

Homogeneous Liquid Phase Transfer of Graphene Oxide into Epoxy Resins

Amirova L., Surnova A., Balkaev D., Musin D., Amirov R., Dimiev A.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2017 American Chemical Society. The quality of polymer composite materials depends on the distribution of the filler in the polymer matrix. Due to the presence of the oxygen functional groups, graphene oxide (GO) has a strong affinity to epoxy resins, providing potential opportunity for the uniform distribution of GO sheets in the matrix. Another advantage of GO over its nonoxidized counterpart is its ability to exfoliate to single-atomic-layer sheets in water and in some organic solvents. However, these advantages of GO have not yet been fully realized due to the lack of the methods efficiently introducing GO into the epoxy resin. Here we develop a novel homogeneous liquid phase transfer method that affords uniform distribution, and fully exfoliated condition of GO in the polymer matrix. The most pronounced alteration of properties of the cured composites is registered at the 0.10%-0.15% GO content. Addition of as little as 0.10% GO leads to the increase of the Young's modulus by 48%. Moreover, we demonstrate successful introduction of GO into the epoxy matrix containing an active diluent-modifier; this opens new venues for fabrication of improved GO-epoxy-modifier composites with a broad range of predesigned properties. The experiments done on reproducing the two literature methods, using alternative GO introduction techniques, lead to either decrease or insignificant increase of the Young's modulus of the resulting GO-epoxy composites.

<http://dx.doi.org/10.1021/acsmi.7b02243>

Keywords

epoxy resin, graphene oxide, phase transfer, polymer composite, viscosity

References

- [1] Ajayan, P. M.; Tour, J. M. Materials Science: Nanotube Composites Nature 2007, 447, 1066-1068 10.1038/4471066a
- [2] Potts, J. R.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S. Graphene-Based Polymer Nanocomposites Polymer 2011, 52, 5-25 10.1016/j.polymer.2010.11.042
- [3] Gudarzi, M. M.; Aboutalebi, S. H.; Sharif, F. In Graphene Oxide: Fundamentals and Applications; Dimiev, A. M.; Eigler, S., Eds.; Wiley: London, 2017; Chapter 10, pp 314-365.
- [4] Spitalsky, Z.; Tasis, D.; Papagelis, K.; Galiotis, C. Carbon Nanotube-Polymer Composites: Chemistry, Processing, Mechanical and Electrical Properties Prog. Polym. Sci. 2010, 35, 357-401 10.1016/j.progpolymsci.2009.09.003
- [5] Dimiev, A. M.; Zakhidov, D.; Genorio, B.; Oladimeji, K.; Crowgey, B.; Rothwell, E.; Kempel, L. C.; Tour, J. M. Permittivity of Dielectric Composite Materials Comprising Graphene Nanoribbons. The Effect of Nanostructure ACS Appl. Mater. Interfaces 2013, 5, 7567-7573 10.1021/am401859j

- [6] Park, Y. T.; Qian, Y.; Chan, C.; Suh, T.; Nejad, M. G.; Macosko, C. W.; Stein, A. Epoxy Toughening with Low Graphene Loading *Adv. Funct. Mater.* 2015, 25, 575-585 10.1002/adfm.201402553
- [7] Gong, L.; Young, R. J.; Kinloch, I. A.; Riaz, I.; Jalil, R.; Novoselov, K. S. Optimizing the Reinforcement of Polymer-Based Nanocomposites by Graphene *ACS Nano* 2012, 6, 2086-2095 10.1021/nn203917d
- [8] Hu, K.; Gupta, M. K.; Kulkarni, D. D.; Tsukruk, V. V. Ultra-Robust Graphene Oxide-Silk Fibroin Nanocomposite Membranes *Adv. Mater.* 2013, 25, 2301-2307 10.1002/adma.201300179
- [9] Hu, K.; Kulkarni, D. D.; Choi, I.; Tsukruk, V. V. Graphene-Polymer Nanocomposites For Structural and Functional Applications *Prog. Polym. Sci.* 2014, 39, 1934-1972 10.1016/j.progpolymsci.2014.03.001
- [10] Liu, F.; Guo, K. Reinforcing Epoxy Resin Through Covalent Integration of Functionalized Graphene Nanosheets *Polym. Adv. Technol.* 2014, 25, 418-423 10.1002/pat.3256
- [11] Liu, F.; Wu, L.; Song, Y.; Xia, W.; Guo, K. Effect of Molecular Chain Length on the Properties of Amine-Functionalized Graphene Oxide Nanosheets/Epoxy Resins Nanocomposites *RSC Adv.* 2015, 5, 45987-45995 10.1039/C5RA02013A
- [12] Jalili, R.; Aboutalebi, S. H.; Esrafilzadeh, D.; Konstantinov, K.; Moulton, E.; Razal, J. M.; Wallace, G. G. Organic Solvent Based Graphene Oxide Liquid Crystals: a Facile Route Toward the Next Generation of Self-Assembled Layer-by-Layer Multifunctional 3D Architectures *ACS Nano* 2013, 7, 3981-3990 10.1021/nn305906z
- [13] Gudarzi, M. M.; Moghadam, M. H. M.; Sharif, F. Spontaneous Exfoliation of Graphite Oxide in Polar Aprotic Solvents as the Route to Produce Graphene Oxide-Organic Solvents *Liquid Crystals Carbon* 2013, 64, 403-415 10.1016/j.carbon.2013.07.093
- [14] Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-Based Composite Materials *Nature* 2006, 442, 282-286 10.1038/nature04969
- [15] Xu, Y. X.; Bai, H.; Lu, G. W.; Li, C.; Shi, G. Q. Flexible Graphene Films via the Filtration of Water-Soluble Noncovalent Functionalized Graphene Sheets *J. Am. Chem. Soc.* 2008, 130, 5856-5857 10.1021/ja800745y
- [16] Wang, S.; Chia, P.-J.; Chua, L.-L.; Zhao, L.-H.; Png, R.-Q.; Sivaramakrishnan, S.; Zhou, M.; Goh, R. G.-S.; Friend, R. H.; Wee, A. T.-S.; Ho, P. K.-H. Band-like Transport in Surface-Functionalized Highly Solution-Processable Graphene Nanosheets *Adv. Mater.* 2008, 20, 3440-3446 10.1002/adma.200800279
- [17] Cao, Y. W.; Lai, Z. L.; Feng, J. C.; Wu, P. Y. Graphene Oxide Sheets Covalently Functionalized with Block Copolymers via Click Chemistry as Reinforcing Fillers *J. Mater. Chem.* 2011, 21, 9271-9278 10.1039/c1jm10420a
- [18] Umer, R.; Li, Y.; Dong, Y.; Haroosh, H. J.; Liao, K. The Effect of Graphene Oxide (GO) Nanoparticles on the Processing of Epoxy/Glass Fiber Composites Using Resin Infusion *Int. J. Adv. Manuf. Technol.* 2015, 81, 2183-2192 10.1007/s00170-015-7427-1
- [19] Bortz, D. R.; Heras, E. G.; Martin-Gullon, I. Impressive Fatigue Life and Fracture Toughness Improvements in Graphene Oxide/Epoxy Composites *Macromolecules* 2012, 45, 238-245 10.1021/ma201563k
- [20] Wan, Y. J.; Tang, L. C.; Gong, L. X.; Yan, D.; Li, Y. B.; Wu, L. B.; Lai, G. Q. Grafting of Epoxy Chains onto Graphene Oxide for Epoxy Composites with Improved Mechanical and Thermal Properties *Carbon* 2014, 69, 467-480 10.1016/j.carbon.2013.12.050
- [21] Liu, Q.; Zhou, X.; Fan, X.; Zhu, C.; Yao, X.; Liu, Z. Mechanical and Thermal Properties of Epoxy Resin Nanocomposites Reinforced with Graphene Oxide *Polym.-Plast. Technol. Eng.* 2012, 51, 251-256 10.1080/03602559.2011.625381
- [22] Nair, A. B.; Abraham, B. T.; Beehum, P. M. S.; Thachil, E. T. Microwave Exfoliated Reduced Graphene Oxide Epoxy Nanocomposites for High Performance Applications *Polymer* 2014, 55, 3614-3627 10.1016/j.polymer.2014.05.032
- [23] Guan, L. Z.; Wan, Y. J.; Gong, L. X.; Yan, D.; Tang, L. C.; Wu, L. B.; Jiang, J. X.; Lai, G. Q. Toward Effective and Tunable Interfaces in Graphene Oxide/Epoxy Composites by Grafting Different Chain Lengths of Polyetheramine onto Graphene Oxide *J. Mater. Chem. A* 2014, 2, 15058-15069 10.1039/C4TA02429J
- [24] Valles, C.; Beckert, F.; Burk, L.; Mulhaupt, R.; Young, R. J.; Kinloch, I. A. Effect of the C/O Ratio in Graphene Oxide Materials on the Reinforcement of Epoxy-Based Nanocomposites *J. Polym. Sci., Part B: Polym. Phys.* 2016, 54, 281-291 10.1002/polb.23925
- [25] Yang, H.; Shan, C.; Li, F.; Zhang, Q.; Han, D.; Niu, L. Convenient Preparation of Tunably Loaded Chemically Converted Graphene Oxide/Epoxy Resin Nanocomposites from Graphene Oxide Sheets Through Two-Phase Extraction *J. Mater. Chem.* 2009, 19, 8856-8860 10.1039/b915228h
- [26] Li, Z.; Wang, R.; Young, R. J.; Deng, L.; Yang, F.; Hao, L.; Jiao, W.; Liu, W. Control of the Functionality of Graphene Oxide for its Application in Epoxy Nanocomposites *Polymer* 2013, 54, 6437-6446 10.1016/j.polymer.2013.09.054
- [27] Dimiev, A. M.; Alemany, L.; Tour, J. M. Graphene Oxide. Origin of Acidity and Dynamic Structural Model *ACS Nano* 2013, 7, 576-588 10.1021/nn3047378
- [28] Dimiev, A. M.; Polson, T. A. Contesting the Two-Component Structural Model of Graphene Oxide and Reexamining the Chemistry of Graphene Oxide in Basic Media *Carbon* 2015, 93, 544-554 10.1016/j.carbon.2015.05.058

- [29] Dimiev, A. M.; Tour, J. M. Mechanism of Graphene Oxide Formation *ACS Nano* 2014, 8, 3060-3068 10.1021/nn500606a
- [30] Eigler, S.; Dimiev, A. M. In *Graphene Oxide: Fundamentals and Applications*; Dimiev, A. M.; Eigler, S., Eds.; Wiley: London, 2017; Chapter 3, pp 85-120.
- [31] Wan, Y.-J.; Gong, L.-X.; Tang, L.-C.; Wu, L.-B.; Jiang, J.-X. Mechanical Properties of Epoxy Composites Filled with Silane-Functionalized Graphene Oxide Composites, Part A 2014, 64, 79-89 10.1016/j.compositesa.2014.04.023
- [32] Suvarna, S.; Ambekar, S. Y.; Saletori, M.; Biswas, C.; Rajanna, A. V. Cure Kinetics of Multifunctional Epoxies with 2, 2'-Dichloro-4, 4'-Diaminodiphenylmethane as Hardener *J. Appl. Polym. Sci.* 2000, 77, 2097-2103 10.1002/1097-4628(20000906)77:10<2097::AID-APP1>3.0.CO;2-4
- [33] Roşu, D.; Caşcaval, C. N.; Mustăta, F.; Ciobanu, C. Cure Kinetics of Epoxy Resins Studied by Non-Isothermal DSC Data *Thermochim. Acta* 2002, 383, 119-127 10.1016/S0040-6031(01)00672-4
- [34] Urbaczewski, E.; Pascault, J. P.; Sautereau, H.; Riccardi, C. C.; Moschiar, S. S.; Williams, R. J. J. Influence of the Addition of an Aliphatic Epoxide as Reactive Diluent on the Cure Kinetics of Epoxy/Amine Formulations *Makromol. Chem.* 1990, 191, 943-953 10.1002/macp.1990.021910420
- [35] Chen, Z.-K.; Yang, G.; Yang, J.-P.; Fu, S.-Y.; Ye, L.; Huang, Y.-G. Simultaneously Increasing Cryogenic Strength, Ductility and Impact Resistance of Epoxy Resins Modified by N-butyl Glycidyl Ether Polymer 2009, 50, 1316-1323 10.1016/j.polymer.2008.12.048
- [36] Valles, C. In *Graphene Oxide: Fundamentals and Applications*; Dimiev, A. M.; Eigler, S., Eds.; Wiley: London, 2017; Chapter 4, pp 121-146.
- [37] Vallés, C.; Young, R. J.; Lomax, D. J.; Kinloch, I. A. The Rheological Behaviour of Concentrated Dispersions of Graphene Oxide *J. Mater. Sci.* 2014, 49, 6311-6320 10.1007/s10853-014-8356-3
- [38] Kumar, P.; Maiti, U. N.; Lee, K. E.; Kim, S. O. Rheological Properties of Graphene Oxide Liquid Crystal Carbon 2014, 80, 453-461 10.1016/j.carbon.2014.08.085
- [39] Kim, J.; Cote, L. J.; Kim, F.; Yuan, W.; Shull, K. R.; Huang, J. Graphene Oxide Sheets at Interfaces *J. Am. Chem. Soc.* 2010, 132, 8180-8186 10.1021/ja102777p
- [40] Bourgeat-Lami, E.; Faucheau, J.; Noel, A. Latex Routes to Graphene-Based Nanocomposites *Polym. Chem.* 2015, 6, 5323-5357 10.1039/C5PY00490J