

In situ reduction of graphene oxide dispersed in a polymer matrix

M. Traina · A. Pegoretti

Received: 4 December 2011 / Accepted: 25 February 2012
© Springer Science+Business Media B.V. 2012

Abstract An alternative route for the production of graphene-polymer nanocomposites is proposed. First graphene oxide lamellae are homogeneously dispersed in a polyvinyl alcohol matrix. In a second step, mild thermal treatments are carried out on composites in order to promote a thermal reduction of the graphene oxide into reduced graphene oxide. The occurrence of an in situ reduction of graphene oxide is confirmed by various experimental techniques, such as differential scanning calorimetry, thermogravimetric analysis and electrical resistivity measurements.

Keywords Graphene oxide · Reduction · Nanocomposites · Electrical conductivity · Thermal treatment

Introduction

Graphene surely represents one of the most promising nanofillers for polymer nanocomposites nowadays (Stankovich et al. 2006; Zhao et al. 2010). In order to produce a large amount of graphene, chemical methods are typically adopted (Dreyer et al. 2010; Park and Ruoff 2009). Typically, graphite powder undergoes treatments with strong acids in order to obtain graphite oxide,

which is successively exfoliated into single layers of graphene oxide (GO) by sonication treatments in solution. Finally GO is reduced by chemical or thermal treatments. In the case of polymer nanocomposites (Kuilla et al. 2010; Potts et al. 2011), great care is necessary when GO is reduced because agglomeration phenomena could take place. In fact, graphene layers naturally tends to rearrange as in the parent graphite structure. For this reason, if graphene is used as filler for nanocomposites, massive reduction of GO or reduction of GO in solution with successive solvent removal should be avoided. GO is generally reduced in presence of stabilizing agents, such as polymer chains which could also be part of the resulting polymer matrix, or it is chemically modified in order to be stable in the solvent after reduction. Graphene structure could also be restored by thermal reduction of GO (Kim et al. 2011; McAllister et al. 2007). Elevated temperatures are generally required (ranging from 300 to 1,000 °C) so that thermal reduction in presence of a polymer matrix is practically limited by the polymer thermal stability.

In this communication we report on the possibility to perform in situ reduction of GO dispersed in a polymer matrix by using mild thermal treatment.

Experimental section

Materials

Fully hydrolyzed polyvinyl alcohol (PVOH) Celvol 350 (molecular weight = 100 kDa) was kindly

M. Traina · A. Pegoretti (✉)
Department of Materials Engineering and Industrial Technologies, University of Trento, Via Mesiano 77, 38123 Trento, Italy
e-mail: alessandro.pegoretti@unitn.it

supplied by Celanese (Dallas, USA). Graphite powder (particle size < 20 μm) and hydrazine hydrate solution (yield = 50–60 %) were purchased from Sigma-Aldrich. All reagents were analytical grade and used without any further purification.

Sample preparation

GO was obtained from graphite according to the modified Hummers method (Hummers and Offeman 1958; Kovtyukhova et al. 1999). GO powder was dispersed in distilled water by using high power sonication treatment (tip sonication, Hielscher UP400S, 30 min). The obtained dispersion was centrifuged at 4,000 rpm for 1 h in order to remove non-exfoliated GO. Brownish homogenous suspensions of GO with concentration up to 10 mg/mL were obtained.

GO colloidal dispersion was added to aqueous solutions of PVOH (50 mg/mL) for nanocomposite preparation. The mixture was sonicated for 1 min and then poured into an open silicon mould to allow the evaporation of the solvent. Nanocomposites were also prepared by using chemically reduced GO (rGO). The chemical reduction of GO was performed according to the literature indications (Li et al. 2008; Ren et al. 2011). In particular, hydrazine hydrate solution was added to aqueous PVOH-GO solution with a GO/hydrazine weight ratio of 1. The mixture was kept at 95 $^{\circ}\text{C}$ for 24 h under magnetic stirring and subsequently cast as previously described. Finally, cast films were dried at 60 $^{\circ}\text{C}$ for 15 h under vacuum and conditioned at 23 $^{\circ}\text{C}$ and 50 % RH for 1 week. The obtained films had a thickness of about 25 μm . Nanocomposites with a filler content up to 9.4 wt% were produced.

Neat GO and rGO films with a thickness of about 1 μm were also prepared by casting water-GO and water-rGO solutions.

Characterization

Nanocomposites were fractured in liquid nitrogen, mounted on aluminium stub using a conductive adhesive without any further metallization and analyzed with a Zeiss Supra 40 field emission scanning electron microscope (FESEM).

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC 30 calorimeter. A first heating ramp from 0 up to 240 $^{\circ}\text{C}$ was

followed by a cooling stage from 240 to 0 $^{\circ}\text{C}$ and by a second heating ramp up to 240 $^{\circ}\text{C}$. Both the heating and cooling rates were fixed at 10 $^{\circ}\text{C}/\text{min}$, and all tests were conducted in nitrogen flushing at 100 mL/min.

Thermogravimetric analysis (TGA) measurements were performed with a Mettler TG50 thermobalance at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 40 to 600 $^{\circ}\text{C}$ under nitrogen flow (200 mL/min).

The surface electrical resistivity of the films as a function of time at 180 $^{\circ}\text{C}$ under vacuum was measured by using a Keithley 6517A electrometer in accordance with ASTM D 257 standard. The resistivity was continuously monitored as a function of the time during the thermal treatment.

Results and discussion

As shown in Fig. 1a, the adopted Hummers procedure yields GO in form of highly exfoliated lamellae. FESEM micrographs of the cryofractured surface of nanocomposites evidence a highly homogenous dispersion of GO lamellae in the polymer matrix. In particular, at low filler content (1.0 wt%), single fully exfoliated lamellae with average dimension of 150–250 nm can be observed (see Fig. 1b). Also for composites with high filler content (9.4 wt%) a quite homogeneous filler dispersion can be observed. Image analysis on these micrographs allowed us to estimate a surface area of about 1,730 m^2/g for GO dispersed in PVOH. This result has been obtained by analyzing the FESEM micrographs by an open source image processing and analysis software (Image J).

As depicted in Fig. 2, TGA curves on pure GO evidence a mass loss of about 36 wt% occurring in the temperature range from 175 to 205 $^{\circ}\text{C}$, which can be certainly attributed to the removal of chemical moieties generated on the GO lamellae by the oxidation treatment (Dreyer et al. 2010). On the other hand, TGA curve of rGO sample evidences the complete absence of mass loss related to residual functional groups, as expected. TGA curves of PVOH-GO composites present several degradation steps in the mass loss curve. A first one, at about 100 $^{\circ}\text{C}$, is related to the release of the adsorbed moisture, while the last one is related to the polymer degradation for temperature over 250 $^{\circ}\text{C}$ and it is the more intense. In addition, a small mass loss step can be detected between 150 and 200 $^{\circ}\text{C}$, as evidenced in the inset of

Fig. 1 SEM micrographs of **a** neat GO and cryo-fracture surfaces of nanocomposites containing **b** 1.0 wt% and **c** 9.4 wt% of GO

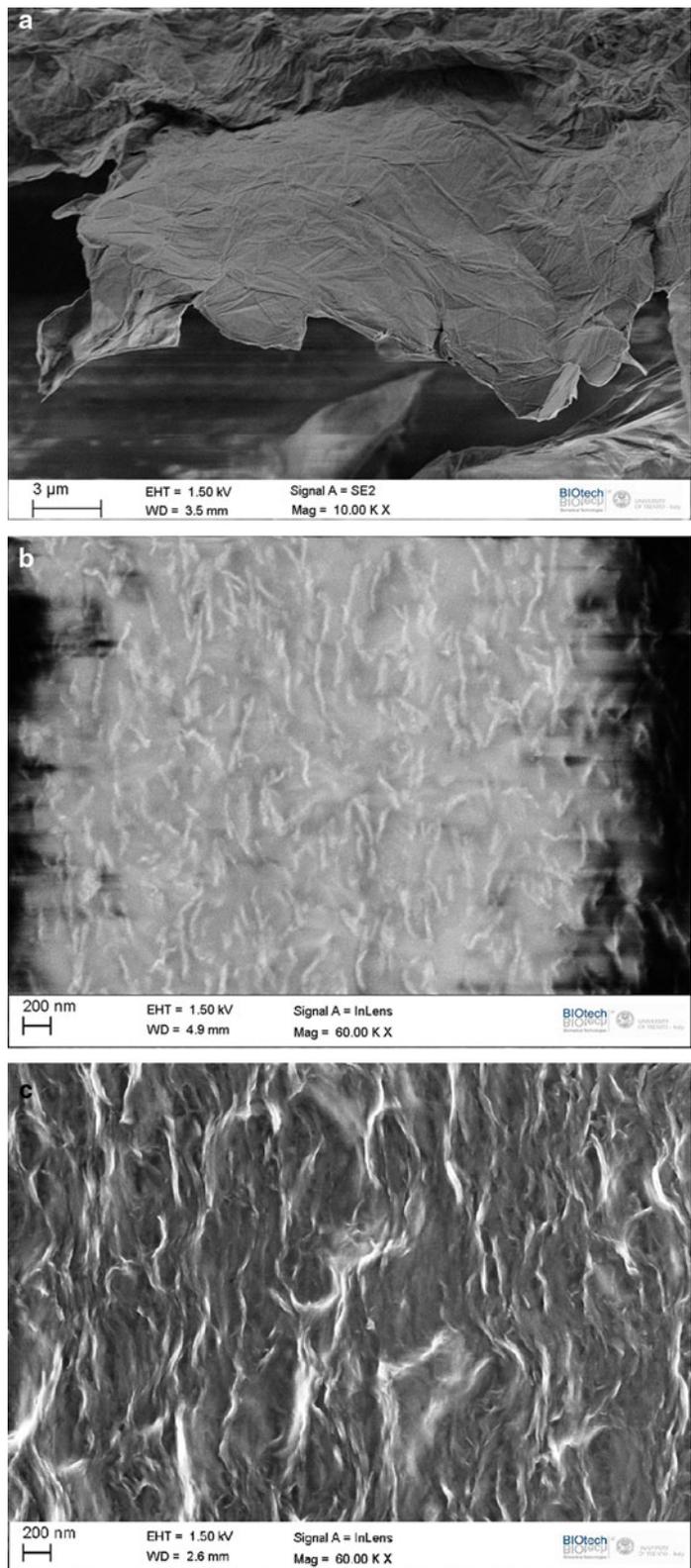


Fig. 2. This last step can be observed on all composites, but not on pure PVOH matrix. Therefore, it can be surely attributed to the in situ reduction reaction of GO filler.

As evidenced by DSC thermograms of Fig. 3, the reduction of GO is accompanied by a highly exothermic peak centred at about 196 °C with a heat release of 556 J/g : as expected this peak is absent on the DSC thermogram of chemically rGO (this thermogram has not been reported for brevity). On the DSC thermograms of neat PVOH matrix a glass transition temperature can be detected at about 47 °C, and an

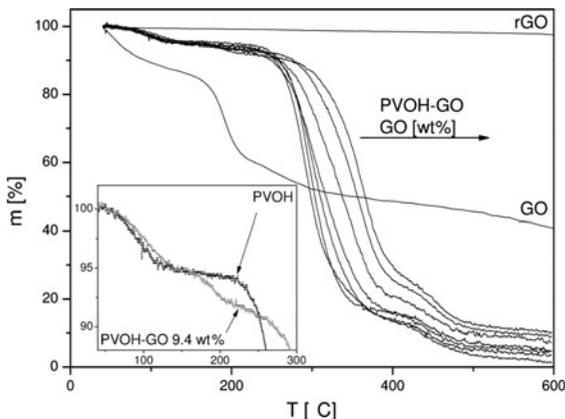


Fig. 2 TGA curves of GO, rGO and PVOH-GO nanocomposites at various GO content (increasing in the plots as indicated by the arrow). The filler content of PVOH-GO composites is 0, 1.0, 2.0, 3.8, 5.7, 7.4 and 9.4 wt%. The inset shows a detail of TGA curves for PVOH and PVOH-GO 9.4 wt%

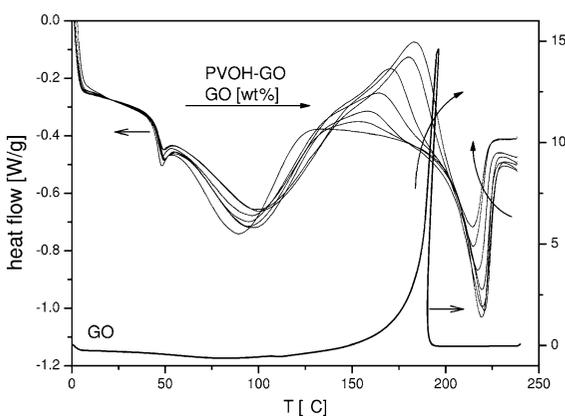


Fig. 3 DSC curves of GO, rGO and PVOH-GO nanocomposites at various GO content (increasing in the chart as indicated by the arrow). The filler content of PVOH-GO composites is 0, 1.0, 2.0, 3.8, 5.7, 7.4 and 9.4 wt%. The data of PVOH-GO composites refer to left axis while GO and rGO refer to right axis

endothermic peak corresponding to water evaporation can be observed at about 100 °C (which disappears in the second heating scan). Finally, an endothermic melting signal can be evidenced, with a peak at temperatures higher than 200 °C. When GO is added an additional exothermic signal appears in the temperature range between 120 and 200 °C, which can be certainly attributed to the in situ reduction of GO.

If the peak temperature and the enthalpy of this exothermic signal are plotted as a function of the GO content (see Fig. 4), almost linear trends can be observed. The enthalpy data are in good agreement with the expected values (solid line passing through open circles) estimated considering the GO content in nanocomposites and the enthalpy of the reduction reaction of neat GO (556 J/g). The amount of mass loss detected by TGA between 150 and 200 °C is also reported in Fig. 4. As expected, a linear trend can be observed with the GO content. Linear regression of the experimental data (dashed line) allows us to estimate a mass loss value of about 29 wt% for a limiting GO content of 100 wt%. This value is slightly lower than the experimental mass loss detected on neat GO (i.e. 36 wt%). This last consideration could be interpreted as an indirect prove that GO is only partially reduced under the selected mild thermal treatment conditions. The experimental evidences reported above strongly support the hypothesis that GO can be thermally reduced even when dispersed inside a polymer matrix.

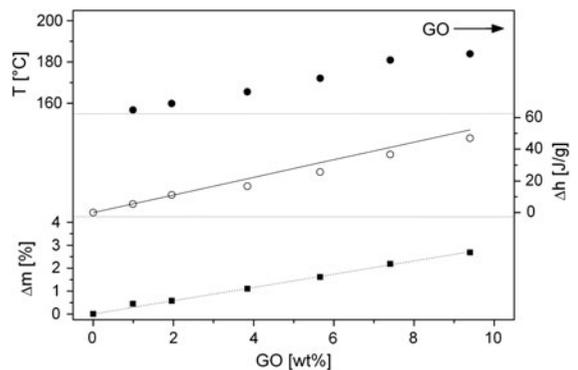


Fig. 4 Peak temperature T (full circles) and enthalpy Δh (open circles) of the exothermic GO reduction for PVOH-GO composites as a function of the GO content as evaluated in DSC measurements. Arrow indicates the reference temperature of 196 °C measured on neat GO. In the lower part of the plot, the change in residual mass Δm (solid squares) of PVOH-GO composites associated to GO reduction as evaluated by TGA experiments is reported

Isothermal treatments on the produced materials have been performed at 180 °C under vacuum. When the treatment is carried out on pure GO, the materials lose transparency after few minutes, changing in colour and turning into dark black because of the occurrence of reduction, in agreement with the literature (Chen et al. 2010). In a similar way, when the same treatment is applied to PVOH-GO nanocomposites, the materials lose transparency after few minutes, changing colour into dark black. On the other hand, neat PVOH do not manifest colour variation after the same treatment. Since graphene is a good electrical conductive material, the occurrence of GO reduction is generally accompanied by an increase of electrical conductivity because of the restored electronic conjugation (Jung et al. 2009). As reported in Fig. 5, the surface electrical resistivity of the investigated materials has been continuously monitored during the heat treatment. As expected, the resistivity of GO drastically decreases from 1.6×10^{10} ohm/sq to 2.0×10^3 ohm/sq after 160 min at 180 °C. The major part of the observed resistivity decay occurs within the initial 60 min of treatment. On the other hand, chemically rGO displays a lower resistivity value of 3.6×10^2 ohm/sq, that remains practically constant during the heat treatment. While neat PVOH matrix maintains a constantly high resistivity value of about 1.3×10^9 ohm/sq, PVOH-GO composites with high filler content (9.4 wt%) manifests a drastic resistivity decrease from 6.6×10^8 to 2.6×10^6 ohm/sq.

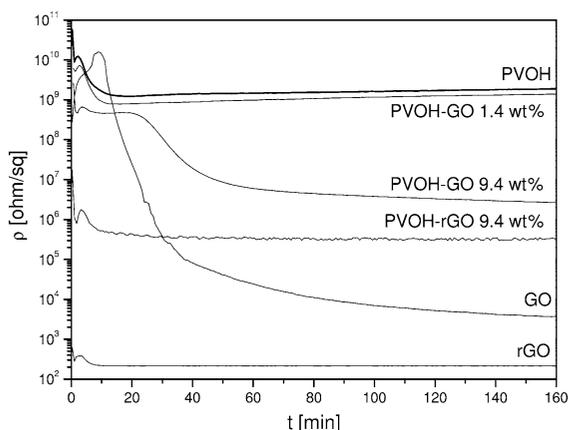


Fig. 5 Surface electrical resistivity as a function of time during isothermal treatment at 180 °C under vacuum of neat PVOH, of PVOH-based nanocomposite with 1.0 wt% and 9.4 wt% of GO, of PVOH-based nanocomposites with 9.4 wt% of rGO, of neat GO and neat rGO

Most of this decay occurs during the initial 60 min with a kinetics similar to that observed for neat GO. On the other hand, the resistivity of PVOH-rGO composites at a filler loading of 9.4 wt% remains practically constant at 3.1×10^5 ohm/sq during the entire treatment time, i.e. about one order of magnitude lower than the value obtained for PVOH-GO composites at the same filler content. This behaviour evidences that GO reduction can take place also in a solid polymer matrix at relatively mild temperature. It is important to underline that the selected treatment temperature is higher than the glass transition of the polymer matrix, thus increasing diffusive phenomena and the reaction kinetics. At the same time, the treatment temperature is low enough to avoid thermal degradation of the same polymer matrix.

Nevertheless, resistivity and TGA data evidence that the thermal treatment under the investigated conditions does not induce a complete reduction of GO. This fact is probably related to the mild treatment temperature and to the different reduction mechanism of GO lamellae when surrounded by a polymer matrix in comparison to neat GO. Moreover, PVOH-GO composites with low filler content (1.0 wt%) are characterized by constantly high resistivity values over the entire treatment time (Fig. 5). This fact could be explained by considering SEM micrographs (Fig. 1) where single GO lamellae can be observed: after in situ thermal reduction, highly homogenous dispersion is maintained and no extensive contacts between the single rGO lamellae can be observed. As a consequence, conductive interconnected network of conductive filler particles is not formed and the electrical behaviour of the composite is still dominated by the insulating polymer matrix. Moreover, we cannot exclude that only a partial reduction of the GO layers has been achieved by the mild thermal treatment selected in this study. In other words, low filler content and good dispersion do not permit to reach percolative conditions (Stankovich et al. 2006). On the other hand, PVOH-GO composites with a higher filler content (9.4 wt%) are characterized by a highly homogeneous dispersion, and GO lamellae may build an interconnected network. In addition, combining SEM information and TGA mass loss, it is possible to estimate a surface area of 2,490 m²/g for in situ rGO dispersed in PVOH. This value is very close to the theoretical value of 2,630 m²/g of graphene layers (Peigney et al. 2001).

Conclusion

In conclusion, this study evidences how GO layers dispersed in a solid polymer matrix can be reduced by mild thermal treatment. The reduction process has been monitored by DSC, TGA and electrical conductivity measurements. The selection of a proper temperature for the thermal treatment is a critical issue to promote GO reduction and to preserve the organic matrix from degradation phenomena. From a general point of view, this alternative route could allow one to use GO in place of graphene for the preparation of polymer nanocomposites. The main advantage of GO over graphene for the preparation of polymer nanocomposites is that GO can be more easily and homogeneously dispersed in polymer matrices due to its lower propensity to aggregation.

References

- Chen W, Yan L, Bangal PR (2010) Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves. *Carbon* 48(4):1146–1152. doi:10.1016/j.carbon.2009.11.037
- Dreyer DR, Park S, Bielawski CW, Ruoff RS (2010) The chemistry of graphene oxide. *Chem Soc Rev* 39(1):228–240. doi:10.1039/b917103g
- Hummers WSJ, Offeman RE (1958) Preparation of graphitic oxide. *J Am Chem Soc* 80(6):1339. doi:10.1021/ja01539a017
- Jung I, Field DA, Clark NJ, Zhu Y, Yang D, Piner RD, Stankovich S, Dikin DA, Geisler H, Ventrice CA, Ruoff RS (2009) Reduction kinetics of graphene oxide determined by electrical transport measurements and temperature programmed desorption. *J Phys Chem C* 113(43):18480–18486. doi:10.1021/jp904396j
- Kim C-J, Khan W, Park S-Y (2011) Structural evolution of graphite oxide during heat treatment. *Chem Phys Lett* 511(1–3):110–115. doi:10.1016/j.cplett.2011.06.016
- Kovtyukhova NI, Ollivier PJ, Martin BR, Mallouk TE, Chizhik SA, Buzaneva EV, Gorchinskiy AD (1999) Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem Mater* 11(3):771–778. doi:10.1021/cm981085u
- Kuilla T, Bhadra S, Yao D, Kim N, Bose S, Lee J (2010) Recent advances in graphene based polymer composites. *Prog Polym Sci* 35(11):1350–1375. doi:10.1016/j.progpolymsci.2010.07.005
- Li D, Müller MB, Gilje S, Kaner RB, Wallace GG (2008) Processable aqueous dispersions of graphene nanosheets. *Nat Nanotechnol* 3:101–105
- McAllister MJ, Li J-L, Adamson DH, Schniepp HC, Abdala AA, Liu J, Herrera-Alonso M, Milius DL, Car R, Prud'homme RK, Aksay IA (2007) Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem Mater* 19(18):4396–4404. doi:10.1021/cm0630800
- Park S, Ruoff RS (2009) Chemical methods for the production of graphenes. *Nat Nanotechnol* 4(4):217–224. doi:10.1038/NNANO.2009.58
- Peigney A, Laurent C, Flahaut E, Bacsa RR, Rousset A (2001) Specific surface area of carbon nanotubes and bundles of carbon nanotubes. *Carbon* 39(4):507–514. doi:10.1016/s0008-6223(00)00155-x
- Potts J, Dreyer D, Bielawski C, Ruoff R (2011) Graphene-based polymer nanocomposites. *Polymer* 52(1):5–25. doi:10.1016/j.polymer.2010.11.042
- Ren P-G, Yan D-X, Ji X, Chen T, Li Z-M (2011) Temperature dependence of graphene oxide reduced by hydrazine hydrate. *Nanotechnology* 22(5):055705. doi:10.1088/0957-4484/22/5/055705
- Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, Piner RD, Nguyen ST, Ruoff RS (2006) Graphene-based composite materials. *Nature* 442(7100):282–286. doi:10.1038/nature04969
- Zhao X, Zhang Q, Chen D, Lu P (2010) Enhanced mechanical properties of graphene-based poly(vinyl alcohol) composites. *Macromolecules* 43(5):2357–2363. doi:10.1021/ma902862u