Study of Epoxy/CNT Nanocomposites Prepared Via Dispersion in the Hardener

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In this study, carboxylated (SWCNT-c) and pristine (SWCNT) single-walled carbon nanotubes were randomly dispersed in a hardener prior to mixing it with an epoxy resin. The influence of several parameters on the dispersion process were investigated. The produced samples were characterized by infrared spectroscopy, differential scanning calorimetry, dilatometry, dynamic mechanical analysis, scanning electron microscopy and mechanical testing (tensile, flexural and microhardness). The results obtained with the nanocomposites with SWCNT-c suggested that the lowest time and amplitude of sonication improved the mechanical properties. The use of a solvent (acetone) was important to improve dispersion, ultimately increasing microhardness and Young's Modulus up to 32%. Nanocomposites with 0.25 wt. (%) SWCNT-c presented superior mechanical properties compared to those with 0.50 wt. (%) SWCNT. Two simple mathematical models (rule of mixtures and Halpin-Tsai) were used to predict Young's Modulus of the composites yielding results very close to the experimental ones.

1. Introduction

In the last decade, much attention has been drawn to carbon nanotubes (CNTs) and their use in a variety of applications. However, major difficulties related to the use of CNTs in polymers remain, including the exfoliation of their original bundled structure, their distribution in polymeric matrices and their homogeneous dispersion using a minimum of 0.5-1.0 wt. (%) CNT content. These issues are in great part a consequence of the significant attractive forces among carboxylated (SWCNT-c) and pristine (SWCNT) single-walled carbon nanotubes, which are in the order of 0.5 eV (approximately 0.8×10^{-19} J) per nanometer throughout the nanotube-to-nanotube contact. This level of energy resembles that of a typical covalent bond[1].

In general, physical methods, such as sonication, are used to promote CNTs dispersion, even though this may damage their physical structure due to the very high shear stress and shear rate involved, which can reach 70 GPa and 10^7 s^{-1}, respectively. It should also be pointed out that the nanofillers must have a medium with an appropriate viscosity to allow diffusion[1]. The use of solvents, for instance, is also an alternative to reduce the generally high viscosity of thermoset resins used for nanocomposites.

Another possibility is to initiate the CNTs dispersion in the hardener rather than in the resin. Only few works reported this procedure[2-4]. Gojny and Schulte[2] verified that the best dispersion was achieved by suspending the nanotubes in the hardener, followed by mild sonication, mixing with the epoxy resin, and an extra sonication step. On the other hand, Chen et al.[3] compared wear rate measurements of samples with CNTs first dispersed in the hardener or in the resin, by asymmetric centrifugation, and found that they were not significantly different. Furthermore, the use of surfactants or solvents to aid this process is still an open issue. A previous study[4] showed that significant increase in some mechanical properties is achieved by dispersing carboxylated SWCNTs in the hardener, indicating this to be a possible route for preparing nanocomposites.

The other major issue related to nanocomposites regards the need for good interfacial adhesion between nanotubes and the polymer matrix in order to allow efficient stress transfer between them, which is strongly dependent on the type of CNTs and the nature of the polymer matrix. On this context, functionalization of the nanotube surface and the use of surfactants are believed to enhance interfacial adhesion[5], even though this process may also damage the surface of the carbon nanotube[6].

An additional benefit associated with functionalization is that it may also aid dispersion due to a strong interaction with the dispersion medium[2,7]. Although covalent functionalisation of CNTs may be helpful for mechanical reinforcement, it can be deleterious for electrical conductivity. It is possible that functionalization can even hinder the dispersion, specially if the nanotubes become too reactive. Nevertheless, CNTs are able to increase, for instance, the electrical conductivity of an epoxy resin due to their high tendency to form conducting networks as well as lower percolation thresholds. However, impurities, entanglement/dispersion degree and CNT diameter and length complicate the transfer of their good electrical and mechanical properties to the nanocomposites[8].

In this work, two types of CNTs were dispersed in the hardener, using sonication, a solvent and/or a surfactant, and different stirring techniques for mixing the hardener with the epoxy resin. The effect of these process variants on the properties of CNTs/epoxy nanocomposites was investigated. Besides, two simple micromechanical models to estimate Young's Modulus of the nanocomposites were employed to compare theoretical and experimental results.

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2. Materials and Methods

SWCNT-c and SWCNT used in this work were supplied by the Nanomaterials Laboratory at the Federal University of Minas Gerais (UFMG-Brazil) and were produced by electrical arc discharge with 92% purity (supplier information). The bifunctional diglycidyl ether of bisphenol A (DGEBA) epoxy resin was obtained from Huntsman as Araldite GY251, together with the hardener Aradur HY956. The solvent used was analytical grade acetone, from Cinética Química/Brazil and, the surfactant, Triton X-100 supplied by Vetec Química Fina/Brazil.

Figure 1 shows a generic route used for preparing all nanocomposites studied in this work. For sonication, a Sonics Vibration 750 equipment was employed. Previous studies published by the group on sonication conditions (i.e. power and time) may be found elsewhere[4,9] and the final evolution of the solvent was followed via mass balance. The samples were named as shown in Table 1, considering the various parameters studied. For comparison purposes, neat epoxy samples were also prepared using the same curing conditions.

2.1. Characterization

Mechanical tests were performed according to ASTM D638M using an EMIC DL30000 universal testing machine with a 1000 kgf load cell operating at a cross-head speed of 5 mm/min. Flexural properties were determined according to ASTM D790 in the same equipment, with a 100 kgf load cell operating at 2.6 mm/min. Vickers hardness was measured using 25 g load and 10 seconds loading time in a Shimadzu HMV-2T equipment. Surface morphology of the tensile fractured specimens was observed under a Zeiss DSM 940A scanning electron microscope (SEM) operating at 10 kV. The samples were previously gold-coated using a sputtering device.

The various nanocomposite specimens were also analyzed in a Netzsch 402C dilatometer. The samples were first heated from room temperature to 150 °C (at 10 °C/min and under N_2 atmosphere), followed by a fast cool down to room temperature and a new heating (second run) under the same conditions. Dynamic-mechanical analysis (DMA) on dual cantilever mode was carried out from room temperature to 150 °C at 5 minutes in a TA Instruments (model 2980) equipment. All measurements were conducted under 0.01% strain and 1 Hz frequency. DSC was conducted in a DSC2010 TA Instruments equipment at a heating rate of 10 °C/min, using a heating/cooling/heating cycle. Fourier transform infrared transmission spectroscopy (FTIR) analysis, in the 400-3500 cm^{-1} region, was carried out in a Perkin-Elmer equipment using the KBr pellet technique.

Raman spectroscopy was employed to characterize specific bands of the SWCNT-c, between 800 and 3400 cm^{-1}, on a Labram Jobim Yvon Micro Raman Spectrometer (wavelength: 632.8 nm). In addition, Fourier transform infrared (FTIR) transmission spectra were collected with a Nexus microscope (magnification 10×, probed
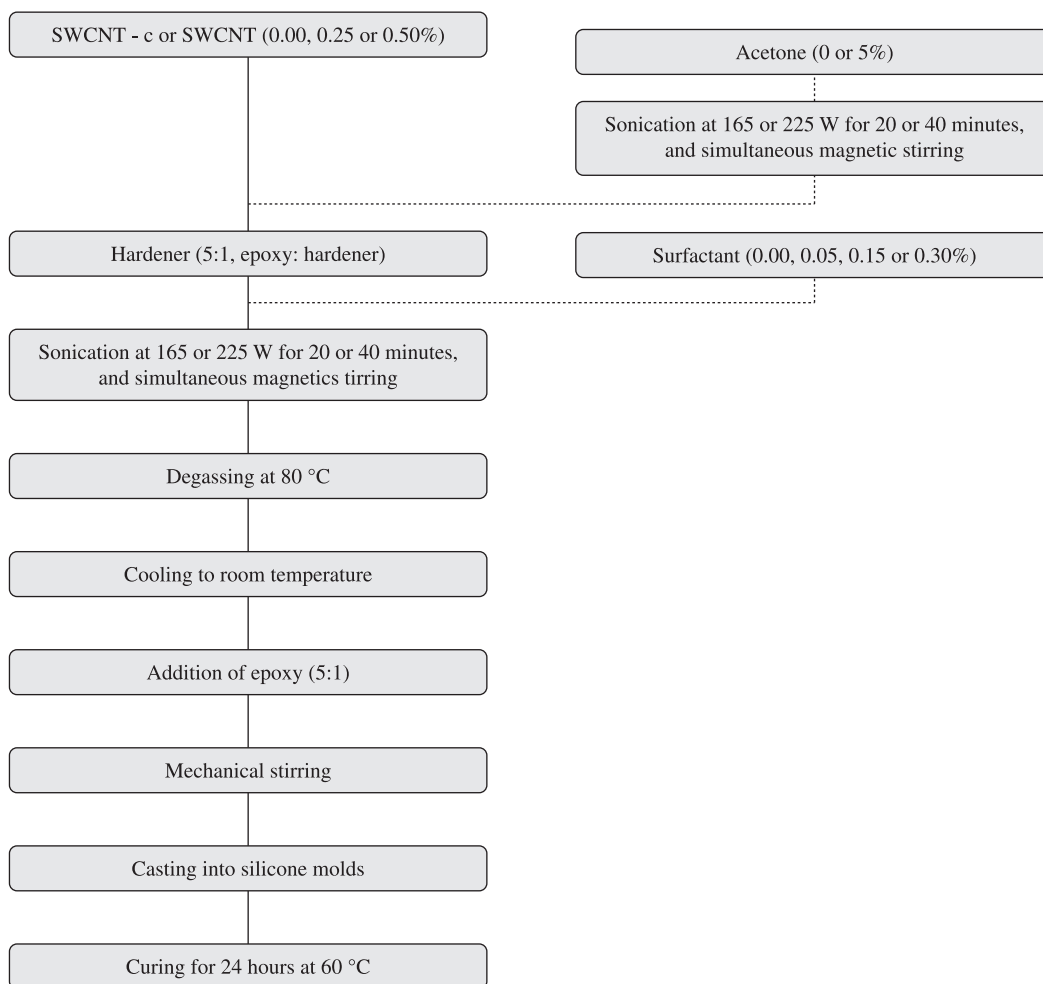

Figure 1. Route used in this work for the preparation of the various nanocomposites.

Table 1. Nomenclature used for all samples prepared in this work.

Sample	CNT content (%)	Sonication period (minutes)	Sonication power (W)	Solvent used	Amount of surfactant (%)	Degassing at 80 °C
SWCNT-c_C25_ T20_A22_Man	0.25	20	165	---	---	---
SWCNT-c_C25_ T20_A22_Mec	0.25	20	165	---	---	---
SWCNT-c_C25_ T20_A22_Mec_Ace	0.25	20	165	Acetone	---	Yes
SWCNT-c_C25_ T40_A30_Mec	0.25	40	225	---	---	---
SWCNT-c_C25_ T40_A30_Mec_Ace	0.25	40	225	Acetone	---	Yes
SWCNT_C50_ T40_A30_Mec	0.50	40	225	---	---	---
SWCNT_C50_ T40_A30_Mec_Ace	0.50	40	225	Acetone	---	Yes
SWCNT_C50_T40_A30_Mec_Ace_S0.15	0.50	40	225	Acetone	0.15	Yes
SWCNT_C50_T40_A30_Mec_Ace_S0.30	0.50	40	225	Acetone	0.30	Yes

Man: Manual stirring; Mec: Mechanical stirring at 2000 rpm.

region 150 × 150 mm^2) attached to a Nicolet spectrometer, in the mid-infrared region (650-3500 cm^{-1}). The measurements were performed under nitrogen purge, with 4 cm^{-1} of spectral resolution, by averaging 64 scans.

3. Results and Discussion

3.1. Physical and thermal properties

Table 2 presents the glass transition temperature (T_g) determined during the second heating of the DSC analyses of the nanocomposites. T_g appears independent on the nanotube content and the processing parameters for the samples with carboxylated CNT. In general, no significant change in T_g was observed, except when surfactant was used, even though no clear trend could be identified since the addition of 0.30 wt. (%) Triton X-100 increased T_g, but lower surfactant content (0.15 wt. (%)) decreased T_g maintaining all other processing parameters unchanged. This may suggest a critical micelle concentration within 0.15-0.30 wt. (%) Triton X-100 for 0.50 wt. (%) SWCNT nanocomposites. The rather small variation in T_g of the nanocomposites prepared using acetone suggests that nearly all solvent was removed, as indicated by the mass balance conducted during the experiments. Indeed, according to Moniruzzaman[10], complete solvent removal before curing is expected to yield similar cross-linking degree in neat epoxy or epoxy nanocomposites, leading to similar glass transition temperatures.

FTIR was used to monitor the presence of the epoxide group indicated by the presence of an absorption band in the 910-920 cm^{-1} range, related to the contraction of the C-C bond and the stretching of both C-O bonds of the epoxy ring[11]. As can be seen for all samples shown in Figure 2, this peak has almost disappeared after curing, which is an evidence of a high degree of crosslinking in the nanocomposites and in the neat epoxy. Similar results may be found in the literature[12].

In Figure 3, the Raman spectrum of SWCNT-c is presented and two peaks around 1570 and 1350 cm^{-1} can be seen, referring to the G band and the disorder-induced D band, respectively. The intensity of the D band compared with the G band indicates high content of disordered structures and defects[13]. The Raman spectra of the non-carboxylated SWCNT was presented elsewhere[14], showing a very low intensity D band. The high intensity of the D band presented here is expected since covalent functionalization with a carboxylic group changes the physical and chemical structure of SWCNT[15].

In Figure 4, FTIR spectra of the SWCNTs before and after the oxidation process are presented. It should be noted that the spectrum of the pristine SWCNT is quite similar to others presented in the

Table 2. Glass transition temperature and storage modulus (at 40 °C) of the SWCNT and SWCNT-c/epoxy nanocomposites.

Sample	T_g (°C)	Storage modulus (GPa)
Neat Epoxy_Mec	107	2.0
SWCNT-c_C25_T20_A22_Man	106	2.5
SWCNT-c_C25_T20_A22_Mec	107	2.3
SWCNT-c_C25_T20_A22_Mec_Ace	107	2.1
SWCNT-c_C25_T40_A30_Mec	107	2.2
SWCNT-c_C25_T40_A30_Mec_Ace	106	2.2
SWCNT_C50_T40_A30_Mec	107	2.4
SWCNT_C50_T40_A30_Mec_Ace	110	2.5
SWCNT_C50_T40_A30_Mec_Ace_S0.15	101	2.3
SWCNT_C50_T40_A30_Mec_Ace_S0.30	115	2.4
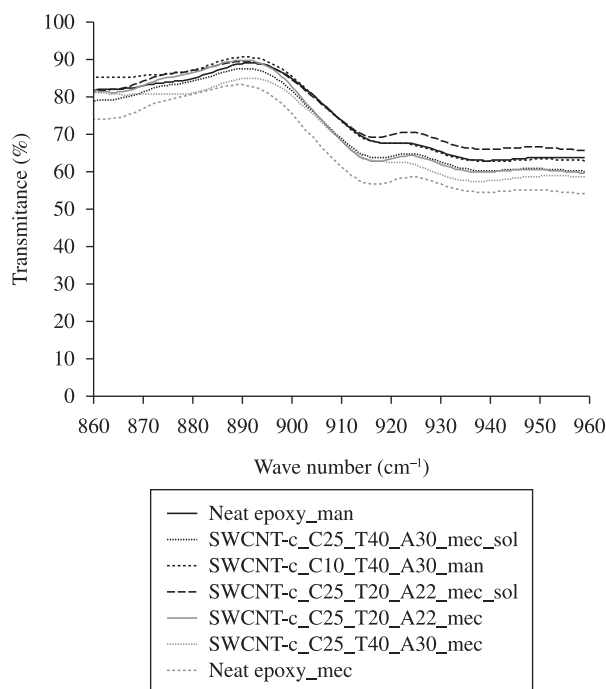
Figure 2. FTIR spectra of SWCNT/epoxy nanocomposites prepared under different conditions.

literature[16,17]. The presence of typical C=O and O-H bonds are due to the formation of COOH groups on the nanotubes after acid treatment. This is evident in the IR spectrum shown in Figure 4. The very broad shoulder peak at 3100-3600 cm⁻¹ is assigned to the O-H stretches of terminal carboxyl groups, the peak at 2918 cm⁻¹ can be assigned to the C-H stretch, and the peaks near 1730 cm⁻¹ correspond to the carboxylic C=O stretching vibrations. The peak at 1585 cm⁻¹ is attributed to the -C=C- stretching mode of the SWCNTs[17].

The dilatometric behavior of some of the nanocomposites studied in this work is presented in Figure 5. All nanocomposites presented higher dilation than neat epoxy. Besides, higher linear dilation was associated with mild sonication parameters (20 minutes and 165 W). According to Gonnet[18], carbon nanotubes have a negative coefficient of thermal expansion due to the sp² network and their nanocomposites should present thermal dilation smaller than neat epoxy even at very low CNT content, but this was not confirmed by the results of this work.

3.2. Mechanical properties

Figures 6a and 6b present DMA curves of storage modulus versus temperature for the nanocomposites. The storage modulus was found to increase with the addition of CNTs in the range of interest of the epoxy nanocomposites. The highest storage modulus at 40 °C (see Table 2) was found for the 0.25 wt. (%) SWCNT nanocomposite prepared using acetone and harsh sonication (SWCNT-c_C25_T40_A30_Ace). However, similarly high values were observed for the nanocomposite with higher SWCNT loading (0.50 wt. (%)) prepared without solvent and under the same sonication conditions (SWCNT_C50_T40_A30). This suggests that the use of the solvent was effective in improving storage modulus since higher values were found with lower nanofiller content.

In general, the addition of CNTs, either SWCNT or SWCNT-c, was responsible for an increase in storage modulus, and the highest values were found for SWCNT-c_C25_T20_A22_Man and SWCNT_C50_T40_A30_Mec_Ace. Addition of surfactant also yielded an increase in storage modulus for longer sonication periods. Liao[19] observed that the use of acetone was important for CNTs debundling in epoxy matrices, increasing in up to 50% the storage modulus of the matrix. However, in this work, the most significant increase for the nanocomposites prepared with the aid of acetone was 25%.

Table 3 presents the Vickers microhardness values obtained for all samples. These results suggest an increase in hardness with the use of solvent for the carboxylated SWCNT. For the nanocomposites with SWCNT-c, an increase of up to 31% was observed in comparison with neat epoxy. Suave[9] studied CNTs dispersion in the resin using tetrahydrofuran (THF) as solvent and observed a small negative variation in this property (ca. 7% for 0.25 wt. (%) SWCNT-c), whereas Lau[20] found an increase of around 20% (when compared to neat epoxy), reaching 13 HV when using 2 wt. (%) SWCNT prepared using ethanol. It should be noted that the hardness values obtained in this work are much higher than those reported for similar CNTs/epoxy systems.

Table 3 also presents the tensile properties of the nanocomposites. All samples, except SWCNT_C50_T40_A30_Mec, presented higher Young´s modulus than neat epoxy. The more pronounced increase in this property was obtained for the composite with 0.25 wt. (%) SWCNT-c prepared under harsh sonication conditions (40 minutes at 225 W) and using the solvent. Surprisingly, this same sample presented a significant decrease in tensile strength. Regarding tensile strength, the highest value was found for carboxylated nanotubes (0.25 wt. (%)) dispersed under mild sonication conditions (20 minutes at 165 W) and using acetone but, even in this case, the increase was not significant considering the standard deviation and therefore it was
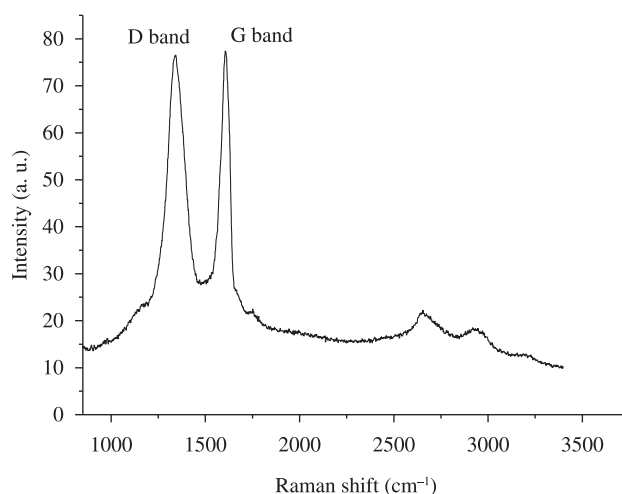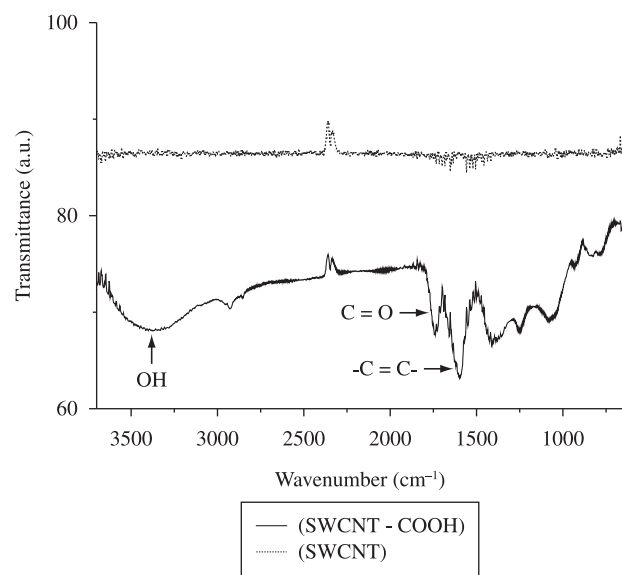

Figure 3. Raman spectra of SWCNT-c.
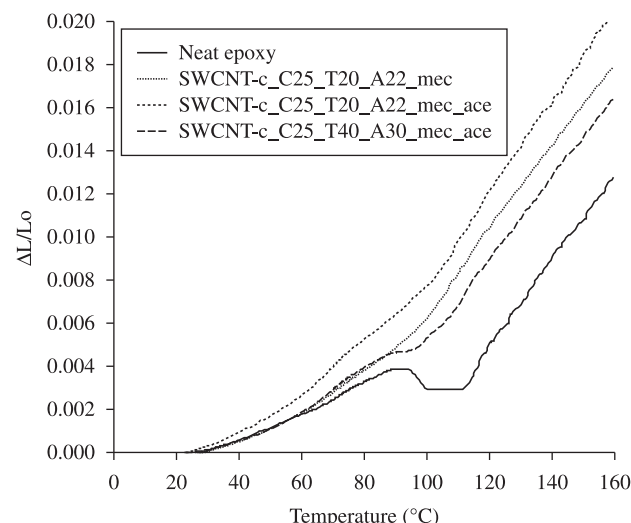

Figure 4. FTIR of pristine SWCNT and SWCNT-c.

Figure 5. Dilatometric behavior of some SWCNT-c/epoxy nanocomposites (second heating).
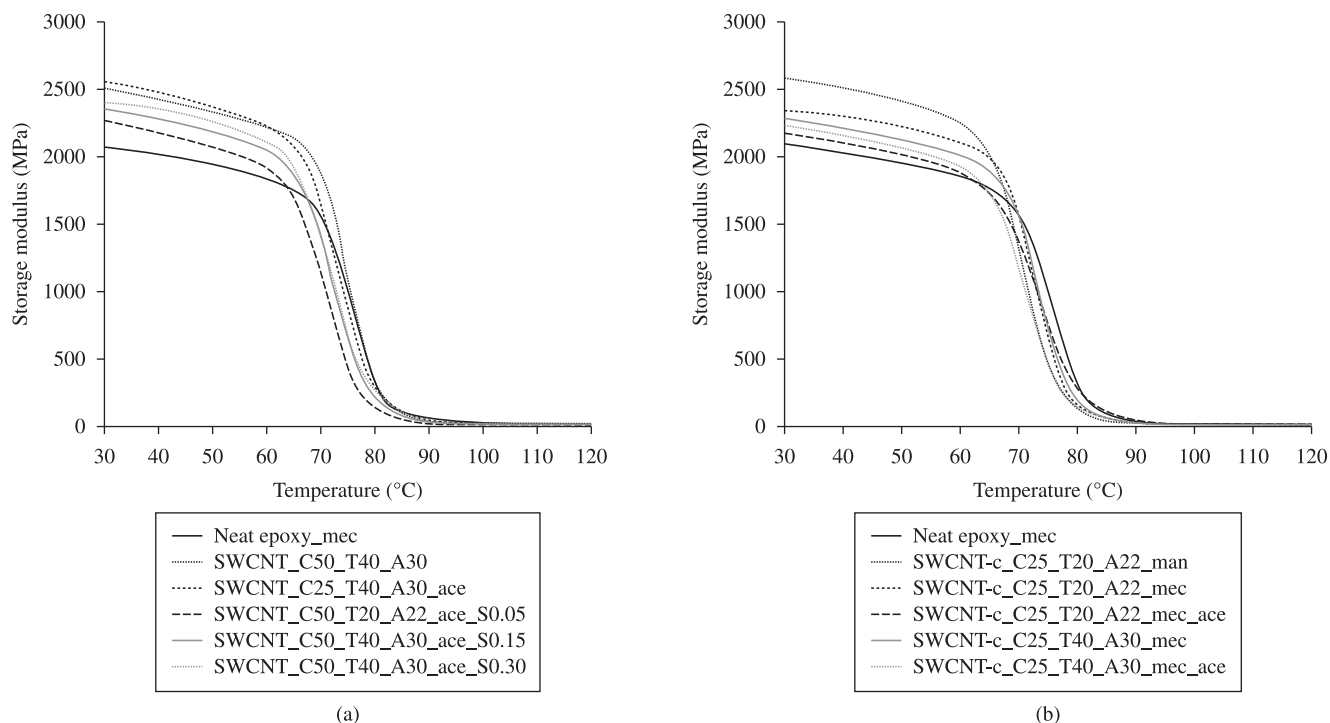
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Figure 6. Storage modulus for nanocomposites with SWCNT (a) and SWCNT-c (b).

Table 3. Vickers microhardness and tensile properties of the SWCNT and SWCNT-c/epoxy nanocomposites.

Sample	Hardness (HV)	Young´s modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Neat Epoxy* Man or Mec	19 ± 1	3.5 ± 0.4	39.7 ± 4.8	1.2 ± 0.2
SWCNT-c_C25_T20_A22_Man	16 ± 1	4.1 ± 0.3	28.3 ± 4.7	0.7 ± 0.1
SWCNT-c_C25_T20_A22_Mec	21 ± 1	3.5 ± 0.6	33.0 ± 11.1	1.1 ± 0.5
SWCNT-c_C25_T20_A22_Mec_Ace	25 ± 1	4.2 ± 1.2	45.1 ± 7.6	1.2 ± 0.6
SWCNT-c_C25_T40_A30_Mec	19 ± 1	3.7 ± 0.7	30.0 ± 6.5	0.9 ± 0.3
SWCNT-c_C25_T40_A30_Mec_Ace	23 ± 2	4.6 ± 2.3	19.8 ± 5.4	0.5 ±0.3
SWCNT_C50_T40_A30_Mec	24 ± 3	3.3 ± 0.2	38.4 ± 10.9	1.1 ± 0.3
SWCNT_C50_T40_A30_Mec_Ace	20 ± 1	4.3 ± 1.0	41.8 ± 9.1	0.9 ± 0.2
SWCNT_C50_T40_A30_Mec_Ace_S0.15	19 ± 1	4.0 ± 0.9	42.8 ± 9.8	1.2 ± 0.3
SWCNT_C50_T40_A30_Mec_Ace_S0.30	16 ± 1	3.7 ± 1.1	36.3 ± 10.1	1.2 ± 0.5

*For the neat epoxy, 30 specimens were tested (N = 30), in the other cases, N = 8-10.

not possible to find a clear correlation between processing parameters and tensile strength.

Nevertheless, the use of the solvent shows a clear trend in helping increasing Young´s modulus for both SWCNT and SWCNT-c, differently from what was found from observation of the microhardness results. This may have occurred since microhardness (which is not a material property) measurement is much more sensitive to local heterogeneities which may have affected some of the experimental readings.

The results of the flexural tests performed on the nanocomposites prepared with SWCNT-c are summarized in Table 4. No significant variation in flexural modulus was observed. On the other hand, flexural strength showed, in general, a significant improvement when compared to neat epoxy, especially for the 0.25 wt. (%) SWCNT sample sonicated under mild conditions and with manual mixing of the hardener with the epoxy, which presented an increase of 28%. In a similar study by Chen[3], modulus and strength were found to decrease when compared to neat epoxy, which was credited to a non-uniform dispersion of CNTs. By adding 2 wt. (%) SWCNT to epoxy, Lau[20] found a decrease of 33% in flexural strength, which was explained by the presence of aggregates in the nanocomposites.

Scanning electron micrographs of the surface of a tensile fractured nanocomposite obtained in this work are presented in Figure 7. The specimens in general exhibited a relatively smooth surface which is indicative of a brittle fracture. No evidence of poor dispersion was found in Figure 7a and the pull-out of carboxylated SWCNTs taking place at the fractured surface shown in Figure 7b indicates poor adhesion between nanotubes and epoxy. The pull-out phenomenon[21] captured in this SEM image for nanocomposites with CNTs is scarcely seen in the literature.

3.3. Micromechanical modeling

A rough estimate of the Young's modulus of a polymeric (nano) composite with randomly oriented CNTs may be theoretically found using the rule of mixtures (Equation 1):

Table 4. Flexural properties of the SWCNT-c/epoxy nanocomposites.

Sample	Flexural modulus (GPa)	Flexural strength (MPa)
Neat Epoxy Man or Mec	2.8 ± 0.3	70.4 ± 5.7
SWCNT-c_C25_T20_A22_Man	2.6 ± 0.2	90.2 ± 12.6
SWCNT-c_C25_T20_A22_Mec	2.8 ± 0.3	85.5 ± 19.1
SWCNT-c_C25_T40_A30_Mec	2.6 ± 0.3	70.0 ± 9.8
SWCNT-c_C25_T40_A30_Mec_Ace	2.5 ± 0.2	73.2 ± 19.6

$$E_c = \alpha\beta E_f V_f + \left(1 - V_f\right) E_m \qquad (1)$$

where: E is the Young´s modulus, and subscripts c, f and m refer to the nanocomposite, the nanofiller (in this case, CNTs) and the matrix, respectively, and V_f is the CNTs volume fraction in the nanocomposite. The β parameter is equal to 0.2 when the CNTs are considered to be arranged in a 3-D random orientation or equal to 0.35 for in-plane (2-D) random orientation. The α parameter may be found using Equation 2:

$$\alpha = 1 - \left[\frac{\tanh\left(\alpha\frac{L}{D}\right)}{\alpha\frac{L}{D}}\right] \qquad (2)$$

where: $\alpha = \sqrt{\dfrac{-3E_m}{2E_f \ln V_f}}$, L e D are the mean length and diameter of the CNTs, respectively.

The Halpin-Tsai theoretical model, given by Equation 3, may also be used to estimate E_c. The Young's modulus and the aspect ratio (L/D) of the nanotubes may be considered to vary within 500-1000 GPa and 500-1000, respectively. More details about these equations and the values used here can be found in Coleman[22] and Gojny[23].

$$\frac{E_C}{E_m} = \frac{3}{8}\left[\frac{1 + \frac{2L}{D}\eta_L V_f}{1 - \eta_L V_f}\right] + \frac{5}{8}\left[\frac{1 + 2\eta_T V_f}{1 - \eta_T V_f}\right] \qquad (3)$$

where: $\eta_L = \dfrac{\dfrac{E_f}{E_m} - 1}{\dfrac{E_f}{E_m} + \dfrac{2L}{D}}$ and $\eta_T = \dfrac{\dfrac{E_f}{E_m} - 1}{\dfrac{E_f}{E_m} + 2}$.

Using 3.5 GPa as the Young's modulus of the unreinforced polymeric matrix (i.e. neat epoxy) and applying these equations for 0.10-0.50 wt. (%) CNTs yields the results shown in Table 5. Thus, the experimental results found in this work and in the literature[4,22] for SWCNTs, MWCNTs and SWCNTs-c with epoxy fitted the estimated range of values found for up to 0.50 wt. (%) CNTs. For detailing purposes, the SWCNT-c_C25_T20_A22_Mec_Ace sample (experimental Young´s modulus of 4.2 GPa) was chosen for comparison. The theoretical estimation of Young's modulus for 0.25 wt. (%) nanofillers varied within 3.7-4.4 GPa, thus the agreement between experimental and calculated values was very good, and perhaps an intermediate arrangement between pure 2-D and pure 3-D orientation could be expected. Therefore, the obtained experimental results were quite close to the theoretical results obtained using two very simple models. According to the literature, epoxy and other nanocomposites systems[4,24] may yield results just as accurate as more sophisticated models.
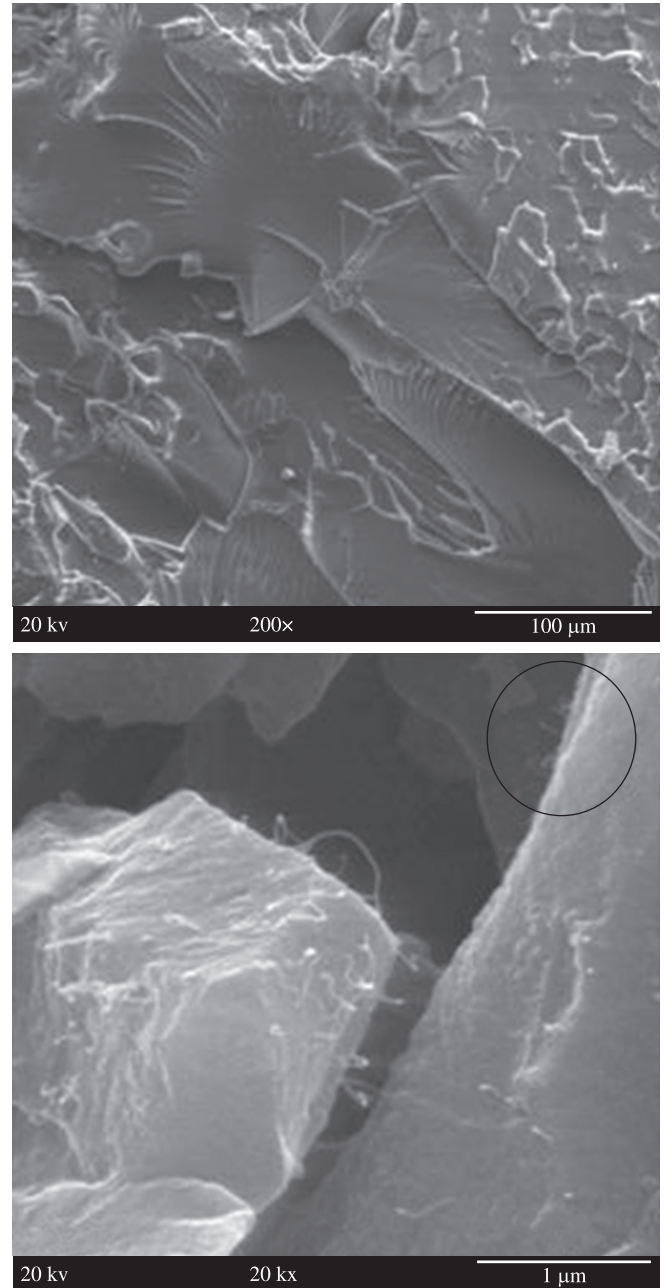
Figure 7. Scanning electron micrographs of the 0.25 wt. (%) SWCNT-c/epoxy nanocomposite prepared under mild sonication conditions.

Table 5. Predicted (theoretical) Young's modulus of the composites.

E_f (GPa)	L/D	V_f	E_c – Rule of Mixtures (GPa)		E_c - Halpin-Tsai (GPa)
			$\beta = 0.20$	$\beta = 0.35$	
500	500	0.0025	3.7	3.9	4.0
500	1000	0.0025	3.7	3.9	4.0
500	500	0.0050	4.0	4.4	4.4
500	1000	0.0050	4.0	4.4	4.4
1000	500	0.0025	4.0	4.4	4.2
1000	1000	0.0025	4.0	4.4	4.3
1000	500	0.0050	4.4	5.2	5.0
1000	1000	0.0050	4.5	5.3	5.2

4. Conclusions

In this work, nanocomposites were prepared by first dispersing carbon nanotubes, carboxylated or not, in the hardener. Different dispersion techniques were investigated, including mechanical/manual stirring, use of solvent, use of surfactant and sonication (under distinct conditions). None of the variations significantly affected the final degree of curing of the nanocomposites, since no peak related to post-curing was observed in the first-run of the DSC analyses and also because the FT-IR yielded similar curves in the 910-920 cm⁻¹ absorption range for neat and filled epoxy resins after curing.

The highest increase in glass transition temperature (8 °C) was obtained for a nanocomposite prepared with surfactant, solvent and under longer sonication at higher power. All nanocomposites presented higher thermal dilation than neat epoxy, even though the literature suggests that even small amounts of these nanofillers should decrease dilation. The storage modulus increased for all nanocomposites up to c.a. 65 °C, being c.a. 20% the highest increase, and the use of surfactant or solvent was not found imperative in influencing this property. Nanocomposites prepared with SWCNT-c presented higher microhardness than those prepared with SWCNT, except for SWCNT_C50_T40_A30_Mec, and it appears that solvent, time and power of sonication affect this property.

In general, tensile modulus increased with the addition of nanotubes to the epoxy but a less significant increase was found for tensile strength, which indicates poor CNTs/matrix adhesion even for the functionalized carboxilated CNTs studied. For both properties, higher values were found for nanocomposites prepared with a combination of solvent and surfactant. Flexural testing, on the other hand, indicated an increase in strength for some of the studied samples, whereas other samples showed similar strength and modulus in comparison with the neat resin.

SEM micrographs showed pull-out of carbon nanotubes in tensile tested specimens and suggested a reasonably homogeneous dispersion of the nanofillers, with an approximate distance of 100-200 nm. Two simple theoretical micromechanical models were used to predict the expected range of Young´s modulus of the nanocomposites and the calculated values were found to agree with the experimental results for most of the studied nanocomposites.

Acknowledgements

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