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Functionalization of carbon nanotubes with (3-glycidyloxypropyl)-trimethoxysilane: Effect of wrapping on epoxy matrix nanocomposites

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ABSTRACT: In this work, multiwalled carbon nanotubes (MWCNT), after previous oxidation, are functionalized with excess (3-glycidyloxypropyl)trimethoxysilane (GLYMO) and used as reinforcement in epoxy matrix nanocomposites. Infrared, Raman, and energy-dispersive X-ray spectroscopies confirm the silanization of the MWCNT, while transmission electron microscopy images show that oxidized nanotubes presented less entanglement than pristine and silanized MWCNT. Thickening of the nanotubes is also observed after silanization, suggesting that the MWCNT are wrapped by siloxane chains. Field-emission scanning electron microscopy reveals that oxidized nanotubes are better dispersed in the matrix, providing nanocomposites with better mechanical properties than those reinforced with pristine and silanized MWCNT. On the other hand, the glass transition temperature of the nanocomposite with 0.05 wt % MWCNT-GLYMO increased by 14 °C compared to the neat epoxy resin, suggesting a strong matrix–nanotube adhesion. The functionalization of nanotubes using an excess amount of silane can thus favor the formation of an organosiloxane coating on the MWCNT, preventing its dispersion and contributing to poor mechanical properties of epoxy nanocomposites. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44245.

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INTRODUCTION

Multiwalled carbon nanotubes (MWCNT) are often investigated as reinforcement in polymer matrices, due to their outstanding mechanical and electrical properties.[1–5] Actually, the incorporation of small amounts of carbon nanotubes in a polymer matrix, usually between 0.1 and 5 wt %, can potentially provide structural materials with higher modulus and mechanical strength, as well as improvements in thermal and electrical performances.[2–6] These nanocomposites can find applications in automotive, aerospace, marine, defense, energy, and electronics industries.[1,3,6]

On the other hand, it is known that the intermolecular interactions (mainly van der Waals) are responsible for the formation of MWCNT agglomerates. Thus, for homogeneous dispersion, the strong nanotube–nanotube interactions must be overcome.[6] Another complication is the appropriate interaction between MWCNT and the polymeric matrix. These obstacles can reduce the efficiency of MWCNT in the final properties of the nanocomposites, making them sometimes less attractive than conventional composites.[6] To address these problems, a widely used approach is functionalization, that is, the surface modification of the MWCNT with functional groups strongly interacting or forming covalent bonds with the polymer chains of the matrix. In the recent literature, there are a number of papers reporting MWCNT functionalization with carboxylic and siloxane groups, among others, to enhance the interaction between the MWCNT and the polymer matrix.[7–11] Silanes have been widely studied as coupling agents, in MWCNT/polymer nanocomposites, to enhance the mechanical properties, especially increasing elastic and flexural modulus,[12] wear and thermal resistance,[13] with an increase of the glass transition temperature (T_g) of the matrix.

Epoxy resins are one of the most important classes of thermosetting polymers and often used in engineering composites. Seeking to enhance their mechanical properties such as modulus and tensile strength,[14–16] as well as wear and thermal resistances,[17–19] a number of researchers have been studying the reinforcement of these materials with MWCNT. The electrical properties of MWCNT/epoxy nanocomposites are also noteworthy and have been recently used to monitor strain and damage in composites under cyclic strain.[20]

The functionalization of MWCNT with (3-glycidyloxypropyl)trimethoxysilane (GLYMO) to reinforce epoxy matrices has also been reported.[21–23] GLYMO is a bifunctional organosilane having three methoxy groups in one side of the structure and an epoxy group on the other side. Like other organosilanes, GLYMO is easily hydrolyzable, and the methoxy groups are substituted by hydroxyl groups, forming a trisilanol.[21] The advantage of MWCNT functionalization with GLYMO for reinforcing epoxy matrices is the presence of an epoxy end group in its structure. Thus, in addition to the physical interaction between the MWCNT-GLYMO and the resin epoxy groups, there is also the possibility of a chemical bond between MWCNT-GLYMO and the hardener, so that it is interwoven throughout the network polymer chains.[21,23]

Studying the effect of MWCNT-GLYMO in epoxy matrix nanocomposites, Ma and coworkers observed that the thermal stability increased with the addition of silanized MWCNT. This is possibly related to the fact that MWCNT act as a physical barrier, preventing the spread of decomposition reactions in the nanocomposite. The authors also observed an increase of over 20 °C in T_g for a 0.25 wt % MWCNT-GLYMO nanocomposite, while pristine nanotubes at the same concentration provided an increase of 8 °C.[21] In another work, with composites cured by electron beam irradiation, the functionalization with GLYMO also enhanced MWCNT/matrix adhesion, ensuring an increase of 34.1% in the elastic modulus of the matrix with 0.25 wt % of MWCNT-GLYMO, while there was no increase with pristine MWCNT. Moreover, the T_g was increased by 18.4 °C for 0.25 wt % MWCNT-GLYMO nanocomposites.[22] Nie and Hübert functionalized carbon nanofibers (CNF) with GLYMO and observed that, unlike other silanes, GLYMO, at high concentrations, formed multilayers on CNFs, suggesting that it is adsorbed easier on the surface than other silanes. Scanning electron micrographs showed that the functionalization with GLYMO improved dispersion of CNF in epoxy matrix. For 1 wt % CNF-GLYMO composites, there was an increase in the storage modulus, but a decrease in T_g, which was attributed to an excess of epoxy groups, resulting in a nonstoichiometric resin/hardener ratio.[23]

However, there are no specific studies in the literature concerning the effects of nanotube wrapping on the properties of epoxy matrix nanocomposites. Wrapping studies are, in general, related to noncovalent functionalization, especially with block copolymers, aiming to preserve the electronic structure and electrical properties of the nanotubes.[24,25] On the other hand, when an excessive amount of the functionalization agent (e.g., a silane) is used, it could lead to the formation of nanotube clusters and, consequently, unsatisfactory mechanical and/or thermal properties.

This work aims to study the wrapping of MWCNT with GLYMO and its effect on the mechanical and thermal properties of epoxy matrix nanocomposites, at low MWCNT-GLYMO concentrations (0.05–0.1 wt %), in comparison with oxidized and pristine MWCNT. The dispersion of functionalized and pristine MWCNT in the polymer matrix was revealed by transmission and scanning electron microscopy and correlated with mechanical and thermal properties.

EXPERIMENTAL

Materials

MWCNT were supplied by Chengdu Organic Chemicals (Chengdu, China). The epoxy resin used was Araldite GY 251, based on diglycidyl ether of bisphenol A (DGEBA), cured with HY 956 hardener, both manufactured by Huntsman (São Paulo, Brazil). Sulfuric acid 98% (Cinética Química, São Paulo, Brazil), nitric acid 65% (Merck, Rio de Janeiro, Brazil), and GLYMO 98% (Sigma Aldrich, St. Louis) were used as acquired. PVDF filters (Pall, Washington) with a pore size of 0.45 μm were used in filtration processes.

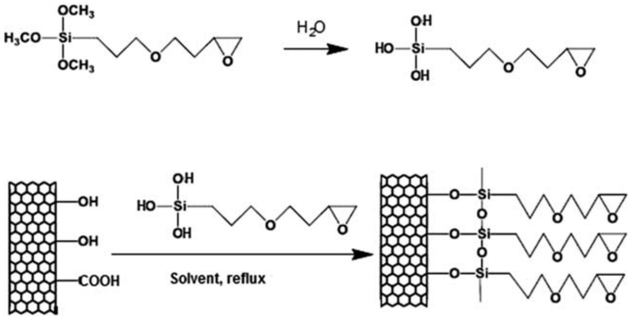

Figure 1. The hydrolysis of GLYMO and the formation of covalent bonds with an oxidized carbon nanotube.

Functionalization

MWCNT were first carboxylated using an oxidizing solution and further silanized using GLYMO. Figure 1 represents the GLYMO hydrolysis and the interaction with oxidized MWCNT. The hydrolysis process generally takes place in the presence of an acid catalyst, for example, sulfuric, hydrochloric or acetic acids, although even water can act as the acid catalyst, although the efficiency is lower.[26] Silanol groups can readily reacts with hydroxyl and carboxyl groups present on oxidized MWCNT, forming covalent bonds.

For the oxidation, 25 mL of a nitrating solution (sulfuric acid/nitric acid, 70/30, v/v) was added to 0.05 g of pristine MWCNT, and the system was maintained under stirring for 12 h, at room temperature. The MWCNT was then filtered and washed with deionized water in a PVDF filter until pH around 7 and subsequently dried at 80 °C for 24 h.

For the silanization, 0.1 g of oxidized MWCNT (MWCNT-COOH) was added to 40 mL of acetone, and the system was maintained in ultrasonic bath for 60 min at 50 °C. After this, 100 μL of GLYMO were added to 20 mL de acetone, and the mixture was maintained under stirring for 60 min. Finally both systems were mixed in a Duran-Schott bottle and maintained under stirring for 12 h at room temperature. The silanized carbon nanotubes (MWCNT-GLYMO) were then filtered, washed with acetone, and dried in a vacuum oven at 80 °C for 24 h. To test a possible wrapping effect, the MWCNT/GLYMO ratio used (ca., 1:1) was considerably higher than those used in other studies.[12,21,23]

Fabrication of Specimens

Pristine, oxidized, and silanized MWCNT were first disentangled by tip sonication (Sonics Vibration, 750 W, 20 kHz) in acetone for 20 min at amplitude of 22%. The MWCNT samples, in concentrations of 0.05, 0.075, and 0.1 wt %, were then added to DGEBA, and the mixtures were sonicated for 20 min at amplitude of 30%. After sonication, the residual solvent (acetone)

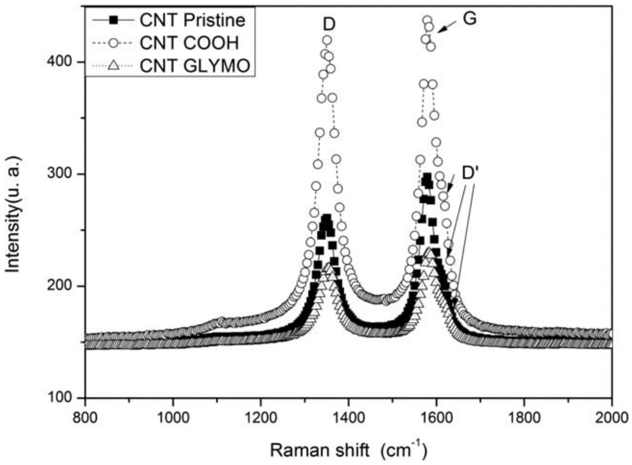

Figure 2. Raman spectra of samples of pristine MWCNT, MWCNT-COOH (oxidized), and MWCNT-GLYMO (silanized).

was eliminated by heating the system to 65 °C under vacuum until constant mass. The samples were prepared by mixing the MWCNT/DGEBA system with the required amount of hardener (100 parts of epoxy resin to 20 parts of hardener), according to the manufacturer, under mechanical stirring for 5 min. The specimens were prepared by casting in silicone molds. The curing was made at ambient temperature for 24 h, according to the manufacturer's recommendation.

Characterization

Pristine and functionalized MWCNT were characterized by Raman spectroscopy (Wintec, argon laser, $\lambda = 532$ nm) and Fourier transform infrared spectroscopy (FTIR). FTIR spectra were collected with a Perkin Elmer Spectrum One B spectrometer in the 600–4000 cm^{-1} range, using resolution of 4 cm^{-1} and 32 scans. The spectra of dried samples were obtained in KBr pellets (Merck, spectroscopic grade) containing 0.2 wt % of MWCNT. The morphology and chemical composition of the nanoparticles were investigated by scanning electron microscope with field emission gun (FESEM) and energy-dispersive X-ray spectroscopy (EDS) in a JEOL 6701F equipment operating at 10 kV.

Thermogravimetric analyses (TGA) were carried out on a Netzsch STA 449C equipment from room temperature to 1000 °C at 10 K/min under nitrogen atmosphere at a flow rate of 70 cm^3/min. Differential scanning calorimetry (DSC) analyses were conducted in a DSC Q50 da TA Instruments from room temperature to 250 °C at 10 K/min under nitrogen atmosphere.

Tensile tests were performed in a universal testing machine (Instron Model 3382), with a load cell of 5.0 kN. The samples were molded by casting in silicone molds of approximately 6 cm × 4 cm. Five specimens were tested for each sample. The analyses of the fracture surfaces of tensile tested specimens were performed on a FESEM (JEOL-6701F), while a transmission electron microscope (TEM) (JEOL-2100) was used to evaluate the dispersion and dimensions of MWCNT in the polymer matrix.

RESULTS AND DISCUSSION

Carbon Nanotubes Characterization

Raman Spectroscopy. Raman spectra of pristine, oxidized (MWCNT-COOH), and silanized (MWCNT-GLYMO) nanotubes are shown in Figure 2. By functionalizing MWCNT, it is expected that its graphitic structure, with sp^2-hybridized carbon atoms, will be somewhat altered by the insertion of functional groups, which leads to the formation of bonds with carbon atoms having sp^3 hybridization. It is expected that functionalization will increase the relative intensity of the bands representing disorder (or defects), D and D′ bands, while the G bands, representing the MWCNT graphitic structure, is unchanged or decreases. Thus, the ratio between the intensities of D and G bands is generally used to access the quality and/or modifications of the MWCNT structure.[27]

Table I shows the D, G, and D′ bands wavenumber positions (in cm^{-1}) and the I_D/I_G ratios (calculated from the peak areas) for pristine, oxidized (MWCNT-COOH), and silanized (MWCNT-GLYMO) carbon nanotube samples.

For pristine MWCNT, the ratio is 0.87, while it increases to 1.08 for MWCNT-COOH. The values of I_D/I_G for pristine and oxidized MWCNT are in agreement with the literature, confirming that the oxidation process was effective. For example, Silva *et al.* calculated I_D/I_G values of 0.84 for pristine and 0.93 for MWCNT oxidized with a mixture of nitric and sulfuric acid in the same proportions used in this study.[27]

Samples of MWCNT-GLYMO present no further increase in the I_D/I_G ratio in comparison to the oxidized MWCNT. This behavior has also been described by other authors that functionalized previously oxidized MWCNT with 3-(mercaptopropyl)-trimethoxysilane.[28] The bands of Raman spectra represent details of the crystal structure of MWCNT and the defects caused by the insertion of chemical groups. After the process of hydrolysis, the silane interacts with oxygenated groups that cover the nanotube walls, leading to the formation of covalent bonds with the carbon nanotubes. Thus, there is no further change in the molecular structure of the MWCNT.

Fourier Transform Infrared Spectroscopy. Figure 3 shows the infrared absorbance spectra of pristine, oxidized, and silanized MWCNT samples. For pristine MWCNT, it is observed the presence of a band at 1635 cm^{-1}, attributed to conjugated C=C stretching, small bands at 2945 cm^{-1} and 2850 cm^{-1}, relative

Table I. D, G, and D′ Band Positions and I_D/I_G for Pristine and Functionalized MWCNT

Sample	D band (cm^{-1})	G band (cm^{-1})	D′ band (cm^{-1})	I_D/I_G
Pristine	1350	1580	1615	0.87
MWCNT-COOH	1349	1576	1613	1.08
MWCNT-GLYMO	1353	1582	1622	1.05

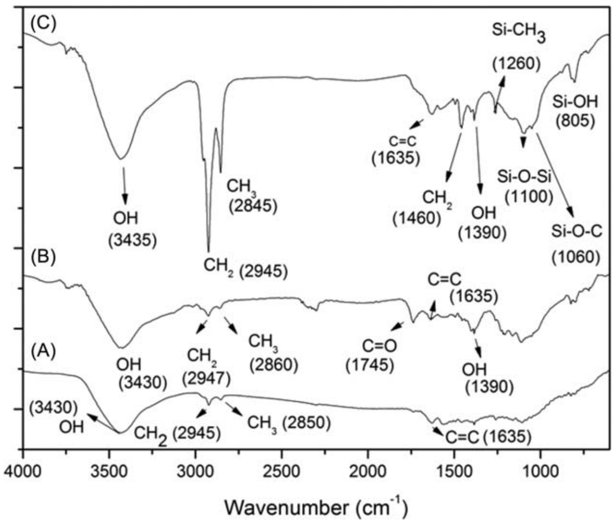

Figure 3. FTIR spectra of (A) pristine MWCNT, (B) MWCNT-COOH, and (C) MWCNT-GLYMO.

to $\mathrm{C{-}H}$ stretching, and a wide $\mathrm{O{-}H}$ band at 3430 $\mathrm{cm^{-1}}$. The latter is attributed to adsorbed water and is present in all of the spectra. The MWCNT-COOH spectrum reveals $\mathrm{C{=}O}$ and $\mathrm{C{-}O{-}C}$ absorption bands at 1745 $\mathrm{cm^{-1}}$ and ca. 1180 $\mathrm{cm^{-1}}$, respectively, both assigned to carboxylic groups attached to nanotube walls after the oxidation procedure.[29] Conjugated $\mathrm{C{=}C}$, related to the carbon nanotube structure, and CH bands are also still present.

The spectrum of the MWCNT-GLYMO sample shows the disappearance of the band at 1745 $\mathrm{cm^{-1}}$ and the appearance of four bands: at 1100 $\mathrm{cm^{-1}}$ and 1060 $\mathrm{cm^{-1}}$, assigned to $\mathrm{Si{-}O{-}Si}$ and $\mathrm{Si{-}O{-}C}$ bonds; at 1260 $\mathrm{cm^{-1}}$, from $\mathrm{Si{-}CH_3}$ groups; and at 1460 $\mathrm{cm^{-1}}$, attributed to $\mathrm{CH_2}$ scissoring from glycidoxy groups.[23,30] It is also noteworthy that the relative intensities of CH stretching bands, related to $\mathrm{{-}CH_2}$ and $\mathrm{{-}CH_3}$ groups, mostly from attached GLYMO, are significantly increased. These FTIR spectra confirm the successful functionalization of oxidized MWCNT with GLYMO. Nevertheless, the presence of OH bands at 1390 $\mathrm{cm^{-1}}$ and around 805 $\mathrm{cm^{-1}}$ can be attributed to silanol ($\mathrm{Si{-}OH}$) groups, indicating that an excess of GLYMO probably produced a coating of silsesquioxane chains over the nanotubes, at least partially noncovalently bonded to the nanotube walls. The functionalization of the MWCNT with a silane can thus result in individual siloxane-nanotube bonds; however, more likely, the formation of a siloxane network takes place, which ultimately encapsulate the MWCNT.[23,31,32]

Morphological Characterization and EDS Analysis. The FESEM images (Figure 4) show no significant differences in the appearance of MWCNT before and after the oxidation, and in both cases it is observed that most of the tubes are long and undamaged, showing that these MWCNT are resistant to the oxidation process. This behavior was also observed by Kathi *et al.*[32] for a similar oxidation procedure, although some other studies on MWCNT acid oxidation reported the fragmentation of the nanotubes.[23,31] This can be explained by the different quality of the nanotubes and the lower oxidation temperature used in this work. The appearance of the nanotubes changes little after further silanization with GLYMO. The diameters of pristine MWCNT and MWCNT-COOH were within the range of 30–55 nm, whereas for MWCNT-GLYMO it was observed an increase of about 10 nm in the diameters (up to 65 nm). This thickening of the nanotubes is an indication of the MWCNT wrapping[14,33,34] after the silanization process.

EDS analysis confirmed the presence of Si in the MWCNT-GLYMO sample. Table II summarizes the wt % values for

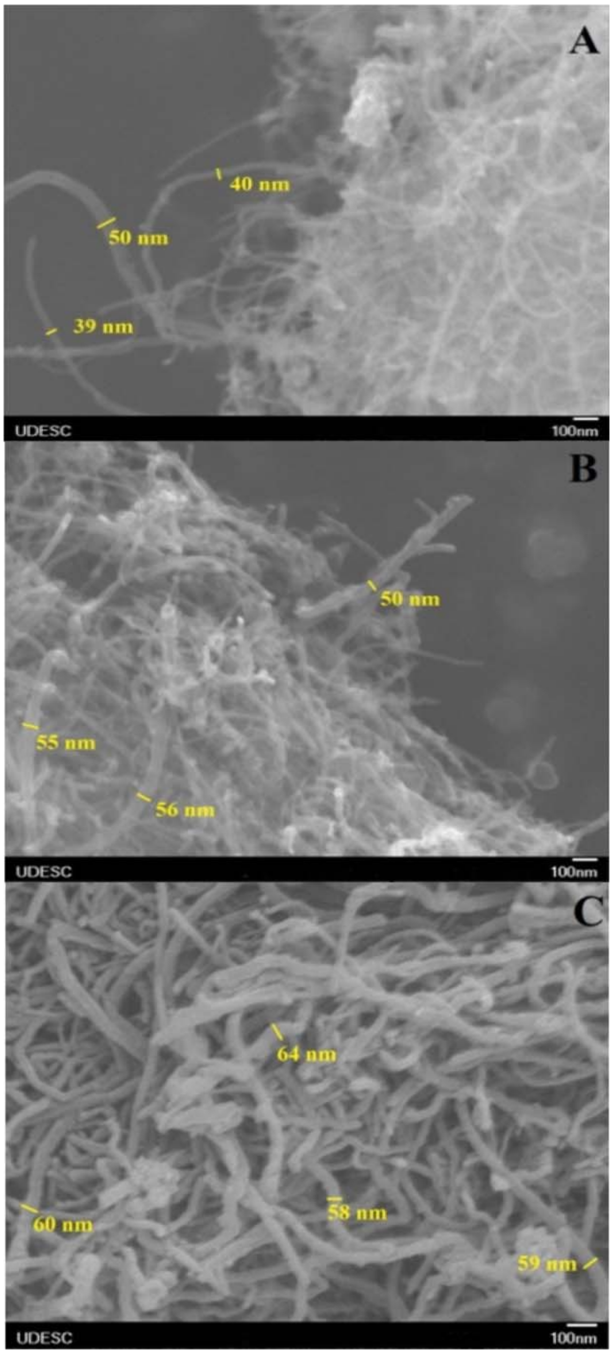

Figure 4. FESEM images at 10 kV of: (A) pristine MWCNT, (B) MWCNT-COOH, and (C) MWCNT-GLYMO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. EDS Analysis of MWCNT Pristine, MWCNT-COOH, and MWCNT-GLYMO

Sample	C (wt %)	O (wt %)	Si (wt %)
MWCNT pristine	92	8	0
MWCNT-COOH	88	12	0
MWCNT-GLYMO	80	14	6

carbon, oxygen, and silicon. Although this is a semiquantitative technique, it is possible to compare the values for the different MWCNT samples to access the efficiency of the functionalization processes. For example, the increase of the oxygen content after the oxidizing acid treatment is an indication that the oxidation of MWCNT has occurred.

The values of oxygen content and O/C ratios were estimated for pristine MWCNT and MWCNT-COOH. For pristine MWCNT the values were 6.1 mol % and 0.065, respectively, while for MWCNT-COOH the values changed to 9.3 mol % and 0.10, showing that the oxidizing treatment was effective. As indicated by FTIR measurements, most of the oxygenated groups are expected to be hydroxyl and carboxylic groups, which are able to react with hydrolyzed GLYMO (Figure 3). These values are close to others reported in literature for similar oxidizing treatments.[35,36]

For MWCNT-GLYMO the presence of 6 wt % Si was observed, confirming the functionalization of the nanotubes. Other authors reported different EDS values for different conditions of silanization. Nie and Hübert[23] obtained a much lower Si content (1.1 wt %) in their study of functionalization of carbon fibers with GLYMO. In other works, Ma *et al.*[37] obtained a concentration of 1.68% for MWCNT silanized with GLYMO, while Kathi *et al.*[32] found 4.10 wt % Si for the silanization of MWCNT with 3-aminopropyltriethoxysilane. However, Velasco-Santos *et al.*[28] silanized previously oxidized MWCNT with 3-mercaptopropyl trimethoxysilane, obtaining 12 wt % Si. Here, it is important to consider that Nie and Hübert used a 2:1 MWCNT/GLYMO ratio, while Ma *et al.* used a 5:1 ratio. Kathi *et al.* and Velascos-Santos *et al.* used the same MWCNT/GLYMO ratio of this work (1:1) and, therefore, also achieved higher Si contents. Moreover, the relatively high Si content obtained in this work (6 wt %) is consistent with the formation of a silsesquioxane coating on the MWCNT.

Thermogravimetric Analysis. TGA curves (Figure 5) show only one stage of decomposition for the pristine nanotubes, between 450 and 650° C, which is a typical behavior for MWCNT.[29,38] For the functionalized MWCNT samples, mass loss starts at temperatures between 100 and 200 °C. The low thermal stability of the functionalized MWCNT with respect to pristine can be explained by the formation of defects along the MWCNT walls. Such defects are a result of functionalization, wherein the conjugated sp^2 structure of MWCNT is changed by the "graft" functional groups (in this case, —COOH, —OH, lactone, and siloxane groups) to a sp^3 hybridization structure.[38] It is also observed in Figure 5 that the MWCNT-COOH sample shows a significantly lower $T_{\max}$ (temperature of the maximum in the mass loss rate) than MWCNT-GLYMO samples.

Furthermore, MWCNT-GLYMO samples exhibited much higher residual masses than pristine and MWCNT-COOH, at temperatures above 640 °C. This phenomenon may be attributed to the physical barrier produced when a protective silicon oxide layer is formed on MWCNT, which effectively impedes the propagation of decomposition reactions of MWCNT.[39] This hypothesis was confirmed by the fact that a significant yield, that is, 40% of residual mass, was noticed for MWCNT-GLYMO, which was much higher than its counterparts, pristine and MWCNT-COOH, with 3.5% and 3.3%, respectively. This behavior is another evidence of the formation of a thin coating formed by a siloxane network around the MWCNT (wrapping), which can improve thermal stability.[40]

Nanocomposites Characterization

Mechanical Characterization. Stress–strain curves from tensile tests are shown in Figure 6. It is observed that most of the samples present a similar profile, close to the behavior of the neat resin. In the case of nanocomposites reinforced with 0.1 wt %

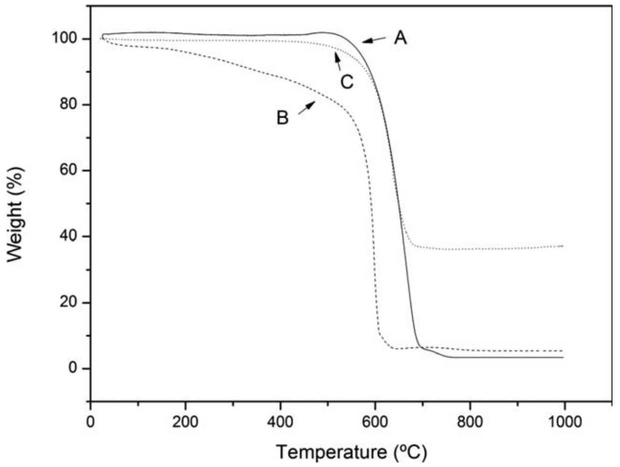

Figure 5. TGA of pristine MWCNT (A), MWCNT-COOH (B), and MWCNT-GLYMO (C).

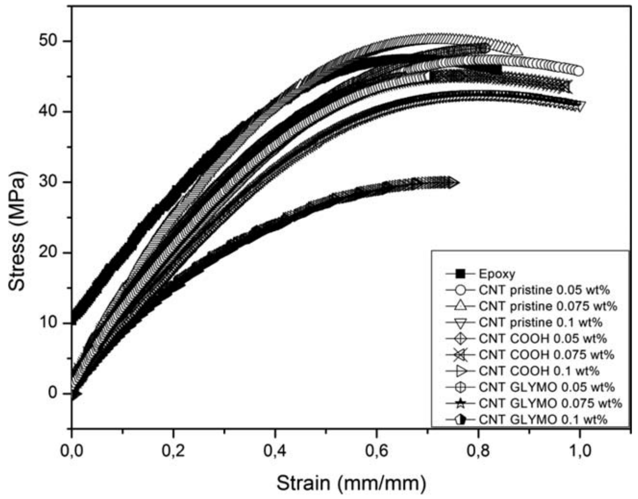

Figure 6. Stress–strain curves from tensile tests for neat resin and nanocomposites.

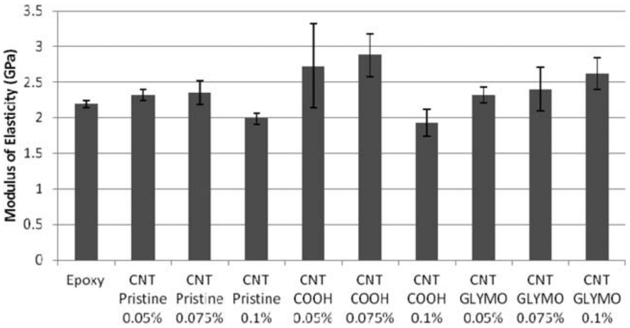

Figure 7. Modulus of elasticity of nanocomposites reinforced with pristine, oxidized (COOH) or silanized (GLYMO) MWCNT.

MWCNT COOH, however, a significant decrease in maximum tensile stress and elongation at break is observed. This can be related to the formation of large agglomerates (as will be discussed later), probably due to the high viscosity of the samples with higher MWCNT COOH amounts and/or a stronger interaction between oxidized nanotubes, hindering homogenization.

Most of the work on the functionalization of MWCNT correlates the increases of the modulus of elasticity and the tensile strength with better interactions between the polymer matrix and the nanotubes. The elastic modulus is strongly influenced by dispersive states of the nanoparticles and their interfacial interaction with polymer matrix.[41] Thus, the elastic modulus can be used as a parameter for evaluating the efficiency of the functionalization and the state of dispersion of nanoparticles.

Figures 7 and 8 show the values for the modulus of elasticity and tensile strength, respectively, of nanocomposites reinforced with pristine and functionalized MWCNT.

It is observed that, for most of the nanocomposites, there was no significant variation of the modulus of elasticity compared with the neat epoxy resin. For the nanocomposites reinforced with pristine MWCNT, there is a tendency of increase of the modulus of elasticity for the lower concentrations of MWCNT (0.05 and 0.075 wt %). The low intermolecular interaction between pristine MWCNT and the epoxy matrix is probably responsible for the small increase in the storage modulus.

For MWCNT-COOH, there was an increase of about 30% in elastic modulus for nanocomposites with 0.05 and 0.075 wt % of nanotubes, while a decrease of the modulus was observed for nanocomposites with 0.1 wt % MWCNT-COOH. The increased elastic modulus for the nanocomposites reinforced with 0.05 and 0.075 wt % MWCNT-COOH evidences the influence of oxidation in the decrease of molecular interactions (van de Waals forces) between the MWCNT, improving dispersion.[42] However, for the highest concentration (0.1 wt %), the formation of agglomerates, which become stress concentrators, possibly decreases the modulus of elasticity.[43]

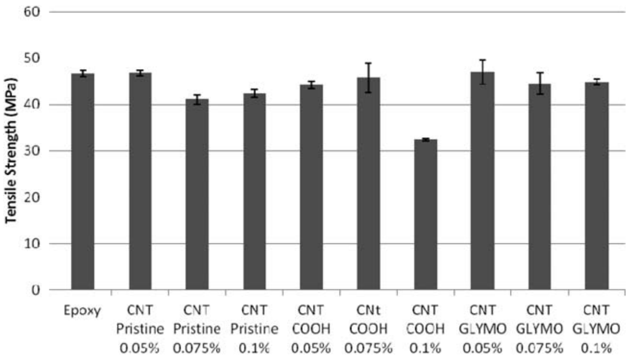

Figure 8. Tensile strength of nanocomposites reinforced with pristine, oxidized (COOH), or silanized (GLYMO) MWCNT.

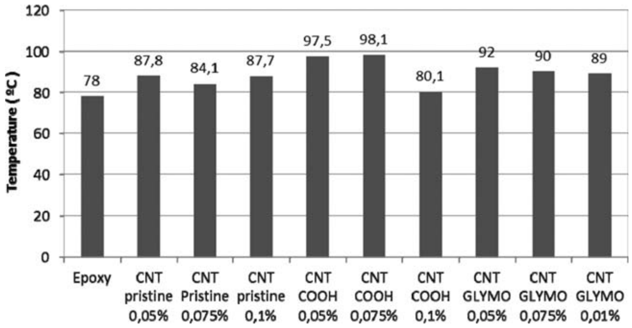

Figure 9. Glass transition temperatures for the neat epoxy and the nanocomposites.

For MWCNT-COOH and pristine MWCNT, the values of tensile strength also remained virtually the same as those for the neat resin. These results show that the interactions between carboxyl groups and the resin is limited.[44] Finally, for pristine MWCNT there was a decrease on the tensile strength for the samples with 0.075 and 0.1 wt % of MWCNT. This decrease is possibly related to a poor dispersion, also suggested by the decrease of the elastic modulus, and the lack of interfacial interaction with the epoxy resin.

In the case of MWCNT-GLYMO, there is a tendency to increase the modulus for all concentrations. However, these values are lower than those observed for MWCNT-COOH reinforced nanocomposites. Several studies in the literature report the increase of the modulus of elasticity of nanocomposites with MWCNT-GLYMO. In general, it is related to the decrease of the intermolecular interactions between nanotubes, and the simultaneous improve of the nanotube-matrix interfacial adhesion.[21,44] It is also noted that most of the tensile strength values are close to that of the neat epoxy resin, which suggests that there was a small interfacial adhesion between MWCNT-GLYMO and the polymer matrix. This can be related to the wrapping of the nanotubes with a silsesquioxane coating, from the excess silane available in the functionalization process, as indicated by the characterization of MWCNT-GLYMO. Such relatively thick coating seems to prevent the dispersion and the interaction of the nanotubes with the epoxy matrix.

DSC Characterization. Figure 9 shows the T_g values for the neat epoxy resin and the epoxy/MWCNT nanocomposites. It was observed an increase of up to 20 °C in T_g for MWCNT-COOH samples, with the only exception of the sample with 0.1 wt % of oxidized MWCNT. The same sample presented a decrease on the tensile strength, which reinforces the fact that at higher MWCNT concentrations agglomeration takes place. For

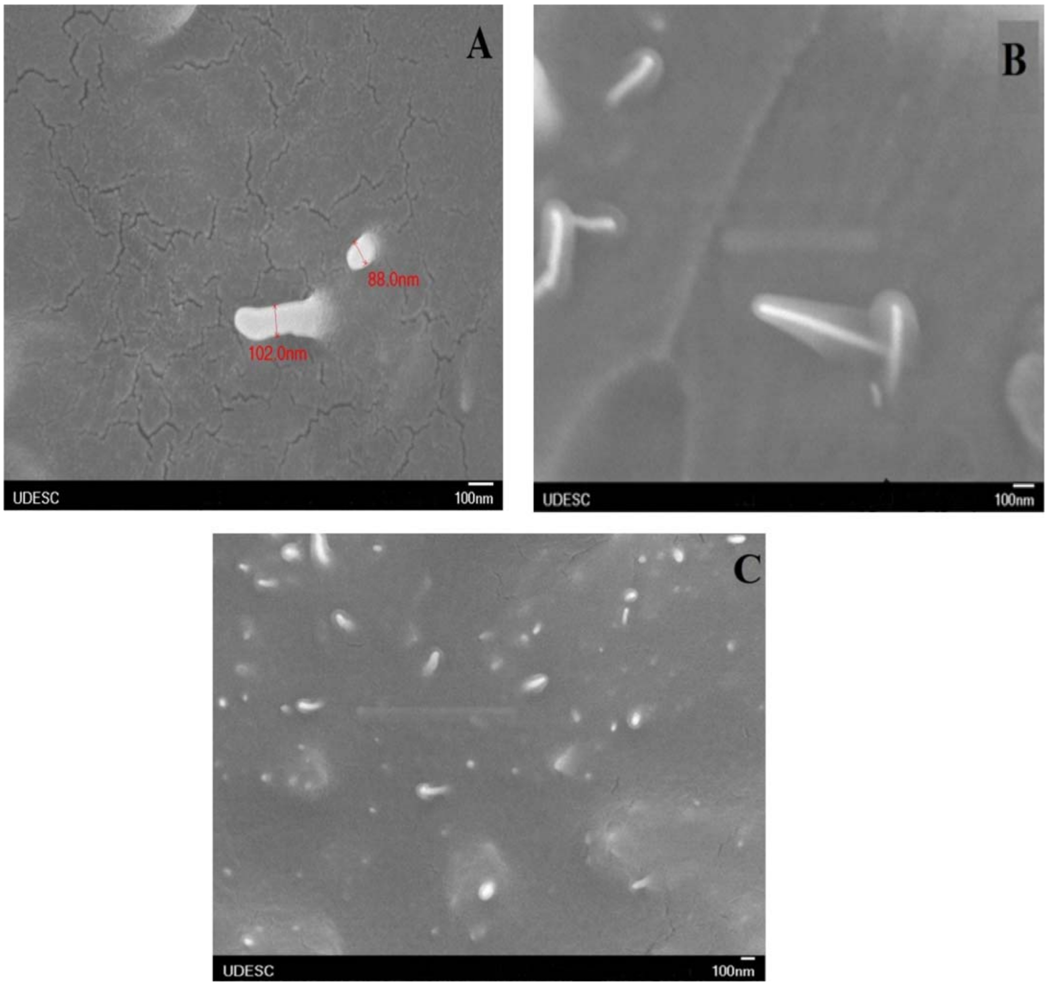

Figure 10. FESEM images of epoxy–matrix nanocomposites reinforced with: (A) MWCNT pristine 0.075%, (B) MWCNT-COOH 0.075%, and (C) MWCNT-GLYMO 0.1 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MWCNT-GLYMO concentrations of 0.05, 0.075, and 0.10 wt %, T_g increases of 14, 12, and 11 °C, respectively, were obtained.

A similar behavior has been also observed by other researchers.[22,32] Kathi *et al.*[32] reported an increase of 10 °C in the T_g of the epoxy matrix when 0.2 wt % of oxidized MWCNT was added, while Ma *et al.*[21] verified increases of around 14 °C for epoxy matrix nanocomposites with 0.25 wt % of MWCNT-GLYMO.

An enhancement in T_g can be produced by several factors, such as (i) an increase in the crosslink density, (ii) a restriction in molecular motions at the molecular level, and (iii) a decrease in the free volume;[45] although for nanocomposites reinforced with CNT it is normally attributed to an improvement in adhesion, which will cause restriction in molecular mobility.[40] The increase in T_g in our study may be attributed to the restriction in rapid coordinated molecular motion and thereby a decrease in free volume [factors (ii) and (iii)], as considering the relatively low GLYMO concentration, that could affect the stoichiometric ratio only very slightly, and further characterizations made in this work we can rule out factor (i). Therefore, the T_g can give an indirect indication of the formation of an interphase region[33] and, consequently, the increase in T_g can be a hint of the interaction between the nanoparticle and the polymer matrix.

Thus, the significant increase observed for epoxy systems reinforced with MWCNT-GLYMO suggests an enhanced nanotube/matrix interfacial adhesion, which is attributed to the formation of covalent bonds between the amine-curing agent and the epoxy ring present in the molecule of GLYMO.[21]

Morphological Characterization. Figure 10 shows FESEM images of the fractured surface of epoxy matrix nanocomposites with pristine, oxidized, and silanized MWCNT. Most samples showed small differences in the morphology, maintaining the characteristics of a brittle material typical of epoxy matrices,[46] which is in agreement with the mechanical characterization, while pulled out pristine MWCNT indicated a weak interaction between the matrix and the nanotubes.[47–52] However, the phenomenon looks different for each type of MWCNT sample. For MWCNT-COOH and MWCNT-GLYMO there is a thin polymer layer around the nanotubes pulled out from the matrix, indicating that there is an important interaction between these materials.[47]

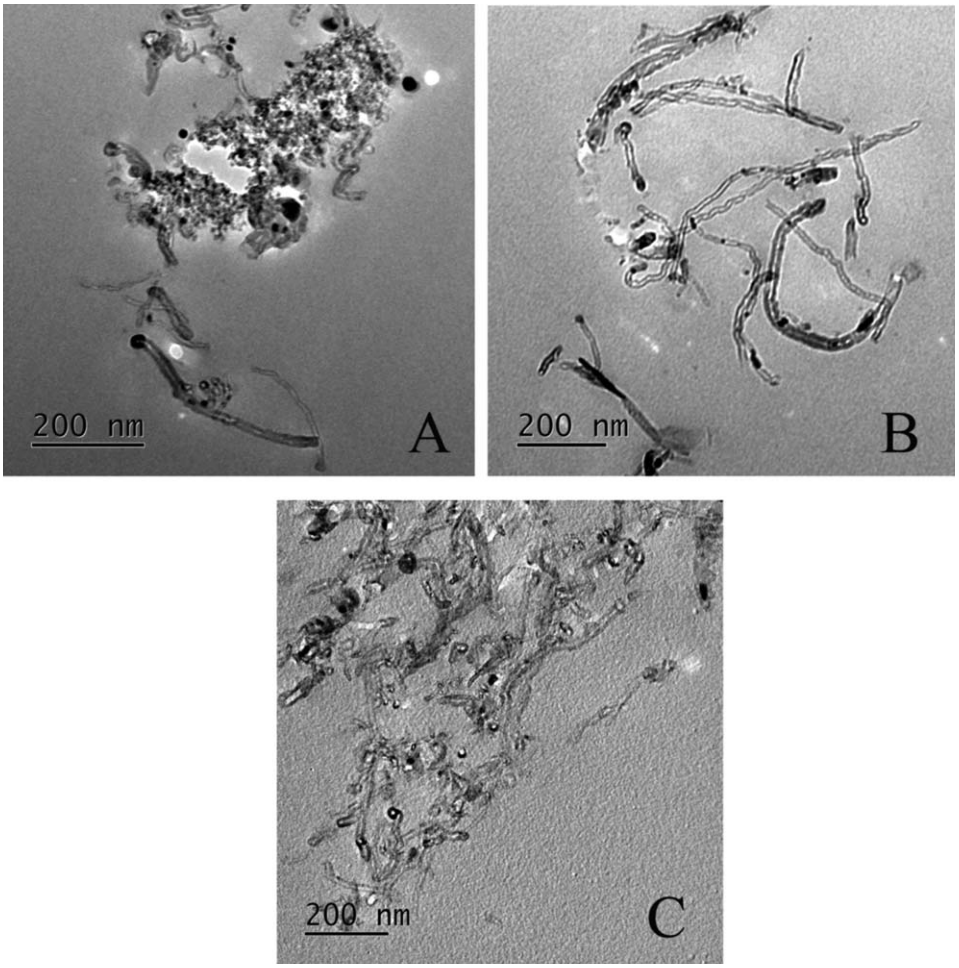

Figure 11. TEM images of epoxy matrix nanocomposites reinforced with: (A) pristine MWCNT, (B) MWCNT-COOH, and (C) MWCNT-GLYMO.

Moreover, the pulled out MWCNT-COOH and MWCNT-GLYMO were very short and accompanied by the deformation of nearby matrix, confirming a strong interaction between these nanotubes and the epoxy matrix. This suggests the formation of covalent bonds by the reaction of carboxylic and epoxy groups attached to the nanotube walls with the DGEBA or polyamine (hardener) molecules. This is also in accordance with the significant increase of the T_g observed in the DSC measurements for these nanocomposites. On the other hand, Figure 8(c) clearly shows the presence of large agglomerates of MWCNT-GLYMO in the matrix, probably caused by the excess of GLYMO used in the functionalization procedure. These agglomerates deteriorate load and stress transfer from the weak epoxy resin matrix to the high stiffness nanotubes and prevent an enhancement of mechanical properties. This is in disagreement with most of the studies on the use of covalently functionalized carbon nanotubes as reinforcement of polymer matrices,[3,9,39] which reported a better dispersion of the nanotubes after surface modification. These findings highlight the importance of the MWCNT/GLYMO ratio in the preparation of dispersible reinforcements for epoxy matrices.

TEM images of epoxy/MWCNT specimens (Figure 11) confirm the FESEM conclusions. For the nanocomposites with pristine MWCNT, Figure 9(a), it is verified the presence of relatively large clusters (>200 nm) in the epoxy matrix, while a clear improvement in the dispersion is achieved with oxidized MWCNT, Figure 9(b). However, it seems that after the silanization process, the MWCNT tend to reform agglomerates. This result was not expected and can be attributed to the formation of a silsesquioxane network wrapping MWCNT clusters.[26] The reagglomeration of silanized MWCNT can also explain why the tensile strength does not increase when MWCNT-GLYMO is added to the epoxy resin. As already discussed this is a consequence of the excess of GLYMO during the functionalization process, causing the wrapping of MWCNT and, possibly, crosslinking the nanotubes.

CONCLUSIONS

MWCNT have been successfully functionalized with GLYMO after prior oxidation. FESEM images showed an increase of the MWCNT diameter when it is functionalized with an excess amount of GLYMO, indicating the formation of a siloxane coating on the nanotubes (wrapping). A significant increase in T_g was verified for epoxy systems reinforced with MWCNT-GLYMO, suggesting that the glycidyl groups attached the walls of the MWCNT provided an improved interfacial interaction with the epoxy matrix. On the other hand, there was no enhancement of the mechanical properties due to the reagglomeration of the MWCNT-GLYMO nanotubes in the epoxy matrix. This reagglomeration results from the wrapping and clustering of MWCNT-GLYMO by the formation of a silsesquioxane network. These results highlight the importance of the MWCNT/GLYMO ratio in the preparation of dispersible reinforcements for epoxy matrices. Taking into account the potential structural applications of these materials, it is interesting to point out that, although mechanical and thermal properties can be adjusted by the degree of functionalization of the nanoreinforcement, an excessive amount of functionalization agent can lead to deleterious effects on their performance.

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