Effect of sonication on thermo-mechanical properties of epoxy nanocomposites with carboxylated-SWNTs

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Abstract

In this work, a 2k factorial design was used to determine the interaction between sonication time, ultrasound amplitude, and carboxylic-functionalized single-walled carbon nanotubes (c-SWNT) content and their effect on the tensile, dilatometric, and dynamic-mechanical properties of casted epoxy nanocomposites reinforced with c-SWNTs. The nanocomposites were prepared with the help of a solvent (tetrahydrofuran) to reduce resin viscosity. Tensile strength increased with sonication for higher amplitudes and shorter times (20 min). The addition of 0.25 wt% c-SWNT enhanced the mechanical properties, increasing the Young’s modulus up to 30% in comparison with neat epoxy prepared under the same conditions. Dilatometry tests showed that shrinkage takes place at the epoxy glass transition, while dynamic-mechanical analyses confirmed the tensile results and suggested that the presence of nanotubes yielded a more homogeneous epoxy resin network, probably due to the minimization of residual solvent.

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1. Introduction

Carbon nanotubes (NTs), reported by Iijima in 1991 [1], are currently being investigated as a possible reinforcement for polymer composites. NTs are considered candidates for this application due to their unique structure, which exhibits a remarkable combination of mechanical, electrical and thermal properties [2].

The use of a small amount of NTs in polymer matrices, generally below 1 wt% [3–5], has the potential to yield nanocomposites with improved properties. However, the reported effect has been, in most cases, much lower than envisaged by theoretical predictions.

The effective mechanical reinforcement by NTs in polymers may be achieved once two major challenges are faced: homogeneous dispersion of NTs in the matrix, and good interfacial adhesion between nanotubes and matrix [3,6–8].

Chemical functionalization at the surface of NTs has a great potential for enhancing physical and chemical properties of the final materials by promoting adhesion and a more efficient stress transfer at the NT/matrix interface. For instance, soluble nanotubes may be used to produce mechanically reinforced nanocomposites [9].

In this work, a 2k factorial design was used to statistically determine the interaction between the main parameters in the production of epoxy-matrix nanocomposites reinforced with randomly dispersed carboxylic-functionalized single-walled carbon nanotubes (SWNTs). The fabrication process studied here was based on a tip sonication technique with the use of solvents to achieve a uniform dispersion of SWNTs in the matrix. The influence of the SWNT content on the mechanical and thermal properties of the epoxy-matrix nanocomposites was also investigated.

2. Experimental

2.1. Materials

Single-walled carbon nanotubes functionalized with carboxylic groups (c-SWNT) used in this work were produced by electrical arc discharge and supplied by the Nanomaterials Laboratory at the Federal University of Minas Gerais (UFMG)-Brazil.

The bifunctional diglycidyl ether of bisphenol A (DGEBA) epoxy resin was obtained from Huntsman as Araldite GY 251®, together with the hardener Aradur HY 956®, based on a polyamine. The sol-

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vent used was analytical grade tetrahydrofuran (THF), from Cinetica Quimica-Brazil.

2.2. Experimental design

In order to achieve a homogeneous dispersion of c-SWNTs in the epoxy-matrix, the nanocomposites were prepared with the help of a solvent (THF), to reduce resin viscosity, and tip sonication. A typical 2³ factorial design was used to study the effect of the sonication parameters (power and time of sonication) and the c-SWNT content on the final properties of the material. These factors and their studied levels are identified in Table 1 and the statistical analysis of the results was carried out using the software Statistica®. The parameters and levels chosen in this work were defined based on the former experience of the group and after testing several other possibilities [10,11].

2.3. Preparation of c-SWNT/epoxy nanocomposites

For the preparation of nanocomposites, a certain amount of carboxylated-SWNTs (0.10 or 0.25 wt% relative to the epoxy) was dispersed in THF (10 wt%, in relation to the epoxy) under simultaneous magnetic stirring and sonication (Sonics Vibration 750) at 165 or 225 W, for 20 or 40 min. The nanotube (NT) suspension was then added to the epoxy under the same conditions of simultaneous magnetic stirring and sonication. The mixture was later degassed under vacuum and magnetic stirring at 70 °C for 1.5 h and cooled down to room temperature. After that, the hardener was added to the c-SWNT/epoxy system under mechanical stirring, at a epoxy:hardener weight ratio of 5:1. Finally, the mixture was cast into silicone molds and left to cure at 60 °C for 24 h. For comparison, another sample, called epoxy/THF, was prepared following this procedure except that in this sample no SWNT was added.

2.4. Characterization

Thermogravimetric analysis (TG) was performed on a TA Instruments equipment (model 2050). The samples were heated from room temperature to 1000 °C at 10 °C min⁻¹ under nitrogen atmosphere at a flow rate of 70 cm³ min⁻¹. Dilatometric measurements were conducted on a Netzsch 402C equipment. The specimens were heated from room temperature to 160 °C at 2 °C min⁻¹, under N₂ atmosphere, followed by a fast cooling down to room temperature and a new heating (second run) under the same conditions of the first run.

The behavior of the epoxy/THF and the nanocomposite specimens was evaluated by various mechanical tests. Tensile tests (ASTM D638M-93) were carried out in an EMIC DL 30000 universal testing machine using a 1000 kgf load-cell, at 5 mm min⁻¹, and for every experimental condition, a minimum of 10 specimens were tested.

The surface morphology of the tensile fractured specimens was observed under a Zeiss DSM 940A scanning electron microscope (SEM) operating at 10 kV.

Dynamic-mechanical analysis (DMA) on dual cantilever mode was carried out from room temperature to 250 °C, at 5 °C min⁻¹, in a TA Instruments (model 2980) equipment. All measurements were conducted at a strain of 0.01% and a frequency of 1 Hz.

The molecular weight distribution of sonified epoxy samples was obtained using a Waters 510 Gel Permeation Chromatograph equipped with a Waters 410 refractometer detector and PS/DVB Styragel® columns thermostated at 40 °C. Standards of polystyrene were used for calibration and tetrahydrofuran as eluent. The flow rate was 1.0 mL min⁻¹ and the injection volume 200 μL.

3. Results and discussion

3.1. Thermogravimetry

Fig. 1 shows the weight loss curves for cured samples of neat epoxy and epoxy sonicated with 10 wt% THF, i.e. epoxy/THF. A higher weight loss in the 100–300 °C range was observed for the epoxy/THF, which is related to the elimination of residual solvent. This is similar to what was reported by Lau et al. who observed the presence of residual dimethylformamide in SWNT/epoxy nanocomposites [12]. The loss of weight above around 300 °C is related to the decomposition of the polymer.

Fig. 2 shows thermograms of c-SWNT/epoxy nanocomposites, where the presence of residual THF is again observed. The estimated...
Table 2
Residual THF concentration, $T_{peak}$ and glass transition temperatures ($T_g$, from DMA measurements) for all studied samples following experimental design: sonication power/sonication time/c-SWNT content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Residual THF (wt%)</th>
<th>$T_{peak}$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>N/A</td>
<td>373</td>
<td>72</td>
</tr>
<tr>
<td>Epoxy/THF</td>
<td>5.1</td>
<td>370</td>
<td>78</td>
</tr>
<tr>
<td>165 W/20 min/0.10%</td>
<td>4.8</td>
<td>369</td>
<td>72</td>
</tr>
<tr>
<td>225 W/20 min/0.10%</td>
<td>4.5</td>
<td>364</td>
<td>68</td>
</tr>
<tr>
<td>165 W/40 min/0.10%</td>
<td>3.2</td>
<td>366</td>
<td>78</td>
</tr>
<tr>
<td>225 W/40 min/0.10%</td>
<td>3.7</td>
<td>365</td>
<td>76</td>
</tr>
<tr>
<td>165 W/20 min/0.25%</td>
<td>3.8</td>
<td>374</td>
<td>74</td>
</tr>
<tr>
<td>225 W/20 min/0.25%</td>
<td>3.4</td>
<td>367</td>
<td>68</td>
</tr>
<tr>
<td>165 W/40 min/0.25%</td>
<td>3.1</td>
<td>369</td>
<td>82</td>
</tr>
<tr>
<td>225 W/40 min/0.25%</td>
<td>1.5</td>
<td>369</td>
<td>77</td>
</tr>
</tbody>
</table>

amount of THF trapped in each sample is presented in Table 2. The samples with higher c-SWNT contents presented a lower amount of residual solvent. It also appears that the content of trapped THF decreases for longer sonication periods. Above ca. 350 °C, all the samples decompose and the curves overlap. The decomposition temperatures ($T_{peak}$ in Table 2) were slightly higher for nanocomposites with 0.25 wt% of c-SWNT than for 0.10 wt% prepared under the same conditions.

Distinct results may be found in the literature regarding the thermal stability of NT-reinforced nanocomposites. Shen et al. [13] reported an improvement in thermal stability when the nanotubes are well dispersed and a single interfacial region between matrix and NTs is present, whereas Miyagawa and Drzal [14] observed a decrease in the thermal stability of epoxy with the addition of fluorinated SWNTs, which may occur due to the NTs interference in the cure stoichiometry, reducing the density of crosslinks, which leads to lower degradation temperatures.

3.2 Dynamic-mechanical analysis

Fig. 3(a) illustrates the DMA curves of storage modulus versus temperature for neat epoxy (prepared with or without THF addition) and nanocomposites with 0.25 wt% c-SWNT. The storage modulus was found to increase with the c-SWNT content and the sonication time, and decrease with the sonication power. For the best sonication conditions (165 W and 40 min), the addition of 0.25 wt% of c-SWNTs yielded a 57% increase in storage modulus (at 40 °C), in comparison with epoxy/THF samples, and a 42% increase in comparison with neat epoxy (prepared without solvent). In fact, the storage modulus reached values above 3.0 GPa at 40 °C, significantly higher than similar composites recently reported in the literature [15,16].

The loss factor ($\tan \delta$) versus temperature curves for neat epoxy (with or without THF addition) and various nanocomposites are shown in Fig. 3(b). Glass transition temperatures, determined from the position of the $\tan \delta$ peak, varied from 71 to 78 °C (see Table 2).

The peak factor ($\Gamma$), defined as the full width at half maximum of the $\tan \delta$ peak divided by its height [15], was used to estimate the homogeneity of the epoxy network. Lower $\Gamma$ values, i.e. higher homogeneity, were found for stricter sonication conditions (225 W and 40 min). The variation with the c-SWNT content, however, was very small, changing from 20.8 °C (for 0.10 wt%) to 19.9 °C (for 0.25 wt%). The epoxy/THF sample showed the highest $\Gamma$ value, 39.6 °C, indicating a less homogeneous network, probably due to the presence of trapped solvent. For the nanocomposites the average $\Gamma$ value was 25.7 °C, showing that the presence of nanotubes somehow promoted a more homogeneous network, probably due to the minimization of residual solvent, as confirmed by TG analysis.

3.3 Dilatometry

Fig. 4(a) presents the first run (heating) dilatometric curves for some of the c-SWNT/epoxy nanocomposites, showing volume contraction at temperatures around $T_g$, related to free volume and post-cure processes. In the second run (Fig. 4(b)), most samples exhibited a plateau near $T_g$, evidencing some reorganization of
polymer chains due to stress relaxation during the heating process.

It was also noted that the nanocomposites showed a slightly lower thermal dilation than epoxy/THF. González [17] correlates this effect to the negative thermal expansion coefficient of carbon nanotubes, due to its sp² network. Indeed, theoretical data suggest that even nanocomposites with low SWNTs content should have a lower thermal dilation than the unreinforced resin [17].

3.4. Tensile properties

Table 3 summarizes the tensile tests results of the nanocomposites and epoxy/THF. It may be observed that c-SWNT/epoxy nanocomposites presented a higher Young’s modulus than the epoxy/THF, whereas variations in tensile strength and elongation at break were less significant and more dependent on the processing parameters. It has already been reported in the literature that the elastic modulus of NT/epoxy nanocomposites increases with the NT content regardless of the dispersion level, but tensile strength and elongation at break are more critically related to a homogeneous distribution in the matrix [7]. Agglomerates of NTs, which may lead to rapid crack propagation [15], and poor NT/matrix interfacial adhesion are the main factors associated with low tensile strength of nanocomposites [18].

The results of the statistical analysis are reported in Table 4. It was found that the c-SWNT content factor has no significant interaction with the others (for a significance level of 5%), i.e. it can be interpreted isolated, and is the most significant factor to enhance tensile strength. There is also a trend to increase tensile strength for longer sonication times, which could be related to lower resin viscosity and better dispersion of c-SWNTs in the matrix. Similar, but less important, effects were found regarding elongation at break and Young’s modulus.

Considering tensile properties, lower sonication power (165 W), longer sonication time (40 min) and higher c-SWNT content (0.25 wt%) were found to be the most adequate conditions to prepare c-SWNT/epoxy nanocomposites.

Micrographs of tensile fractured surfaces of epoxy/THF and some of its nanocomposites are shown in Fig. 5. All specimens exhibited a relatively smooth surface indicating a typical brittle fracture behavior and no significant changes were observed in the nanocomposites with c-SWNTs.

### 3.5. Gel permeation chromatography

The GPC results for 10 wt% epoxy/THF sonicated solutions and neat non-sonicated epoxy are presented in Table 5. The number average molecular mass (Mn), the chromatogram profile, and the concentration of monomer (DGEBA) and oligomers of the non-sonicated epoxy were similar to those reported in the literature [19]. The concentration of oligomers tends to decrease when the samples are sonicated due to the scission of polymer chains. However, the most significant decrease in the oligomer concentration occurred under milder sonication conditions (165 W), while the samples submitted to 225 W showed a lower decrease in
the oligomer concentration, what is possibly related to branching and crosslinking processes due to the recombination of radicals. On the other hand, the number-average molecular masses do not vary significantly with the sonication parameters. Anyway, sonication of epoxy samples under the conditions used in this work, does not cause a considerable change in resin properties.

4. Conclusions

A systematic statistical study of the influence of sonication parameters and nanotube content on thermal and mechanical properties of c-SWNT/epoxy nanocomposites was carried out using a $2^2$ factorial design. The route chosen for the preparation of nanocomposites was proved to be not strict enough, allowing the presence of some trapped solvent (THF) in the cured samples, as confirmed by TG measurements.

Tensile tests showed an increase in Young’s modulus (up to 30%) with the addition of 0.25 wt% c-SWNT. Tensile strength and elongation at break results, however, suggested that dispersion and/or c-SWNT/matrix adhesion should be enhanced to achieve more satisfactory mechanical properties. The findings of the statistical analysis showed that the lowest sonication power (165 W), the longest sonication time (40 min) and the highest c-SWNT content (0.25 wt%) were the best conditions to prepare c-SWNT/epoxy nanocomposites using THF as solvent.
DMA results have shown an increase in storage modulus for the nanocomposites, reaching 3.0 GPa for the best sonication conditions and 0.25 wt% c-SWNT content. Analysis of the peak factor ($\Gamma$), calculated from the tan $\delta$ curves, suggests that the presence of nanotubes promoted a more homogeneous epoxy network, probably due to the minimization of residual solvent, which corroborates other findings of this work.

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