Hybrid Nanocomposites Based on Epoxy/silsesquioxanes Matrices Reinforced with Multi-walled Carbon Nanotubes

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The aim of this work was the synthesis of hybrid organic-inorganic epoxy-copolysilsesquioxane nanocomposites reinforced with multi-walled carbon nanotubes (MWCNT). Copolysilsesquioxanes oligomers from 3-aminopropyltriethoxysilane (APTES) and phenyltriethoxysilane (PTES) precursors have been synthesized by a sol-gel process and chemically incorporated to an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA). MWCNT (0.25 wt%) was added to the hybrid matrixes with different degrees of condensation. Fourier transform infrared analysis showed that a high degree of cure was achieved, suggesting that the MWCNT did not affect the curing reaction of the hybrid matrixes. Hybrid nanocomposites obtained by sonication technique presented improvement on thermal stability, exhibiting onset degradation temperatures higher than 340 °C under N_2. Tensile tests presented Young's modulus and maximum stress values up to 2.9 GPa and 47 MPa, respectively, indicating that the new hybrid epoxy/MWCNT nanocomposites show a moderate enhancement of the mechanical properties in comparison with the neat epoxy resin.

Keywords: *epoxy resin, silsesquioxanes, carbon nanotubes, hybrid nanocomposite*

1. Introduction

Epoxy resins are one of the most important classes of thermosetting polymers being applied in advanced composites mainly due to its chemical resistance, high tensile and compressive strength, low shrinkage during cure process and satisfactory adhesion, as well as structural stability and ease of processing[1-3].

An usual method to enhance epoxy properties is the chemical modification by inorganic structures. Silsesquioxanes are typical organic-inorganic materials and can be incorporated into almost any kind of thermoplastic or thermosetting polymer to improve their properties[4]. Epoxy/silsesquioxane hybrids present improvements in thermal stability[5], dielectric properties[6], corrosion resistance[7], and mechanical properties[8], as well as reduced flammability[9], in comparison with neat epoxy resin. In this context, increases in glass transition temperature (T_g) with chemical modifications of epoxy matrixes by random[10] or organized[11] structures with polysilsesquioxanes are scarcely reported. Ni & Zheng[10] studied the chemical modification of DGEBA epoxy resins by the addition of poly(phenylsilsesquioxane). The authors related an increase of 6 °C in the T_g value of the epoxy/silsesquioxane system with the incorporation of 5 wt% silsesquioxane, however, the addition of 15 and 20 wt% of silsesquioxane reduced the epoxy T_g values in 4 and 6 °C, respectively. Wu and co-workers[12] produced a functional polyhedral oligomeric silsesquioxane (POSS) with two epoxy groups, which was incorporated in an epoxy resin, resulting in a hybrid

material with improved flame retardancy and thermal stability. Furthermore, the authors proposed the degradation mechanism of this hybrid material, suggesting that the POSS is responsible to retard the movement and scission of epoxy polymeric chains, forming a stable charred layer that prevents the underlying materials from further combustion. In our previous work[13], an epoxy/silsesquioxane containing amino and phenyl groups was successfully synthesized with a novel interpenetrating network approach. The co-condensation of the silsesquioxanes were obtained with different degrees of condensation showing the possibility to control the sol-gel process in order to produce liquid silsesquioxanes oligomers that can be used as reactive precursors for further chemical modifications, e.g. between amino groups and epoxy groups. This combination leads to an epoxy/silsesquioxane hybrid matrix with potential for coating and structural applications.

Nanocomposites between epoxy resins and carbon nanotubes (CNT) are well known[1,14,15]. The current interest on the use of nanometer reinforcement in polymeric matrixes is due to the ability of these fillers to provide potentially unique properties to the polymer material as a result of their nanometer dimension. A number of materials can be produced at nanometer size, but carbon nanotubes (CNT) have gained much attention due to its exceptional aspect ratio (over 1000), low density, high strength and rigidity[14,16]. However, in general, an homogeneous dispersion of nanoparticles throughout the matrix is required in order to benefit from its excellent reinforcement characteristics. Sonication techniques and mechanical mixing with high

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speed shearing are the most effective way to improve the dispersion of CNT in a polymer matrix[17,18].

In the present work the synthesis and characterization of novel nanocomposites based on hybrid epoxy/silsesquioxanes matrixes reinforced with multi-walled carbon nanotubes (MWCNT) was investigated. The nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), dilatometry, thermogravimetry (TGA) and mechanical tensile tests.

2. Experimental

2.1. Materials

Araldite LY 1316 epoxy resin (epoxy value = 6.5 eq kg⁻¹) based on bisphenol A diglycidyl ether (DGEBA) monomer and Aradur HY 1208 hardener (amine value = 950 mg KOH g⁻¹) were purchased from Huntsman. MWCNT Baytubes® C 150 HP (Lot-No: E0009AAD07; Drum-No: 034) were kindly supplied by BAYER Materials Science. APTES (99.9%) and PTES (99.5%) were purchased from Sigma-Aldrich (St. Louis, USA).

2.2. Synthesis of copolysilsesquioxane APTES/ PTES and hybrid epoxy/silsesquioxanes preparation

The syntheses of copolysilsesquioxane from equimolar mixture of APTES and PTES, as well as the DGEBA matrix chemical modification with APTES/PTES copolysilsesquioxanes,

were conducted as reported in a previous work[13]. Briefly, the hydrolysis and condensation reactions of APTES and PTES were acid catalyzed (HCl 0.1 M) and interrupted after 18 or 24 h, achieving condensation degrees of 76 and 81%, respectively. The viscous product (APTES/PTES copolysilsesquioxane) reacted with DGEBA matrix producing hybrid organic-inorganic with 7.5 wt% copolysilsesquioxane mass fraction. Scheme 1 illustrates the copolysilsesquioxane oligomer chemically bonded to epoxy matrix.

2.3. Nanocomposite processing

Propanone (20 wt%) and MWCNT (0.25 wt%) – percentages relative to the hybrid total mass – were sonicated at 165 W (Sonics Vibra Cell, VCX 750 W) during 20 minutes. The hybrid epoxy/silsesquioxane was then added to the propanone/MWCNT system which was sonicated for 30 min at 187.5 W[17] with simultaneously magnetic stirring[17,18]. The solvent was removed under vacuum at 65 °C until constant mass.

The nanocomposite curing process (using polyamine-based hardener) was performed by two methodologies: (a) curing immediately after chemical modification of the DGEBA resin with the copolysilsesquioxane, and (b) curing after 7 days of the chemical modification, in order to allow the formation of higher molecular weight hybrids[13]. In both methods 12 phr of hardener were added and the homogenization was conducted mechanically for 5 minutes at 250 rpm. Then, the hybrid nanocomposites were cured in specific templates
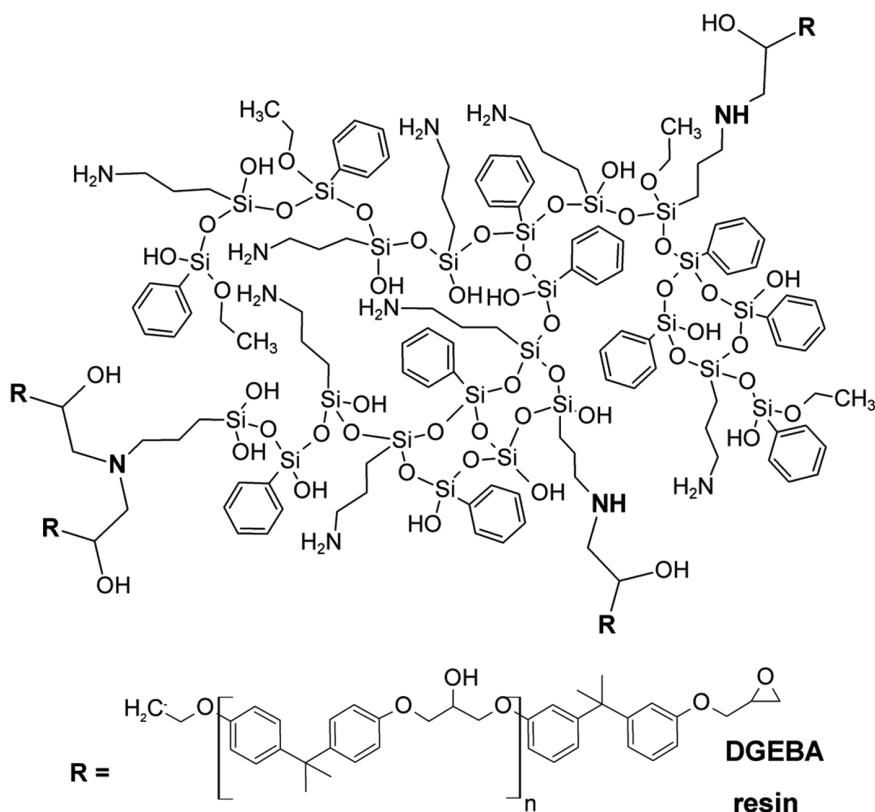
Scheme 1. Chemical structure of epoxy-APTES/PTES silsesquioxane hybrid matrix. Numbers 1 and 2 shows the possible nitrogen bonds from the reaction between APTES amine groups with one or two DGEBA epoxy groups, respectively.

(e.g. dilatometry and mechanical tests) for 2 h at 80 °C and subsequently submitted at 160 °C for another 2 h[10].

The samples were named according to Table 1. Briefly, LY refers to DGEBA resin; 18 or 24 indicate the hydrolysis and condensation reaction times (in hours); 0 or 7, is the cure gap after chemical modification (in days); CNT, indicated the MWCNT incorporation (0.25 wt%). Thus, LY-18-7-CNT is the hybrid nanocomposite with APTES/PTES copolysilsesquioxane obtained by 18 h of sol-gel process, cured 7 days after chemical modification and containing 0.25 wt% MWCNT.

2.4. Characterization

FTIR analyses were performed on a Perkin-Elmer Spectrum One B in attenuated total reflectance (ATR) mode, with resolution of 4 cm^{-1} and range between 4000-650 cm^{-1}.

Morphological characterization was conducted in a scanning electron microscope (SEM) Zeiss DSM 940A operating at an accelerating voltage of 20 kV. Tensile fracture surfaces of samples were coated with a thin gold layer on a Baltec SCD 050 sputter coater.

T_g values were obtained from dilatometry analyses performed on a Netzsch 402C Dilatometer. T_g is determined by dilatometry from the $\Delta L/L_o$ curve as the point of intersection of the tangents below and above the slope change, according to ASTM E1545[19]. Typically, the samples ca. $22 \times 5 \times 5$ mm were heated from 30 °C to 160 °C at 10 K min^{-1} heating rate under nitrogen atmosphere. Then the samples were cooled and

a second heating cycle was done under the same conditions as before, eliminating the samples' thermal history.

Thermogravimetric analyses (TGA) were conducted on a Netzsch STA 449C. The samples ca. 15 mg were heated from 30 °C to 900 °C under a heating rate of 10 K min^{-1} under nitrogen atmosphere.

Mechanical tests were carried out in a universal mechanical testing machine (Emic DL 30000), according to ASTM D638[20].

3. Results and Discussion

3.1. Epoxy/silsesquioxanes hybrid nanocomposites: spectroscopic analysis

Although the cure process of epoxy resins starts with hardener addition, the APTES/PTES copolysilsesquioxane is also able to open the epoxy ring as well as the hardener. The primary amine group present in APTES reacts with epoxy ring turning into secondary amine. Furthermore, the secondary amine may react with another epoxy ring producing a tertiary amine (Scheme 1). This is an autocatalytic process once hydroxyls formed can also open epoxy rings[4,21]. However, the concentration of amine groups present in the copolysilsesquioxane is unable to promote the total cure process and, thus, the hybrids were further cured with a polyamine-based hardener.

The cure degrees of the epoxy matrix were verified by FTIR analysis as shown in Figure 1. The characteristic

Table 1. Schematic nomenclature of the samples.

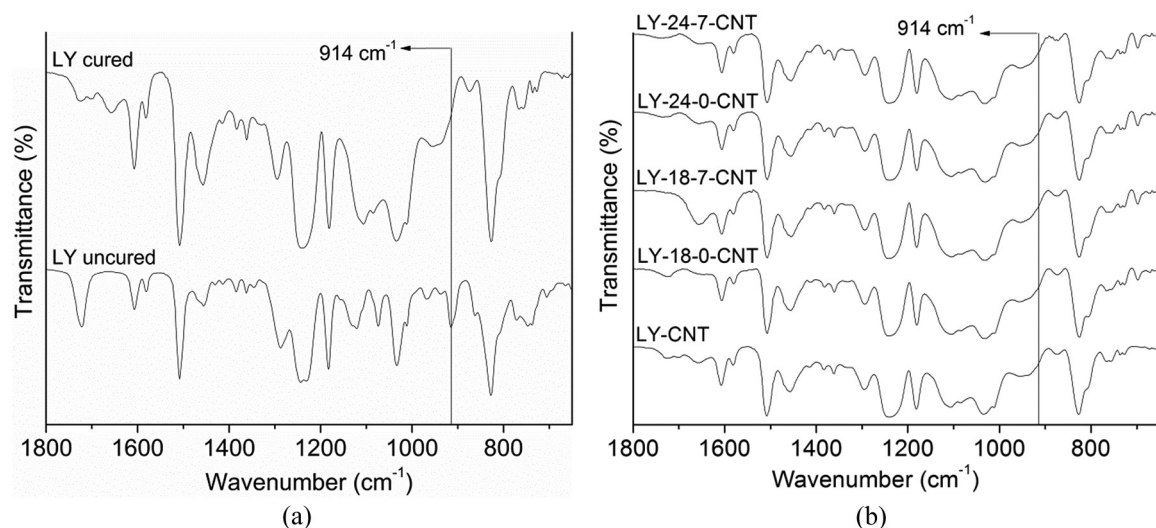| Sample name	DGEBA resin	Hydrolysis and condensation reaction times (h)	Cure gap (day)	0.25 wt% MWCNT
LY	LY	-	-	-
LY-CNT	LY	-	-	CNT
LY-18-0-CNT	LY	18	0	CNT
LY-18-7-CNT	LY	18	7	CNT
LY-24-0-CNT	LY	24	0	CNT
LY-24-7-CNT	LY	24	7	CNT

Figure 1. (a) FTIR spectra of uncured and cured LY matrix. (b) FTIR spectra of cured hybrid nanocomposites.

absorption peak of epoxy ring appeared in 950-810 cm^{-1} range[22]. This region is attributed to the asymmetric axial stretching of the epoxy ring, where the C-C bond is elongated during the contraction of the C-O bond. The DGEBA epoxy resin showed the epoxy ring stretching band at 914 cm^{-1}. Figure 1a also shows clearly the extinction of the characteristic epoxy ring absorption peak in the DGEBA epoxy resin cured ("LY cured") in relation to the uncured neat epoxy resin ("LY uncured"). This behavior was also observed in Figure 1b, indicating that a high degree of cure was achieved with the applied cure conditions. Although some reports have shown that CNT may change the cure reaction parameters of epoxy resins[23-25], the FTIR spectra also show that the incorporation of 0.25 wt% MWCNT did not affect the final cure process of the neat or hybrid epoxy matrix. No spectroscopic change was observed with the incorporation of the MWCNT due, probably, to the low concentration of MWCNT presented in the nanocomposite and also because no reaction between MWCNT and epoxy/silsesquioxanes was expected.

The spectra of samples presented in Figure 1 are very similar. The analysis of Si-C bending at approximately 700 cm^{-1} is necessary in order to differentiate these spectra. Figure 2 compares the characteristic absorption band relative to Si-C bending presented in the hybrid matrixes. Since only hybrid matrixes have Si-C bonds (Scheme 1), the LY matrix did not present absorption band in the specific region of 715-670 cm^{-1}. On the other hand, the APTES/PTES copolysilsesquioxane present Si-C bonds in your structure. Furthermore, hydroxyls from silanol groups can also open epoxy rings during the cure reaction[4,21], forming new Si-C bonds between the APTES/PTES copolysilsesquioxane and the LY matrix. For these reasons, the hybrid matrixes presented Si-C absorption bands and the hybrid matrixes cured after 7 days of chemical modification presented slightly higher intensity for the Si-C bonds, comparing with the respective hybrid matrixes cured immediately after chemical modification.

3.2. Morphology characterization

Figure 3 exhibits SEM images of epoxy and hybrid nanocomposites surfaces after tensile fractures. All samples showed typically brittle fracture morphologies, moreover, it was not possible to observe significant changes in the matrices' fracture mechanisms with the addition of 0.25 wt% MWCNT. In our previous work[17], we observed a similar behavior when carboxylated single-walled carbon nanotubes (SWCNT) were incorporated to similar epoxy resin.

On the other hand, regions with high concentration of MWCNT were also observed in the fracture surfaces of nanocomposites. Figure 4 highlights these concentrated regions spread by the fracture surface (white dots) on the LY-18-0-CNT hybrid matrix. Although the MWCNT showed good interaction with epoxy/silsesquioxane hybrid matrix, such remaining agglomerations can contribute to a localized stress concentration and consequently reduce the composite's stiffness[14,16,26].

3.3. Thermal properties

Dilatometric analyses were used to evaluate the T_g of the nanocomposites and the values are listed in Table 2. The incorporation of MWCNT to the hybrid epoxy matrixes did not present any tendency regarding the T_g values for hybrid epoxy matrixes. Thus, the oscillation of T_g values depends not only on how the free volume is affected by MWCNT incorporation, but also depends on the interaction between MWCNT and epoxy matrix which is subjected to different molecular architectures or condensation degrees.

Once FTIR analysis (Figure 1) revealed that a high cure degree was achieved for both matrixes (neat and hybrid epoxy), the decrease of T_g values for nanocomposites in relation to LY-CNT could be hindered by MWCNT incorporation in the reaction between the NH$_2$ group of APTES/PTES copolysilsesquioxane and the epoxy ring. Furthermore, this decrease of T_g may be associated with commercial CNT impurities. In general, reports shown[27] that SWCNT and MWCNT may lead to a decrease and an increased or unchanged Tg values of the nanocomposites, respectively.

Other studies also reported decreases in the T_g value of DGEBA epoxy matrixes with the incorporation of CNT[23,25,28]. Furthermore, a decrease in the T_g value with the incorporation of a random[5,7,8,29] or organized polysilsesquioxane structures[2,30,31] in epoxy matrix have been reported in literature. On the other hand, in our previous work[13], the incorporation of the APTES/PTES copolysilsesquioxane provided improvement on T_g up to 13 °C in relation to neat LY matrix.

The results of the TGA measurements of the hybrid nanocomposites and LY epoxy resin are showed in Figure 5. The hybrid nanocomposites and LY resin presented similar thermograms with only one main degradation event. The mass loss observed in the 100-250 °C range (approximately 2 to 4%) can be attributed to (1) the loss of the retained
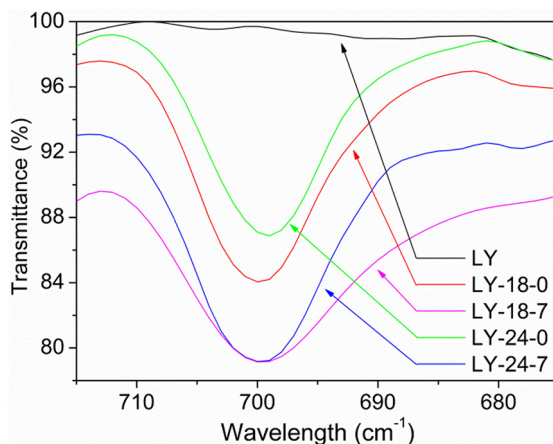

Figure 2. FTIR spectra in the range of 715-670 cm^{-1} of neat epoxy resin (LY) and the respective hybrid matrixes.

Table 2. Glass transition temperatures values obtained by dilatometry.

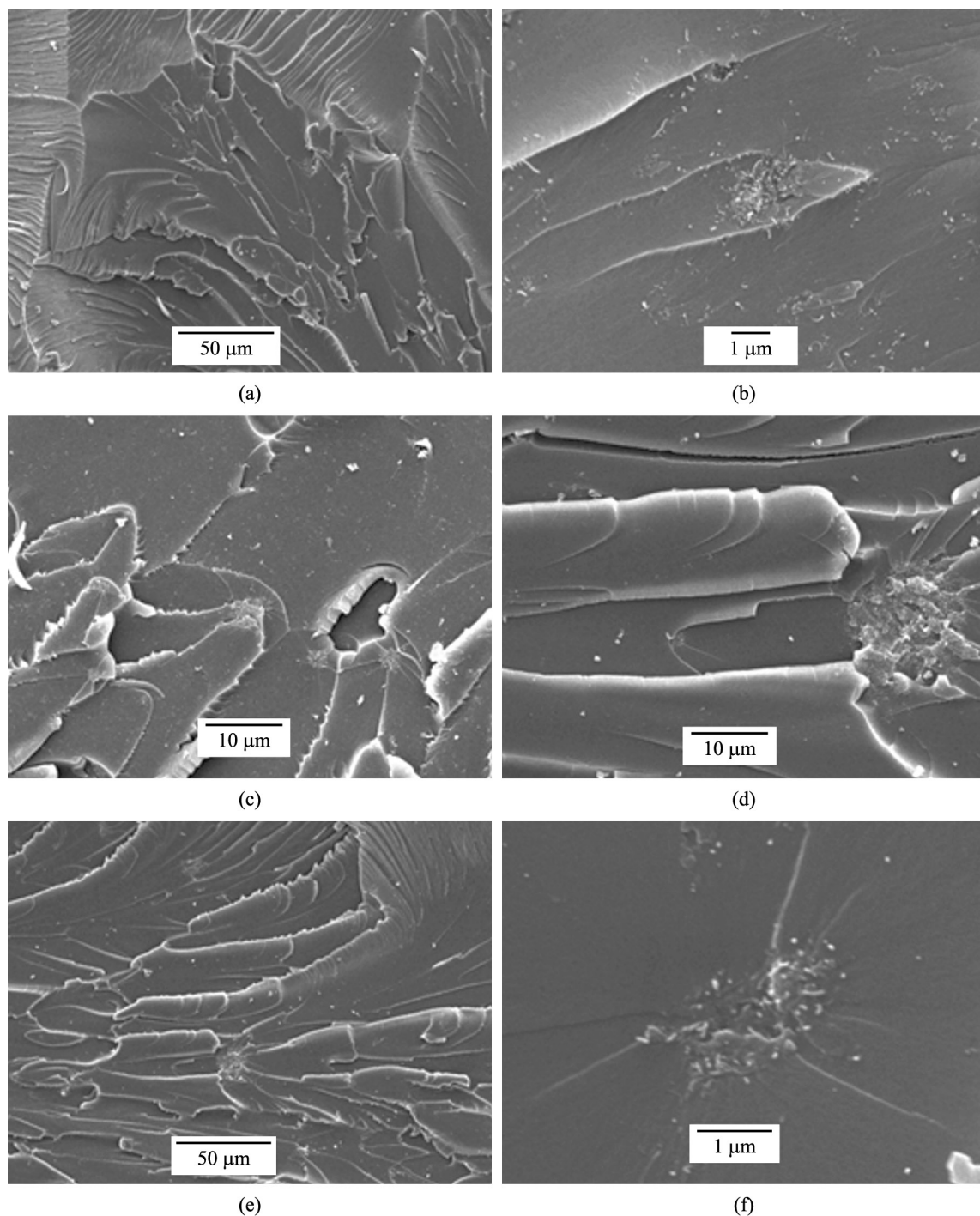| Samples	T_g (°C)
LY	121
LY-CNT	120
LY-18-0-CNT	116
LY-18-7-CNT	128
LY-24-0-CNT	109
LY-24-7-CNT	113

Figure 3. SEM images of fracture surface tensile: (a) LY; (b) LY-CNT; (c) LY-18-0-CNT; (d) LY-18-7-CNT; (e) LY-24-0-CNT; (f) LY-24-7-CNT.

volatiles in the hybrid matrix due to the incomplete polycondensation reactions of residual silanol[32] or (2) the elimination of residual solvent (propanone) added during sonication stage[17,33]. Thermal stability parameters, including initial decomposing temperature (temperature of 5% weight loss, T_{d5}), temperature of 30% weight loss (T_{d30}), statistic heat-resistant index temperature (T_s) and mass residual at 800 °C are described in Table 3. The percentages of volatiles

were taken into account to obtain T_{d5} and T_{d30} values. T_s value was determined from T_{d5} and T_{d30} values, according to the following equation[34-36]:

$$T_s = 0.49 \, [T_{d5} + 0.6x(T_{d30} - T_{d5})] \tag{1}$$

T_{d5} value of the hybrids nanocomposites increased around 4 to 7 °C in relation to the DGEBA epoxy resin.

Table 3. Thermal stability parameters obtained from TGA of the hybrid nanocomposites.

Samples	T_{d5} (°C)	T_{d30} (°C)	T_s (°C)	Residual mass at 800 °C (%)
LY	337	378	177.2	9.2
LY-CNT	332	377	175.9	2.7
LY-18-0-CNT	344	381	179.4	19.2
LY-18-7-CNT	341	387	180.6	18.0
LY-24-0-CNT	343	385	180.4	20.2
LY-24-7-CNT	344	382	179.7	20.0

(a)　　　　　　　　　　　　　　　　(b)
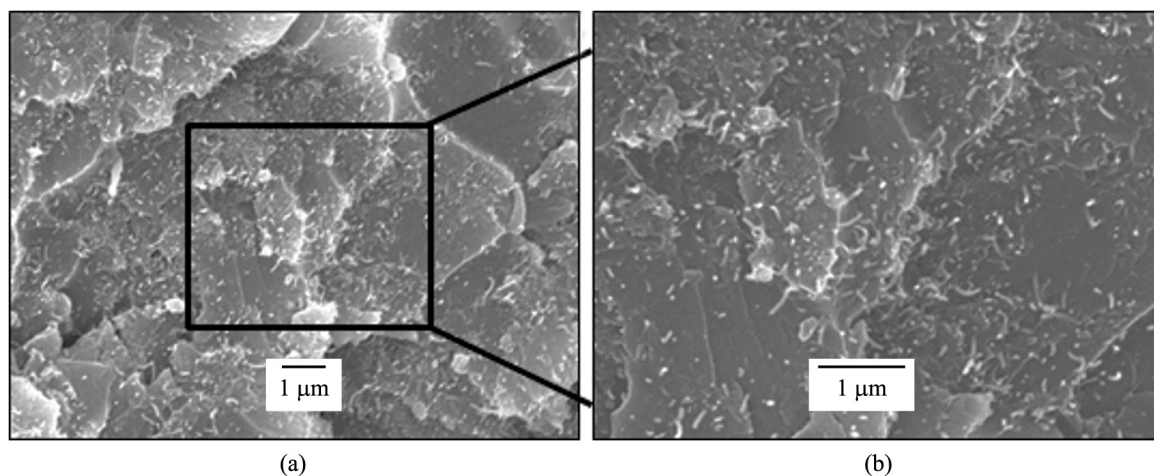
Figure 4. Regions of high concentration of MWCNT in the LY-18-0-CNT hybrid matrix.
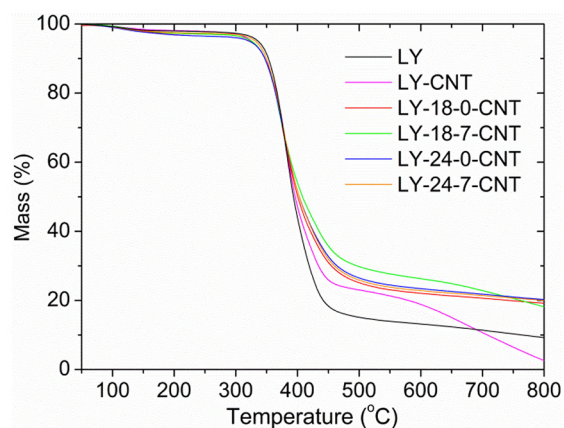
Figure 5. TGA thermograms of hybrid nanocomposites.

This behavior was also observed for T_{d30} value, however in this case, the increase was around 3 and 9 °C. On the other hand, the incorporation of 0.25 wt% MWCNT to the neat LY nanocomposite (LY-CNT) caused a decrease around 5 °C in T_{d5} value and no significant change was observed to T_{d30} value. The T_s value for DGEBA epoxy resin is in agreement to the reported values in literature[8] for similar DGEBA epoxy resin in terms of eq g^{-1}, however, in the present work, a slight increase of this parameter was observed, contrary to other reported works.

Analyzing the residual mass at 800 °C, it is clearly observed that the residual mass of the hybrid nanocomposites were higher than those obtained to LY and LY-CNT samples. The esidual mass values at 800°C for the hybrid nanocomposites were twice that of LY and LY-CNT samples. This significant increase in the residual mass is due to the high thermal stability of Si–O–Si bonds present in the APTES/PTES copolysilsesquioxanes[13,32,37]. The incorporation of MWCNT to LY resin caused an almost fully degradation of the matrix at 800 °C. This thermal stability decrease was also observed in literature[23] and is attributed to the high thermal conductivity of carbon nanotubes, which favored the degradation process of the epoxy matrix. As reported by Puglia and co-workers[38] the residual mass of epoxy resins can vary with their nature and processing conditions; for aromatic systems these differences were attributed to char formation properties. For example, a sensible higher residual mass is obtained for lower heating rates while at higher rates (ca. 30 °C min^{-1}) almost no residual mass remains at the end of the degradation step. As the carbon nanotubes can enhance the local heating transfer, it also affects the degradation process, lowering the residue amount.

On the other hand, the CNT presence in the epoxy/silsesquioxane matrixes did not favored the degradation of theses matrices, confirming the higher thermal stability provided by silsesquioxanes[5,9].

3.4. Mechanical characterization

A typical curve obtained from mechanical test of LY sample is shown in Figure 6. All samples prepared in this work do not show any plastic deformation, failing during elastic
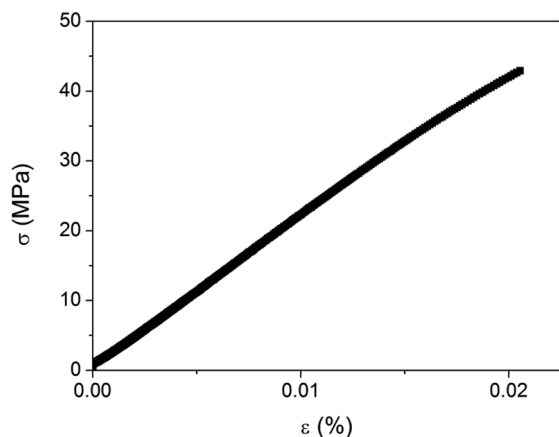
Figure 6. Stress-strain curve obtained from mechanical test of LY sample.

Table 4. Young's modulus (E) and tensile strength (σ_{max}) mean values obtained by mechanical tests. Values between parentheses are the standard deviation with $\alpha = 0.05$.

Samples	E (GPa)	σ_{max} (MPa)
LY	2.1 (± 0.1)	41.0 (± 5.4)
LY-CNT	2.2 (± 0.3)	39.3 (± 5.0)
LY-18-0-CNT	2.6 (± 0.8)	41.3 (± 6.2)
LY-18-7-CNT	1.9 (± 0.2)	47.0 (± 1.5)
LY-24-0-CNT	2.1 (± 0.1)	43.0 (± 5.7)
LY-24-7-CNT	2.1 (± 0.3)	37.8 (± 7.2)

deformation. This brittle behavior showed by all samples is in agreement with observed by SEM images. Student's *t*-tests were performed to compare the main values obtained in mechanical testing (Table 4) of the hybrid nanocomposites and their respective hybrid matrices. Confidence limit of 95% (with significance level, $\alpha = 0.05$) was adopted.

The incorporation of MWCNT into epoxy matrix, in general, did not statistically affect the Young's modulus and tensile strength of the nanocomposites (according to the applied *t*-test). The only statistically significant difference in Young's modulus was observed for LY-18-0-CNT, when an increase of 24% was observed with the incorporation of

0.25% MWCNT. Although the MWCNT incorporation did not affect the Young's modulus of LY-18-7-CNT nanocomposite, an increase of 15% was observed in its tensile strength in relation to LY matrix. In this context, Patankar and co-workers[3] also prepared nanocomposites based on epoxy/MWCNT by sonication technique and reported an improvement of 9% in the tensile strength with a loading of 0.15% MWCNT.

Assuming no chemical incompatibility between hybrid matrix and MWCNT, the mechanical properties are in agreement with SEM images (Figures 3 and 4) in which MWCNT clusters and a relatively poor dispersion was observed. These regions with high MWCNT concentration may lead to a lower charge transfer through the matrix/reinforcement interface, avoiding improvements in mechanical tests[14,16,26]. The heterogeneity observed in SEM images lead us to conclude that there is no tendency regarding the improvement of mechanical properties with MWCNT incorporation.

4. Conclusions

A new kind of hybrid nanocomposites based on epoxy/MWCNT was prepared by chemical modification of the epoxy matrix and dispersion of MWCNT by sonication. FTIR spectra showed that a high degree of cure was achieved, suggesting that the MWCNT loading did not affect the curing reaction of these hybrid matrices. Morphological observations of tensile fractured surfaces of the nanocomposites made by SEM revealed some regions with high MWCNT concentration, suggesting that the dispersion of pristine MWCNT by sonication technique is still a challenge. TGA results indicated that MWCNT incorporation reduced the thermal stability of epoxy matrix; on the other hand, the hybrid nanocomposite exhibited improvements in all the studied thermal stability parameters. Hybrid nanocomposites increased the Young's modulus and the maximum stress of the epoxy matrix up to 2.6 GPa and 47 MPa, respectively. The results show that the novel hybrid nanocomposite is suitable for applications requiring superior thermal stability, such as special coatings for aeronautical components.

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