Non-covalent exfoliation of graphite in aqueous suspension for nanocomposite production with waterborne polyurethane

Eunice Cunha¹, M. Conceição Paiva¹, M. Fernanda Proença², Fernando Duarte¹

¹ Instituto de Polímeros e Compósitos/I3N, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

²Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

eunice.cunha@dep.uminho.pt

Abstract

Graphene has emerged as a new class of nanomaterials, since its isolation by mechanical exfoliation of graphite in 2004. [1] The excellent electronic, mechanical, thermal and optical properties of graphene [2] have reveled potential applications in various fields including in the polymer nanomaterials science. [3] As so, graphene has been considered as an ideal reinforcing agent for high strength polymer nanocomposites. One of most used method to produce graphene in large scale is through oxidation of graphite followed by exfoliation and reduction of the oxidation products. However, this method leads to the production of graphene with structural defects which strongly affect the excellent initial properties of this material. [4] Recently, the production of graphene based on graphite exfoliation through non-covalent interactions between graphene/pyrene derivatives was reported. [5] This approach may be used for the exfoliation and stabilization of graphene in water, leading to the production of few- and single- layer graphene without damaging its structure. The suspension of graphene in water allows its easy mixture with polymers that form stable suspensions, or are soluble in water.

Polyurethane presents excelent physical properties, namely high tensile strength, abrasion and tear resistance, and the use of WPU in surface coatings is an environmentally friendly process, avoiding the emission of volatile organic compounds (VOCs). The development and application of WPU has been increasing, especially in the field of coating industry where the reduction of VOCs is critical. The potential applications of waterborne polyurethane/ graphene thin films in antistatic coatings, electromagnetic shielding and corrosion-resistant coatings have also been reported.[6-10]

The present work reports the preparation of stable aqueous suspensions of few-layer graphene, or highly exfoliated graphite, using solutions of pyrene derivatives at low concentration, and the production of thin films of WPU/ few-layer graphene at low loading level (from 0,025% to 0,5% wt). The aqueous suspensions of few-layer graphene were analyzed by UV-Visible spectroscopy. The graphene/exfoliated graphite-based materials were deposited on surfaces and analyzed by Raman spectroscopy, to characterize the effectiveness of the exfoliation of pristine graphite. The nanoparticles were observed by scanning transmission microscopy. The mechanical properties of the thin films were measured by tensile testing showing an increase up to 39% of the Young's modulus. Figure 1a presents the Raman spectra of graphite and few-layer graphene obtained by exfoliation with a pyrene derivative (Py-XGnP), illustrating a downshift of the 2D band at 2669 cm⁻¹ (633nm laser), that indicates that the exfoliation occurred. Figure 1b shows the Young's modulus of the WPU film and WPU nanocomposites reinforced with graphene.

Acknowledgement

The authors acknowledge FCT, project PEst-C/CTM/LA0025/2011 and PhD grant SFRH/BD/87214/2012.

References

[1] K. Novoselov, A. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva and A. Firsov, Science, **306** (2004) 666-669.

[2] A. Geim and K. Novoselov, Nature Materials, 6 (2007) 183-191.

[3] V. Singh, D. Joung, L. Zhai, S. Das, S. Khondaker and S. Seal, Progress in Materials Science, 56 (2011) 1178–1271.

[4] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, and A. Ferrari, Materials today, 15 (2012) 564-589.

[5] D. Parviz, S. Das, H. Ahmed, F. Irin, S. Bhattacharia, and M. Green, ACS Nano, 6 (2012) 8857–8867.

[6] B. Ramezanzadeh, E. Ghasemi, M. Mahdavian, E. Changizi, M. Moghadam, Carbon, 93 (2015) 555-573.

[7] X. Luo, P. Zhang, J. Ren, R. Liu, J. Feng, B. Ge, Applied Polymer Science, 132 (2015) 42005 (8pp).
[8] J. Ding, Y. Fan, C. Zhao, Y. Liu, C. Yu, N. Yuan, Journal of Composite Materials, 46 (2011) 747-752.
[9] S. Hsiao, C. Ma, H. Tien, W. Liao, Y. Wang, S. Li, C. Yang, S. Lin, R. Yang, ACS Applied Materials and Interfaces, 7 (2015) 2817-2826.

[10] T. Gupta, B. Singh, R. Tripathi, S. Dhakate, V. Singh, O. Panwar, R. Mathur, RSC Advances, 5 (2015) 16921-16930.



Figure 1: a) Raman spectra of pristine graphite (XGnP) and exfoliated graphite using pyrene derivative (Py-XGnP); b) Mechanical properties of PU/XGnP thin films.