Electric field assisted thermal annealing reorganization of graphene oxide/polystyrene latex films

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Abstract. Graphene/polymer films were prepared by casting water dispersion of graphene oxide (GO) in the presence of polystyrene (PS) latex particles. The samples were heated up to 180°C and exposed to an external electric voltage during their annealing. We observed that for the GO/PS films deposited before the electric field assisted thermal annealing the polymer latex was embedded in the graphene sheets, while the electric field assisted thermal annealing induces a phase separation with the enrichment of the PS phase above an underlying GO layer. For the films annealed under an external electric field we have also found that as the electric current passes through the GO film, GO could be recovered to reduced GO with decreased resistance.

Keywords: nanocomposites, coatings, graphene oxide, electrical properties

1. Introduction

Graphene, one-atom thick two-dimensional molecule made of sp² hybridized carbon atoms, is generally prepared by mechanical exfoliation [1], epitaxial growth [2] and chemical methods [3]. Among these methods the most common route toward large quantities of reduced graphene begins with the oxidation of graphite to graphene oxide (GO).

The oxidation of graphite to GO breaks the sp² hybridized structure generating defects that increase the distance between adjacent sheets from 0.335 nm in graphite to 0.68 nm for GO powder [4]. This increased spacing reduces interaction between sheets, thus facilitating the delamination of GO into single layer graphene oxide sheets upon exposure to water in a sonication bath. The main disadvantage of this material is that the charge carrier transport (i. e. electrons) observed in nearly ideal graphene are absent in GO, but at the same time the easy processing and the versatile properties of GO make the reduction

methods for such material attractive for fundamental research as well as for applications [5].

To date, most work in the area of graphene based polymer nanocomposites has focused on property modification using small amounts of graphene [6]. This emphasis can be partially attributed to the intrinsic properties of the graphene (high mechanical properties, high thermal conductivity, high electrical conductivity, etc.), which result in remarkable property improvements at low graphene concentrations. Notably, nanocomposites with randomly oriented graphene sheets, commonly exhibit isotropic properties.

Among the strategies to disperse graphene onto polymer matrix (i. e. solvent processing, in situ polymerisation and melt processing), latex technology represents a novel method for manufacturing polymer/graphene nanocomposites [7–9].

While composites prepared from aqueous graphene dispersions mixed with polystyrene latex and sub-

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sequent compression molding was accomplished with an increase of the electrical conductivity of several order of magnitude [8] there is no literature so far on the morphological and physical properties of graphene oxide/polystyrene latex films deposited under an electric field assisted thermal annealing treatment.

Here we report on the deposition of graphene oxide/polystyrene composite films by electric field assisted thermal annealing method. It was found that the thermal annealing induces a self-organization of the GO sheets with respect to the polymeric phase and that the application of an external electric field during the thermal treatment leads to the reduction of the GO sheets decreasing their surface resistivity.

2. Experimental part

Graphene oxide (GO) were purchased from Cheaptubes (single layer GO, Cheaptubes, Brattleboro – VT, USA; thickness 0.7–1.2 nm by AFM see Figure 1a). Distillated water dispersion (1 mg/1 ml) was prepared and sonicated (CV33, Bioblock Scientific, Madrid, Spain, 750 W, 60% amplitude) for 1 hr to yield a yellow suspension. GO/polymer samples were prepared by adding 1:1 volume ratio of water polystyrene latex particles dispersion (PS latex S130-1, Agar Scientific, Stansted, England, 10 wt% dispersion in water with surface-bound sulfate groups as stabilizer, average particle diameter 125 nm). Glass slides (2 cm × 2 cm) were used as substrates. The glass surface was first cleaned by the ethanol and then cleansed sequentially with deionized water and finally dried in high purity nitrogen. The glass surface was plasma treated in oxygen atmosphere (10 min., 10 Pa, with the substrate polarized with a radiofrequency plasma enhanced chemical vapour deposition system (PECVD 100,

Kenosystec, Milan, Italy) at –300 V to improve its wettability and modified by a thin layer of GO/PS solution which were drop-cast on the plasma treated substrate. After the evaporation of the water a top metal electrodes, which were made up of Al and spaced 1mm, were deposited on the dried composite film by vacuum evaporation ($\approx 133 \cdot 10^{-4}$ Pa) with an optimized thickness of 60 nm. The samples were heated up to 180°C (heating rate 10°C/min) and exposed for 10 min to a DC electric voltage of 20 V applied between the aluminium electrodes. The samples were then cooled down to room temperature leaving the electric field applied. A similar procedure was then repeated by applying the electric field to the samples at 50°C. The morphology of the prepared samples was characterized by field emission scanning electron microscopy (FESEM) (Supra 25, Carl Zeiss, Oberkochen, Germany). The surface resistance has been measured with four-point probes (4200 SCS, Keithley Instruments, Cleveland-Ohio, USA). GO/PS latex casted films were characterized with UV-Vis measurements (Lambda 35, Perkin-Elmer, San Jose-California, USA); for all samples, a quartz slide was used as the reference. The Fourier transformed infrared spectra (FTIR) (Jasco 615, Jasco Analytical Instruments, Easton-MD, USA) of the deposited film were recorded in transmission mode between 250 and 2500 cm^{-1} . Contact angles were measured with an optical contact angle meter at ambient temperature. Water droplets were dropped carefully onto the surfaces and the contact angle was monitored as a function of time. Raman spectroscopy was carried out using a LabRam (HORIBA Jobin Yvon SRL, Opera Milano, Italy) Raman spectrometer. The laser excitation of the He–Ne laser was 633 nm and the power was kept at 2 mW. The spot size of the laser was about 1–2 μm .

Figure 1. a) AFM image (left panel) and AFM height profile (right panel) of GO flakes. b) Vials containing GO/PS latex dispersion before (left panel) and after sonication (right panel), respectively.

3. Results and discussion

Figure 1b shows the water solution of the vial with before its sonication; it contains visible precipitates while the dark brown dispersion of GO dispersed in PS latex particles contains no visible precipitates after its sonication.

The morphology of neat PS latex and GO/PS latex films, formed after the evaporation of water at 50°C, were imaged by means of FESEM and reported in Figure 2a–b, respectively. It is evident that the polymer latex is embedded in the graphene sheets (Figure 2b). It should be noted that the graphene sheets, in spite of their ultrathin thickness, have very high aspect ratio and are considerably larger with respect to the spherical PS latex particles. It should be noted that the application of an external electric field during the evaporation of water at 50°C did not cause any effect onto the film morphology.

The electric field assisted thermal annealing at 180°C induces a change in the film morphology (Figures 2c) inducing the formation of separated phases as suggested by the cross-section SEM image in Figure 2d and schematized in Figure 2e.

This phenomenon was monitored by contact angle measurements. The contact angle measurements of the GO/PS latex blend evaporated at 50°C with and without electric field show an increase of the wettability with respect to the PS latex samples processed in the same way, this effect being due to the presence of carboxylic functionalities on the GO sheets position at the film/air interface (Table 1). On the contrary the hydrophobic contact angle value measured for electric field assisted thermal annealed GO/PS latex blend at 180°C is similar to that observed for neat PS latex processed with the same conditions (Table 1). This phenomenon could be explained with the enrichment of the polymer phase

Figure 2. a) FESEM image of neat PS latex film. FESEM images of GO/PS latex film cast at b) 50°C and c) under the application of an external bias of 20 V for 10 min. at 180°C. d) Cross section FESEM image of GO/PS latex film cast at 180°C under the application of an external bias of 20 V for 10 min. e) Scheme of GO/PS latex film formation before (left) and after (right) electric field assisted thermal annealing, respectively.

Table 1. Contact angle and surface resistivity (R_s) values for the prepared samples at 50°C, 50°C under electric field, 180°C and 180°C under electric field, respectively

Sample	Sample preparation conditions	Contact angle [°]	R_s^a [Ω/cm^2]
PS latex	50°C	60	$0.2 \cdot 10^9$
PS latex	50°C under electric field	76	— ^b
PS latex	180°C	60	$0.3 \cdot 10^9$
PS latex	180°C under electric field	79	$0.4 \cdot 10^9$
GO/PS latex	50°C	36	$0.1 \cdot 10^9$
GO/PS latex	50°C under electric field	40	$3.7 \cdot 10^8$
GO/PS latex	180°C	70	$0.3 \cdot 10^9$
GO/PS latex	180°C under electric field	78	$9.0 \cdot 10^6$

^aFour-probe measurements of surface resistance^bSurface resistance larger than $10^{11} \Omega/\text{cm}^2$

onto the GO sheets as shown in Figure 2d and proposed in Figure 2e where the thermal annealing induces the formation of PS hydrophobic domains that repel the water at the film/liquid interface.

Along with the thermal annealing effect, it should be noted that only for the GO/PS latex samples treated with the presence of an external electric field, a decrease of the surface resistance was observed (Table 1) being this effect more pronounced for the thermal annealed samples at 180°C.

The high resistance of GO/PS latex films is due to the existence of oxygen-containing groups, which could introduce defects to graphene [5]. It is well known how the deoxygenation could recover the GO conductivity to some extent. For example it has been shown that deoxygenation occurs in GO when it is heated above 200°C resulting in a thermal reduction [10, 11]. In our case the annealing in absence of an external electric field did not produce any significant change on the surface resistivity of our samples. On the contrary the electric field assisted thermal annealing of GO/PS latex film induces a marked decrease of the film surface resistivity. Recently, it has been reported that Joule heat will be generated when applying a large current through a graphene materials-based device [12, 13]. This makes it possible that the reduction of our GO is due to Joule heating.

The chemical changes occurring upon applying an external electric field to our GO sheets can be observed by FTIR spectroscopy in Figure 3. The most characteristic features in the FTIR spectrum of GO are the adsorption bands corresponding to the C=O carbonyl stretching at 1733 cm^{-1} and the O–H

Figure 3. FTIR spectra of GO annealed at 180°C and annealed at 180°C and exposed to an external electric field, respectively

deformation vibration at 1412 cm^{-1} [14, 15]. A broad and intense signal at 1621 cm^{-1} can be assigned to the vibrations of the adsorbed water molecules, but may also contain components from vibrations of un-oxidized graphitic domains. Upon plasma treatment, the C=O stretching vibration at 1733 cm^{-1} and the O–H deformation vibration at 1412 cm^{-1} of the GOP is gradually attenuated.

As demonstrated by the values reported in Table 1 and by the graph of the electric current vs. time recorded on our samples (Figure 4), it is interesting to note that only the application of the electric field during the thermal annealing displays a distinct decrease of the sheet resistance with an increase of the current passing through the film. The electric current decreases with time when we apply the electric field at 50°C. The current signal recorded at the start of the experiment is due to the presence of water that evaporates during the experiment leading to an insulating hybrid interface made of PS latex

Figure 4. Current vs. time curves of GO/PS latex films under the application of an external bias of 20 V for 10 min. at 50°C and at 180°C, respectively

and GO sheets as reported in Figure 2b. On the contrary the electric current increases when the electric field was applied at 180°C, in this case the medium for the electric current flow is not the water that evaporates instantaneously but leads to the formation of a conductive pathway for the electron flux. The only one component of the hybrid composite able to be conductive is the reduced GO component that has to segregate in a conductive pathway to avoid interruption of the electron charge carrier flow by the presence of intercalated insulating PS latex particles. Accordingly to Figure 2d and Figure 3 this finding suggests that: (i) the thermal annealing segregates the GO between the substrate/polymer interface leading to (ii) a percolation pathway for the electric current induced reduction of the GO film.

The optical absorption in the whole UV-Vis spectral region has been investigated for the GO/PS latex samples (see the supporting information for the UV-Vis spectra of the PS latex samples), as shown in Figure 5. The increase in the absorption for the annealed sample at 180°C is due to the GO sheet aggregation between the substrate/polymer interface; the further decrease of the optical transparency for the electric field assisted thermal annealed sample indicates deoxygenation of GO. The observed increase of the absorption suggests that the flow of the electric current through the GO layer reduces the degree of deoxygenation of GO restoring the degree of aromaticity in the graphene plane [5]. The structural model presented by Eda *et al.* [5] illustrated that the reduction restores sp^2 carbon in GO sheet plane; this reduction leads to a

Figure 5. UV-Vis spectra of the prepared samples before and after electric field assisted water evaporation at 50°C and before and after electric field assisted thermal annealing at 180°C, respectively

Figure 6. Raman spectra of GO/PS latex film thermal annealed at 180°C without the external electric field (top) and GO/PS latex film thermal annealed at 180°C with the external electric field (bottom), respectively

greater connectivity among the original sp^2 domains increasing the optical absorbance and leaving the graphene layer thickness unaltered.

In order to prove these argumentations Raman analysis was used to provide further insight into the structural changes of the graphene oxide flakes, as shown in Figure 6 [16]. The attenuation of the second-order zone boundary phonon (2D) peak at 2646 cm^{-1} together with a shoulder peak at $\sim 2920\text{ cm}^{-1}$ observed for the GO/PS latex film annealed at 180°C without the external electric field was due to the presence of residual oxygen functional groups [17].

The first-order spectrum of the prepared samples is also characterized by a strong band at $\sim 1590\text{ cm}^{-1}$ (G band) and a band at $\sim 1340\text{ cm}^{-1}$ (D band). From the Raman spectra it is also possible to see that the full width at half maximum of the D band decreases for the GO/PS latex film when it underwent to electric field assisted thermal annealing; specifically, this value varies from 186 cm^{-1} for the GO/PS sample annealed at 180°C without electric field to 149 cm^{-1} after the electric field assisted thermal annealing at 180°C. Accordingly to Yang *et al.* [18] we attribute these findings to the removal of oxygen from the GO sheet.

4. Conclusions

In summary, the graphene oxide/polystyrene composite films have been fabricated by electric field assisted thermal annealing method. It has been reported how the GO sheets can be transported

between the substrate/polymer interface by thermal annealing; the combination of the thermal treatment with the application of an electric current lead to the reduction of the GO sheets decreasing their surface resistivity. Therefore, self organization of this 2D material within a polymer matrix could lead to many exciting functional graphene-based polymer nanocomposites.

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