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Effect of non-covalent functionalization of graphene-based nanoparticles on the local electrical properties of epoxy nanocomposites

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Abstract. In this study, we put forward a non-covalent π - π interaction between graphene nanoparticles (G) and a pyrene-based molecule (py) to give the functionalized graphene (G-py). The proposed modification has proven to be a winning solution aimed at safeguarding the graphene's striking electronic properties, while favoring a more effective nanofiller dispersion due to a decrease in viscosity with consequent improvement of the rheological properties of the formulated nanocomposites. Tunneling Atomic Force Microscopy (TUNA) analysis was carried out using G-py weight percentages both below and above the Electrical Percolation Threshold (EPT) to investigate the electrical behavior of the conductive nanodomains of the epoxy/graphene systems. The electrical results are in perfect agreement with the rheological ones. The non-covalent modification greatly enhances the thermal stability of the graphene-based nanoparticles, also causing an increase in the oxidative thermostability of the formulated nanocomposites.

1. Introduction

In recent years, graphene which is a two-dimensional nanostructured form of carbon with sp^2 hybridization is increasingly becoming the subject of in-depth studies [1] since it is endowed with extraordinary properties such as astonishing thermal conductivity [2], high Young's modulus [3], and high electrical conductivity [4]. These properties can undergo notable improvements when passing from the simple polymer to the corresponding graphene-based composite while keeping the lightness and flexibility almost unchanged. Consequently, graphene which is being more and more wanted in the production of the various micro-electrical devices, batteries, supercapacitors, and composites [5–9] has attracted the attention of those who are strongly engaged in the field of research on materials and nanotechnologies and who are currently trying to explore its full potential in various application sectors. In order to allow for an effective load transfer through the graphene / matrix interface [10], it is necessary to avoid the formation of graphene nanoplatelet aggregates in the matrix, mainly due to the extended surface of the graphene layers, as well as to the intense van der Waals intermolecular forces. In this regard, a homogeneous dispersion of the graphene nanoparticles within the polymeric matrix is crucial for obtaining a substantial improvement of the final properties of the nanofilled materials. An appreciable amelioration in the graphene nanoparticle dispersion can be achieved by covalent and non-covalent chemical modifications [11,12]. In this paper, the effectiveness of non-covalent functionalization by π - π stacking interaction between unfunctionalized graphene (G) and a pyrene-



based molecule (py) originating the functionalized graphene (G-py) has been proven. In fact, the functionalization carried out in this work had a positive impact on the nanofiller dispersion by causing an increase in electrical and rheological properties of the resulting nanocomposites. Tunneling Atomic Force Microscopy (TUNA) was used to analyze electrical nanodomains of samples filled with G-py weight percentages both above and below EPT. In this regard, we have shown that for the unfunctionalized G-based samples, EPT is in the range 0.025–0.1 wt% [13]. The chemical functionalization counteracts the formation of agglomerates in the matrix, thus permitting improvement in the processability [14–17] of the nanocomposites without changing their electrical performance. The electrical results agree with the rheological results [18]. In addition, the non-covalent functionalization determines a considerable improvement of the thermal stability of the graphene-based nanoparticles, also increasing the oxidative thermostability of the formulated nanocomposites.

2. Experimental section

2.1. Materials

The unfilled resin, here marked with the letter R, consists of: 1) an epoxy precursor, tetraglycidylmethylenedianiline (TGMDA), 2) a reactive diluent, 1-4 butanedioldiglycidyl ether (BDE), and 3) a cross-linking agent, 4,4'-diaminodiphenyl sulfone (DDS) [8,17,18]. All these chemical compounds have been supplied by Sigma-Aldrich. In this work, we used the conductive graphene nanoparticles G obtained through an intercalation/exfoliation process starting from natural graphite [13].

2.2. Preparation

Non-covalently modified graphene nanoparticles (G-py) were obtained starting from 1-pyrenebutyric acid (py) and conductive nanofillers (G) in the presence of CH_2Cl_2 dry [18]. The graphene-based nanoparticles were ultrasonicated into the unfilled matrix R at different loading concentrations ranging from 0.05 wt% up to 1.8 wt%. The resulting nanocomposites were cured in an oven for one hour at 125°C and for three hours at 200°C.

2.3. Methods

The conductivity mapping at nanoscale level of the graphene-based samples was performed by TUNA analysis. For TUNA measurements, the control parameters were the following: DC sample bias between 1 and 3 V, current sensitivity equal to 1pA/V, scan rate equal to 0.500 Hz s⁻¹, pixel resolution: 512x512. In order to observe more clearly the distribution of the filler in the epoxy matrix [8,18], the morphological analysis on the solid samples was carried out after they were previously kept in an oxidizing solution [8,13,17] which caused the removal of the resin around the graphene sheets.

Rheological measurements of the liquid uncured systems were performed using a Physica MCR 301 (Anton Paar) rotational rheometer [18].

Thermal analysis was performed using a Mettler DSC 822 differential scanning calorimeter. The Cure Degree (DC) of the samples was assessed using the calorimetric data [17–20].

Thermogravimetric analysis (TGA) was performed using a Mettler TGA/SDTA 851 thermobalance [18].

3. Results and discussions

Carbon nanostructure distribution of the etched nanocomposites R0.1%G-py and R1%G-py can be detected in Figures 1–4 showing the four TUNA pictures, that is Height, Deflection Error, Friction and TUNA Current (on the left) and the corresponding three-dimensional (3D) shapes (on the right). As it is evident in the TUNA current images, from the strong contrast of the color tones which are associated with areas of the samples characterized by higher or lower current density, it is possible to obtain a conductivity map. Although in all the TUNA Current images the presence of conductive particles is detectable, however, the sample R0.1%G-py containing a lower quantity of functionalized G-py shows lower electrical conductivity than that detected for the sample R1%G-py containing a higher filler load.

In fact, the current values for sample R0.1%G-py are between 1.3 pA and 1.8 pA (see Figure 2), while for sample R1%G-py they are between 4.5 pA and 12.8 pA (see Figure 3). From these values, it is easy to deduce that, for the sample R0.1%G-py, the EPT has not yet been achieved and, consequently, there are few interconnections in the matrix with the absence of percolating electrical paths in many areas of the sample. Instead, for the sample R1%G-py, above the EPT, we can observe an extensive conductive network that crosses the entire surface with strong interfacial interactions. Anyhow, the effectiveness of the functionalization of graphene nanoparticles is proven by the good electrical properties shown by the formulated nanocomposites. In fact, even for the sample below the EPT, it is still possible to measure low currents.

Furthermore, the functionalization carried out improved the electrical performance of the investigated nanocomposites. More precisely, the electrical conductivity value for the nanocomposite containing 1 wt% of pristine G is worth 4.82×10^{-3} S/m while, on the other hand, for the nanocomposite containing the same weight percentage (above the EPT) of functionalized G-py, an increase in electrical conductivity of two size orders and equal to 0.1 S/m was recorded.

In Figure 5 on the left, the black TGA curve in air shows that the thermal degradation of the functionalized sample G-py begins to occur at a temperature approximately 70°C higher than that of unfunctionalized graphene G (see the blue curve). This clearly demonstrates that the non-covalent modification of graphene with pyrene derivative greatly enhances the thermal stability of the pristine graphene G, thus tellingly raising the composite oxidative thermostability caused by a shift in the evolution of CO₂ towards higher values. In Figure 5 on the right, the TGA curves in air of the cured epoxy samples show the presence of two steps of weight loss at 330°C and 490°C, while the final residue at 670°C is about 3%. Therefore, functionalization had a significant impact on increasing the thermal stability of the starting graphene with a consequent growth in the oxidative thermostability of the filled resins.

The curing behavior of the filled resins was investigated through dynamic and isothermal DSC. In Figure 6, the first graph on the left exhibits dynamic cure (first run) and the central graph exhibits isothermal cure (second run) DSC thermograms of the resins loaded with G-py cured at 200°C. We can clearly detect that, in the dynamic conditions, the curing reactions of all the investigated samples occur in the 125°C-250°C temperature range. From the last graph on the right of Figure 6 showing the DC values of resins nanocharged with G and G-py isothermally cured, we can found out that, for all the formulations studied, a curing degree of about 90% has been achieved. This high value largely meets the technical requirements established by the aeronautical industry.

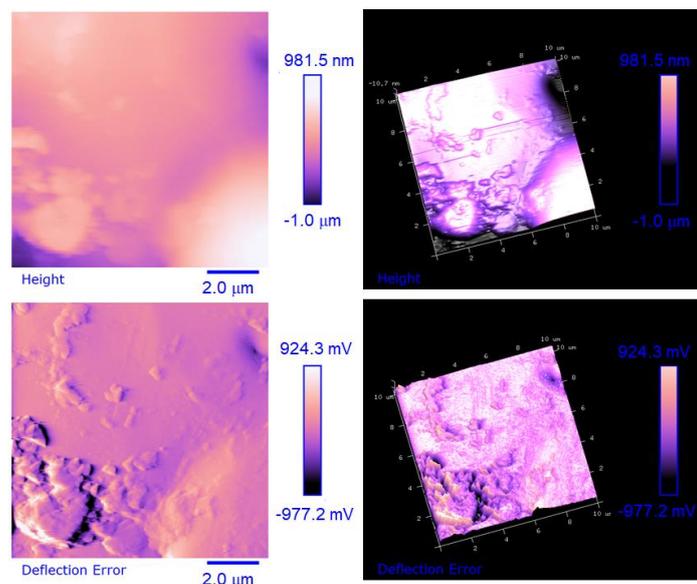


Figure 1. TUNA images (Height and Deflection Error profiles) of the R0.1%G-py fracture surface.

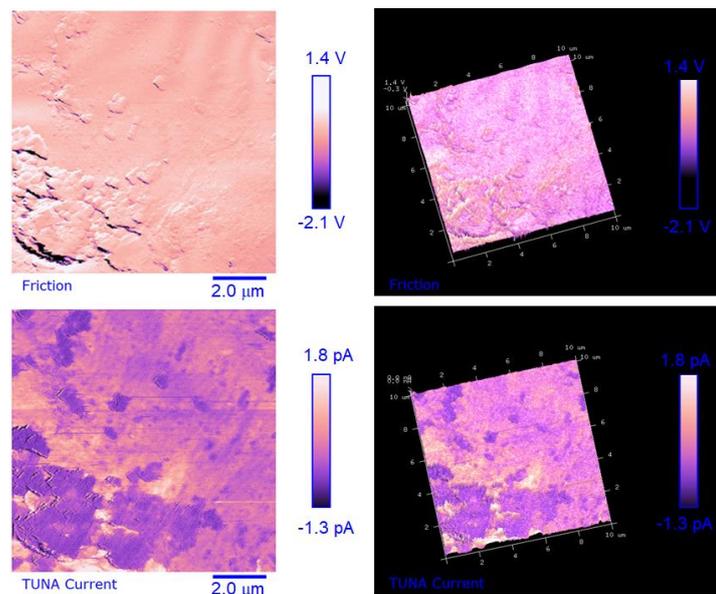


Figure 2. TUNA images (Friction and TUNA current profiles) of the R0.1%G-py fracture surface.

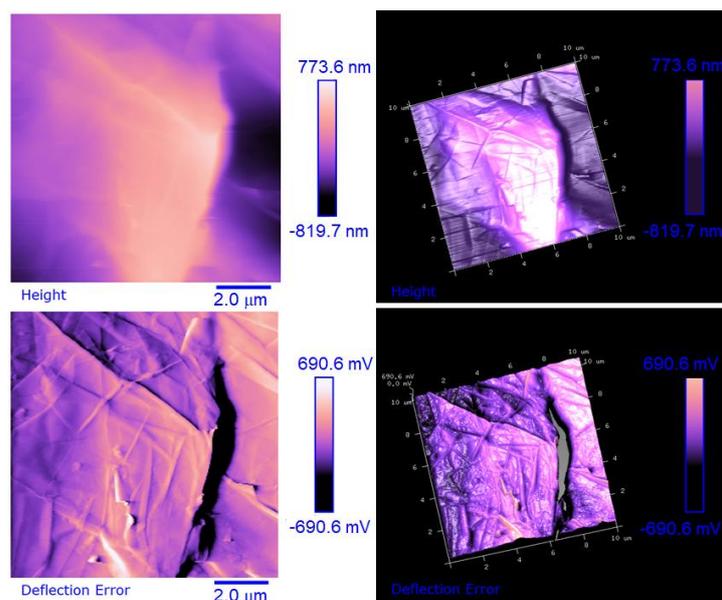


Figure 3. TUNA images (Height and Deflection Error profiles) of the R1%G-py fracture surface.

Figure 7 shows the complex viscosity (η^*) vs frequency (ω) at $T=25^\circ\text{C}$, $T=50^\circ\text{C}$ and $T=75^\circ\text{C}$ for the R uncured epoxy matrix, the R0.5%G and the R0.5%G-py liquid dispersions. For all three different temperatures investigated, we can ascertain that the incorporation in the unfilled liquid resin R of the unfunctionalized G leads to an increase in the resin R viscosity, while the incorporation of the functionalized G-py causes a relevant reduction of the complex viscosity in the whole frequency range examined.

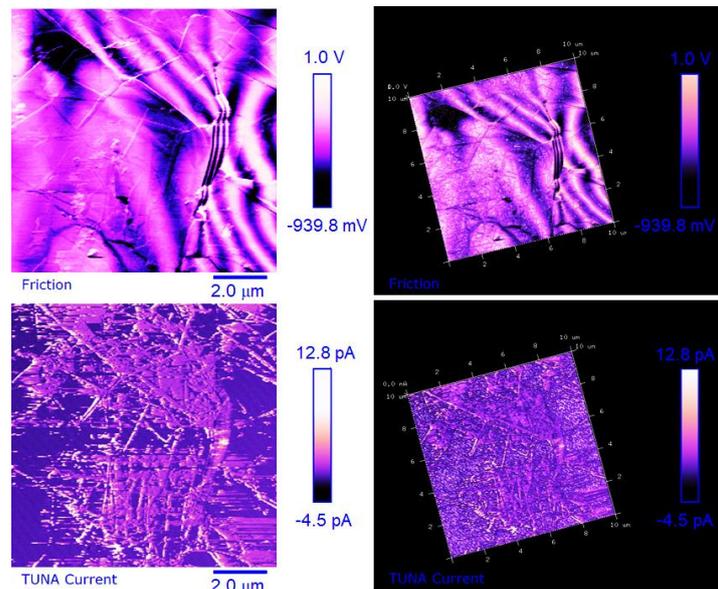


Figure 4. TUNA images (Friction and TUNA current profiles) of the R1%G-py fracture surface.

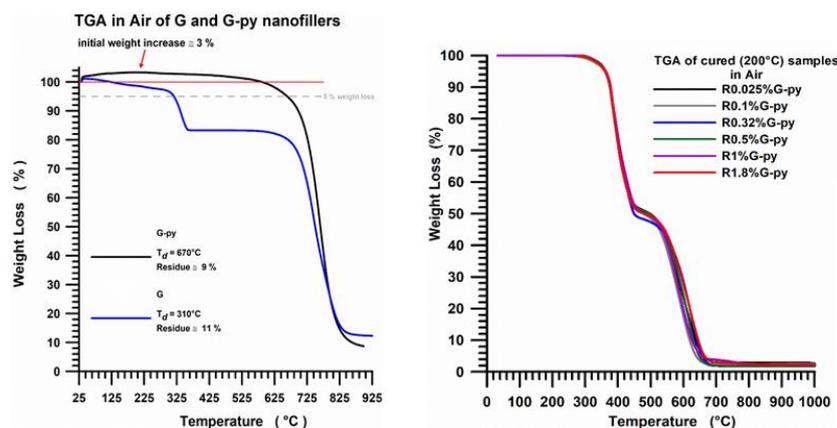


Figure 5. TGA curves in air of G and G-py nanoparticles (on the left) and the G-py based samples (on the right).

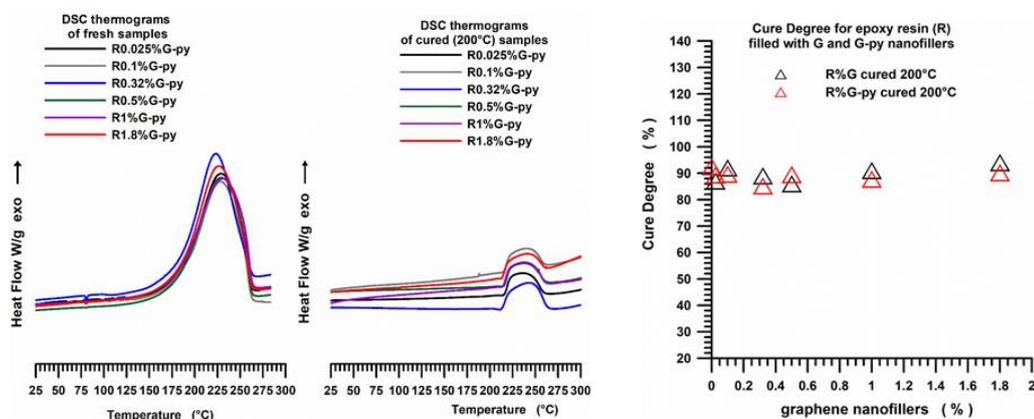


Figure 6. Dynamic cure (first run) DSC curves (first graph on the left), isothermal cure (second run) DSC thermograms (central graph) of the epoxy resins containing different G-py weight percentages and DC values of the resins nanocharged with G and G-py isothermally cured (last graph on the right).

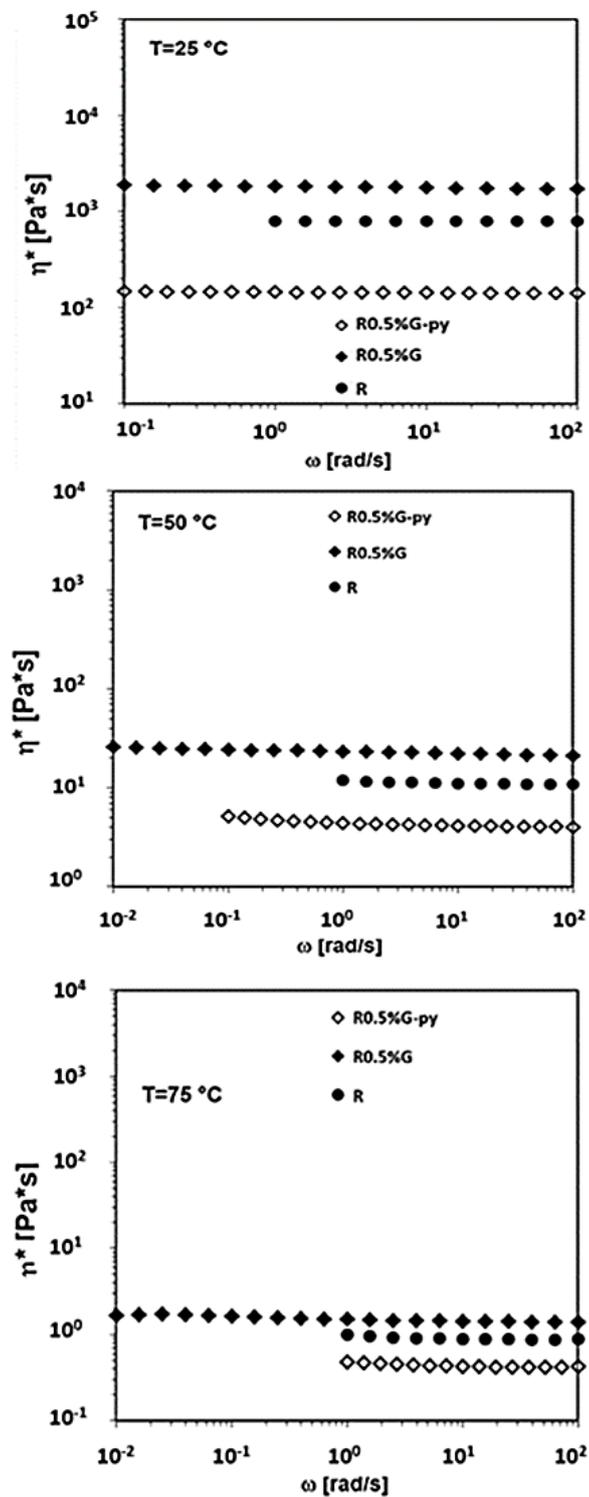


Figure 7. Complex viscosity vs frequency at T=25°C, T=50°C and T=75°C for the R uncured epoxy matrix, the R0.5%G and the R0.5%G-py by wt liquid dispersions.

4. Conclusions

Non-covalent π - π interaction between graphene nanoplatelets (G) and a pyrene-based compound (py) has been explored together with its great ability to positively impact many crucial properties for the resulting nanocomposites.

This type of functionalization proved to be the winning strategy for improving the rheological properties of the samples investigated in this work. In fact, thanks to its ability both to avoid the formation of agglomerates of graphene nanoparticles when they are dispersed in the resin and to lower the viscosity of the epoxy systems, it is remarkably advantageous in guaranteeing effective processability of the material even when this contains loads of nanofiller above the EPT.

The exploration of the electrical performance that characterizes the conductive nanodomains of nanocharged resins was carried out through TUNA analysis using G-py quantities both below (0.1 wt%) and above (1 wt%) the electrical percolation threshold (EPT), thus awarding new insights for a better understanding of current conduction mechanism. Specifically, many areas of the nanocomposite containing the G-py lowest concentration have not electrically conductive paths, whilst for the nanocomposite having the G-py highest concentration, the conductive network detection demonstrates that the sample is above the EPT. Nevertheless, the detection of low currents even in the sample with a filler load below the EPT shows the excellent electrical properties of the nanocomposites, thus effectively confirming the doing of the non-covalent functionalization.

The electrical results agree perfectly with the rheological results. In this regard, the incorporation of 0.5 wt% of functionalized G-py determined the complex viscosity abatement of the resin. On the contrary, the addition of 0.5 wt% of unfunctionalized G caused an increase in viscosity.

It is worth noting that the non-covalent functionalization also significantly improved the thermal stability of the graphene-based nanoparticles, resulting in an increment in the oxidative thermostability of the formulated nanocomposites.

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