

THE IMPACT OF SONICATION TIME THROUGH POLYSULFONE-GRAPHENE OXIDE COMPOSITE FILMS PROPERTIES

S.I. VOICU, M.A. PANDELE, E. VASILE, R. RUGHINIS, L. CRICA, L. PILAN, M. IONITA*

University Politehnica of Bucharest, Bucharest, 060042, Romania

In this research we studied the influence of sonication time through the properties of polysulfone (PS)-graphene oxide (GO) composites. Nanocomposites of PS-GO 0.5 wt. % were prepared by phase inversion and were exposed to sonication treatment for 30, 60 and 90 minutes. The presence of largely dispersed graphene oxide was evidenced by Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) and Raman spectroscopy. Fourier transform infrared (FT-IR) investigation indicated no occurrence of interaction between graphene oxide nanosheets and PS. The obtained composites exhibit similar mechanical and thermal properties with those of PS.

(Received August 18, 2013; Accepted October 11, 2013)

Keywords: Polysulfone, Graphene oxide, Thermal stability, Mechanical properties

1. Introduction

The field of nanoscience has been the centre of attention during the past twenty years, and the importance will increase as miniaturisation becomes more important. Progress in this area depends fundamentally on the ability to synthesize nanoparticles as well as to assemble them efficiently into complex architectures [1]. In this regard, the discovery of graphene and graphene-polymer nanocomposites is playing a key role in modern nanoscience and nanotechnology [2-3]. The inclusion of graphene and its derivatives into polymer and exploring different production routes or material properties has been widely considered [4-5]. However, fabrication of graphene-polymer nanocomposites faces a number of challenges in terms of dispersion and interfacial interaction. Several methods were used to incorporate graphene or graphene derivatives within the polymer matrix such as melt blending or solution mixing. There have been numerous studies revealing that direct mixing of graphene particles and polymer solution is not effective method to disperse graphene [3]. Polysulfone (PS) is one of the most important polymeric materials widely used in separation or biomedical fields such as artificial organs and medical devices used for blood purification. However, from mechanical strength and stability point of view PS proves to be vulnerable. Blending the PS with carbon nanotubes (CNTs) has a positive effect but material becomes unrealistic expensive [6-7]. Graphene / graphene oxide (GO) is predicted to present similar outstanding physical and mechanical properties as CNTs and to be cost effective.

In this study is presented the synthesis of a new nanocomposite material PS-GO. To address the challenge concerning GO dispersion within PS matrix after solution mixing we applied different sonication treatment (30, 60 and 90 minutes). Further the influence of exposure to sonication on PS-GO composite materials morphology, structure, mechanical and thermal properties was investigated.

* Corresponding author: mariana.ionita@polimi.it

2. Materials and methods

2.1 Materials

Graphene oxide was purchased from National Institute for Research and Development in Microtechnologies (Romania) and prepared according to Hummers method. Polysulfone, Ultrason S3010, was provided by BASF. N,N'-Dimethylformamide (DMF) 99.8 % purity and absolute ethanol used as polymer solvent, non-solvent respectively were purchased from Sigma Aldrich.

2.2 Preparation of polysulfone-graphene oxide nanocomposites

Polysulfone was dissolved in DMF under magnetic stirring, in portions, until the desired mass concentration is achieved (15 %). In 50 mL of polymer solution, which contains 7 g of polysulfone, 0,035 g of graphene oxide (concentration of 0.5 wt. % related to polymer) were added and exposed to sonication (60 Hz) for different times *i.e.* 30 min, 60 min, respectively 90 min. The solution was deposited onto a spectral glass at a standard thickness of 400 μm and the composite matrix polymer-graphene oxide was precipitated in ethanol. After synthesis, the PS-GO composite films were washed and kept in deionized water.

2.3 Characterization of polysulfone-graphene oxide nanocomposites

A morphological characterisation of PS-GO composites was carried out by Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM). TEM images were recorded on a TECNAI F30 G2 S-TWIN equipment provided with 300 kV emission gun. The Scanning Electron Microscopy was performed using a FEI instrument and the samples were gold plated before analysis [10-11]. The structure of the PS and PS-GO composites was investigated by Fourier transform infrared (FT-IR) measurements, performed on SHIMADZU 8900 equipment. The FT-IR spectra were assessed in $600 \div 4000 \text{ cm}^{-1}$ range with 4 cm^{-1} resolution. Raman spectra were performed on a DXR Raman Microscope from Thermo Scientific using a 633 nm laser line and a number of 10 scans. The laser beam was focused with the 10x objective of the Raman microscope. Mechanical tests were performed employing an universal mechanical tester (Instron, Model 3382, USA). The relative humidity was 45–50% and a speed of 2 mm/min was considered. The size of the sample was 10 cm in length and 1 cm in width. Seven-ten samples were tested for each composite film and the average values are reported. Thermogravimetric analysis (TGA) was performed on a Q500 TA Instruments equipment, in nitrogen atmosphere from room temperature to 800 °C and a heating rate of 10 °C/min.

3. Results and discussion

3.1 Morphological characterisation of PS and PS-GO composites

TEM image of GO (Fig. 1 a) and GO dispersed within PS matrix (Fig. 1b) by applying sonication treatment of 60 minutes are reported. TEM revealed the network of GO (Fig. 1a) to be composed of stacks of several sheets of GO. From the microscopic investigation of the composites (Fig. 1 b) it can be noticed the ability of processing methods (mixing and sonication) to separate the GO flakes to single layers. For PS-GO composites exposed to sonication for 60 and 90 minutes GO were highly exfoliated. Conversely, it seems that by exposing the composite to 30 minutes sonication treatment GO is well dispersed but the occurrence of few isolated aggregation of the nanofiller was observed.

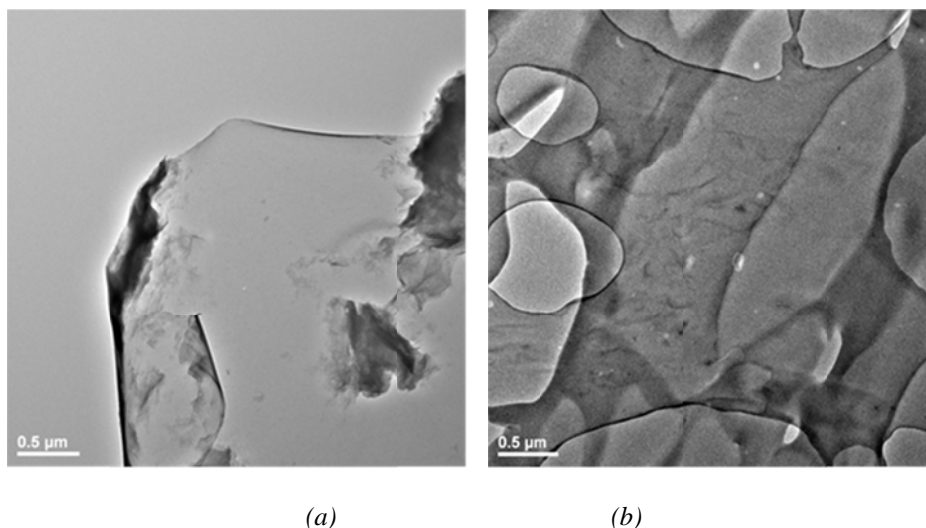


Fig. 1. TEM images of (a) pristine GO and (b) PS-GO after mixing and sonication

The morphology of the composite films surface was characterized by SEM. Figure 2 exhibits typical SEM image of the PS and PS-GO composites surface. Unlike the pure polymer (Figure 2 (a)), which structure is smooth with some roughs, the composites exhibits a porous surface. It can be observed that by increasing the sonication time, the porosity and pore dimensions increase. This can be explained by the fact that better dispersibility of graphene oxide is achieved and the cross flow of DMF through polymer film is favoured due to the interaction with hydrophobic surface of the GO. The porosity and pore dimensions are approximately 3-4 times higher at the film with GO sonicated for 60 and 90 min than the film with GO sonicated 30 min. The films present a clean surface with no traces of impurities or polymer particles.

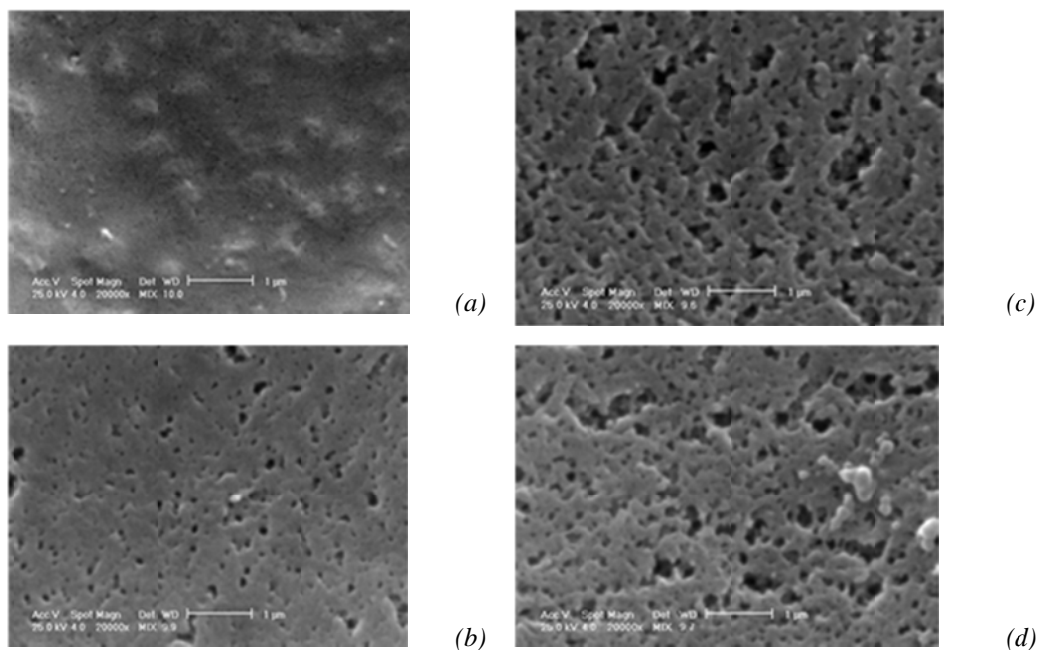


Fig 2. SEM images of surface (a) PS, (b) PS-GO 0.5 wt. % sonicated 30 min, (c) PS-GO 0.5 wt. % sonicated 60 min and (d) PS-GO 0.5 wt. % sonicated 90 min

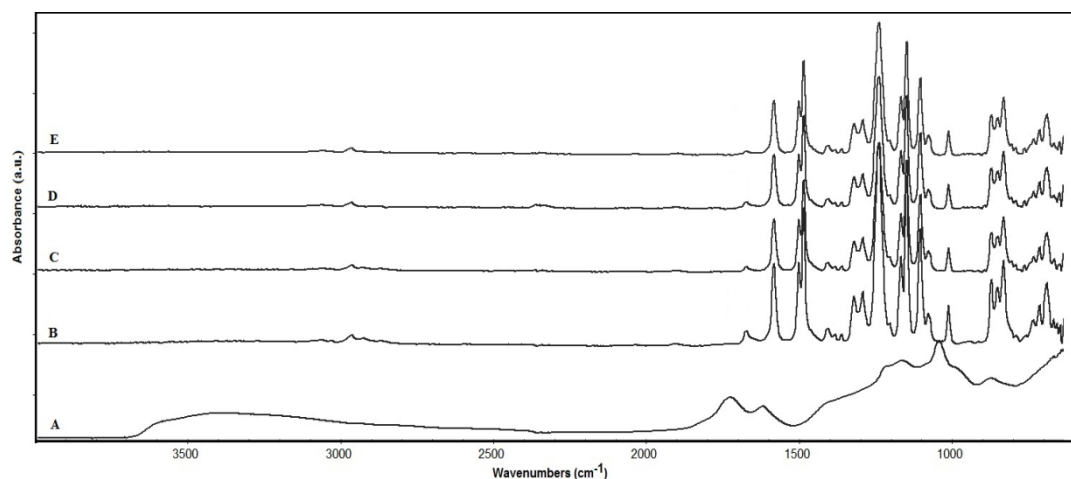


Fig 3. FT-IR spectra of the A) GO, B) PS, C) PS-GO 0.5 wt. %, sonicated 30 minutes, D) PS-GO 0.5 wt. %, sonicated 60 minutes and E) PS-GO 0.5 wt. %, sonicated 90 minutes

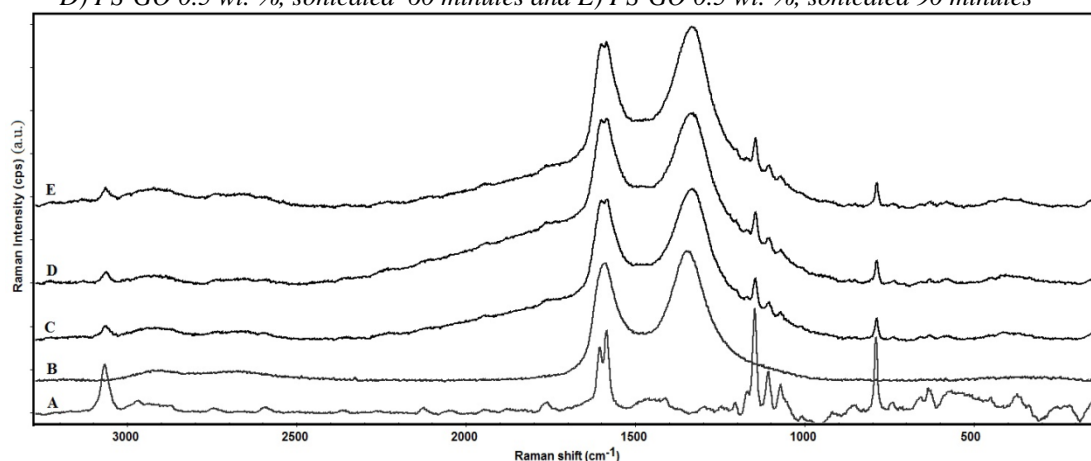


Fig. 4. Raman spectra of A) PS, B) GO, C) PS-GO 0.5 wt. %, sonicated 30 minutes, D) PS-GO 0.5 wt. %, sonicated 60 minutes and E) PS-GO 0.5 wt. %, sonicated 90 minutes

Table 1. Mechanical properties and Td_{3%} (temperature at which the mass loss is 3%) for PS and PS-GO nanocomposites after exposure to different sonication time

Sample	Exposure to sonication, [min]	Young's modulus, [MPa]	Tensile strength [MPa]	Td _{3%} , [°C]
PS		182.07±14.43	3.54±0.29	497.95
PS-GO (0.5 wt. %)	30	183.15±18.70	3.86±0.40	503.80
PS-GO (0.5 wt. %)	60	183.05±24.01	3.60±0.24	509.21
PS-GO (0.5 wt. %)	90	187.04±17.40	3.18±0.29	503.63

3.2 Structural characterisation of PS and PS-GO composites

The FT-IR analyses were performed to examine the interaction between the PS and GO. GO spectrum (Figure 3 A) displays two characteristics bands at 1736 cm^{-1} and 1618 cm^{-1} assigned to C=O stretching vibration of the carboxylic group and C=C stretching mode of the sp^2 network [12]. The most important absorption bands present in PS spectrum (Figure 3 B) are: 1150 cm^{-1} (SO_2 group from polysulfone), 1294 cm^{-1} (plane stretching symmetric vibration C=C from aromatic ring), 834 cm^{-1} (C-H from aromatic ring), 1488 cm^{-1} (asymmetric vibration attributed to C-H from methyl groups), 1169 cm^{-1} (stretching vibration of etheric between aromatic rings and oxygen) [6-7]. PS-GO composites (Figure 3 C, D and E) exhibit a similar spectrum with the pristine PS, with no shifting or occurrence of new bands. This is an indication that no chemical

interaction between graphene oxide and polysulfone takes place. Furthermore no change in the material structure was observed by increasing to sonication time.

Figure 4. shows the Raman spectra of pristine GO, PS and PS-GO composites. In the GO spectrum (Figure 4 B) two peaks at ~ 1354 and ~ 1603 cm^{-1} assigned to D band and G band are observed. The D band indicates the disorder in the GO structure while G band corresponds to the ordered sp^2 bonded carbon [13]. It can be seen from Figure 4 A that PS spectrum shows lines at ~ 790 , ~ 1151 , ~ 1600 and 3065 cm^{-1} [14]. From Figure 4 C, D and E it can be observed that PS-GO composites exhibit spectra which present peaks characteristic of pristine GO and PS, with a slight shifting of D band to ~ 1339 cm^{-1} . The presence of the peaks characteristic of GO within composites spectra is indicating the presence of this compound within the composite.

3.3 Mechanical results

The results of mechanical tests are reported in Table 1 and Fig. 5. A small effect of the insertion of GO within PS matrix on Young's modulus that increase of about 5 % with respect to neat PS was recorded. Tensile strength also present just a marginal enhancement, changing from 184 to 187 MPa by adding 0.5 wt. % GO to the PS matrix and sonication exposure of 90 min. This results can be explained considering that the addition of reinforce has a major effect on mechanical properties just if a good interface adhesion of polymer matrix with reinforce is realised. Analogous results were obtained in our previous work where epoxy resin or polyaniline was reinforced with different CNTs. The addition of CNTs within the epoxy resin leads to an increase of Young's modulus when good interface adhesion occurred [15-16]. On the other hand this can be explained considering stress distribution in composites. Tensile stress is initially sustained by polymer matrix if good interface adhesion with nanofiller occurs and effective transfers to the reinforce take place [4]. No correlation of mechanical properties and duration of sonication time were found. This could be associated on the one hand with largely good GO dispersion achieved even when short (30 min) sonication treatment was applied and on another hand, to the fact that here an important role in composite material mechanical behaviour is played by the quality of interface adhesion of polymer matrix with GO

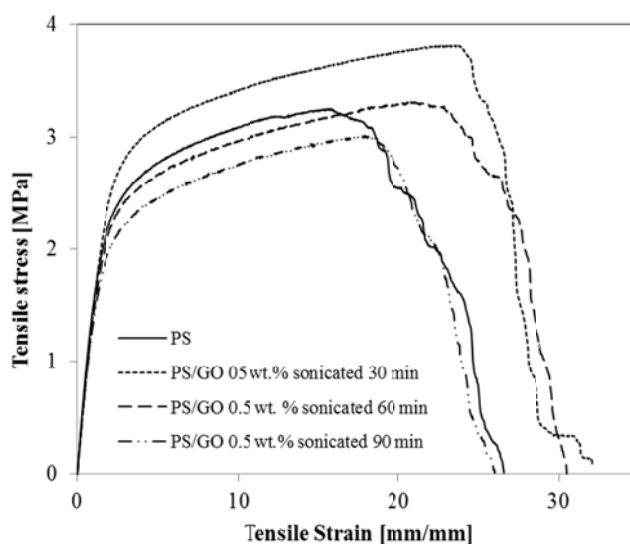


Fig. 5. Typical stress-strain curves of PS and PS-GO nanocomposites after exposure at different sonication time

3.4 Thermal characterisation

The TGA investigation indicated that when GO is loaded into the polymer matrix the degradation stages were just slightly shifted toward higher values. The Td3% (temperature at

which the mass loss is 3%) values obtained for the pure PS and the PS-GO composites are summarized in Table 1. The Td3% increased about 6-11 °C in the case of the composites phenomenon which is attributed to the good dispersion of the filler into PS matrix which probably slightly suppress the polymer chain mobility. No important influence of the duration of sonication treatment was observed on thermal stability of the material.

4. Conclusion

In this study, PS and PS-GO nanocomposites materials were obtained and the effectiveness of GO as reinforce in PS was discussed.

TEM images revealed good dispersion of GO within PS matrix particularly for exposure of the composites of sonication treatment of 60 and 90 minutes. In the case of exposure to sonication treatment of 30 minutes formation of few, small GO aggregates was observed. FT-IR investigation suggests no chemical or non-bond interaction between PS and GO thus, the disruption of the GO van der Waals interaction and furthermore the GO dispersion is produced by sonication treatment.

The lack of good adhesion between PS and GO matrix generate just a marginal effect on the mechanical properties of the composite materials.

The thermal stability of the PS-GO composites was slightly higher than that of pure PS.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, UEFISCDI, project number PN-II-TE- 17/26.04.2013.

References

- [1] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, J. H. Lee, *Prog. Polym. Sci.*, **35**, 11 (2010).
- [2] S. Stankovich, D. A. Dikin, G. H. Dommett, K. M. Kohlaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature*, **442**, 7100 (2006).
- [3] M. M. Gudarzi, F. Sharif, *J. Colloid Interface Sci.*, **366**, 1 (2012).
- [4] M. Ionita, M. A. Pandele, Iovu H., *Carbohydr. Polym.* **94**, 1 (2013).
- [5] A. M. Pandele, S. Dinescu, M. Costache, E. Vasile, C. Obreja, H. Iovu, M. Ionita, *Polym. Compos.*, (2013), DOI: 10.1002/pc.22620.
- [6] S.I. Voicu, A. Dobrica, S. Sava, A. Ivan, L. Naftanaila, *J. Optoelectron. Adv. Mater.*, **14**, 11-12 (2012).
- [7] S. I. Voicu, A. C. Nechifor, B. Serban, G. Nechifor, M. Miculescu, *J. Optoelectron. Adv. Mater.*, **9**, 11 (2007).
- [8] F. R. Lamastra, D. Puglia, M. Monti, A. Vella, L. Peponi, J. M. Kenny, F. Nanni, *Chem. Eng. J.*, **195-196**, (2012).
- [9] W. S. Hummers, R. E. Offeman, R. E., *J. Am. Chem. Soc.*, **80**, 6 (1958).
- [10] F. Miculescu, L. T. Ciocan, M. Miculescu, A. Ernuteanu, *Dig. J. Nanomater. Bios.*, **6**, 1 (2011).
- [11] F. Miculescu, I. Jepu, C. P. Lungu, M. Miculescu, M. Bane, *Dig. J. Nanomater. Bios.*, **6**, 2 (2011).
- [12] W. Zhang, C. Zhou, W. Zhou, A. Lei, Q. Zhang, Q. Wan, B. Zou, *Bull. Environ. Contam. Toxicol.*, **87**, 1 (2011).
- [13] M. Fang, J. Long, W. Zhao, L. Wang, G. Chen, *Langmuir*, **26**, 22 (2010).
- [14] S. J. Shilton, K. A. Prokhorov, S. A. Gordeyev, G. Yu. Nicolaeva, I. R. Dunkin, W. E. Smith, P. P. Pashinin, *Laser, Phys. Lett.*, **1**, 7 (2004).
- [15] M. Ionita, *Composites Part B*, **43**, 8 (2012).
- [16] M. Ionita, I.V. Branzoi, L. Pilan. *Surf. Inter. Anal.*, **42**, 6-7 (2010).