuits. On the other hand, “graphene in solution” can offer lower cost and higher throughput for the production of graphene based nanocomposites as well as relatively larger sized films than other methods<sup>11</sup>. However, the method is relatively

complicated and involves a personal-dependant procedures due to the use of several chemicals involving oxidation, funtionalization and reduction processes. Researchers most commonly use Hummer’s method<sup>12</sup> to produce well dispersed graphene oxide (GO) solutions in account of its hydrophilic property. However, the as-prepared graphene oxide is an electrical insulator. Therefore, a chemical reduction to recover its conductivity is necessary. Nevertheless, the reduced GO still exhibits lower conductivity than pristine graphene<sup>11,13</sup>. Some researchers have introduced different re-intercalation and dispersion methods to circumvent the oxidation of graphene<sup>14,15</sup>. Although Xiaolin<sup>14</sup> and others<sup>16</sup> suggested methods for high yield and quality graphene suspensions, their method is quite complicated with a lengthy process time because the process to form a homogeneous suspension without the oxidation of graphene consists of 6~8 steps. Notwithstanding these efforts, the production of stable suspensions of graphene in water or organic solvents is an important goal for the fabrication of graphene based devices. In this study, the expanded graphite was synthesized using a fluorinated graphite intercalation compound in only one step exfoliation comprising a single intercalation and thermal expansion process within 5~6 hours. The expansion state of the easy soluble expanded graphite can allow dispersion in organic solvents or even water by ultrasonication with normal surfactants used for carbon nanotubes (CNT), such as sodium dodecylbenzene sulfonate (SDBS). After the dispersion state examination, we demonstrated that ESEG could be considered as the preferable reinforcing filler in polymer matrices.

## 2 EXPERIMENT

### 2.1 Synthesis of fluorinated graphite intercalation compound (FGIC) - $C_2F_nClF_3$

A Teflon reactor was filled with 30 g of liquid  $ClF_3$  and cooled with liquid nitrogen. Five grams of pure natural graphite (ash content < 0.05 mass %, particle size = 200–300 microns, Zaval’evsk coal field, Ukraine) was then added. The reactor was sealed hermetically, and the temperature was increased slowly to 22°C and kept at that temperature for 5 hours. The excess  $ClF_3$  was removed in a nickel vessel cooled with liquid nitrogen until a constant mass was measured. The intercalation product

(approximately 11 g) had an approximate composition of  $C_2F_0.13ClF_3$ . Elemental analysis data (mass %): C 44.22; F 44.79; Cl 12.49.<sup>17</sup>

## 2.2 Expansion of FGIC

The intercalation compound,  $C_2F_0.13ClF_3$  (~50 mg), was decomposed thermally in a quartz reactor (V~500 ml) heated to 600-700°C. After 4 minutes, the compound was decomposed using a thermal shock process and the ESEG filled the larger volume of the reactor.

## 2.3 Synthesis of graphene-polymer composite

These ESEG were dispersed in 50mL freshly distilled N,Ndimethylacetamide (DMAc). The suspension was ultrasonicated for 1 hour and 2 g of diamine(ODA) 4,4-diaminodiphenylether was added, then magnetically stirred for 1 h. The suspension was transferred into a three-neck round-bottom flask equipped with a mechanical stirrer and filled with nitrogen gas. After stirring, 2.94 g of the dianhydride (s-BPDA) was added. The reaction was kept for 3 h and formed an graphene-poly(amic acid) solution.

A series of graphene-poly(amic acid) solutions with different solid contents was obtained using the same process. In order to obtain graphene-polyimide composite films, the latter were imidized by heating as follows. The graphene-polyamic acid solutions prepared were cast onto glass plates and dried in a dry air-flowing chamber. Subsequently, the dried films were cured at 110, 170, 210, and 250°C for 1 h each in an air-circulating oven to obtain solvent free films. Then, the composite films were imidized at 350°C for 1 h under vacuum and MWNT-polyimide composite films were formed.

## 3 RESULTS AND DISCUSSION

Before characterizing the mechanical properties of the graphene-polyimide composite, the solubility of ESEG in DMAc was examined. The photograph in Fig. 1 (a) shows that the graphene suspension in DMAc was quite stable. A few drops from this solution were collected onto the copper-grids for HRTEM analysis. The central part of the graphene layers was mostly uniform, homogeneous and featureless. However, the folding edges provided a clear indication of the number of graphene sheets (Fig. 1 (b) and (c)). The incident electron beam was locally parallel to the folding edge. Hence, a fold exhibits one dark fringe for each graphene layer. A large number of folding edges were examined and a cluster of 3-6 graphene sheets with a thickness 1~2 nm were observed. The spacing between neighboring fringes was measured to be 3.6~3.9 Å, which is considerably larger than the planes of bulk graphitic layers (3.35 Å).<sup>17</sup> In a previous paper, it was demonstrated that the yield of a few layers of graphene in DMAc was

approximately 93% and the yields of graphene were approximately 23%.<sup>18</sup>

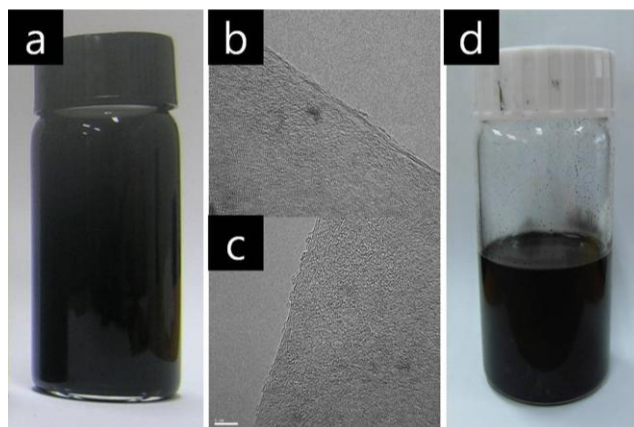


Figure 1: photograph of ESEG suspension in DMAc (a), TEM images of dispersed graphene sheets (b), (c) and photograph of ESEG (0.1 wt%) based polyimide paste (d).

Due to the good stability of graphene-DMAc suspension, graphene-polyimide paste also had the good dispersion state. After film formation, the tensile properties of polyimide and graphene-polyimide nanocomposites were examined. Table 1 is showing the mechanical properties of neat polyimide and graphene-polyimide composites. The enhanced mechanical properties of epoxy nano-composites at low graphene content is reported.<sup>19</sup> At low nano-filler content graphene platelets perform significantly better than carbon nanotubes in terms of enhancing a variety of mechanical properties including tensile strength, Young's modulus, fracture toughness, fracture energy, and resistance to fatigue crack growth.<sup>19</sup> In our study, graphene-polyimide composite had the similar mechanical enhancement at low graphene concentration. As increase the graphene content to 0.05 wt%, the tensile strength was increase from 100kgf/cm<sup>2</sup> to 111.9kgf/cm<sup>2</sup>. However, as graphene content increased further, at the graphene content about 0.1 wt%, tensile strength was decreased to the 89.8kgf/cm<sup>2</sup>. There are several possible reasons for this. At the low graphene content, enhanced specific area of graphene and improved mechanical adhesion of the graphene and matrix interface can make the graphene-polyimide composite has the good enhanced mechanical properties. As increase the reinforcing agent, however, graphene disturb the polymerization process.

Graphene (wt%)	Room temperature tensile strength (kgf/cm <sup>2</sup> )	Elongation at break (%)
0	100	20
0.05	111.9	16.03
0.1	89.8	15.7

Table 1: neat polymer and graphene-polyimide composite mechanical characterization.

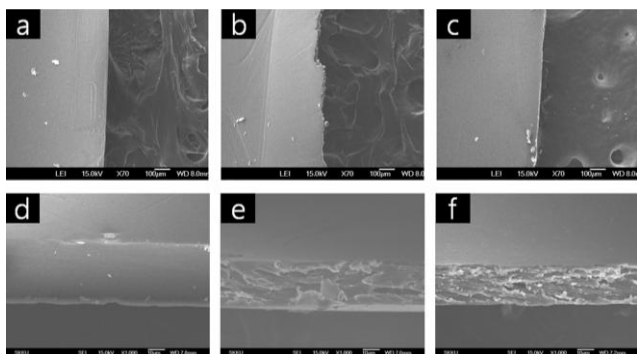


Figure 2: SEM images of the polymer and graphene composite films after fracture examination. neat polyimide (a) and (d), 0.05wt% (b) and (e), 0.1wt% (c) and (f). upper images are plane view and bottom parts are cross-sectional view.

Figure 2 is showing the SEM images of the neat polyimide and graphene-polyimide composite films after fracture experiments. The image of fracture plane could be a vital clue. As increase the graphene content, the fracture plane became more rough (Fig. 2 (b) and (e)). Until the adequate graphene content, graphene can act as a reinforcing agent. However, after adequate graphene content, graphene disturbs the polymerization of polyimide. As a result, the elongation property became poor.

## 4 CONCLUSION

Easy soluble expanded graphite (ESEG) was prepared from a fluorinated graphite intercalation compound (FGIC) -  $C_2F_nClF_3$  containing inorganic volatile intercalating agent  $ClF_3$  was examined as the reinforcing agent. Well-dispersed graphene in DMAc solutions has the good dispersability. We demonstrated that ESEG could be considered as the preferable reinforcing filler in polymer matrices. As increase the graphene content to 0.5wt%, the tensile strength was increased to 12% higher than that of neat polyimide film.

## REFERENCES

- [1] Geim, A. K. & Novoselov, K. S. "The rise of graphene" *Nature Mater.* 6, 183–191 (2007).
- [2] Novoselov, K. S. et al. "Two-dimensional gas of massless Dirac fermions in graphene." *Nature* 438, 197–200 (2005).
- [3] Blake, P. et al. "Graphene-based liquid crystal device." *Nano Lett.* 8, 1704–1708 (2008).
- [4] Dikin, D. A. et al. "Preparation and characterization of graphene oxide paper." *Nature* 448, 457–460 (2007).
- [5] Novoselov, K. S. et al. "Electric field effect in atomically thin carbon films." *Science* 306, 666–669 (2004).

- [6] Novoselov, K. S. et al. "Two-dimensional atomic crystals." *Proc. Natl Acad. Sci. USA* 102, 10451–10453 (2005).
- [7] Li, D., Muller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. "Processable aqueous dispersions of graphene nanosheets." *Nature Nanotech.* 3, 101–105 (2008).
- [8] Stankovich, S. et al. "Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate)." *J. Mater. Chem.* 16, 155–158 (2006).
- [9] Berger, C. et al. "Electronic confinement and coherence in patterned epitaxial graphene." *Science* 312, 1191–1196 (2006).
- [10] Berger, C. et al. "Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphenebased nanoelectronics." *J. Phys. Chem. B* 108, 19912–19916 (2004).
- [11] Goki eda, et al. "Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material." *Nature Nanotech.* 3, 270–274 (2008)
- [12] Hummers, W. S. & Offeman, R. E. "Preparation of graphite oxide." *J. Am. Chem. Soc.* 80, 1339 (1958).
- [13] Stankovich, S. et al. "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide." *Carbon* 45, 1558–1565 (2007).
- [14] Yenny Hernandez, et al. "High-yield production of graphene by liquid-phase exfoliation of graphite." *Nature Nanotech.* 3, 563–568 (2008)
- [15] Xiaolin li, et al. "Highly conducting graphene sheets and Langmuir Blodgett films." *Nature Nanotech.* 3, 538–542 (2008)
- [16] Mohammad Choucair, et al. "Gram-scale production of graphene based on solvothermal synthesis and sonication." *Nature Nanotech.* 4, 30–33 (2009)
- [17] Lee JH, Shin DW, Makotchenko VG, Nazarov AS, Fedorov VE, Kim YH, et al. "One step exfoliation synthesis of easily soluble graphite and transparent conducting graphene sheet" *Adv. Mater.* 21, 4384–4387 (2009)
- [18] Lee JH, Shin DW, Makotchenko VG, Nazarov AS, Fedorov VE, Yoo JB. "Superior dispersion property of easily soluble graphite." *Small*, 1, 58–62 (2010)
- [19] Mohammad A. Rafiee, Javad Rafiee, Zhou Wang, Huaihe Song, Zhong-Zhen Yu, and Nikhil Koratkar. "Enhanced mechanical properties of nano composites at low graphene content" *ACS Nano*, 3, 3884–3890 (2009)