

Effect of the epoxy/amine stoichiometry on the properties of carbon nanotube/epoxy composites

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Abstract The effect of different amine/epoxy ratios on different properties of an epoxy resin was evaluated. Also, different amounts of carbon nanotubes (CNT) were added in order to analyse which of these two factors is more relevant. Dynamic thermomechanical analysis and flexural tests were carried out. The results obtained for the epoxy resin are in agreement with that reported by several researchers. The glass transition temperature of the resin and composites is maximal for the amine/epoxy stoichiometric ratio, while the highest glassy storage and flexural modulus correspond to the epoxy-rich systems, showing that the most crosslinked network is not the stiffest one. The effect of changing the stoichiometry is more relevant than adding CNT to the epoxy resin used in this work. However, the addition of CNT causes more remarkable changes in the epoxy-rich resin, promoting an increase of the glass transition temperature and the elastic modulus.

Keywords Epoxy · Carbon nanotubes · Stoichiometry · Dynamic thermomechanical analysis · Flexural tests

Introduction

Epoxy resins are very used thermoset polymers because of their good combination of high elastic modulus and mechanical strength and good chemical and thermal resistance. One of their main limitations, the low fracture toughness, is trying to be solved by adding carbon nanotubes (CNT). This is expected to improve the mechanical

and thermal behaviour of the epoxy resins, increasing also their electrical conductivity [1–3]. However, in the last years, it was proven that the effect of the addition of CNT to epoxy resins was not that expected, mainly in regard to the mechanical properties. The two main reasons for this behaviour are: (1) the low interfacial matrix/nanofiller adhesion, and (2) the inability of the current manufacturing procedures to provide a homogeneous dispersion of the CNT in the epoxy matrices. Several strategies are being explored with the aim of solving these limitations [1, 4–6].

There is also a problem when trying to extrapolate the results from one to another CNT/epoxy composite. As it was expected, the results obtained are highly dependent on the nanofiller type (length, number of walls, functionalization, etc.) [1, 2]. But, even for the same CNT, their effect depends on the properties of the neat epoxy resin, which are also affected by its chemical composition and cross-linking degree obtained during the cure reaction. For example, Ci and Bai [7] analysed the effect of multiwalled CNT on epoxy resins with different crosslinking degree, founding that the reinforcement effect is less significant in the stiffer matrix. Similar results obtained Guzmán de Villoria et al. [8], using in this case single-walled CNT.

In previous studies, we have also probed the influence of the matrix properties when CNT are added to epoxy resins. We have used two epoxy resins based on diglycidyl ether of bisphenol A (DGEBA), with two different aromatic amines with very similar chemical composition as hardeners: 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulphone (DDS). In both cases, the addition of amino-functionalized multiwalled CNT raises the glassy storage modulus E_G' of the matrix, but the increase is more pronounced in the more crosslinked epoxy matrix (DGEBA/DDS). In particular, in composites with 0.25 wt% CNT, E_G' increases 27% with DDS and 16% with DDM [9, 10]. With

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respect to the glass transition temperature (T_g), the effect of CNT changes completely from one epoxy resin to other. When added to the system DGEBA/DDM, they decrease the T_g , but in DGEBA/DDS there is a small increase of this property. This agrees with the controversy found in the bibliography. It seems that CNTs cause several counteracting effects in the glass transition of epoxy resins [11], and the result is in some cases an increase and in other a decrease or even keeps it constant [2, 11].

In short, our previous results indicate that the beneficial effect of CNT is more marked in a more crosslinked epoxy network. Anyway, as it was previously mentioned, the chemical composition of the resins is not exactly the same. In order to analyse properly, the effect of the crosslinking degree, the same epoxy matrix should be used. There are two ways of changing this parameter: varying either the curing conditions or the epoxy/amine ratio. In this study, we have chosen the second one, using three different epoxy/hardener ratios: stoichiometric, an excess of epoxy and an excess of hardener. First, it was analysed the effect of stoichiometry on the properties of the epoxy resin, and then two different contents of CNT were added in order to assess how their effect is influenced by the crosslinking degree of the same epoxy matrix.

Experimental

Materials

The epoxy resin used was based on DGEBA, with 178 g/epoxy equivalent. The curing agent used was DDM with 49.6 g/amine equivalent. Both were supplied by Sigma-Aldrich.

Amino-functionalized multiwalled CNT Nanocyl-3152 were used as fillers. Their main morphological characteristics are an average diameter of 9.5 nm, length shorter than 1 μm and are formed by 5–10 walls.

In order to disperse the nanotubes properly in the epoxy matrix, a three-roll calender Exakt 80 E was used. CNT were previously added to the epoxy prepolymer (DGEBA) and mixed by hand. The gap size between the first and the second roll is always three times the separation between the second and the third roll, and they were changed for each step. The procedure used consisted of seven stages with the following gaps (in μm): (1) 120–40, (2) 75–25, (3) 45–15 and (4) 15–5. The fourth step was repeated four times. Also, each roll rotates at different speed, being the rotation speed 27.8, 83.3 and 250 rpm for the first, the second and the third roll, respectively. These rolls were refrigerated at 30 $^{\circ}\text{C}$.

As the CNT are functionalized with amine groups, a thermal treatment was applied in order to promote the

chemical reaction between these groups and the oxirane rings of the epoxy prepolymer (DGEBA). In previous studies, it was demonstrated that this pre-curing treatment, performed at 130 $^{\circ}\text{C}$ for 1 h, increases the interfacial adhesion between the nanofillers and the epoxy matrix, improving the mechanical behaviour of the composites [9, 12].

After the pre-curing treatment, the curing agent was added to the DGEBA/CNT mixtures. Composite materials with 0.1 and 0.25 wt% CNT were manufactured. For each CNT content and also for the neat epoxy resin, three different amine/epoxy ratios, r , were used: 0.8 (excess of epoxy), 1 (stoichiometric ratio) and 1.2 (excess of amine). In all cases, the curing process was carried out at 150 $^{\circ}\text{C}$ for 3 h and then 180 $^{\circ}\text{C}$ for 1 h.

Characterization

Thermal dynamic mechanical properties were determined with a DMTA Q800 V7.1 from TA Instruments, operating in single cantilever mode with an oscillation frequency of 1 Hz and a heating rate of 2 $^{\circ}\text{C}/\text{min}$, from 25 to 250 $^{\circ}\text{C}$.

A Mettler Toledo balance, with a precision of ± 0.001 mg, equipped with a density determination kit by means of the buoyancy technique was used to evaluate the density of the epoxy resin and CNT/epoxy composites. Ten measurements of density for each sample were carried out.

The mechanical characterization was carried out by flexural tests, with an universal testing machine Instron 4465, following the procedure B of the standard ASMT D-790 at a crosshead speed of 8 mm/min. Five samples of each composition were tested.

The dispersion degree of the CNT into the epoxy matrix of the cured samples was analysed with a high resolution microscope, by Field Emission Gun Scanning Electron Microscopy (FEG-SEM, Nova NanoSEM FEI 230). For it, the samples were broken into liquid nitrogen in order to cause fragile fracture. Then, the surfaces were sputter-coated with a thin layer of Au(Pd).

Results and discussion

Epoxy resin

The glass transition temperature, T_g , was determined as the maximum of the $\tan \delta$ peak. The maximum T_g (186.7 $^{\circ}\text{C}$) is obtained for the stoichiometric amine/epoxy ratio ($r = 1$). Samples with an excess of epoxy ($r = 0.8$) present the lowest glass transition temperature (125.3 $^{\circ}\text{C}$), while with an excess of hardener ($r = 1.2$) the result is an intermediate value (169.6 $^{\circ}\text{C}$). This behaviour had been observed in epoxy resins by different researchers [13–17]. As explained by Calventus et al. [13], for $r = 1$ all amine

hydrogens react with all epoxide groups, giving a network of interconnected rings. These rings consist of two or three epoxidic chains, which have reacted with the corresponding amine group. In the epoxy-rich resin all the primary and secondary amines react with 80% of the epoxy groups of the DGEBA molecules. Therefore, 20% of the epoxy groups do not react, giving a network with some bulky groups situated at the end of the epoxidic chains. This increase of the number of chain ends increases the free volume of the resin, decreasing the glass transition temperature.

In the resin with an excess of amine, all the epoxy groups react with all the primary amine groups (NH_2) but there are unreacted secondary amine groups (NH). According to Morgan et al. [18], under these conditions, the epoxy tends to give branched structures, and occasionally may give ring consisting of the partially reacted triamine molecules and the epoxidic chain. These structures contribute to an increase of the free volume of the system and, as a consequence, show a lower glass transition temperature [13].

It is noteworthy that the presence of unreacted epoxy groups has a more remarkable effect on the T_g than the same amount of unreacted amine groups, as may be deduced by the lowest glass transition temperature in the first case.

The height of the $\tan \delta$ peak is related to the crosslinking degree of the epoxy network. Epoxy-rich resin ($r = 0.8$) present higher $\tan \delta$ peak, while an excess of amine does not affect this parameter, with regard to the stoichiometric mixture (Fig. 1). An increase of the height indicates a less crosslinked network [19], with lower restriction of the chain mobility, agreeing with the lower values of T_g . Similar trend was observed previously by other authors [15, 19].

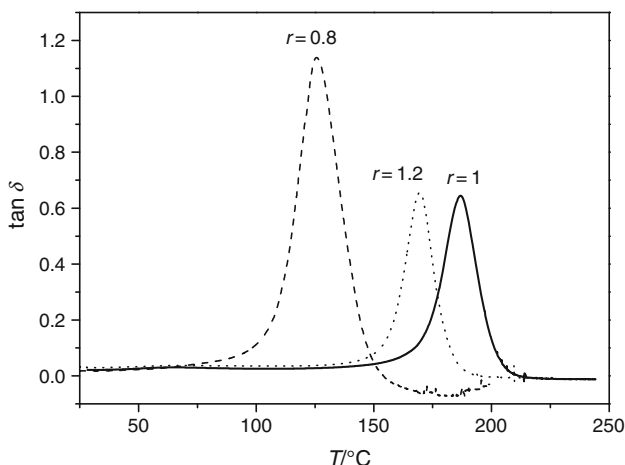


Fig. 1 $\tan \delta$ curves of the epoxy resin with different stoichiometric ratios

The storage modulus, determined by DMTA, follows a different trend depending on the temperature. At the glassy state, at a temperature 50 °C lower than T_g , the maximum value of E' is obtained for the epoxy-rich system (2.6 GPa), while the stoichiometric amine/epoxy ratio provides the lowest value (1.6 GPa). These results indicate that higher glass transition temperature does not imply a stiffer epoxy network.

The values of the rubbery storage modulus, at a temperature 30 °C above T_g (Table 1), were used to calculate the average molecular weight between crosslinking points with the following equation from the theory of rubbery elasticity:

$$E'_R = \frac{3dRT}{M_c}$$

where E'_R is the rubbery storage modulus (MPa), d is the density (g/cm^3), R is the universal gas constant ($8.314 \text{ J}/\text{mol K}$), T is the temperature (K) and M_c is the average molecular weight between crosslinks (g/mol). As it may be seen in Table 1, M_c decreases with increasing amounts of hardener. Lower values of M_c indicate higher crosslinking degree. For the epoxy-rich and stoichiometric systems, this result agrees with the glass transition temperature. The calculated average molecular weight is the same order of magnitude than the obtained by other researchers studying similar epoxy systems [15, 16, 20].

The flexural modulus follows the same trend than the glassy storage modulus, being highest for $r = 0.8$ (3.3 GPa) and lowest for $r = 1$ (2.7 GPa). Although these results are in agreement with reported results for several epoxy systems [14, 15, 17], it seems to contradict the explanation given for the trend of the glass transition temperature. The more crosslinked network ($r = 1$) was expected to present the highest stiffness, but it is just the opposite. Several authors explain that these results invoking the concept of

Table 1 Average molecular weight between crosslinking points and the parameters used for its calculation, as a function of the percentage of CNT and the amine/epoxy ratio

wt% CNT	r	$T_g + 30/$ K	$E'_{T_g+30}/$ MPa	Density/ g cm^{-3}	$M_c/$ g mol^{-1}
0	0.8	428.4	6.9	1.2012	1860
	1	490.0	39.5	1.2028	372
	1.2	472.7	42.7	1.2047	333
0.1	0.8	443.5	10.4	1.1985	1275
	1	483.2	40.4	1.1965	357
	1.2	476.9	27.1	1.1950	525
0.25	0.8	427.8	13.8	1.2006	928
	1	484.6	32.5	1.1953	445
	1.2	475.3	34.7	1.1961	409

free volume [14, 15]. This property should be analysed in depth, using techniques such as positron annihilation [21], in order to establish the correlation between free volume, elastic modulus and glass transition temperature.

CNT/epoxy composites

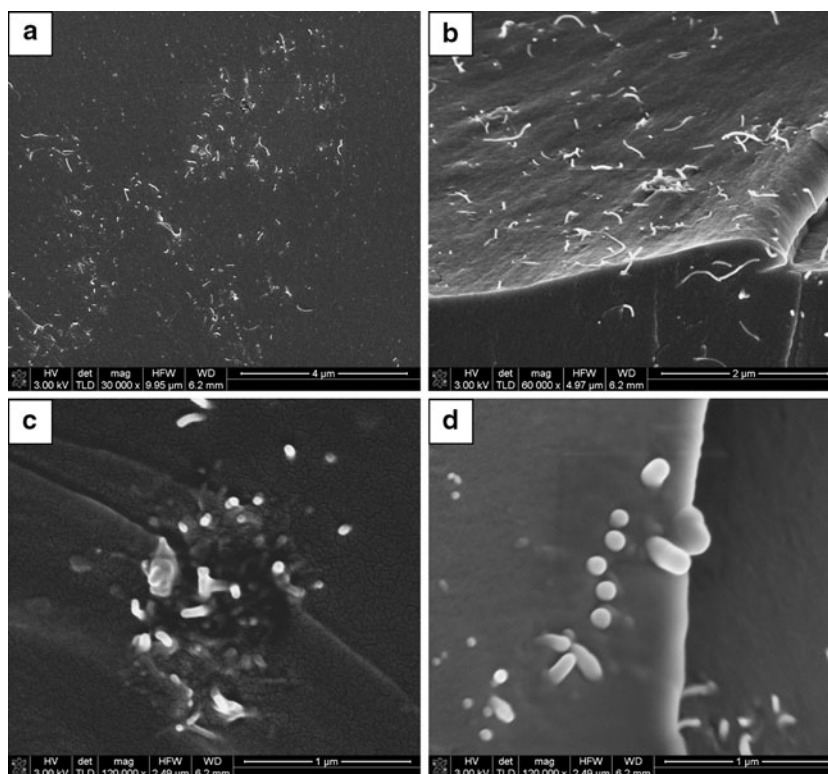
The dispersion procedure used allows obtaining a quite good dispersion degree of the CNT into the epoxy resin. Although some agglomerates of CNTs were found, there are several areas with isolated CNT. Figure 2 collects some micrographs of CNT/epoxy composites at different magnification levels, where it is possible to confirm the high quality of the dispersion. One of them (Fig. 2c) shows a detail of an agglomerate. The number of found agglomerates is low, although it increases with the amount of nanotubes added. In all cases, the size of the agglomerates is not larger than a few microns (1–2 μm in diameter). In spite of the presence of some agglomerates, which implies a not perfect dispersion, it is worthy to note that there are not problems of wettability into them. In fact, in Fig. 2c, it is possible to observe epoxy resin inside the agglomerate. Other interesting observation about the morphology of these composites is the length of the pulled-out CNT (Fig. 2d). This length is short, indicating a high interaction between the nanofiller and matrix. As it was confirmed in a previous work, the stronger chemical interaction between these materials is due to the improvement of the chemical

reaction in the interface caused by the pre-curing reaction [9].

Before the presentation of the experimental results about the effect of the stoichiometry on the final properties of CNT/epoxy composites, which is the main objective of this study, it is important to show a summary of the effect of these nanofillers on the curing reaction of the matrix. In fact, in a previous study [22], we confirmed by differential scanning calorimetry (DSC) that the addition of amino-functionalized CNT induces a light delay of the chemical reaction (increasing the exothermic peak temperature) and a small decrease of the reaction enthalpy. It was confirmed that the decrease of the enthalpy is associated to: (1) a selective adsorption of curing agent molecules inside the nanotubes, and (2) the previous reaction of the amine groups anchored to the nanotubes and the oxirane rings of DGEBA. The study of the curing reaction of CNT/epoxy composites with different amine/epoxy ratios allowed us confirming that an excess of amine groups ($r = 1.2$) induces a light increase of exothermic enthalpy, associated to the catalytic effect of primaries amines. Finally, the authors have demonstrated that the curing reaction mechanism is neither affected by the addition of CNT nor affected by the modification of the matrix stoichiometry. The reaction kinetic orders remained constant [22].

The addition of CNT to the epoxy resin with stoichiometric amine/epoxy ratio causes a light decrease of the glass transition temperature. However, in the non-stoichiometric

Fig. 2 Micrographs of fracture surface CNT/epoxy composites



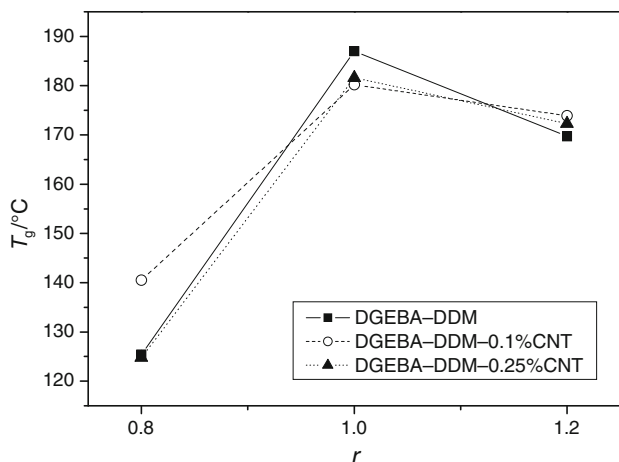


Fig. 3 Glass transition temperature of epoxy resin with different CNT contents as a function of amine/epoxy ratio

epoxy systems, the effect is just the opposite (Fig. 3). In these cases, the T_g is slightly increased by the presence of CNTs. The reason could be that, when the resin is not fully cross-linked, there is more free volume which may be occupied by CNT, restricting the molecular motion and thus increasing the glass transition temperature. The reaction of amine groups on CNTs with the oxirane groups of DGEBA may also contribute to the increase of crosslinking degree. In highly crosslinked epoxy resins ($r = 1$), this chemical reaction improves the filler/matrix interfacial adhesion, but it is detrimental for the crosslinking degree because it causes the presence of unreacted hardener molecules. These epoxy composites are comparable to epoxy resins with $r > 1$, thus, presenting lower T_g values than the stoichiometric system. The drawn conclusions are consistent with the results of the kinetic curing study, which show a slight decrease of the reaction enthalpy of the composites with regard to that of the neat epoxy resin. This implies that the epoxy matrix in stoichiometric composites is not totally cured and therefore their glass transition temperature decreases.

The effect of CNT on the glassy storage modulus is not so clear (Fig. 4). The composite with 0.25 wt% CNT follows the same trend than the epoxy resin as a function of the stoichiometry. For the epoxy-rich system, this amount of CNT increases E_G' , but for the two other amine/epoxy ratios they produce a small decrease of this property. However, the differences are not very remarkable in any case, and the effect of the amine/epoxy ratio is always more important than the effect of the CNT addition. Taking into account that the composites present higher real amine/epoxy ratio than the resin with the same value of r , due to the amine-functionalization of the nanotubes added, with $r = 0.8$ the glassy storage modulus should be higher for the resin and with $r = 1$ and $r = 1.2$ it should be higher for the composites, but the results are just the opposite. This

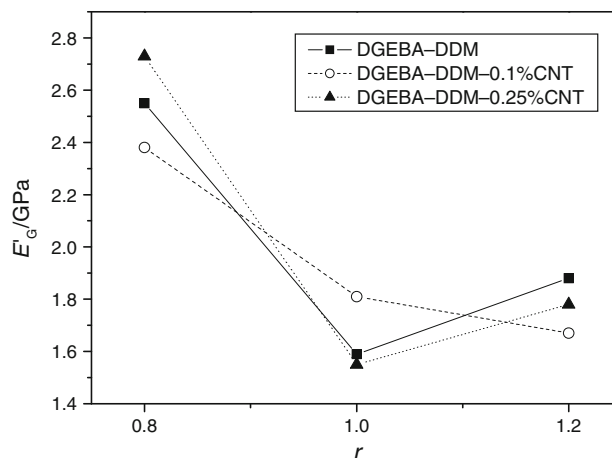


Fig. 4 Storage modulus at a temperature 50 °C below T_g

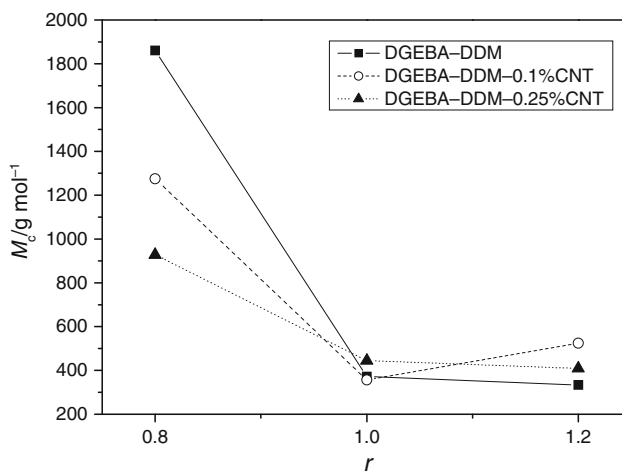


Fig. 5 Average molecular weight between crosslinking points for the epoxy resin with different CNT contents as a function of amine/epoxy ratio

indicates that, unlike the glass transition temperature, the difference in E_G' between CNT/epoxy composites and epoxy resin is not related to the amine groups on CNT but to the CNT themselves.

The average molecular weight between crosslinking points is scarcely influenced by the presence of CNT in the stoichiometric and amine-rich epoxy systems (Fig. 5; Table 1). However, they reduce the values of M_c in the epoxy-rich resin ($r = 0.8$), indicating a higher crosslinking degree. This is again indicating that amino-functionalized CNT may counteract in part the defect of amine groups when the amine/epoxy ratio is smaller than 1.

Figure 6 shows the elastic modulus of the different epoxy systems obtained in flexural tests. Although the values are different, the trends are almost the same than that obtained for the glassy storage modulus. The addition of CNT has a more remarkable effect in the epoxy-rich

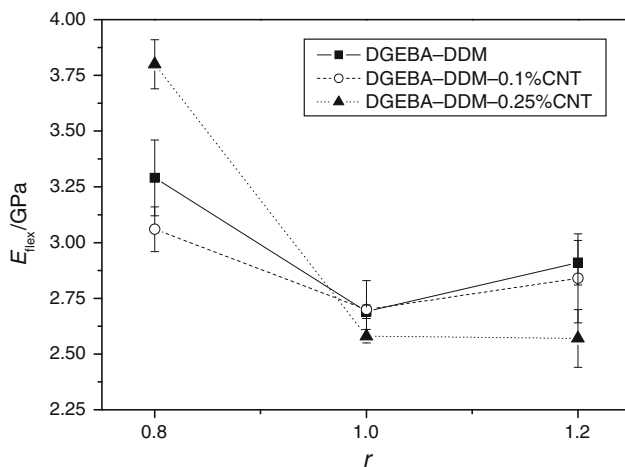


Fig. 6 Flexural modulus of the epoxy resin with different CNT contents as a function of amine/epoxy ratio

resin, causing an increase of the modulus of 15% with 0.25% CNT. This indicates that the stiffer resin is susceptible to be more stiffened by CNT. The low sensitivity of the resins with $r = 1$ and $r = 1.2$ to the presence of CNT may be related to one of these factors: (1) their lower stiffness, (2) their higher crosslinking degree. The obtained results indicate that the reason is likely associated with the crosslinking degree. In a highly crosslinked network, the presence of a third element may have a detrimental effect during the cure, delaying the peak of reaction or preventing the resin to obtain their optimum properties [23–25]. In fact, this was confirmed in our particular CNT/epoxy system by a DSC kinetic study [22], in which the results indicate that the addition of amino-functionalized multiwalled CNT has a retardation effect on the chemical reaction and induces a decrease of the reaction enthalpy.

Conclusions

The main conclusion is that the changes in the amine/epoxy ratio have a greater effect on the properties of the epoxy resin than the addition of CNT. Although the stiffer resin is that with an excess of epoxy groups, the stoichiometric resin shows the highest glass transition temperature. The effect of CNT is more remarkable in the epoxy-rich resin, promoting an increase of the glass transition temperature and the elastic modulus. For stoichiometric and amine-rich resins, the effect of CNTs is almost negligible. This indicates that the reinforcement effect of CNT is higher in the stiffer and less crosslinked network, while in highly crosslinked epoxy networks they are not able to improve the resin properties.

The authors have demonstrated that the effect of the stoichiometry on the nanocomposite is very complex and it requires to be studied in depth. On the one hand, the effects of

different amine/epoxy ratios on the neat epoxy resins are clear and they have been well studied. However, some of them are not totally right explained. On the other hand, the study on epoxy composites with amino-functionalized nanotubes implies a higher amount of experimental parameters which can affect to their final properties.

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References

1. Gojny FH, Wichmann MHG, Fiedler B, Schulte K. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites—a comparative study. *Compos Sci Technol*. 2005;65:2300–13.
2. Chen X, Wang J, Lin M, Zhong W, Feng T, Chen X, Chen J, Xue F. Mechanical and thermal properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes. *Mater Sci Eng A*. 2008;492:236–42.
3. Song YS, Youn JR. Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. *Carbon*. 2005;43:1378–85.
4. Xie XL, Mai YW, Zhou XP. Dispersion and alignment of carbon nanotubes in polymer matrix: a review. *Mater Sci Eng R*. 2005;49: 89–112.
5. Chen W, Auad ML, Williams RJJ, Nutt SR. Improving the dispersion and flexural strength of multiwalled carbon nanotubes-stiff epoxy composites through β -hydroxyester surface functionalization coupled with the anionic homopolymerization of the epoxy matrix. *Eur Polym J*. 2006;42:2765–72.
6. Lau KT, Lu M, Lam CK, Cheung HY, Shen FL, Li HL. Thermal and mechanical properties of single-walled carbon nanotube bundle-reinforced epoxy nanocomposites: the role of solvent for nanotube dispersion. *Compos Sci Technol*. 2005;65:719–25.
7. Ci L, Bai J. The reinforcement role of carbon nanotubes in epoxy composites with different matrix stiffness. *Compos Sci Technol*. 2006;66:599–603.
8. Guzmán de Villoria R, Miravete A, Cuartero J, Chiminelli A, Tolosana N. Mechanical properties of SWNT/epoxy composites using two different curing cycles. *Composites B*. 2006;37:273–7.
9. Prolongo SG, Gude MR, Ureña A. Improving the flexural and thermomechanical properties of amino-functionalized carbon nanotube/epoxy composites by using a pre-curing treatment. *Compos Sci Technol*. 2011;71:765–71.
10. Prolongo SG, Gude MR, Ureña A. Synthesis and characterisation of epoxy resins reinforced with carbon nanotubes and nanofibers. *J Nanosci Nanotechnol*. 2009;9:6181–7.
11. Shen J, Huang L, Wu L, Hu Y, Ye M. The reinforcement role of different amino-functionalized multi-walled carbon nanotubes in epoxy nanocomposites. *Compos Sci Technol*. 2007;67:3041–50.
12. Prolongo SG, Gude MR, Ureña A. Rheological behaviour of nanoreinforced epoxy adhesives of low electrical resistivity for joining carbon fiber/epoxy laminates. *J Adhes Sci Technol*. 2010; 24:1097–112.
13. Calventus Y, Montserrat S, Hutchinson JM. Enthalpy relaxation of non-stoichiometric epoxy-amine resins. *Polymer*. 2001;42: 7081–93.

14. Meyer F, Sanz G, Eceiza A, Mondragon I, Mijović J. The effect of stoichiometry and thermal history during cure on structure and properties of epoxy networks. *Polymer*. 1995;36:1407–14.
15. Fernandez-Nograro F, Valea A, Llano-Ponte R, Mondragon I. Dynamic and mechanical properties of DGEBA/poly(propylene oxide) amine based epoxy resins as a function of stoichiometry. *Eur Polym J*. 1996;32:257–66.
16. Vallo CI, Frontini PM, Williams RJJ. The glass transition temperature of nonstoichiometric epoxy-amine networks. *J Polym Sci B*. 1991;29:1503–11.
17. Palmese GR, McCullough RL. Effect of epoxy-amine stoichiometry on cured resin material properties. *J Appl Polym Sci*. 1992;46:1863–73.
18. Morgan RJ, Kong FM, Walkup CN. Structure-property relations of polyethertriamine-cured bisphenol-A-diglycidyl ether epoxies. *Polymer*. 1984;25:375–86.
19. Guerrero P, De la Caba K, Valea A, Corcuera MA, Mondragon I. Influence of cure schedule and stoichiometry on the dynamic mechanical behaviour of tetrafunctional epoxy resins cured with anhydrides. *Polymer*. 1996;37:2195–200.
20. Gupta VB, Brahatheeswara C. Molecular packing and free volume in crosslinked epoxy networks. *Polymer*. 1991;32:1875–84.
21. Jeffrey K, Pethrick RA. Influence of chemical structure on free volume in epoxy resins: a positron annihilation study. *Eur Polym J*. 1994;30:153–8.
22. Prolongo SG, Gude MR, Ureña A. The curing process of epoxy/amino-functionalized MWCNTs: calorimetry, molecular modeling, and electron microscopy. *J Nanotechnol* 2010; ID 420432.
23. López J, Rico M, Montero B, Díez J, Ramírez C. Polymer blends based on an epoxy-amine thermoset and a thermoplastic. *J Therm Anal Calorim*. 2009;95:369–76.
24. Rico M, López J, Bouza R. Thermal behavior of blends based on a thermoplastic-modified epoxy resin with a crosslinking density variation. *J Therm Anal Calorim*. 2011;105:599–606.
25. Bae J, Jang J, Yoon SH. Cure behavior of the liquid-crystalline epoxy/carbon nanotube system and the effect of surface treatment of carbon fillers on cure reaction. *Macromol Chem Phys*. 2002;203:2196–204.