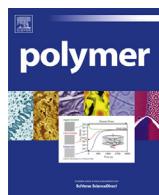




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## Polymer communication

## Catalytic activity of graphite-based nanofillers on cure reaction of epoxy resins



Marco Mauro <sup>a</sup>, Maria Rosaria Acocella <sup>a</sup>, Carola Esposito Corcione <sup>b</sup>, Alfonso Maffezzoli <sup>b</sup>,  
Gaetano Guerra <sup>a,\*</sup>

<sup>a</sup> Dipartimento di Chimica e Biologia e Unità di Ricerca INSTM, Università di Salerno, Fisciano, SA, Italy

<sup>b</sup> Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Lecce, Italy

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## ABSTRACT

The strong influence of graphite oxide (GO) nanofiller on the glass transition temperature ( $T_g$ ) of epoxy resins, generally attributed to restricted molecular mobility of the epoxy matrix by the nanofiller or to the crosslinking of GO layers via the epoxy chains, is investigated. The study confirms that large increases of the glass transition temperature of the nanocomposite can be observed in presence of GO. However, similar  $T_g$  increases are observed, when the filler is a high-surface-area graphite (HSAG), lacking oxidized groups. Moreover, these  $T_g$  differences tend to disappear as a consequence of aging or thermal annealing. These results suggest that the observed  $T_g$  increases are mainly due to a catalytic activity of graphitic layers on the crosslinking reaction between the epoxy resin components (epoxide oligomer and diamine), rather than to reaction of the epoxide groups with functional groups of GO. This hypothesis is supported by investigating the catalytic activity of graphite-based materials on reactions between analogous monofunctional epoxide and amine compounds.

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## 1. Introduction

Polymer nanocomposites have attracted great interest from researchers and technologists, due to unique properties derived from the extended interface between the polymer matrix and the filler [1–4]. Nanocomposites with carbon-based fillers have been widely investigated and, in particular, many studies have been focused on nanocomposites with graphite oxide (GO) [5–10], i.e. a layered material, (generally obtained by chemical oxidation of graphite with strong acids and oxidants) [11–13], whose layers mainly contain hydroxyl and epoxide groups at the surface and carbonyl and carboxyl groups at the edges [14]. The large increase of the interlayer spacing and the disordered arrangement of the functional oxidized groups on the layer surfaces lead to weak interlayer attractive forces, making easy the GO exfoliation by dispersion in a suitable polymer matrix [15–17]. These studies on GO reinforced nanocomposites show relevant improvements of physical properties of epoxy resins, which are mainly due to the polymer-filler improved adhesion, arising from the oxygenated groups [5–10].

In particular, although most nanoparticles generally disrupt crosslinking density and decrease  $T_g$  in high  $T_g$  thermosets [18–20], several studies describe significant  $T_g$  increases for polymer matrices, in the presence of GO nanofiller [21–27]. In fact, according to literature data, this increase is negligible for apolar polymers like isotactic polypropylene [21], of 4.5 °C for polystyrene [22], of nearly 8 °C for poly(propylene carbonate) [23] and definitely higher for polymethylmethacrylate (in the range 7–17 °C) [24,25]. By far the largest  $T_g$  increases, in the presence of GO nanofiller, have been observed for epoxy resins (in the range 10–36 °C) [26,27]. These extremely high  $T_g$  increases would be due to restricted molecular mobility of the epoxy matrix by the nanofiller [26] or to the possible crosslinking of GO layers via the epoxy chains. The latter hypothesis, in principle, could be supported by recent results of Berry et al. [28] on the functionalization of GO by ring opening reaction of epoxidized methyl oleate, as well as of Zheng et al. [29] on the coupling of epoxy resin onto GO sheets via the “grafting to” method.

In this paper, comparative thermal analyses of epoxy resins filled with different carbon nanofillers (a high-surface-area graphite, HSAG and a graphite oxide), for different thermal histories, are conducted. The main aim is to understand the molecular origin of the influence of GO on the  $T_g$  of epoxy resins.

\* Corresponding author. Tel.: +39 089969558.

E-mail address: [gguerra@unisa.it](mailto:gguerra@unisa.it) (G. Guerra).

## 2. Results and discussion

Experimental details are listed in the [Supporting Information](#). The used high surface area graphite (HSAG,  $308 \text{ m}^2/\text{g}$ ) exhibits the X-ray diffraction pattern of [Fig. 1A](#), showing an interlayer distance of  $0.339 \text{ nm}$ , a high shape anisotropy ( $D_{\parallel}/D_{\perp} = 3.1$ ) and a low degree of order in the relative position of parallel graphitic layers (i.e. a tendency toward the so-called turbostratic graphite) [17,30].

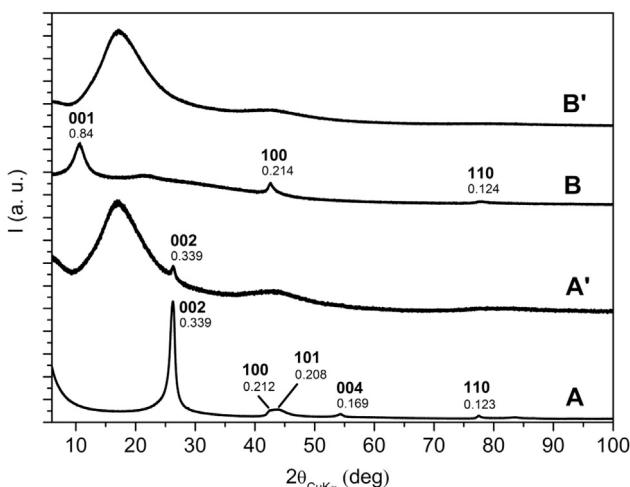
The Hummers' oxidation of HSAG leads to a GO, with an oxygen content of  $32 \text{ wt\%}$  (excluding the water content) and a decrease of surface area down to  $1.4 \text{ m}^2/\text{g}$  (See [Supporting Information](#)). These surface area values agree well with those reported for GO samples by Bielawski et al. [31–33], while they are definitely lower than other literature values [34–36].

The X-ray diffraction pattern of the derived GO, reported in [Fig. 1B](#), shows an interlayer distance increase from  $0.339 \text{ nm}$  to  $0.84 \text{ nm}$ . It is worth noting that the out-of-plane correlation length decreases from  $9.8 \text{ nm}$  to  $4.2 \text{ nm}$ , while the in-plane correlation length remains almost unchanged ( $D_{\parallel} \approx 30 \text{ nm}$ ). Hence, GO presents a high shape anisotropy  $D_{\parallel}/D_{\perp} = 7$ , associated with a strongly reduced order in the direction perpendicular to the graphitic layers.

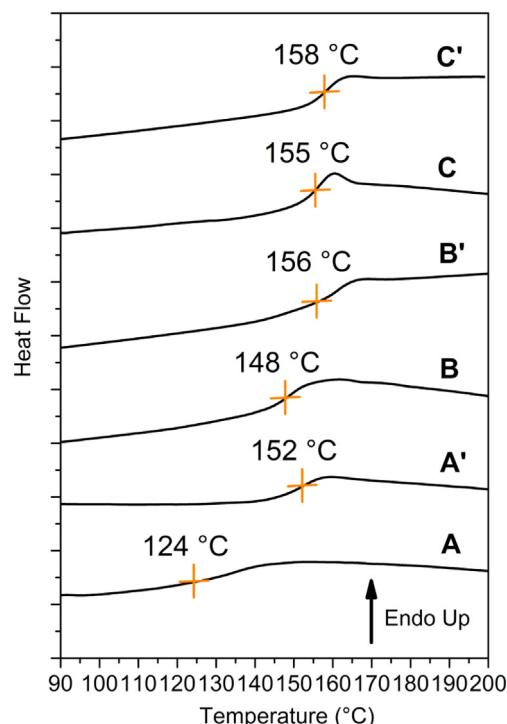
The WAXD patterns of epoxy-based nanocomposites, filled with  $3 \text{ wt\%}$  of HSAG and GO are shown in [Fig. 1A'](#) and [B'](#), respectively. The WAXD pattern of the nanocomposite with HSAG shows a sharp  $002$  reflection, clearly showing that the graphite in the epoxy matrix still consists of multilayer stacks. In the WAXD pattern of the nanocomposite with GO, on the contrary, reflections of the filler cannot be identified. This indicates the occurrence of high disorder in the direction perpendicular to the graphitic layers, possibly corresponding to a complete exfoliation of the graphene oxide layers.

DSC heating scans of the neat epoxy resin and of the corresponding nanocomposites with  $3 \text{ wt\%}$  of HSAG and GO, as cured at  $150 \text{ }^{\circ}\text{C}$ , are shown in [Fig. 2A–C](#) and the derived  $T_g$  data are listed in the second column of [Table 1](#).

An increase of  $T_g$  of about  $24 \text{ }^{\circ}\text{C}$  and  $31 \text{ }^{\circ}\text{C}$ , with respect to the neat epoxy resin ( $T_g = 124 \text{ }^{\circ}\text{C}$ , [Fig. 2A](#)), is observed in presence of HSAG and GO ([Fig. 2B](#) and [C](#)), respectively. The similar  $T_g$  increases for nanocomposites with graphite and graphite oxide clearly indicates that the formation of covalent bonds between the graphene oxide layers and the crosslinked epoxy is not the main mechanism inducing these  $T_g$  increases.



**Fig. 1.** X-ray diffraction patterns ( $\text{CuK}\alpha$ ) of HSAG (A) and GO (B) and of the epoxy-based composites with  $3 \text{ wt\%}$  of HSAG (A') and GO (B'). Miller indexes and  $d$  spacings (nm) are indicated close to the main diffraction peaks.



**Fig. 2.** DSC heating scans of the neat epoxy resin (A, A') and of the epoxy-based nanocomposites, filled with  $3 \text{ wt\%}$  of HSAG (B, B') and GO (C, C'): (A, B, C) samples cured at  $150 \text{ }^{\circ}\text{C}$ ; (A', B', C') the same samples after annealing at  $200 \text{ }^{\circ}\text{C}$ . The evaluated  $T_g$  are indicated close to the curves.

Moreover, large increases of  $T_g$  are observed only for freshly prepared samples. In fact the  $T_g$  of the same samples after aging at room temperature for 3 months become much closer, due to a large aging-induced increase for the neat resin ( $\approx 20 \text{ }^{\circ}\text{C}$ ) and a negligible variation for the nanocomposites. After aging, the  $T_g$  difference between the GO nanocomposite and the neat resin becomes close to  $10 \text{ }^{\circ}\text{C}$ .

Also informative are the  $T_g$  values of the neat resin ([Fig. 2A'](#)) and of the nanocomposites with G and GO ([Fig. 2B'](#) and [C'](#)), after annealing at  $200 \text{ }^{\circ}\text{C}$ , which are also listed in the 3rd column of [Table 1](#). After annealing, the  $T_g$  of the neat resin increases of  $28 \text{ }^{\circ}\text{C}$  while that one of the GO nanocomposite increases of only  $3 \text{ }^{\circ}\text{C}$  and as a consequence the  $T_g$  difference between the GO nanocomposite and the neat resin becomes as low as  $6 \text{ }^{\circ}\text{C}$ .

The whole set of data relative to  $T_g$  ([Table 1](#)) clearly suggests that most of the  $T_g$  increase, which is observed for epoxy resins including GO, has a kinetic rather than a thermodynamic origin. The simplest hypothesis to rationalize the described behavior is a possible catalytic effect of graphitic layers on the crosslinking reaction of the epoxy resin, between the used epoxide oligomer and di-amine. In fact, it is well known that both graphite and graphite oxide show catalytic effects on many organic reactions [31,37–41], being for some reactions more effective and selective than other catalysts [41]. Moreover, a catalytic activity of carbon nanotubes on

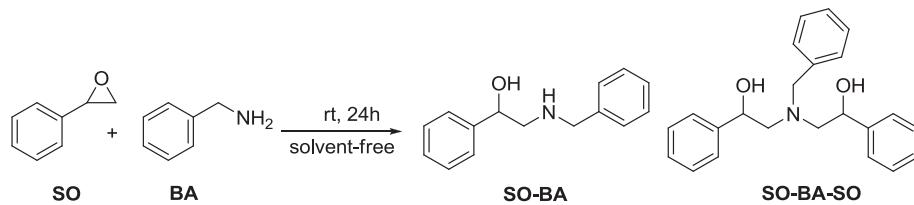
**Table 1**

$T_g$  of the epoxy resin and its nanocomposites with HSAG and GO, as cured at  $150 \text{ }^{\circ}\text{C}$  and subsequently annealed at  $200 \text{ }^{\circ}\text{C}$ .

Sample	$T_g$ , $150 \text{ }^{\circ}\text{C}$	$T_g$ , $200 \text{ }^{\circ}\text{C}$
Neat epoxy resin	124	152
Epoxy + $3 \text{ wt\%}$ HSAG	148	156
Epoxy + $3 \text{ wt\%}$ GO	155	158

**Table 2**

Ring opening reaction of styrene oxide (SO) by benzylamine (BA).



Entry	Molar ratio SO/BA	Catalyst (3 %wt)	Time (h)	Yield (%) <sup>a</sup>
1	1/1.2 or 3/1	—	24	—
2	1/1.2	HSAG	24	54 (SO-BA)
3	1/1.2	GO	24	45 (SO-BA)
4	3/1	GO	18	45 (SO-BA)
5	3/1	GO	48	64 (SO-BA-SO)

<sup>a</sup> All the yields refer to isolated chromatographically pure compounds, whose structures were confirmed by analytical and spectroscopic data.

epoxy resin curing reactions has been clearly established (mainly by dynamic and isothermal DSC studies) [41–47], which has been attributed to the high thermal conductivity of carbon nanotubes [43] or to the presence of impurities in commercially available carbon nanofillers [46].

The possible catalytic activity of HSAG and GO, for reactions between monofunctional low molecular mass epoxides and amines, such as styrene epoxide and benzylamine, is presently studied. The choice of monofunctional reactants is of course due to an easier characterization of uncrosslinked reaction products.

The epoxide ring opening reaction was conducted at room temperature in presence of 3 wt% of the considered high-surface-area graphite (HSAG) or of the derived GO, under solvent free conditions.

As reported in Table 2, already at room temperature and in the presence of both nanofillers, substantial yields of the addition product **SO-BA** are achieved (entries 2 and 3 in Table 2) while the uncatalyzed reaction does not proceed at all (entry 1 in Table 2).

As for analogy with crosslinking of epoxy resins, particularly interesting is exploring the possible catalytic activity of the graphitic nanomaterials on the reaction of the secondary amine **SO-BA** with a further epoxide molecule. This study has been conducted by using the same reaction conditions but a higher epoxide/amine ratio (3/1, entries 4 and 5 in Table 2): for short and long reaction times, products **SO-BA** and **SO-BA-SO** are prevailingly obtained, which correspond to addition of one or two epoxide molecules.

It is worth adding that, for both products **SO-BA** and **SO-BA-SO**, differently from reactions in water solutions [48,49], the ring opening reaction as catalyzed by graphite-based nanofillers is highly regioselective, following an *S<sub>N</sub>2* type reaction with the nucleophile attacking the less substituted end (see reaction on the top of Table 2).

These experiments clearly show that the considered nanocarbons exert a catalytic activity not only on reactions between primary amines and epoxide groups but also on reactions between secondary amines and epoxide groups, like those needed to crosslink epoxy-amine resins. Moreover, because our experiments have been conducted in isothermal conditions, the possibility that the observed catalytic activity is due to the high thermal conductivity of the graphitic materials can be ruled out.

### 3. Conclusion

In summary, comparative thermal analysis of epoxy resins filled with different carbon nanofillers, confirms the occurrence of large

*T<sub>g</sub>* increases in GO nanocomposites. In particular, these *T<sub>g</sub>* increases observed in presence of GO, for the considered epoxy resin cured at 150 °C, is higher than 30 °C. However, similar *T<sub>g</sub>* increases (24 °C) are observed, when the filler is a high-surface-area graphite (HSAG), lacking oxidized groups. The similar results obtained for GO and graphite nanofillers, exclude the possibility that the observed large *T<sub>g</sub>* increases could be attributed either to restricted molecular mobility of the epoxy matrix by interactions with the dipolar groups of the GO nanofiller or to the possible crosslinking of GO layers via the epoxy chains.

Additional DSC analyses have shown that these *T<sub>g</sub>* differences tend to disappear as a consequence of aging or annealing at higher temperatures (e.g.,  $\Delta T_{g,\max} \approx 6$  °C, for *T<sub>annealing</sub>* = 200 °C). This clearly indicates that most of the *T<sub>g</sub>* increment, which is observed for epoxy resins including graphite-based nanofillers, has a kinetic rather than a thermodynamic origin.

The higher *T<sub>g</sub>* values observed for low curing temperatures, for epoxy resins with graphite-based nanofillers, can be easily rationalized by a catalytic activity of graphitic layers on the reaction between the epoxy and amine groups of the resin, which leads to higher crosslinking density in milder conditions.

This hypothesis has been clearly supported by experiments showing catalytic activity of the considered graphite-based nanofillers on the epoxide ring opening reaction, for monofunctional epoxide and amine reactants. In particular, the considered nanocarbons exert a catalytic activity not only on reactions between primary amines and epoxide groups but also on reactions between secondary amines and epoxide groups, like those needed to crosslink epoxy resins.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2014.09.019>.

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