TAILORING OF ELECTRO-MECHANICAL PROPERTIES OF GRAPHENE REINFORCED TEMPLATED COMPOSITES

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Abstract

A capillary-driven particle level templating technique was utilized to disperse graphite nanoplatelets (GNPs) within a polystyrene matrix to form multi-functional composites that possess tailored electro-mechanical properties. Utilizing capillary interactions, highly segregated composites were formed via a melt processing procedure. Since the graphene particles only resided at the boundary between the polymer matrix particles, the composites possess tremendous electrical conductivity but poor mechanical strength. To improve the mechanical properties of the composite, the graphene networks in the specimen were deformed by shear. An experimental investigation was conducted to understand the effect of graphene content as well as shearing on the mechanical strength and electrical conductivity of the composites. The experimental results show that both the mechanical and electrical properties of the composites can be altered using this very simple technique and therefore easily be intelligently optimized for desired applications.

1. Introduction

Polymer nanocomposites, in particular, have attracted significant attention in the past decades with the belief that they could become the next generation high performance materials with multifunctional capabilities [1-12]. Significant research has shown that, in particular, carbon-based nanocomposites have proven to demonstrate remarkable physical and mechanical properties by incorporating very small amounts of filler material [13-18]. The extraordinary mechanical and physical properties of graphene make it a very attractive filler material for the next generation of smart materials [13, 14]. Along with the aspect ratio and the surface-to-volume ratio, the distribution of the filler in a polymer matrix has been shown to directly correlate with its effectiveness in improving material properties such as mechanical strength, electrical and thermal conductivity, and impermeability [19]. Although significant research has been performed to develop strategies to effectively incorporate nanofillers into polymers, our ability to control the dispersion and location of graphene-based fillers to fully exploit their intrinsic properties remains a challenge [20-23].

One promising method to exploit certain properties of graphene is to create segregated composites, where the conductive particles within the composite are specially localized on the surfaces of the polymer matrix particles. When consolidated into a monolith, these conductive particles form a percolating three-dimensional network that dramatically increases the conductivity of the composite [24-29]. Sheets do not have to be distributed isotropically throughout a matrix to achieve percolation, overcoming a major limitation. These studies revealed that highly conductive composites can be created when graphene is segregated into organized networks throughout a matrix material. Although the highly segregated networks provide excellent transport properties throughout the composite, they inevitably result in poor mechanical strength, since fracture can occur easily in the continuous segregated graphene phase. Since most multi-functional materials are required to provide excellent transport properties while maintaining sufficient mechanical strength, alternative methods of distributing graphene need to be developed.

Despite recent progresses on the electrical characterization of graphene-based segregated composites, no results have been published yet regarding the combined electro-mechanical behavior of these highly conductive materials. In this work, a novel capillary-driven, particle-level templating technique was utilized to distribute graphite nanoplatelets into specially constructed architectures throughout a PS matrix to form multi-functional composites with tailored electro-mechanical properties. By precisely controlling the temperature and pressure during a melt compression process, highly conductive composites were formed using very low loadings of graphene particles. To improve the mechanical properties, a new processing technique was developed that uses rotary shear during the compression molding process to gradually evolve the honeycomb graphene network into a concentric band structure. Two types of composites, organized and shear-modified, were produced to demonstrate the electro-mechanical tailoring of the composite material. An experimental investigation was conducted to understand the effect of graphene content as well as shearing on the mechanical strength and electrical conductivity of the composites.

2. Material and Specimen

2.1. Material

The graphite nanoplatelets used in this study were xGnP™ Nanoplatelets (XG Sciences, USA). These nanoparticles consist of short stacks of graphene layers having a lateral dimension of ~ 25 µm and a thickness of ~ 6 nm. The polymeric material chosen for this study was polystyrene (Crystal PS 1300, average molecular weight of 121,000 g/mol) purchased from Styrolution, USA. The PS pellets (~ 2 mm) used were elliptical prisms with a total surface area of 1.03 ± 0.01 cm^2.

2.2. Specimen

Two types of composites, organized and shear-modified, were produced to demonstrate the electro-mechanical tailoring of the composite material. A two-step process was utilized to produce the GNP/PS segregated composites [31]. For composites consisting of less than 0.2 % v/v, the desired amount of graphene platelets were measured and added directly to 7 g of dry PS pellets. The GNP spontaneously adheres to the dry polymer particles by physical forces, which may be van der Waals forces or electrostatic attraction associated with surface charges. This coating process works well for GNP loadings below 0.2 % v/v. However, at higher GNP loadings, this dry method leaves behind excess GNP because the charge on the pellets is neutralized after the initial coating.

To provide a means of temporarily attaching larger quantities of the GNP to the surface of the PS, an additional step is implemented during the fabrication procedure as shown in Figure 1. For GNP loadings greater than 0.2 % v/v, the PS is first soaked in a methanol bath. The excess methanol is drained from the PS pellets. GNP is added, and the mixture is then shaken vigorously, creating a dense coating of graphene on each PS pellet. The methanol temporarily moistens the polymer pellets forming small liquid bridges. The capillary pressure created through these bridges allows the GNP to stick easily to the surface of the pellets. During the subsequent hot melt pressing, the temperature and mold pressure are precisely controlled allowing the pellets to be consolidated into a monolith while maintaining boundaries. In our experiments, a stainless steel mold consisting of a lower base and a plunger was heated to 125 ºC. The graphene coated PS was placed inside the cavity of the lower base and the plunger was placed on top. The temperature of both the plunger and the base mold was maintained for 20 min at which point it was hot-pressed at 45 kN using a hydraulic press. By precisely controlling the temperature and pressure during the melt compression process, highly conductive composites were formed using very low loadings of graphene particles.

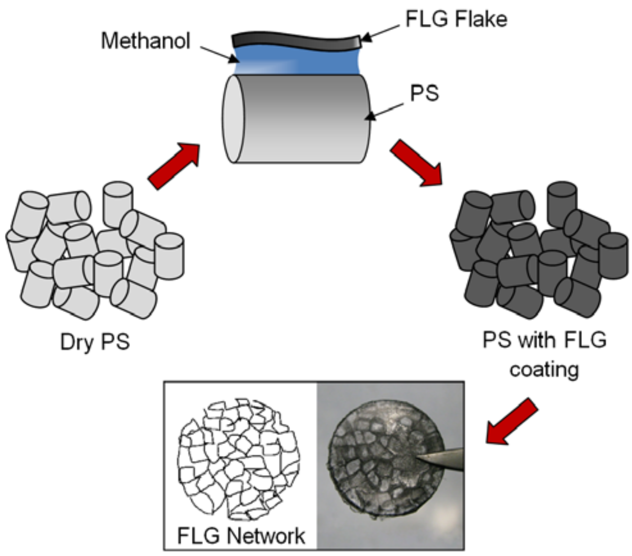

Figure 1. Surface wetting fabrication procedure to obtain highly conductive GNP/PS composites.

Modified particle templated composites were fabricated by incorporating a shearing technique during the melt compression process. Following the same coating process as discussed earlier, the graphene coated pellets were placed inside a modified steel mold, which was equipped with guide pins to ensure that the base remained stationary. The plunger was then placed on top of the material and heated to 160 ºC while the lower base mold was heated to 125 ºC and maintained for 20 min. Next, 45 MPa was applied to the plunger and then rotated to various predetermined angles. All shear-modified composites were fabricated with 0.3 % v/v graphene platelets. By applying such a shear force to the top surface of the material, a gradient of graphene organization/orientation along the sample axis is formed which results in a composite possessing unique properties. A schematic of the compression molding process used to produce both types of segregated composites is shown in Figure 2.

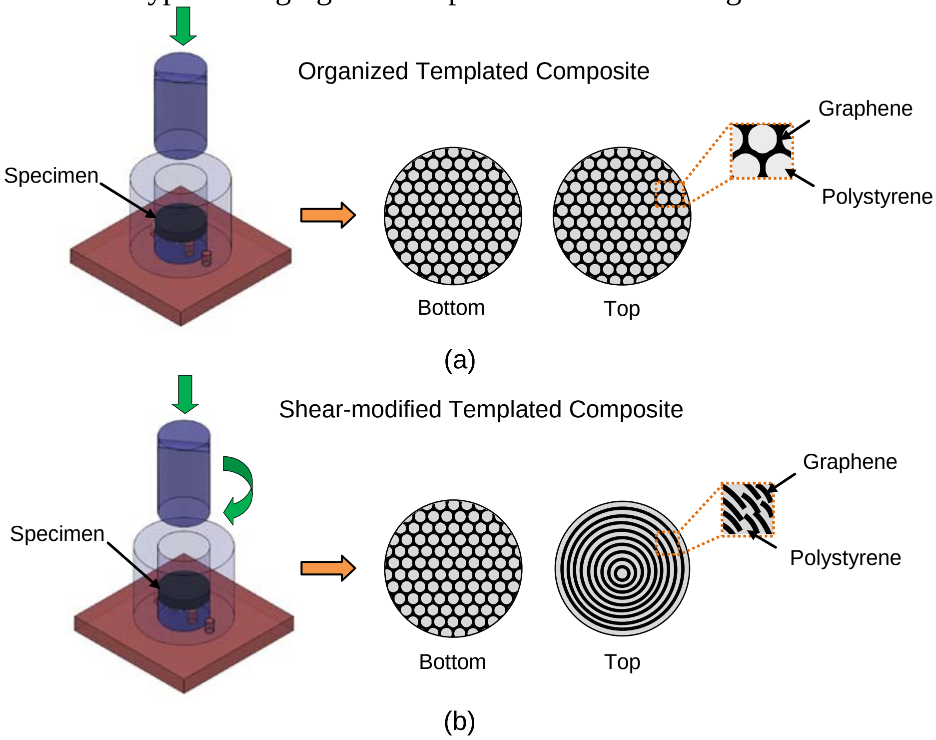

Figure 2. Schematic of compression molding process to produce (a) organized templated composites and (b) shear-modified templated composites

3. Experimental Procedures

3.1 Electrical Characterization

Electrical conductivity measurements were made on the GNP/PS composites using a volumetric two-point probe measurement technique. The bulk electrical conductivity was measured across the thickness of the sample (perpendicular to pressing). The resistance of the material was experimentally determined by supplying a constant current through the specimen while simultaneously measuring the voltage drop across the specimen. A constant current source was used to supply the DC current while two electrometers were used to measure the voltage drop. The difference between the two voltage readings was measured using a digital multimeter.

3.2 Mechanical Characterization

A screw-driven testing machine was implemented to load the specimens in a three point bending configuration. Specimens were cut into 5 x 6 x 38 mm rectangular prisms. A support span of 30 mm was used and the loading was applied at a rate of 0.1 mm/min.

4. Experimental Results & Discussion

Figure 3 shows the electrical conductivity as a function of graphene loading. A significant enhancement in electrical conductivity is demonstrated when 0.01 % v/v GNP was added to the PS. Since the boundaries located between the pellets are maintained, the graphene particles become interconnected throughout the material thus causing a significant increase in conductivity while using very low loadings of graphene. The capillary driven coating process enables more graphene to completely coat the surface of the PS which in turn increases the electrical conductivity of the composite approximately 4-5 orders of magnitude from 0.01 to 0.3 % v/v.

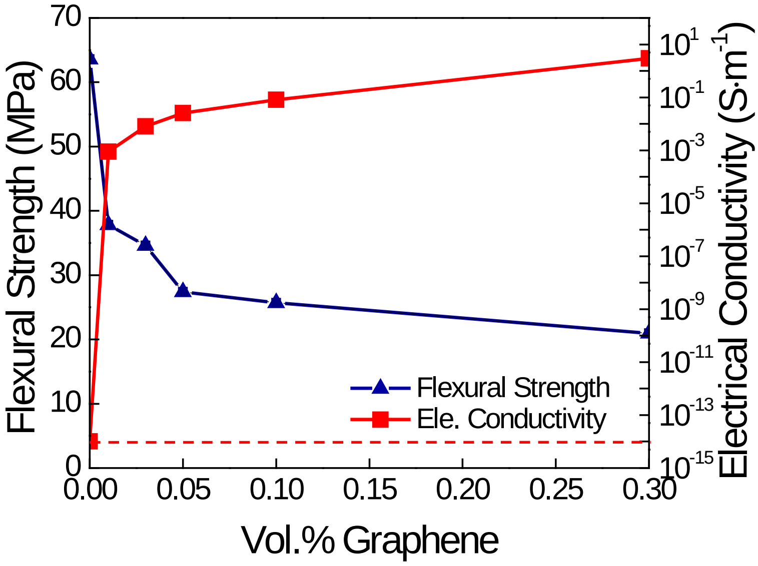

Figure 3. Electro-mechanical behavior of GNP-PS organized particle templated composites loaded parallel to pressing.

Figure 4 shows the electro-mechanical behavior of the shear-modified GNP/PS composites as a function of shear rotation. The capillary driven coating process enabled an increase in electrical conductivity of the composite by approximately 14-15 orders of magnitude as compared to the pristine PS, owing to the dense coating of GNP on the PS pellets. By applying a shear force to the top surface of the highly segregated material, a gradient of graphene organization/orientation along the sample axis is formed which results in a 600 % increase in flexural strength while only sacrificing ~ 1-2 orders of magnitude of conductivity. The effect of shear rotation on the electro-mechanical properties of the shear-modified GNP/PS composites was also investigated.

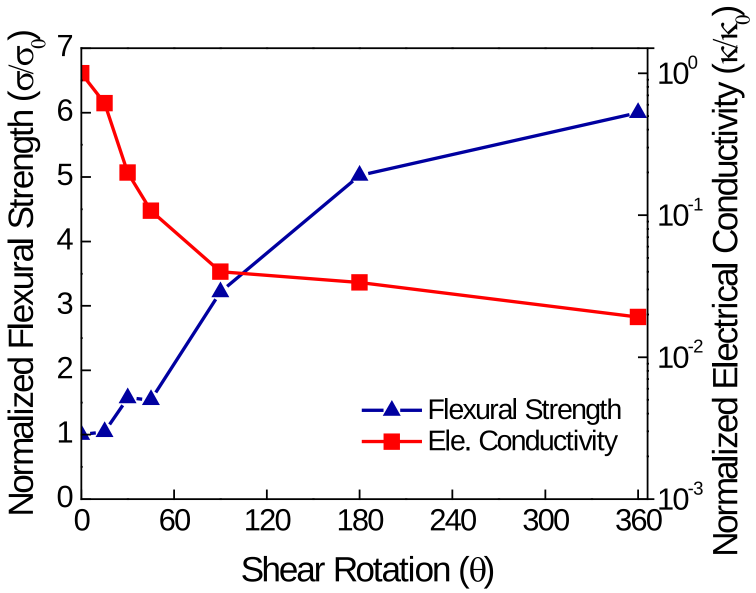

Figure 4. Electro-mechanical behavior of the shear-modified FLG-PS particle templated composites loaded parallel to pressing.

5. Summary

We demonstrate a simple, inexpensive and commercially viable technique that can be used to disperse conductive sheet-like particles, such as graphene, into specially constructed architectures throughout a polymeric material to form multi-functional composites with tailored electro-mechanical properties. Utilizing capillary interactions between polymeric particles and graphite nanoplatelets, liquid bridges on the surface of a polymeric material allows for coating of graphene onto the polymer surfaces. Following a melt compression process, highly conductive composites were formed using very low loadings of graphene particles. Since the graphene particles resided at the boundary between the polymer matrix particles, the composite exhibited poor mechanical strength. To improve the mechanical properties of the composite, a shear force was applied to the top surface of the material which created a gradient of graphene organization/orientation along the sample axis. Results showed that this novel fabrication technique can produce composite materials that possess both excellent transport properties and improved mechanical strength.

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References

[1] P. M. Ajayan and J. M. Tour. Materials Science: Nanotube composites. *Nature*, 447(7148):1066, 2007.

[2] S. M. Cardoso, V. B. Chalivendra, A. Shukla and S. Yang. Damage detection of rubber toughened nanocomposites in the fracture process zone using carbon nanotubes. *Engineering Fracture Mechanics*, 96:380-391, 2012.

[3] F. d. C. Fim, J. M. Guterres, N. R. S. Basso and G. B. Galland. Polyethylene/graphite nanocomposites obtained by in situ polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, 48(3):692-698, 2009.

[4] N. Heeder, A. Shukla, V. Chalivendra and S. Yang. Sensitivity and dynamic electrical response of CNT-reinforced nanocomposites. *Journal of Materials Science*, 47(8):3808-3816, 2012.

[5] N. J. Heeder, A. Shukla, V. Chalivendra, S. Yang and K. Park. Electrical Response of Carbon Nanotube Reinforced Nanocomposites Under Static and Dynamic Loading. *Experimental Mechanics*, 52(3):315-322, 2012.

[6] J. Li, J.-K. Kim and M. Lung Sham. Conductive graphite nanoplatelet/epoxy nanocomposites: Effects of exfoliation and UV/ozone treatment of graphite. *Scripta Materialia*, 53(2):235-240, 2005.

[7] K. P. Pramoda, H. Hussain, H. M. Koh, H. R. Tan and C. B. He. Covalent bonded polymer–graphene nanocomposites. *Journal of Polymer Science Part A: Polymer Chemistry*, 48(19):4262-4267, 2010.

[8] V. K. Vadlamani, V. Chalivendra, A. Shukla and S. Yang. In situ sensing of non-linear deformation and damage in epoxy particulate composites. *Smart Materials and Structures*, 21(7), 2012.

[9] V. K. Vadlamani, V. B. Chalivendra, A. Shukla and S. Yang. Sensing of damage in carbon nanotubes and carbon black-embedded epoxy under tensile loading. *Polymer Composites*, 33(10):1809-1815, 2012.

[10] R. Verdejo, M. M. Bernal, L. J. Romasanta and M. A. Lopez-Manchado. Graphene filled polymer nanocomposites. *Journal of Materials Chemistry*, 21(10):3301-3310, 2010.

[11] L. M. Viculis, J. J. Mack, O. M. Mayer, H. T. Hahn and R. B. Kaner. Intercalation and exfoliation routes to graphite nanoplatelets. *Journal of Materials Chemistry*, 15(9):974-978, 2005.

[12] L. Wang, J. Hong and G. Chen. Comparison study of graphite nanosheets and carbon black as fillers for high density polyethylene. *Polymer Engineering & Science*, 50(11):2176-2181, 2010.

[13] M. H. Chakrabarti, C. T. J. Low, N. P. Brandon, V. Yufit, M. A. Hashim, M. F. Irfan, J. Akhtar, E. Ruiz-Trejo and M. A. Hussain. Progress in the electrochemical modification of graphene-based materials and their applications. *Electrochimica Acta*, 107:425-440, 2013.

[14] X. Huang, X. Qi, F. Boey and H. Zhang. Graphene-based composites. *Chemical Society Reviews*, 41(2):666-686, 2011.

[15] H. Kim, A. A. Abdala and C. W. Macosko. Graphene/Polymer Nanocomposites. *Macromolecules*, 43(16):6515-6530, 2010.

[16] B. Li and W.-H. Zhong. Review on polymer/graphite nanoplatelet nanocomposites. *Journal of Materials Science*, 46(17):5595-5614, 2011.

[17] J. R. Potts, D. R. Dreyer, C. W. Bielawski and R. S. Ruoff. Graphene-based polymer nanocomposites. *Polymer*, 52(1):5-25, 2011.

[18] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker and S. Seal. Graphene based materials: Past, present and future. *Progress in Materials Science*, 56(8):1178-1271, 2011.

[19] 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*, 442(7100):282-286, 2006.

[20] M. Herrera-Alonso, A. A. Abdala, M. J. McAllister, I. A. Aksay and R. K. Prud'homme. Intercalation and Stitching of Graphite Oxide with Diaminoalkanes. *Langmuir*, 23(21):10644-10649, 2007.
[21] J. I. Paredes, S. Villar-Rodil, A. MartiÌ□nez -Alonso and J. M. D. TascoÌ□N. Graphene Oxide Dispersions in Organic Solvents. *Langmuir*, 24(19):10560-10564, 2008.
[22] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 45(7):1558-1565, 2007.
[23] S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen and R. S. Ruoff. Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). *Journal of Materials Chemistry*, 16(2):155-158, 2006.
[24] J. Du, L. Zhao, Y. Zeng, L. Zhang, F. Li, P. Liu and C. Liu. Comparison of electrical properties between multi-walled carbon nanotube and graphene nanosheet/high density polyethylene composites with a segregated network structure. *Carbon*, 49(4):1094-1100, 2011.
[25] N. Heeder, A. Yussuf, F. Guo, I. Chakraborty, M. Godfrin, R. Hurt, A. Tripathi, A. Bose and A. Shukla. Highly conductive graphene-based segregated composites prepared by particle templating. *Journal of Materials Science*, 49(6):2567-2570, 2013.
[26] H. Hu, G. Zhang, L. Xiao, H. Wang, Q. Zhang and Z. Zhao. Preparation and electrical conductivity of graphene/ultrahigh molecular weight polyethylene composites with a segregated structure. *Carbon*, 50(12):4596-4599, 2012.
[27] Y. Mamunya. Carbon Nanotubes-Polymer Nanocomposites, D. S. Yellampalli, Carbon Nanotubes-Polymer Nanocomposites, pages 173-196. InTech, Rijeka, 2011.
[28] H. Pang, Y. Bao, J. Lei, J.-H. Tang, X. Ji, W.-Q. Zhang and C. Chen. Segregated Conductive Ultrahigh-Molecular-Weight Polyethylene Composites Containing High-Density Polyethylene as Carrier Polymer of Graphene Nanosheets. *Polymer-Plastics Technology and Engineering*, 51(14):1483-1486, 2012.
[29] B. Wang, H. Li, L. Li, P. Chen, Z. Wang and Q. Gu. Electrostatic adsorption method for preparing electrically conducting ultrahigh molecular weight polyethylene/graphene nanosheets composites with a segregated network. *Composites Science and Technology*, 89:180-185, 2013.