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Gold functionalized graphene as conductive filler in UV-curable epoxy resin

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ABSTRACT: graphene sheets (GNP) were functionalized with gold nanoparticles via a spontaneous deposition of gold particles on its surface occurred by chemical reduction of (Au^{3+}). Even after only 1 min of reaction, the reduction of Au^{3+} into metallic Au^0 , takes place evidencing the rapid and spontaneous character of the reduction. The particles after only 3 min of deposition have very small diameters, average centered at 17. The Au-GNP nanofillers were dispersed into UV-curable epoxy resin. Conductivity of the epoxy crosslinked samples containing Au-GNP nanofiller were compared to the values obtained for epoxy nanocomposite containing the same amount of bare graphene; the electrical conductivity was significantly increased by the addition of Au-GNP nanofiller, of about 4 orders of magnitude. This could be attributed to a charge transfer mechanism, which is strongly enhanced by the presence of gold NPs.

Keywords: graphene, gold nanoparticles, epoxy resin, Conductivity.

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1. Introduction

Organic materials are a promising candidate for the realization of flexible electronics, due to their high workability, low cost, disposability and low impact [1]. Organic resistors, having a typical resistivity in the range $10^4 \Omega \cdot \text{cm}$ - $10^3 \Omega \cdot \text{cm}$, could be prepared by adding conductive fillers into polymeric matrix in order to increase their electronic conductivity [2]. One of the methods to increase the electronic conductivity of polymeric materials is the addition of conductive fillers like carbon black, graphite, metal powders, metal nanowires [3-5].

Numerous reports have already demonstrated the positive effects of CNTs and graphite on epoxy resins [6-8]. Graphene is following the same trend in the last years [9], but just a few of them are related to UV-photocured nanocomposites [10].

Nowadays, UV-curing processes are becoming a very reliable alternative to the thermal process due to their particular characteristics [11]: fast transformation of the liquid monomer into a thin solid crosslinked coating with tailored physical and chemical properties without the need of using a solvent, so it is considered as environmental friendly processes. This technique is usually performed at room temperature allowing us to save energy. Furthermore, the use of the cationic photopolymerization provides other advantages compared to the radical one [12] such as the absence of oxygen inhibition and reduced shrinkage after curing.

In a recent paper we showed the enhancement of electrical conductivity behavior of a UV-cured epoxy resin containing graphene as conductive filler [10], where electrical conductivity and dielectric permittivity significantly increased in the presence of functionalized graphene sheets. Nevertheless, when the resin was loaded with sheet-like nanofiller the increase of these two properties was much lower compared with the addition of CNTs, and the thresholds appeared at higher concentrations, reaching an antistatic limit of 10^{-8} S/cm .

In order to further enhance the electrical conductivity behaviour of epoxy-graphene UV-cured composites, gold-functionalized graphene sheets were dispersed into the UV-curable epoxy resin and the system was crosslinked. The photocured process was investigated and the obtained films fully characterized.

2. Experimental

2.1 Materials

Graphene sheets were purchased from Graphene Supermarket (**GNP**, Graphene Supermarket, 3 nm flakes, grade AO1, lateral size 10 μm) and consisted on a black powder formed by nm flakes of multilayer graphene sheets. The chemicals Potassium gold (III) chloride (KAuCl_4), ethaol, Bis-cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexyl carboxylate, (**CE**), triphenylsulfonium hexafluoroantimonate (cationic photoinitiator, $\text{Ph}_3\text{S}^+\text{SbF}_6^-$, at 50 wt% solution in propylene carbonate) were purchased from Sigma-Aldrich and used as received.

2.2 Graphene functionalization

GNP were employed as substrates of the gold deposition,. Potassium gold (III) chloride (KAuCl_4) was used as source of gold atoms. In a typical procedure, 10 mg of GNP were dispersed in 10 ml of $\text{H}_2\text{O}/\text{EtOH}$ 50 % in volume by continuous stirring for 1 h and 30 min in ultrasonication bath. Then, a specific amount of KAuCl_4 was added to this dispersion to reach a concentration of 5 mM. Two different deposition times were employed: 3 min and 60 min (for some analysis also a 1 minute deposition was carried out). When the deposition is finished, the particles are washed until neutral pH, filtered and dry at 70 $^\circ\text{C}$ for a night.

The presence of gold nanoparticles on the surface of GNP was evidenced by the analysis of the crystalline structures by X-ray diffraction (XRD). Measurements from $2\theta = 12^\circ$ to $2\theta = 50^\circ$ were carried out on a Bruker D8 Discovery X-ray diffractometer.

Transmission electron microscopy (TEM) images were taken on a Philips CM200 instrument operating at up to 200 kV.

2.3 Sample preparation

Au-GNP was directly dispersed in the range between 0.5 to 2 wt% in the epoxy resin by means of Ultraturrax, a mixing procedure at 30000 rpm for 10 minutes and 10 minutes in an ultrasonic bath was carried out to reach a good dispersion of the carbon filler in the resin. After mixing, 2 wt% of actual content of photo-initiator (triphenylsulfonium hexafluoroantimonate) was added to each formulation. The UV-induced polymerization was promoted by UV irradiation using Fusion lamp, with a light intensity on the surface of the sample of about 2500 mW/cm² (belt speed of about 6 m/min).

2.4 Characterization

The extent of the photo-polymerization reaction was determined by Real-Time-FTIR spectroscopy (RT-FTIR, using the instrument Thermo-Nicolet 5700). 25 µm-thick formulations were coated onto silicon wafers and simultaneously exposed to the UV beam (HAMAMATSU LC8) with an intensity of 35 mW/cm², to induce polymerization, and to the IR beam, to make an in-situ evaluation of the extent of reaction. Epoxy groups conversion was followed by monitoring the decrease in the absorbance of the epoxy groups centred at 750 cm⁻¹ and normalized with the carbonyl peak centred at around 1700 cm⁻¹. The conversion of the cured samples under Fusion lamp was determined by carrying out a single spectrum, before and after irradiation, on a coated film of about 25 µm.

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Dynamic-mechanical thermal analysis (DMTA) was performed on Triton Technology TTDMA. All the experiments were conducted with a temperature ramp of 3°C/min, applying a force with

frequency of 1Hz and with 20 μm of displacement. The storage modulus, E' , and the loss factor, $\tan \delta$, were measured from 25 $^{\circ}\text{C}$ up to the temperature at which the rubbery state was attained. The T_g value was assumed as the maximum of the loss factor curve ($\tan \delta$).

DSC measurements were performed under nitrogen flux of 2 ml/min, in the range of 25 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$ with a heating rate of 20 $^{\circ}\text{C}/\text{min}$, with a Mettler TC 10A/TC15 TA controller instrument.

Electrical measurements were performed by using a Keithley-238 High Current Source Measure Unit as high voltage source and nano-amperometer, multiple measurements in air at room temperature were performed, in the range [-10, 10] V. Electrical properties of the cured films were measured using a two-point probe geometry and using two copper plates as electrodes, bulk conductivity was measured.

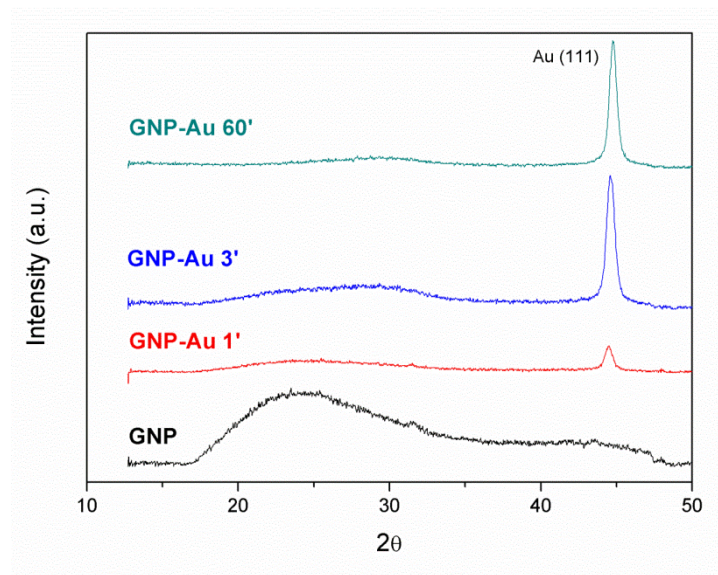
3. Results and discussion

The first step of this investigation was the gold functionalization of GNP. Spontaneous deposition of gold particles on the surface of reduced graphene has already been reported by Kong et al. [13]. The deposition of metallic Au occurs through spontaneous chemical reduction of (Au^{3+}) by the graphene: $\text{AuCl}_4^- + 3\text{e}^- \Rightarrow \text{Au} + 4\text{Cl}^-$. This reaction involves a galvanic displacement and redox reaction by relative potential difference [14, 15]. Following this method the deposition/reduction of gold can be promoted by the presence of electrons on the negatively charged surface of the reduced graphene. The reduction potential of graphene is +0.38 V vs SHE (standard hydrogen electrode), which is lower than the potential of AuCl_4^- (+1.002 V vs SHE) [16]. Therefore, the donation of electrons from the surface of the graphene to reduce Au^{3+} in solution is possible.

Figure 1 shows the XRD diffractogram for the GNP and the gold decorated graphene (Au-GNP). For the Au-GNP samples, at all deposition times, it is possible to observe the characteristic peaks of the crystalline structure of gold at 45 $^{\circ}$ [17]. Even after only 1 min of reaction, the reduction of Au^{3+} into metallic Au^0 , takes place evidencing the rapid and spontaneous character of the reduction. After 3

and 60 min of deposition the XRD patterns evidence sharper peaks, indicating that the amount of gold is higher for the 60 minute deposition than for the 1 min deposition sample. On the other hand, the diffractogram of the GNP presents a broad peak in the region of $2\theta = 25^\circ$, which correspond to the stacked structure of few graphite layers of the GNP. This peak practically disappear for the 1 min and 3 min deposition times of gold and completely disappear after 60 min of deposition. This fact is due to the exfoliation of the GNP by the application of the shear forces during stirring and ultrasonication.

Figure 1: XRD diffractograms of GNP and Au-GNP at three different deposition times.



The morphological characterization of the functionalized GNP was carried out by TEM. Figure 2 shows TEM images for the Au-GNP samples after 3 min and 60 min of deposition respectively. The particles after only 3 min of deposition already have a well-defined spherical geometry with very small diameters, average centered at 17 nm (see the diameter distribution of gold NPs in Figure 3). At longer deposition times (60 min), the particles are much bigger and easy to detect. In this case the average diameter of the gold nanoparticles is 67 nm but their distribution is broadened. For

composite manufacturing and characterization we chose the Au-GNP after 60 min of deposition due to the bigger size of the gold deposited nanoparticles expecting an higher potential to modify the electrical properties of the final nanocomposite by a charge transfer mechanism.

Figure 2: TEM images of the Au-GNP after a deposition of a) 3 min and b) 60 min.

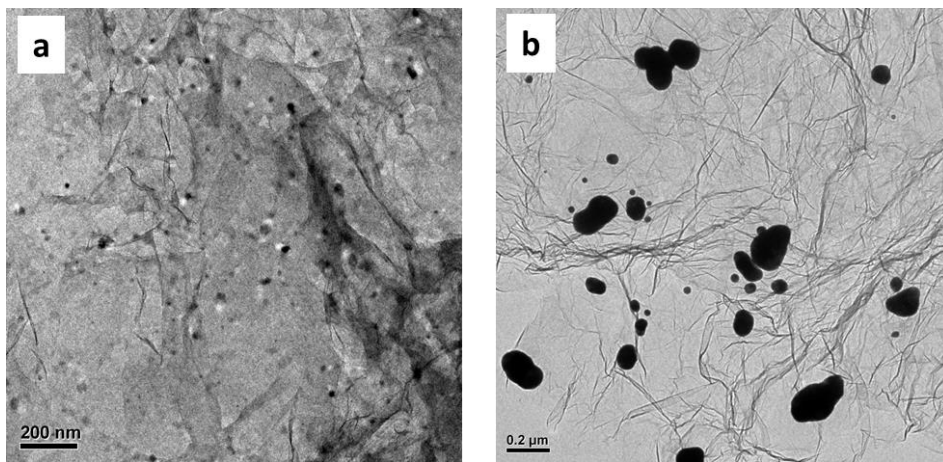
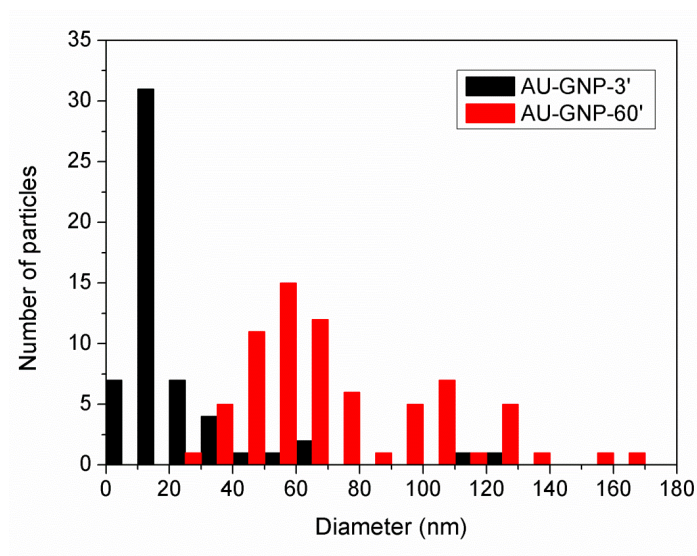
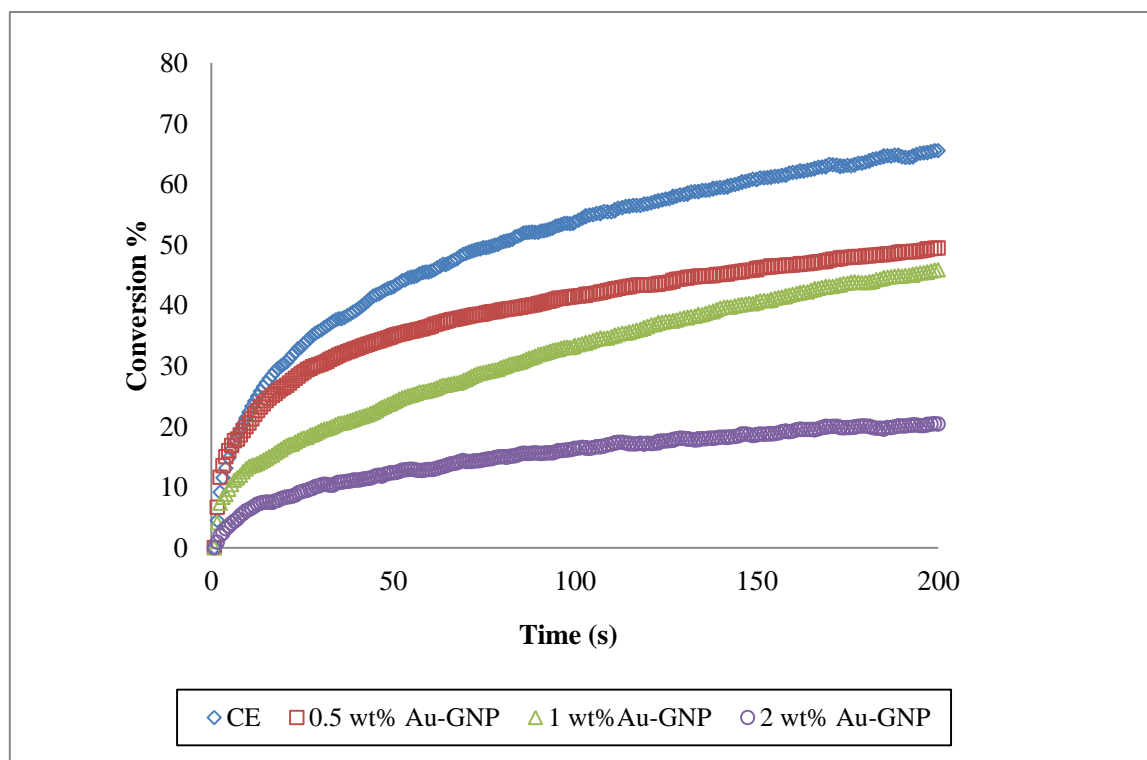


Figure 3: Diameter distribution of the gold nanoparticles.



The influence of the Au-GNP (obtained after 60 minutes of deposition) on the cationic photopolymerization reaction of an epoxy resin was evaluated by real time FTIR. The crosslinking process was monitored following the decrease of the epoxy group band, centered at around 750 cm^{-1} , as a function of irradiation time. The conversion curves as a function of Au-GNP content are reported in Fig. 4 and compared with the curve of the pristine epoxy resin.

Figure 4 RT-FTIR conversion curves as a function of irradiation time for the pristine CE resin and for the formulations containing Au-GNP filler in the range between 0.5 wt% to 2 wt%.



At the initial stages, the reactivity of the epoxy groups was very high for the pristine CE resin, and after 3 minutes of irradiation the final conversion of the epoxy band was around 80%. This phenomenon is a direct consequence of vitrification.

The addition of Au-GNP to the photocurable formulation lead to a decrease of both polymerization rate and final epoxy group conversion as a function of loading fraction of the filler. This behaviour was previously observed and attributed to the UV-light shielding effect of graphene: a lower amount of reactive species is photogenerated resulting in a decrease of the epoxy group conversion. Hence, this competition in terms of light absorption between the nanofiller and the photoinitiator led to a less effective UV-curing process.

In order to overcome this effect, the UV-curable formulations were crosslinked by using a high energy output lamp (Fusion lamp), which was already demonstrated to be useful to achieve an almost fully epoxy group conversion in black formulations containing bare graphene as a filler [10]. Thermal and dynamic-mechanical analysis were performed on the cured films. While DSC analyses gives information about the thermal behaviour, DMTA analyses allows the evaluation for the elastic and viscous component of the modulus of the material over a large temperature range. Therefore, these techniques give a complete characterization of the thermal and viscoelastic properties of the materials. Firstly, the T_g values of the UV-cured films were evaluated by means of DSC analyses. It was possible to observe a strong increase of the T_g values as a function of the graphene content in the UV-curable formulations (see Table 1). The T_g increase could be due to the constraint effect of graphene sheets on the polymeric chain mobility. This results are in accordance with previous investigations [10] and suggest uniform and homogeneous distribution of the graphene platelets within the polymeric network. The T_g values were also determined as the maximum of $\tan\delta$ curves and showed the same trend previously observed by means of DSC analyses. The values are collected in Table 1; it can be observed that the T_g values obtained by DMTA are higher than those obtained by DSC, this is a general behavior previously observed and it was attributed to a frequency effect [18].

Table 1: Properties of UV-cured epoxy films obtained in the presence of graphene filler.

Sample	Conv. [%] ¹	Conv. [%] ²	Gel content [%] ³	T_g [°C] ⁴	T_g [°C] ⁵
CE	70	100	100	150	190
0,5% Au-FGS	45	100	100	163	200
1% Au-FGS	40	95	100	178	210
2% Au-FGS	18	98	99	190	225

1: plateau values of the RT-FTIR conversion curves as a function of irradiation time (UV intensity of 35 mW/cm²)

2: determined by the single spectra taken before and after UV irradiation with Fusion lamp (UV intensity of 2500 mW/cm²)

3: determined gravimetrically ASTM D2765-84

4: determined by DSC analysis, scan-rate 20 °C/min

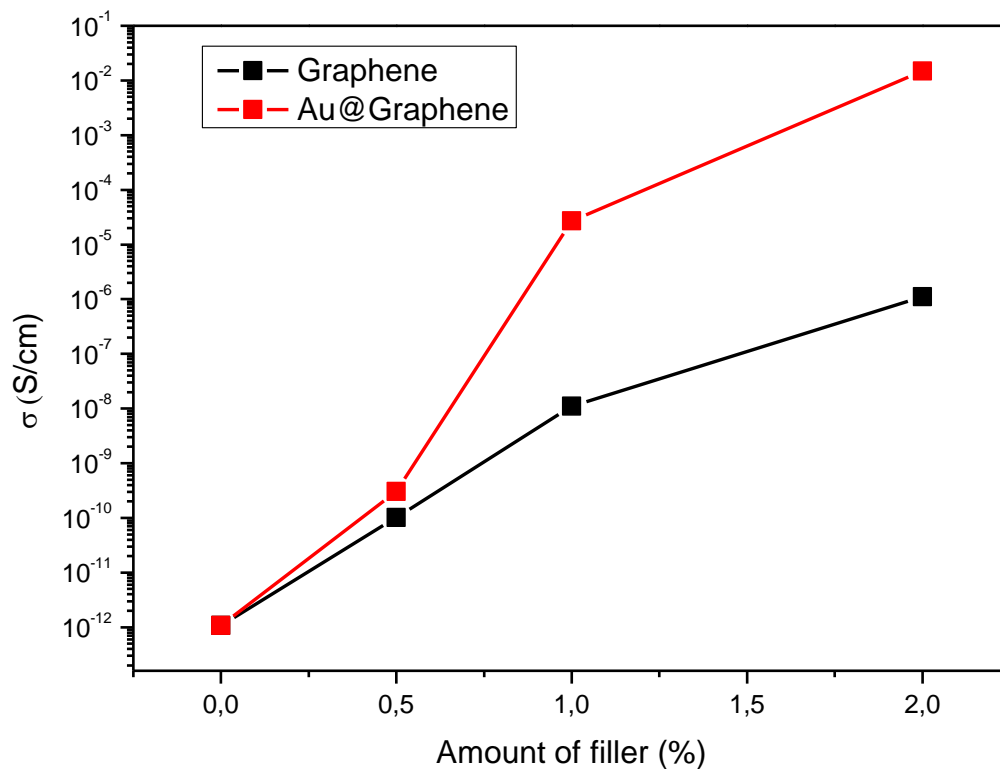
5: determined by DMTA analysis, tensile configuration, 1 Hz frequency

At last, the electrical properties of the photocured epoxy nanocomposites at different nanofiller contents were measured at room temperature. By considering geometrical parameters of the system (electrodes surface area and thickness of each film), bulk conductivity was calculated. Conductivity of the epoxy crosslinked samples containing Au-GNP nanofiller were compared to the values obtained for epoxy nanocomposite containing the same amount of bare graphene. As shown in figure 5, the electrical conductivity was significantly increased by the addition of Au-GNP nanofiller.

It is evident the better performance of the Au-GNP compared to the un-treated GNP. The electrical conductivity of the gold deposited GNP is higher than the bare GNP in the entire range of concentrations employed. When bare GNP was dispersed into UV-curable epoxy resin an antistatic behaviour was reached with a value of 10⁻⁴ S/m when 2 wt. % of the conductive filler was added. When Au-GNP was added, at the same amount, a value of 10⁻² S/cm was reached. Therefore the

UV-cured composite containing Au-GNP showed an enhancement on the electrical conductivity of about 4 orders of magnitude. This could be attributed to a charge transfer mechanism, which is strongly enhanced by the presence of gold NPs. These behaviour is in agreement with literature data in which it was reported that better electronic conduction ability was evidenced for CNTs decorated with gold nanoparticles and dispersed into polymeric matrix [19, 20].

Figure 5: Values of the DC electrical conductivity of the epoxy nanocomposites as a function of the nanofiller content, the reported curve is for Au-GNP 60' composite



4. Conclusions

In this paper graphene sheets (GNP) were functionalized with gold nanoparticles with the aim to obtain higher conductive fillers to be dispersed into UV-curable epoxy resin. Spontaneous deposition of gold particles on the surface of GNP occurred by chemical reduction of (Au^{3+}) by the graphene the deposition/reduction of gold can be promoted by the presence of electrons on the negatively charged surface of the reduced graphene. Even after only 1 min of reaction, the reduction of Au^{3+} into metallic Au^0 , takes place evidencing the rapid and spontaneous character of the reduction. The particles after only 3 min of deposition have very small diameters, average centered at 17. At longer deposition times (60 min), the average diameter of the gold nanoparticles is 67 nm but their distribution is broadened. Fully UV-cured films were achieved by using high energy irradiation. To avoid the detrimental effect of GNP on UV-curing process.

Fully crosslinked epoxy films were obtained with a high gel content values. Thermal and viscoelastic characterization showed that the filler induced an increase of Tg values attributable to an hindering effect of the rigid filler towards the polymer chain mobility.

Conductivity of the epoxy crosslinked samples containing Au-GNP nanofiller were compared to the values obtained for epoxy nanocomposite containing the same amount of bare graphene; the electrical conductivity was significantly increased by the addition of Au-GNP nanofiller: the UV-cured composite containing Au-GNP showed an enhancement on the electrical conductivity of about 4 orders of magnitude. This could be attributed to a charge transfer mechanism, which is strongly enhanced by the presence of gold NPs.

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