

The matrix stiffness role on tensile and thermal properties of carbon nanotubes/epoxy composites

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Abstract In this study, randomly oriented single-walled carbon nanotubes (SWCNTs)/epoxy nanocomposites were fabricated by tip sonication with the aid of a solvent and subsequent casting. Two different curing cycles were used to study the role of the stiffness of the epoxy matrix on the tensile and thermal behavior of the composites. The addition of a small amount of SWCNTs (0.25 wt.%) in rubbery, i.e., soft matrices, greatly increased Young's modulus and tensile strength of the nanocomposites. The results showed that the tensile properties of soft epoxy matrices are much more influenced by the addition of carbon nanotubes than stiffer ones. The significant improvement in tensile properties was attributed to the excellent mechanical properties and structure of SWCNTs, an adequate dispersion of SWCNTs by tip sonication, and a stronger SWCNT/matrix interfacial adhesion in softer epoxy matrices. A slight improvement in the thermal stability of the nanocomposites was also observed.

Introduction

Based on the unique and excellent physical properties of carbon nanotubes (CNTs), their use in structural and smart applications has been proposed. Their mechanical properties (specially tensile strength) considerably exceed those of

currently available synthetic fibers (e.g., graphite, Kevlar[®], stainless steel) [1], making them candidate materials for polymer matrix composites. Indeed, the incorporation of small amounts of CNTs in a polymer matrix, usually between 0.1 and 5 wt.%, has the potential of yielding structural materials with high rigidity and strength [2].

Recent reports have been published on the use of nanotubes in polymer [3], metallic [4], and ceramic [5] matrix composites. However, there are two major challenges that must be faced to enable the development of high performance CNT/polymer nanocomposites: (i) homogeneous dispersion of CNTs in the matrix, and (ii) strong interfacial interaction to allow efficient load transfer from the matrix to the CNTs [6].

Epoxy resins are the most used thermosetting polymer matrices in structural composites, and most of the commercially available epoxy resins are oligomers of diglycidyl ether of bisphenol A [7]. The resins of this class have good stiffness, specific strength, dimensional stability, and chemical resistance, showing considerable adhesion to the embedded reinforcement [8]. It is well known that the physical properties of cured epoxy resins depend on their structure, the curing extent, and the curing time and temperature [7]. For this reason, it is necessary to know and to understand the relationship between the network structure and the final properties of the material, in order to obtain resins suitable for high performance applications [7]. In this context, a delaying effect of the CNTs on the curing kinetics of epoxy has been reported [9] and the reinforcement effect of single-walled carbon nanotubes (SWCNTs) could vary in epoxy composites based on matrices with different stiffness.

In this article, SWCNTs/epoxy nanocomposites were studied. The matrix stiffness was varied by using two different curing cycles and the thermal and mechanical properties of the produced material were evaluated and

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compared in order to address the matrix stiffness effect on those properties.

Experimental

The polymer matrix consisted of bisphenol-A-based epoxy resin (Araldite GY 251) with an amine-based hardener (Aradur HY 956), obtained from Huntsman Advanced Materials. SWCNTs were supplied by Federal University of Rio Grande do Sul (LACER/UFRGS, Brazil), with purity higher than 95%. For the preparation of the nanocomposites, the CNTs (0.25 wt.%) were dispersed in acetone using simultaneous magnetic stirring and sonication. Next, the epoxy was added and the mixture was sonicated and stirred for an hour, being then heated to 50 °C under vacuum for another hour. After that, the solution was left under vacuum for 5 h without heating in order to remove most of the solvent. Later, the hardener was added to the mixture.

Two different curing cycles were used: in cycle I, the epoxy was hardened under vacuum for 24 h followed by 35 h under room temperature and pressure. In cycle II, the system was cured under vacuum for 24 h followed by 135 h under room temperature and pressure. Neat epoxy resin samples were also prepared following the same methodology for comparison, therefore four different epoxy based materials were studied: (i) neat epoxy cured following cycle I, called Epoxy I, (ii) Epoxy reinforced with 0.25 wt.% of SWCNTs cured following cycle I, called Composite I, (iii) neat epoxy cured following cycle II, called Epoxy II, and (iv) Epoxy reinforced with 0.25 wt.% of SWCNTs cured following cycle II, called Composite II.

Thermogravimetric analysis (TGA) was conducted on a Netzsch STA 449 equipment under nitrogen atmosphere from room temperature to 900 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analyses were carried out on a TA 2010 thermal analyzer under nitrogen atmosphere from –50 to 250 °C at 10 °C/min. Tensile tests were carried out using an Emic universal testing machine (model DL 3000) at room temperature and crosshead speed of 5 mm/min according to the ASTM D638M-93 standard. Finally, a scanning electron microscope (SEM, Zeiss DSM 940 A at 15 kV) was used to observe the fractured surfaces of the samples following tensile testing.

Results and discussion

Carbon nanotubes

The SWCNTs used in this study were grown by controlled catalytic chemical vapor deposition. Figure 1

shows SEM and transmission electron microscopy (TEM) images of pristine SWCNTs. It is observed that the tubes are randomly and loosely entangled, with a high purity. The mean diameter and length were 1–5 nm and 2–4 μm, respectively, as determined by image analysis of micrographs.

The Raman spectrum of SWCNTs (Fig. 2) shows peaks around 1,570 and 1,350 cm^{-1} , referring to the G band and the disorder-induced D band, respectively. The intensity of the D band compared with the G band indicates low content of disordered structures and defects [10].

Nanocomposites

Thermal properties

Figure 3 depicts TGA curves of composites cured following cycles I and II. The Composites I and II curves overlap that of Epoxy II, whereas Epoxy I is comparatively less thermally stable in temperatures below 320 °C. A small weight loss of ~5% in the 75–205 °C range is a consequence of the release of trapped acetone, used for the dispersion of CNTs. The weight loss at 205–320 °C is ascribed to the decomposition of lower molecular weight material and the final weight loss, around 320 °C, is attributed to the decomposition of the epoxy matrix.

When comparing similar thermoset polymers, those with higher crosslink density usually display higher degradation temperatures. Crosslink density is maximized when a stoichiometric epoxy:hardener relationship is used [11], but the control of curing time and temperature is also critical, e.g., lower curing time leads to lower crosslinking degree and lower thermal stability.

The glass transition temperature (T_g) of the specimens was evaluated by DSC. The T_g varied from 65 for Epoxy I to 68 °C for Composite I. Although small, this variation of T_g suggests comparable crosslinking degree in both epoxy and nanocomposites [12] and that the incorporation of SWCNTs may have restricted the movement of polymer chains. Literature results show that a small amount of CNTs can alter thermal contraction, crosslinking degree, and other physical–chemical properties during the curing of epoxy resins [13, 14]. In addition, the presence of SWCNT agglomerates in composites was reported to lead to a decrease in T_g [5]. Therefore, the T_g results of this work suggest the absence of significant agglomerates.

Tensile properties

The stress–strain curves of typical specimens submitted to tensile testing are presented in Fig. 4. It may be observed that SWCNTs act as reinforcement in both conditions, although this effect is more pronounced for specimens

Fig. 1 Typical SEM image showing the morphology of SWCNTs (a) and TEM image showing the purified SWCNTs (b)

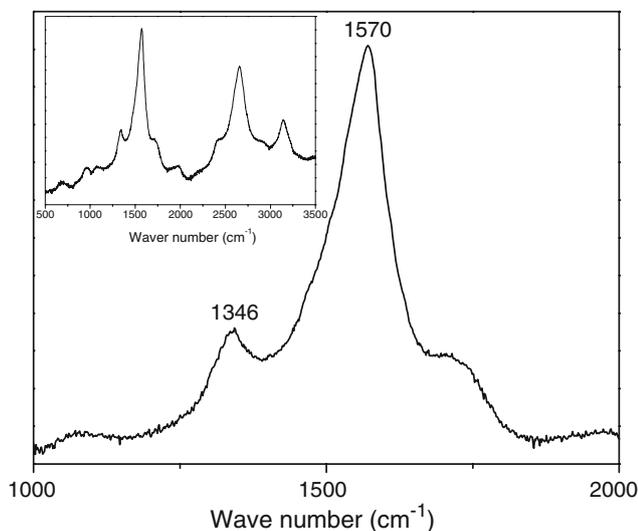
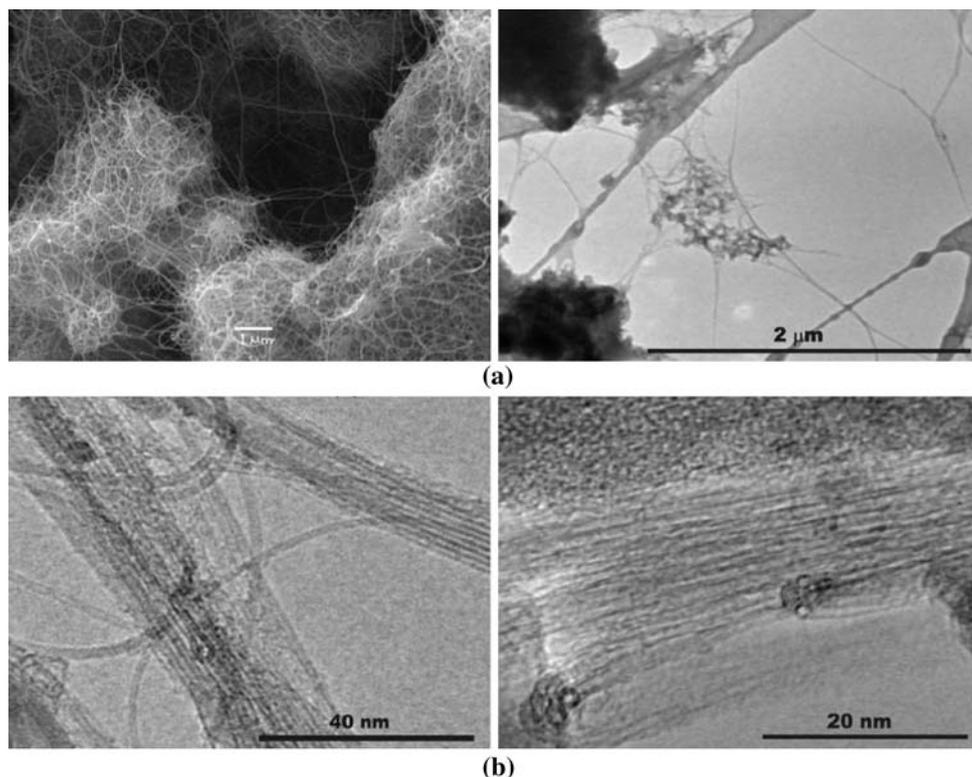


Fig. 2 Raman spectra of the purified SWCNTs

cured following cycle I, in which the matrix showed an original more rubber-like behavior.

Table 1 shows the results of the tensile tests of neat epoxy and SWCNT/epoxy composites. The tensile strength of the composites obtained following curing cycles I and II were 491 and 232% higher in relation to the neat epoxy I and II, respectively. The matrix stiffness effect on the Young's modulus of the nanocomposites was even more significant. The rubbery Composite I showed a modulus 47 times that of Epoxy I, whereas Composite II, a stiffer

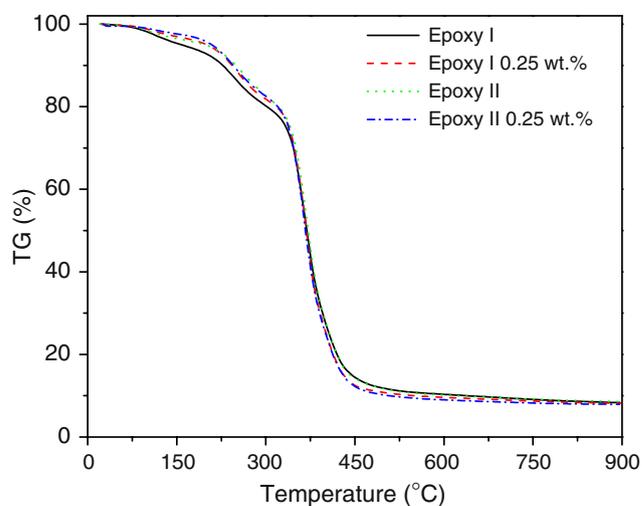


Fig. 3 TGA curves of the neat epoxy and nanocomposites cured using the cycles I and II

sample, showed a modulus six times that of Epoxy II, i.e., the reinforcement effect of the CNTs tends to decrease with the increase in matrix stiffness. The large variation in strain at break for the different composites is another indication that the CNTs may distinctively affect the tensile behavior of the samples. These results suggest that matrixes of different stiffness interact differently with the CNTs [10].

In order to further address the role of the reinforcement in nanocomposites, the tensile properties of single- or multi-walled CNTs composites with epoxy matrices of

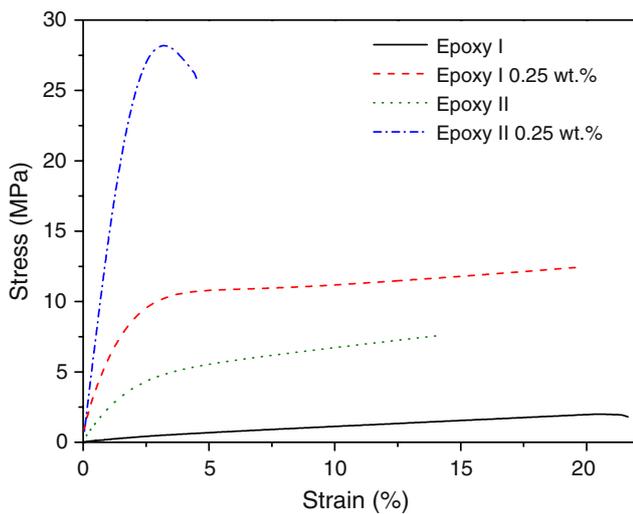


Fig. 4 Stress–strain curves of the neat epoxy and SWCNTs/epoxy composites

Table 1 Tensile properties of the neat epoxy and its nanocomposites

Sample	Modulus (MPa)	Strength (MPa)	Strain at break (%)
Epoxy I	16 ± 2	2.2 ± 0.2	22.5 ± 1.6
Composite I	767 ± 74	13.0 ± 0.6	23.9 ± 4.3
Epoxy II	258 ± 33	8.5 ± 0.5	18.8 ± 1.2
Composite II	1535 ± 155	28.2 ± 0.5	3.2 ± 0.1

different rigidity, which used distinct curing cycles and dispersion methods, were compiled from literature papers (Table 2). Evaluation of Tables 1 and 2 shows that, for epoxy matrices of originally comparable rigidity (around

200–300 MPa) and strength (around 5–10 MPa), higher strength and modulus were reached in this work with the addition of much less CNTs (0.25 wt.% SWNT), suggesting a better nanofiller dispersion in the matrix.

The fact that a more efficient reinforcement with SWCNTs is obtained for matrices with lower crosslinking degree may be an indication that shorter epoxy chains could better interact with nanotubes, possibly by embedding and coating the SWCNTs with polymer sheets [16] to create a more stable interface. Thus, the improvement in tensile properties observed in this study could be attributed to: (i) excellent mechanical properties and structure of SWCNTs, (ii) adequate dispersion of SWCNTs by tip sonication, and (iii) stronger SWCNT/matrix interfacial interaction in softer epoxy matrices.

Figure 5 shows SEM images of tensile fractured surfaces of SWCNTs/epoxy composites. The irregular fracture surface of Composite I (Fig. 5a) indicates a ductile failure behavior. On the other hand, the smoother fracture surface of Composite II (Fig. 5b) indicates a more brittle-like failure mode, as suggested by the stress–strain curves (Fig. 4). When the curing cycle is longer, the crosslinking degree is higher, increasing the stiffness of the epoxy matrix (brittle behavior), whereas shorter curing cycle yields lower reticulation degree and a more ductile material.

Conclusions

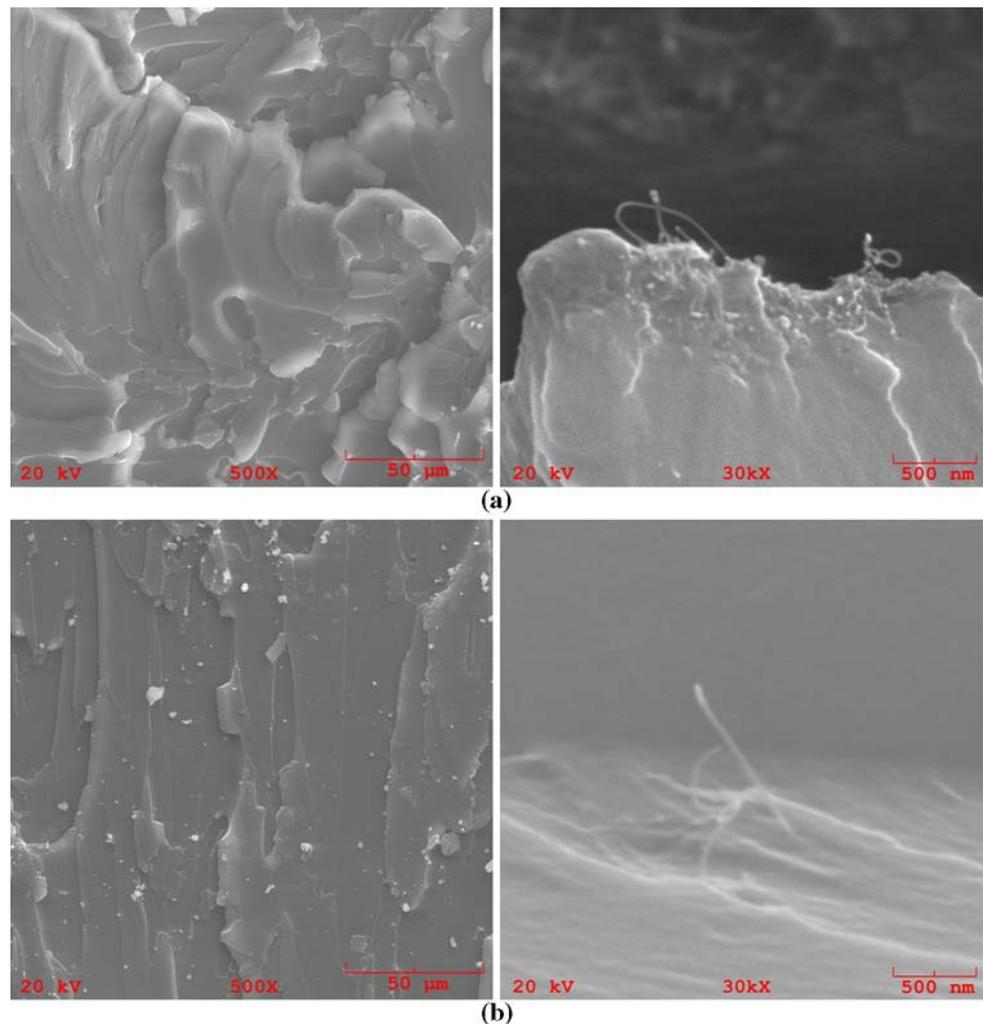
The influence of the matrix stiffness on the reinforcement effect of SWCNTs in epoxy composites was investigated. Matrix stiffness was manipulated by modifying the curing

Table 2 Tensile properties of CNTs/epoxy composites in different studies

Matrix behavior	SWCNTs (wt.%)	Modulus (MPa)	Increase (%)	Strength (MPa)	Increase (%)	References
Rubbery	0.0	118	–	4 ^a	–	[15]
	1.0	236	100	6 ^a	50	
	4.0	465	294	8 ^a	33	
Ductile	0.0	2,473	–	50.6	–	[10]
	0.1	2,875	16	51.9	2.5	
Fragile	0.0	2,875	–	64.8	–	[13]
	0.1	2,910	1.2	68.4	5.6	
Softest	0.0	150	–	5.4	–	[13]
	0.5	440	193	10.9	102	
Soft	0.0	340	–	9.7	–	[13]
	0.5	830	144	14.9	54	
Stiff	0.0	1,630	–	29.6	–	[13]
	0.5	2,000	23	36.4	23	
Stiffest	0.0	2,450	–	45.4	–	[13]
	0.5	2,440	–0.5	47.7	5	

^a Strength was taken as stress at 10% specific strain

Fig. 5 SEM images of the fracture-behavior of the Epoxy I 0.25 wt.% (a) and Epoxy II 0.25 wt.% (b) composites



cycle to yield different materials. Thermal analysis showed the presence of residual solvent and low-molecular-weight material, reflecting an incomplete crosslinking of the epoxy resin.

The addition of 0.25 wt.% SWCNTs showed a significant effect on the tensile properties of the epoxy matrices. This effect was more pronounced for the composites with rubbery matrix, whose modulus reached 47 times that of the neat epoxy prepared under the same conditions. SEM images confirmed the ductile behavior of the rubbery SWCNT/epoxy nanocomposites.

The significant improvement in tensile properties found in this study was attributed to: (i) excellent mechanical properties and structure of SWCNTs, (ii) adequate dispersion of SWCNTs by tip sonication during processing, and (iii) stronger SWCNT/matrix interfacial adhesion in softer epoxy matrices. The fact that reinforcing with SWCNT is more effective in a matrix with lower crosslinking degree suggests that relatively shorter epoxy chains may better interact with the nanotubes, probably by embedding and

coating the SWCNTs with a polymer sheet yielding a more stable interface.

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