ELECTRICAL AND MECHANICAL PROPERTIES OF POLYURETHANE NANOCOMPOSITES CONTAINING SELF-ALIGNED GRAPHENE SHEETS

M. M. GUDARZI, S. H. ABOUTALEBI, Q. B. ZHENG and J.-K. KIM*

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
* Corresponding author(mejkkim@ust.hk)

Keywords*:* Graphene, Polyurethane, Electrical and mechanical properties, Self-aligned

Graphene has emerged as a new class of material in materials science communities in the past few years [1-4]. Discovering excellent properties of graphene and the introduction of new methods to prepare graphene have resulted in significant progress in finding numerous new applications [2-4]. Exploring new methods for mass production of monolayer carbon sheet has made it possible to formulate graphene-based materials [5-6]. Being one of the thinnest and strongest materials with exceptionally high electron mobility and heat conductivity, graphene makes an excellent filler to hybridize with other matrix materials to form composites possessing unique properties [7]. As such, graphene oxide and reduced graphene sheets have attracted significant attention as filler for polymer nanocomposites that are finding diverse applications [8-10]. However, the production of high performance and cost-effective polymer-graphene composites is still a challenge mainly because of the difficulties associated with exfoliation of graphite flakes into mono- or few-layer graphene sheets and uniform dispersion of graphene into polymers [7-10]. Although a remarkable progress has been made in the production of chemically derived graphene sheets [5-6], the incorporation of graphene into polymeric media with fine dispersion and acceptable interfacial bonding is not straightforward [9-10]. Therefore, simple, effective and environment-friendly methods for the production of polymer-graphene composites are in need of development.

In this study, GO was synthesized based on the modified chemical method [6] using expanded graphite (supplied by Asbury Graphite Mills, US). The obtained GO particles were diluted using DI water (~1 mg/ml) and sonicated for 20 min in a bath sonicator, followed by probe sonication for 10 min. The GO dispersion was mixed with aqueous emulsion of polyurethane (PU, Neorez R967 supplied by DSM NeoResin) to obtain a homogeneous aqueous dispersion. Hydrazine solution was added in the ratio of 3:1 to obtain reduced GO (rGO), which was then heat-treated at 80˚C for 24 hr. The mixture was poured into a flat mold and dried in an oven at 50˚C for 6 hr to produce composite films.

Fig. 1 shows the SEM images of the cross-sectional fracture surface of graphene-PU composites. Graphene layers are seen as micrometer long nanosheets embedded in the polymer matrix. We can assume they are uniformly dispersed and there is no sign of aggregation, nor debonding between the graphene and the matrix, judging from the fact that no graphene sheet is directly exposed on the fracture surface. This observation indicates a strong interfacial bond between the composite constituents, which can be attributed to the molecular interaction of polar segments of PU matrix with oxygen groups present on the

graphene sheets. Fine and uniform dispersion of graphene sheets and strong interfacial interaction are two major factors governing the fabrication of strong and tough nanocomposites. In contrast to CNT-polymer composites in which complicated functionalization processes are required for CNTs to maintain good dispersion and interfacial interactions with polymer, a naturally strong interfacial bond was achieved by taking advantage of the presence of polar groups in the chemical structures of both graphene reinforcements and PU matrix.

More interestingly, the examination of the fracture surfaces of composites with high graphene contents over 2wt% revealed significant orientation of graphene sheets, as shown in Fig. 2**.** As graphene concentration approached about 2wt%, graphene layers tended to self-adjust their basal plane perpendicular to the film thickness, resulting in partial alignment of the graphene layers (Fig. 2a, b). Highly aligned graphene layers in the PU matrix were observed at a graphene content of 5wt% (Fig. 2c, d), indicating self-alignment of graphene sheets taking place during the evaporation of water without any external forces.

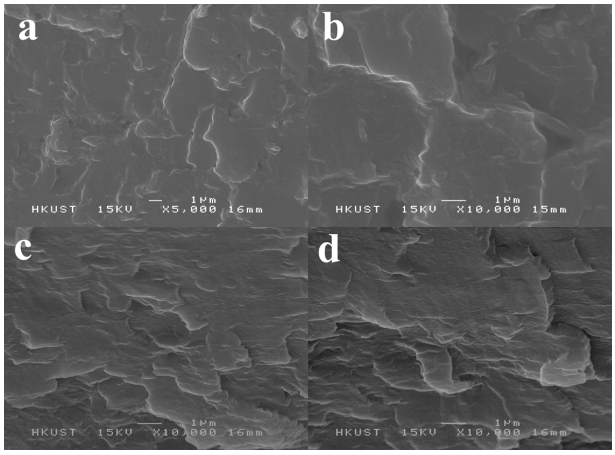

Fig. 1. SEM images of freeze fracture surface of PU nanocomposites containing a,b) 0.5wt% and c,d) 1.0wt% graphene.

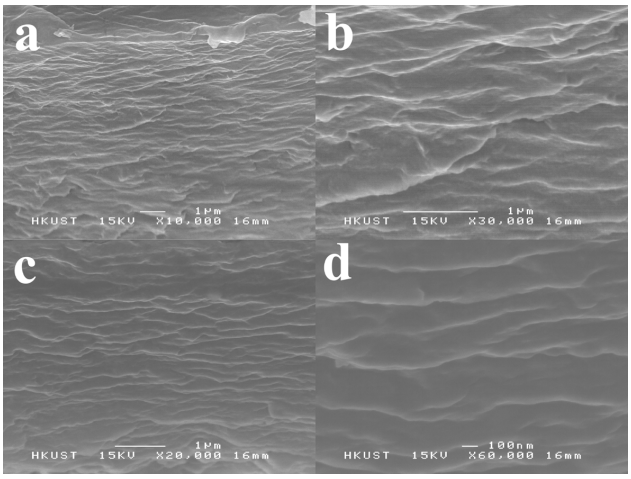

Fig. 2. SEM images of freeze fracture surface of PU nanocomposites containing a,b) 2wt% and c,d) 5wt% graphene.

Fig. 3 depicts the electrical conductivity of PU-rGO composites plotted as a function of graphene content. The electrical conductivity increased exponentially at low graphene contents, followed by a slow growth at high contents. Due to the uniform dispersion of monolayer graphene sheets in the PU matrix, the electrical conductivity rapidly increased by almost 7 orders of magnitude when a very low 0.5wt% graphene was added. A further increase in graphene content beyond 2wt% resulted in a rather saturated conductivity. Nevertheless, an electrical conductivity of 0.09 S/m corresponding to a conducting filler content of 2-5wt% is considered to be sufficient for many applications, such as conductive adhesives and composites for electrostatic and electromagnetic interference shielding.

The percolation threshold, ρ_c , was calculated based on the power law equation:

$$\phi_c = \phi_f (\rho - \rho_c)^n \qquad (1)$$

where ϕ_c is the conductivity of composite, ϕ_f is the filler conductivity, and ρ is the filler content. The inset of Fig. 3 shows the log-log plot of the equation, giving the percolation threshold of ρ_c = 0.16wt%. Taking densities of PU and graphene as 1.05 and 2.2g/cm^3, respectively, a

percolation threshold of about 0.078 vol% was obtained. To the best of the authors' knowledge, this value is the lowest value for homogenous polymer-graphene composites reported in open literature.

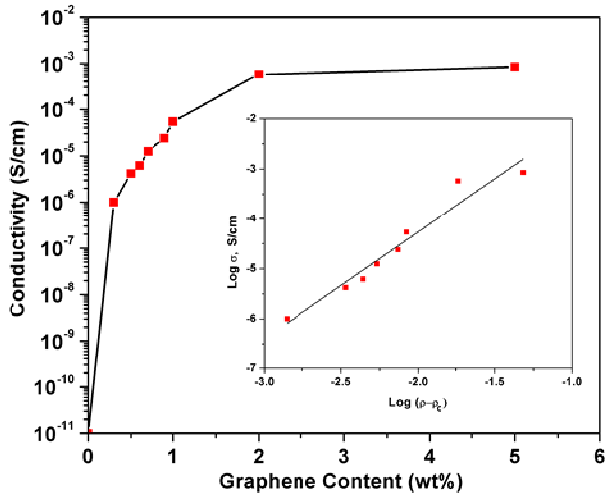

Fig. 3. Electrical conductivity (σ) of PU composite as a function of graphene content (ρ).

The nanoindentation and tensile tests were performed to evaluate the mechanical properties of composites. The elastic modulus and hardness values measured from the unloading curves of nanoindentation are shown in Fig. 4. The modulus and hardness of composites monotonically increased as graphene content increased, partly confirming the presence of well dispersed, aligned graphene sheets in the composite. These observations are in sharp contrast with the recent report in that the Young's modulus and tensile strength of epoxy/graphene composites peaked at only 0.125wt% of graphene with about 50% and 45% improvements, respectively, followed by gradual reductions in these properties with further increase in graphene content. The monotonic increases in mechanical properties without showing saturation in this study are attributed to increasingly better alignment of graphene sheets in the PU matrix. It is worth noting that the incorporation of 5wt% of graphene increased the modulus and hardness of nanocomposites by approximately 1200% and 300%, respectively. These values are even much higher than the previous reports on similar graphene-PU composites containing 4.4wt% GO produced by solution mixing, where 182 and 326% improvements in modulus and hardness, respectively, were recorded.

The above nanoindentation test results are further confirmed by tensile properties. Fig. 5 shows typical tensile stress-strain curves as well as the corresponding tensile moduli and strengths of neat PU and PU-rGO nanocomposites obtained from the tensile DMA tests. Addition of small amounts of graphene controlled the tensile properties of PU: on one hand, incorporation of merely 0.3wt% into PU matrix resulted in 110 and 390% increases in tensile modulus and strength, respectively, while still sustaining the high deformability of the matrix; on the other hand, remarkable 21-fold and 14-fold increases in these tensile properties were achieved with the addition of 3wt% of graphene. Similar to the nanoindentation test results, consistent enhancements in tensile modulus and strength were noted at the expense of ductility or failure strain as the graphene content increased. Such remarkable improvements in tensile modulus and strength of PU composites are attributed to three interrelated factors, namely i) fine exfoliation of graphite nanoplatelets into ultra-large size, monolayer graphene sheets with high aspect ratios; ii) self-alignment of individual graphene sheets when the graphene content is above a threshold value; and iii) strong interfacial interaction between the graphene sheets and PU matrix.

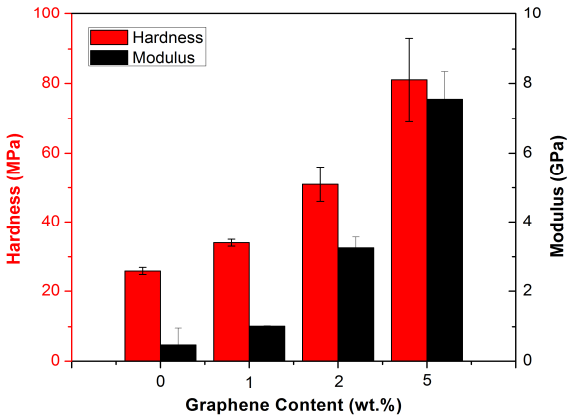

Fig. 4. Nanoindentation test results for PU-rGO composites as function of graphene content.

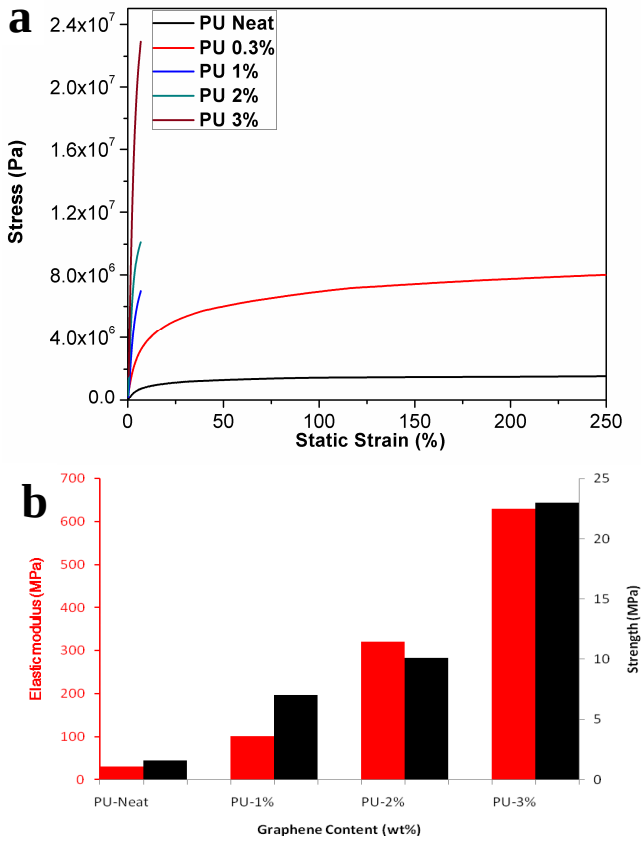

Fig. 5. (a) Typical stress-strain curves and (b) mechanical properties of PU-rGO composites as a function of graphene content. (Change X-axis title from Static strain to Strain (%).

Fig. 6 presents comparisons of the reinforcing efficiency coefficients between the present work and the literature data. It is worth noting that the literature data had consistently very low efficiency coefficients for both modulus and strength, suggesting that the GO in general contributed little to improvement of these mechanical properties in the previous studies. The negative efficiency coefficients, η_2, or reduction of tensile strength shown by the majority of these studies may indicate that the GO sheets were present as multi-layer graphite nanoplatelets without full exfoliation and/or their dispersion was not fine enough to ensure efficient stress transfer through the graphene-matrix interface. In sharp contrast, the current study presented consistently much higher efficiency coefficients than the previous studies: the efficiency coefficient for modulus, η_1, exhibited remarkable values in the range of 6~16%, whereas the efficiency coefficient for strength, η_2, always had positive values around 1%. These values are an order of magnitude greater than the corresponding values found in the previous studies. Another important conclusion drawn from the current study shown in Fig. 6 is that the efficiency coefficients were in general higher for modulus than strength by an order of magnitude, confirming the above observation that the modulus of the polymer can be more easily enhanced using GO sheets than strength as in nanocomposites containing other types of nanoscale fillers.

In summary, a new method based on latex mixing was developed to produce graphene sheet reinforced polymer matrix composites, where polyurethane colloids are mixed with graphene oxide dispersion in water. It was demonstrated that the adsorption of polymer particles onto the surface of graphene oxide was the underlying mechanism behind the stabilized graphene sheets. The morphological examination using the SEM revealed self-alignment of graphene sheets in the PU matrix

when the graphene content was above about 2 wt%, mimicking the microstructure of naturally occurring nacre shells. In addition to the gravitational forces, the "excluded volume" model was used to explain the orientation behavior of graphene sheets of extremely high aspect ratio (>10000) in an aqueous medium. The nanocomposite containing highly-oriented graphene sheets with strong bonding with the PU matrix exhibited excellent mechanical properties: remarkable 21-fold and 14-fold increases in the tensile modulus and strength, respectively, were achieved by the addition of 3wt% of graphene. The experimental tensile moduli were favorably compared with the existing theoretical models for composites containing ellipsoides with random and perfect orientations. The comparative study further confirmed our finding of increasing degree of alignment with increasing the graphene content. The composites also showed excellent electrical conductivity with an exceptionally low percolation threshold of 0.078 vol%, which is one of the lowest values for polymers containing graphene reported in the literature.

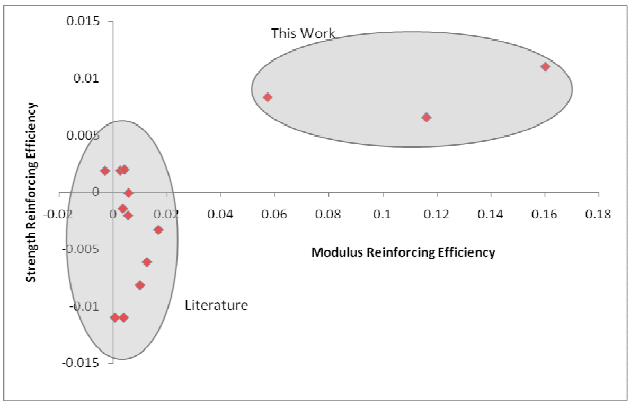

Fig. 6. Comparisons of modulus and strength reinforcing efficiency coefficients of PU-rGO composites containing 3wt% graphene taken from literature data and those with 1-3wt% measured in this work.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov "Electric field in atomically thin carbon films". *Science*, Vol. 306, No. 5696, pp 666-669, 2004.

[2] C. N. Rao, A. K. Sood, K.S. Subrahmanyam, A Govindaraj. "Graphene: The new two-dimensional nanomaterial". *Angewandte Chemie - International Edition*, Vol. 48, No. 42, pp 7752-7777, 2009.

[3] A. K. Geim. "Graphene: Status and prospects". *Science*, Vol. 324, No. 5934, pp 1530-1534, 2009.

[4] C. Soldano, A. Mahmood, and E. Dujardin. "Production, properties and potential of graphene". *Carbon*, Vol. 48, No. 8, pp 2127-2150, 2010.

[5] D. R. Dreyer, S Park, C. W. Bielawski, and R. S. Ruoff "The chemistry of graphene oxide". *Chemical Society reviews*, Vol 39, No. 1, pp 228-240, 2010.

[6] Y. Geng, S. J. Wang, J. K. Kim "Preparation of Graphite Nanoplatelets and Graphene Sheets" J Colloid Interface Sci. Vol 336, No. 2, pp 592-598, 2009.

[7] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff. Graphene-based composite materials. *Nature*, Vol. 442, No. 7100, pp 282-286, 2006.

[8] T. Ramanathan, A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-Alonso, R. D. Piner, D. H. Adamson, H. C. Schniepp, X. Chen, R. S. Ruoff, S. T. Nguyen, I. A. Aksay, R. K. Prud'Homme and L. C. Brinson "Functionalized graphene sheets for polymer nanocomposites". *Nature Nanotechnology*, Vol 3, pp 327-331, 2008.

[9] H. Kim, A. Abdala, and C. Macosko "Graphene/Polymer Nanocomposites". *Macromolecules*, Vol. 43, No. 16, pp 6515-6530, 2010.

[10] D. Cai and M. Song "Recent advance in functionalized graphene/polymer nanocomposites". Journal of Materials Chemistry, Vol. 20, No. 37, pp. 7906-79150, 2010.