Enhanced electrical conductivity of poly(methyl methacrylate) filled with graphene and in situ synthesized gold nanoparticles

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Abstract
The improvement of the electrical conductivity of polymers by incorporating graphene has been intensively studied in recent years. To further boost the electrical conductivity, blending third-party additives into the polymer/graphene systems has been demonstrated as a viable strategy. Herein, we propose a simple route to increase the electrical conductivity of poly(methyl methacrylate) (PMMA)/graphene nanoplatelet (GnP) composites, by the in situ synthesis of gold nanoparticles directly into the solid film. In particular, PMMA, GnP and a gold precursor are solution blended to form the composite films. The subsequent heat-induced formation of gold nanoparticles directly in the solid state film, cause the significant decrease of the percolation threshold of GnPs loading, from 3% to 1% by weight in the composite. This is attributed to the preferential formation of the gold nanoparticles onto the GnPs, with synergistic effects beneficial for the improvement of the electrical conductivity. The formation procedure of the gold nanoparticles, and their arrangement into the composite matrix are studied. We demonstrate that following this straightforward process it is possible to form nanocomposites able to conduct efficiently electric current even at low graphene loadings preserving at the same time the mechanical properties of the polymer matrix.

1. Introduction

After the isolation of few-layer (FLG) [1] and single-layer (SLG) [2] graphene, upon the exfoliation of graphite by micromechanical cleavage [2], this material has attracted tremendous attention thanks to its extraordinary mechanical properties, high electrical ($\sigma$) and thermal conductivity, large surface area and gas impermeability [3]. These properties make both SLG and FLG attractive fillers able to efficiently enhance the properties of the polymers when in composite form [3]. This is currently opening up several application possibilities. In particular, the possibility to produce both SLG and FLG by liquid phase exfoliation of pristine graphite [4], which is scalable at the industrial level [5, 6], is enabling the large-scale applicability of polymer/graphene composites in different fields [3, 7–11].

One of the properties of graphene that can be transferred to a polymer matrix, when these two components are combined to form a composite material, relies on the enhancement of the $\sigma$ of the polymer [3]. This is of crucial importance for applications in which flexible conducting or electromagnetic shielding materials are required [12]. However, adding functionalities in a material should not compromise other properties of the final composite. In fact, in order to develop polymer composite materials with good mechanical properties, low weight, good processability and economic affordability, graphene-based sheets, dispersed in the polymer, should construct percolated conducting pathways for electron transfer at a significantly lower loading compared to conventional additives [13]. The percolation threshold and the maximum $\sigma$ reachable by the composite relies on the structural nature of the graphene-based materials used (i.e., lateral size, thickness, functionality and defects) and their dispersion inside the matrix. In general, graphene sheets with small thickness, large lateral size and limited defects are the most efficient in improving the aforementioned properties of the final composite.
Although their large surface areas are able to support well-developed transport networks, their tendency to agglomerate during processing in the host polymers requires high filler loadings to achieve a satisfactory conductive performance [13, 15], compromising at the same time the mechanical properties of the polymer composites and their economical affordability [15]. Therefore, in the field of polymer composite applications, the investigation on efficient and low-cost methodologies to produce graphene with the aforementioned structural features [5, 6], is performed in parallel with the optimization of the production methods of graphene-based polymer composites with good dispersion and low percolation thresholds.

In particular, modifications of the graphene flakes surface by grafting organic molecules onto flakes themselves to improve their dispersion into the polymers have been extensively investigated [8–10, 16, 17]. However, this functionalization process, usually, negatively affects the pristine graphene’s properties, due to the conversion of carbon’s hybridized state from sp² to sp³, and therefore due to the loss of the free π cloud electrons, or due to the modification of its doping density and of the scattering sites [18]. An alternative route, to achieve a uniform dispersion in a polymer matrix, is the in situ polymerization of monomer-graphene mixtures [19, 20]. Though, the high viscosities achieved upon the polymerization process in the graphene-monomer dispersions and the limited mobility of the monomers due to the presence of the graphene flakes, make the polymerization process more difficult [8, 9]. Recently, preparation methods of conductive polymer composites with segregated networks of graphene flakes have been also developed [15, 21], achieving percolation thresholds at extremely low graphene loadings (e.g. 0.005 vol%) [15].

An alternative way to reduce the electrical percolation threshold of the polymer–graphene based composites is the combination with a third additive. In particular, the combination of carbon nanotubes (CNTs) with reduced graphene oxide (RGO) sheets [22, 23] in the polymer matrix results in the formation of percolation pathways at lower loadings [23], or in composites with higher conductivities compared to the ones formed with the same amount of polymers and the individual fillers [22]. Some inorganic non-conductive fillers, such as layered double hydroxide [24], and silica [25], are also used together with RGO flakes. In fact, although the non-conductive additives do not actively participate to the conducting pathways inside the composites, their presence improves the composites processing, favoring the graphene flakes dispersion. Most importantly, conductive metallic additives, such as silver nanowires [26, 27] or nanoparticles [28–30] are used, contributing both in the formation of percolation pathways and in the reduction of the inter-sheet resistance of the RGO flakes. In these studies, the metallic additives are either pre-fabricated and subsequently mixed with the RGO and the polymer, or pre-anchored on the graphene sheets upon chemical reduction of the corresponding precursors before the mixing with the polymer. However, both routes have severe limitations, due to the multistep and time-consuming processes, which compromise the scalability of these approaches.

Herein, we propose the formation of highly conductive graphene nanoplatelet (GnP)/metallic hybrid polymer composites following a simple two-step process based on the heat-induced in situ formation of gold nanoparticles in the graphene/gold precursor loaded polymer solid film. The in situ synthesis of nanoparticles in polymer films, by photo-irradiation or thermally induced reduction of the embedded metallic precursors, is a facile method, which does not require the use of any chemical reductant. The formed nanoparticles are well dispersed in the polymeric matrix, and their dimensions and density can be easily controlled by the irradiation conditions or the thermal treatment time [31–36]. As we prove, by heating a PMMA/graphene/gold precursor solid film, gold nanoparticles are formed within the composite. The morphological study of the hybrid proves that gold nanoparticles with diameters in the 50–250 nm range are preferentially formed on the GnP sheets, and this causes enhanced electron transfer, reducing significantly the percolation threshold of the composite compared to the PMMA/graphene system. In fact, we demonstrate that the presence of 2 wt% of gold nanoparticles is able to reduce the percolation threshold from 3 to 1 wt% of GnP in the PMMA. Given the fact that the in situ formation of inorganic nanoparticles in solid polymer films a quite general method, different combinations of polymers, graphene flakes and inorganic precursors can be explored, opening up new, simpler ways of processing and fabricating hybrid graphene polymer composites for several applications in key technological areas.

2. Materials and methods

2.1. Materials

Poly(methyl methacrylate) (average molecular weight ~ 120 000 by GPC), gold(III) chloride hydrate (HAuCl₄, contains ~50 wt% of gold after reduction with sulfite), chloroform (CHCl₃, ACS reagent) and tetrahydrofuran (THF, ACS reagent) were purchased from Sigma-Aldrich. GnP, grade Ultra G+®, were obtained from Directa Plus (Italy) [37]. All the materials were used as received.
2.2. Samples preparation

PMMA composite films with \textit{in situ} synthetized Au and different loadings of GnPs (1–15 wt\% with respect to the solid composite) were prepared following the procedure illustrated in figure S1 in the supporting information (SI), which is available online at stacks.iop.org/NANOF/2/025003/mmedia. The specific amount of GnPs and the PMMA were mixed with CHCl₃ (5 to 15 ml depending on the GnPs added) and stirred overnight. Then, the mixtures were treated with ultrasonic bath for 180 min at 59 Hz, and subsequently aliquots of a solution of HAuCl₄ with a concentration of ~0.07 g ml⁻¹ in a 1/10 v/v THF/CHCl₃ mixed solvent were added to the prepared GnPs/PMMA dispersion in order to obtain a precursor concentration of 4 wt\% with respect to the final composite. After stirring for 30 min, the mixtures were poured onto Teflon molds to evaporate the solvent overnight, and then were placed in low vacuum at 40 °C for at least 48 h in order to completely evaporate the solvents. Finally, the dried films were heated in an oven at 100 °C for 24 h to induce the Au nanoparticles formation. For comparison reasons, films of pristine PMMA and PMMA/GnPs at the loadings of 1–30 wt\% were prepared following the same method, without adding any fillers and gold precursor respectively. In a typical experiment, the final weight of the composites was 1 g. To convert the wt\% loading of GnPs in the polymer composites into volume percentage vol\%, the density for GnPs was assumed to be the density of graphite [3] (2.2 g cm⁻³) and the density of PMMA used was 1.2 g cm⁻³ (value given by the producer).

2.3. Characterizations

The morphology of the as-prepared composites was examined by a JEOL JSM 7500FA high-resolution scanning electron microscope (HR-SEM), and a JEOL JEM-1011 transmission electron microscopy (TEM). The observed HR-SEM cross-section surfaces were prepared by samples fractured in liquid N₂ and followed by coating of 10 nm think carbon layer. The images were acquired by collecting the backscattered electrons, in order to reveal information about the composition of the composites. For the TEM analysis, the PMMA was washed away by dissolving the films in CHCl₃ followed by centrifugation in order to collect the GnPs and the formed nanoparticles. This process was repeated for 5 times assuring that the entire polymer was completely removed. At the end of the process, the collected sediments for each process were re-dispersed in CHCl₃, drop casted on 300 mesh Cu grid and dried at room temperature. The statistical Au particle size distribution study was carried out by counting at least 100 particles per sample. In order to estimate the amount of Au nanoparticles formed onto the GnPs flakes, the number of the nanoparticles was measured on at least 50 areas of 1 μm² per sample.

X-ray diffraction (XRD) analyzes were performed on a PANalytical Empyrean x-ray diffractometer equipped with a Cu Kα radiation (λ = 1.5418 Å), and acquisitions were carried out from 5–80° with a step size of 0.05° and a scan speed of 0.33°/s.

Electrical conductivity was measured with a four-probe station and source meter (Keithley, 2612A) in DC regime on 10 mm × 10 mm film specimens. In order to eliminate the contact resistance between the probe and the sample, silver paste electrodes were deposited on the specimens.

Thermogravimetric analysis (TGA) was performed with a TA Q500 instrument, on about 10 mg samples, in Platinum pans, with N₂ fluxes of 60 ml min⁻¹ for. In the heating ramp mode, the heating rate was 10 °C min⁻¹, from 50 to 800 °C. Some samples were also tested with isothermal mode at 100 °C for 24 h.

3. Results and discussion

After their formation, the solid films were treated in the oven at 100 °C in order to induce the reduction of the precursor and the formation of the Au nanoparticles. In order to find the optimal duration of the heat treatment for the completion of the Au nanoparticles formation, a dynamic XRD study is carried out on the PMMA/1 wt\%GnPs/HAuCl₄ and PMMA/HAuCl₄ films at different heating times, and the evolution of the gold diffraction peak at 38.1° is monitored. As shown in figure 1(a), a weak Au (111) diffraction peak emerges after 0.5 h of 100 °C heat treatment. As the duration of the heat treatment increases, the intensity of the Au (111) peak grows gradually, until it reaches a stable value after 20 h of heating. Same behavior is also observed in the PMMA/HAuCl₄ film (see figure S2 in SI), indicating that the GnPs do not affect the kinetics of the Au nanoparticles formation. Both PMMA and GnPs are chemically inert to the Au precursor, since no Au nanoparticles are formed during the solution blending and casting process, as indicated by the absence of Au peaks in the XRD pattern of the precursor containing film before heat treatment (figure 1(b)(b3)). In the same pattern, there is no indication of any Au precursor peak, confirming that Au has been finely dispersed into the composite. However, after the heat treatment of this film, the typical diffraction peaks of Au (111) at 38.1°, (200) at 44.4°, (220) at 64.7° and (311) at 77.6° emerge (JCPDS, card No. 04-0784) (figure 1(b)(b4)), indicating that the heating process induces the \textit{in situ} formation of Au crystalline particles, while the intense peak at 26.5° and the weak peak at 54.6°, assigned to the (002) and (004) planes of graphite [38] are still present, as well as in all samples containing GnPs (figure 1(b)(b2, b3)).
During the heating of the Au precursor containing film, a decomposition process of the precursor is expected to occur, involving release of H$_2$O, HCl and Cl$_2$ leaving just elemental Au in the samples $^{39}$. The newly formed Au act as seeds for the successive growth of the nanoparticles $^{31}$, and, due to the presence of the polymer matrix, their agglomeration is expected to be confined $^{40}$. The loss of gasses upon the precursor thermal treatment is confirmed by the TGA performed on the samples under inert (N$_2$) environment $^{33}$ (figures S3(a) of the SI). Specifically, from the isothermal measurement under 100 °C for 24 h, in the same experimental conditions used for the thermal induced in situ growth of the Au nanoparticles in the films, the Au precursor containing samples lose about 9% of their weight. This value is higher compared to the loss of the pure polymer (6%) or the GnPs/polymer films (5%), and can be attributed to the release of HCl and Cl$_2$ gases upon the thermal decomposition of the Au precursor $^{41}$. The data obtained by the heating ramp measurements of all samples (figure S3(b) of S.I.) up to 800 °C reveals that if the residue of PMMA and GnPs are extracted, the Au residue is ~2 wt%, as in the case of the PMMA/HAuCl$_4$ sample. This implies that the precursor loses half of its weight upon heating, thus leading to the formation of metallic Au regardless the presence of the GnPs.

To assess the morphology and the dispersion of both the GnPs and the in situ synthesized Au nanoparticles inside the polymer matrix, which are key parameters for the good performance of the composite, HR-SEM is performed for all the samples, and some representative images are presented in figure 2.

As shown, the in situ synthesized Au nanoparticles are quite heterogeneous in morphology having spherical, rod and triangle shapes, and sizes in the 0.1–1 μm range. In the PMMA/Au film (figure 2(a)), the Au nanoparticles are distributed homogeneously within the polymer matrix, due to their growth in a homogenous polymeric environment. However, in the GnPs-containing films (figures 2(b), (c)), although some Au nanoparticles are randomly distributed in the composite, their majority is concentrated in specific areas (as indicated with the circles in the images) that coincide with the GnPs present in the film. In fact, as already proved $^{42}$, in the presence of GnPs, the remaining oxidized sites act as nuclei for the growth of Au crystals, resulting in
the localized formation of the Au nanoparticles onto the GnP layers. This is also the case in our system; the GnP's have remaining oxidized sites, as shown by the XPS study presented in the SI figure S4. This hypothesis is further confirmed by the TEM study performed directly on the GnP-Au nanoparticles. As shown in figure 3, Au nanoparticles of different shapes with sizes in the 50–250 nm range (see size distribution histograms in SI figure S5) are localized onto the GnP layers. To prove that the presence of GnP's significantly affects the Au nanoparticles nucleation process and distribution, the surface density of the Au nanoparticles formed after the heat treatment of PMMA/GnP/HAuCl₄ samples with different GnP's concentration is estimated. As shown in figures 3(a) and (b) in the samples with 1 wt% and 7 wt% GnP's respectively, Au nanoparticles are formed on the GnP layers and their amount is less in the 7 wt% sample. The calculated surface density is ~35 Au nanoparticles per μm² of GnP's at the 1 wt% sample and ~15 Au nanoparticles per μm² of GnP's at the 7 wt% sample. In the latter case, the relative amount of the Au precursor with respect to the GnP's is less, which is a direct confirmation of the influence of the GnP's on the Au nanoparticle formation process.

The effect of the hybrid fillers in the samples σ is demonstrated in figure 4. Pure PMMA shows negligible σ of ~10⁻⁹ S cm⁻¹. A similar value is also obtained for the composites with low loading of GnP's (up to 2 wt%). Above this GnP's concentration and up to 5 wt% a drastic increase of σ up to ~6 orders of magnitude is observed, indicating the triggering of electrical percolation. By further increasing the GnP's loading, σ continues to increase, reaching a plateau at the maximum value (σmax) of ~2 S cm⁻¹ up at 25 wt% of GnP's loading. However, this is a very high loading value, which compromises the scalability of the method for any real application. When
The Au precursor is added to the composites, the $\sigma$ behavior is similar to the PMMA/GnP one. This indicates that the presence of the precursor does not affect the overall electrical properties of the polymer composite. Nonetheless, after their thermal treatment at 100 °C for 24 h, (PMMA/GnP/Au films) a significant increase of $\sigma$ occurs at loadings of GnpPs from 0.5–3.0 wt%, whereas it reaches the maximum value of ~2 S cm$^{-1}$ at about half of the GnpPs loading (15 wt%) compared to the PMMA/GnP films. Therefore, with the in situ formation of the Au nanoparticles, the estimated percolation threshold of the PMMA/GnP composites is reduced from 3 wt% (1.65 vol%) to 1 wt% (0.55 vol%).

The electrical percolation behavior can be studied using the equation:

$$\sigma \propto \left[(\phi - \phi_c)/(1 - \phi_c)\right]^t$$

(1)

for $\phi > \phi_c$, where $\phi$ is the volume fraction of the filler, $\phi_c$ is the percolation threshold in volume fraction and $t$ is the universal critical exponent [43]. The parameter $t$ is often used in order to characterize the type of percolation of the system and it is expected to exhibit a value of approximately 1.3 for a two-dimensional (2D) percolating structure, or near 2 for a three-dimensional (3D) percolating structure [14]. As shown in figure 4(b), the percolation behavior is fitted using equation (1) for the PMMA/GnPs and the heat treated PMMA/GnP/HAuCl$_4$. In both cases the fitted universal critical exponent $t$ is a bit higher than 4, ($t$ are 4.02 and 4.76 for PMMA/GnP/HAuCl$_4$ (100 °C treated), respectively). This indicates that the developed films do not follow the behaviors of systems incorporating 2D or 3D conducting structures, but more complex charge tunneling transport processes are involved in their $\sigma$ [44].

The in situ formed Au nanoparticles decrease the percolation threshold of PMMA/GnP from 3 to 1 wt% (~67% reduction). This is comparable, or better than the values previously reported on hybrid graphene-containing polymer composite systems [23, 28, 45]. In particular, polymer composites containing RGO decorated with Ag nanoparticles cause the reduction of ~40% in the percolation threshold, with respect to the graphene/polymer system [28]. Furthermore, the incorporation of CNTs lowered the $\sigma$ percolation threshold of the epoxy/graphene composites by about 30%–70% [23, 45]. Therefore, our proposed method allows the efficient improvement of $\sigma$ of the graphene flakes/polymer systems following the Au in situ synthesis approach directly in the solid films. This method does not require complicated chemical steps, but instead simple processes such as the thermal treatment of the samples.

As the tensile test results indicate (see figure S6 in SI), the increase of the GnpPs loading in the polymer matrix causes the increase of the modulus of the composites and the decrease of the elongation at break, while the presence of Au nanoparticles slightly modifies these properties. In both cases, after 7 wt% loading of the GnpPs, the samples become very brittle, making impossible their use as flexible polymeric conductive films. However, the presence of Au significantly decreases the percolation threshold of the composites, permitting to achieve films of high $\sigma$ at lower GnpPs loadings and, at the same time, with good mechanical properties. In particular, at the 7 wt% GnpPs/PMMA film the $\sigma$ reached $4.95 \times 10^{-4}$ S cm$^{-1}$, while a similar value ($3.27 \times 10^{-4}$ S cm$^{-1}$) is instead reached with 3% loading of GnpPs in the GnpPs/Au/PMMA samples. This is a remarkable result favorable for diverse applications where flexible conducting materials are required. In addition, since the method introduced here is a post- treatment process of already formed films, designs of conducting/non-conducting patterns on the polymeric surfaces can also be realized.

### 4. Conclusions

PMMA composites filled with graphene Au hybrid structures are successfully prepared via solution blending and post-production heat treatment. The Au nanoparticles are formed in situ in the PMMA-GnP solid composite films, upon heat-induced reduction of the Au precursor present in the film. The detailed XRD study confirmed the presence of the metallic gold and together with the thermal analysis for the final composites show that the method followed results in full transformation of the precursor into metallic Au nanoparticles. The morphological studies reveal that GnpPs are dispersed homogeneously in the polymer matrix, whereas the Au nanoparticles are preferentially formed onto the GnpPs layers. This causes a significant decrease of the percolation threshold of the electrical conductivity, with three times less GnpPs needed when combined with Au nanoparticles, compared to the PMMA/GnP film. Specifically, the percolation threshold is decreased from 3 to 1 wt% of GnpPs loading in the presence of the Au. Thanks to the synergistic effect between the GnpPs and Au nanoparticles a smaller total loading is necessary in order to obtain specific conductivity values, which would be beneficial to preserve other desired properties of the polymer matrix, like mechanical flexibility, in the final composites.
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