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# Modeling of dynamic mechanical properties of epoxy and epoxy-phenolic reinforced with multi-wall carbon nanotubes

Juan PM Arias, Mariano Escobar and Analia Vazquez

## Abstract

The viscoelastic properties of nanocomposites based on epoxy and epoxy-phenolic blend matrix reinforced with multi-wall carbon nanotubes were studied. The content of carbon nanotube (0.2 and 0.5 wt.%) and its surface state (pristine vs. oxidized) varied. The characterization of the nanocomposites was done by means of infrared spectroscopy and chemical methods. From the viscoelastic properties of nanocomposites, characteristic properties such as storage modulus ( $E_0$ ),  $\tan \delta$  and damping peak ( $\tan \delta$ ) were obtained. The void content was also determined. Also, Weibull statistics are used to represent the failure of secondary bonds during the relaxation processes that lead to stiffness change over the full range of use temperatures. The incorporation of phenolic resin to an epoxy matrix leads to an increase of the relaxation modulus. The glass transition temperature of the epoxy-phenolic nanocomposites decrease when it is incorporated carbon nanotubes, independently of its state (pristine or oxidized).

## Keywords

Epoxy/MWCNT, phenolic/epoxy/MWCNT, dynamic mechanical properties, relaxation modulus modeling

## Introduction

Epoxy resins are widely used in industries, whose applications range from coatings, materials for electronic devices, adhesives, and even as arrays of fiber-reinforced composite materials, due to their excellent mechanical properties (high strength, hardness), good adhesion, heat resistance and electrical resistance.<sup>1</sup>

Carbon nanotubes (CNT) are the subject of one of the most important areas of research in nanotechnology. Although there are varying reports in the literature on the exact properties of CNT, theoretical and experimental results have shown extremely high elastic modulus, greater than 1 TPa (the elastic modulus of diamond is 1.2 TPa), and reported strengths 10–100 times higher than the steel.<sup>2</sup> Due to its high mechanical advantage, CNT have been used in several composites in order to reinforce the matrix. The reinforcement of epoxy matrix with CNT has been studied by several authors,<sup>3–5</sup> highlighting an improvement in the mechanical properties of resulting nanocomposites.

Phenolic resins are thermosetting polymers with a higher chemical resistance and thermal stability. In addition, phenolic resin has an intrinsic high resistance to ignition, low smoke generation and relatively low

cost.<sup>6</sup> A disadvantage of this kind of resin is the generation of water and formaldehyde during the polymerization process (curing), with the consequent formation of voids. Therefore, the processing of phenolic-based materials requires a very careful control of temperature and a gradual heating to allow the continuous removal of volatile and to reduce the number of defects in the final components. Typically, the required time for these operations is incompatible with the common schedules of industrial processes.<sup>7</sup> Epoxy-phenolic blends are systems that can partially solve this problem and to get good results have been used in industrial applications for many years.<sup>6</sup>

The study of the viscoelastic properties of the modified resins is important to ascertain their thermo-mechanical behaviour of different applications

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considering both load and temperature. The measurement of these viscoelastic properties can be done by a dynamic mechanical analyzer. Mathematical modeling of the relaxation modulus ( $E'$ ) allows fitting the experimental results and permitting to discuss the value of each parameter in function of the material structure.

The goal of this work was to design a nanocomposite with improved properties based on epoxy and phenolic resin using CNT and oxidized CNT as filler. The modeling of the relaxation modulus was also performed in order to discuss the value of each parameter in relation with their structure.

### Theoretical approach for a viscoelastic solid

There are various constitutive models for linear viscoelastic materials: Maxwell, Kelvin–Voigt model and the model of linear viscoelastic solid standard that combines the two previous models. All of them decompose the stress and strain in two summands, one representing the elastic effects and the other representing the viscous effects, which are interpretable in terms of springs and dampers. The Maxwell model is represented by a series arrangement where the spring and damper carry the same stress. The total strain (extension) of the element is the sum of the strains of the spring and damper (Figure 1(a)). The Kelvin–Voigt model is represented by a parallel arrangement (Figure 1(b)). The strain is the same for both the spring and damper. The stress supported by the element is the sum of the stresses in the spring and the damper.

The standard model combines the elements and equations of Maxwell and Kelvin–Voigt models. This leads to a reasonable model for understanding the behaviour of a viscoelastic solid. Equation (1) and Figure 2 present this behaviour.

$$(E_1 + E_2) \frac{d\varepsilon}{dt} = \frac{E_2}{\eta \left( \frac{\eta}{E_2} \frac{d\sigma}{dt} + \sigma - E_1 \varepsilon \right)} \quad (1)$$

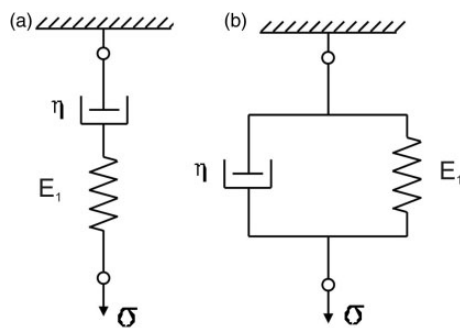


Figure 1. (a) Maxwell model. (b) Voigt–Kelvin model.

where  $E$  is the elastic modulus of the spring,  $\eta$  is the viscosity,  $\sigma$  is the mechanical strength and  $\varepsilon$  is the deformation.

This model is the most used to predict the behaviour of polymer during stress relaxation test. In this case, a constant strain ( $\varepsilon = \varepsilon_0$ ) is imposed on the system and so  $\frac{d\varepsilon}{dt} = 0$

In the model of springs and dampers, let us propose the relaxation time as a representation of local behaviour. Therefore, the relationship between the relaxation modulus and time can be written as:

$$E(t) = \sum_{i=1}^N E_i \exp\left(-\left(\frac{\tau}{\tau_i}\right)\right) \quad (2)$$

where  $E(t)$  is the relaxation modulus,  $E_i$  is the elastic modulus of the spring,  $t$  time and the quantity  $\tau_i = \frac{\eta}{E}$  has the dimension of time and is known as a relaxation time.

The mechanical response is driven by the movement of the smallest chain segments (only a few monomers long). Taking into account the number and strength of the links involved in the relaxation process, we can associate a Weibull parameter  $m_i$ , with the relaxation of a given point. In this case, equation (2), for a transition state becomes equation (3)<sup>8</sup>:

$$E(t) = \exp\left(-\left(\frac{\tau}{\tau_i}\right)^{m_i}\right) \quad (3)$$

Regarding the standard model under a constant strain, the modulus (at glassy state) will have a higher value for short times, which is determined by the sums

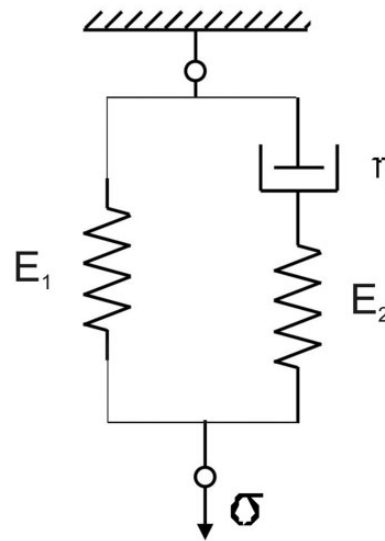


Figure 2. Standard model representation.

of both spring rate constants  $E_0$  and  $E_0-E_1$  (Figure 3). For longer times, the modulus has a low value and is determined by the spring rate  $E_1$ . For small times, the effect of the damper is high and therefore, influencing the behaviour of the springs  $E_0-E_1$  on the level of the modulus is important. In this case,  $E_0 \gg E_1$ , there is a drastic transition from high to low modulus at the relaxation time constant  $\tau_1$ .

Using the relation of time and temperature proposed by Aklonis and MacKnight,<sup>9</sup> it is possible to obtain the relaxation modulus vs. temperature:

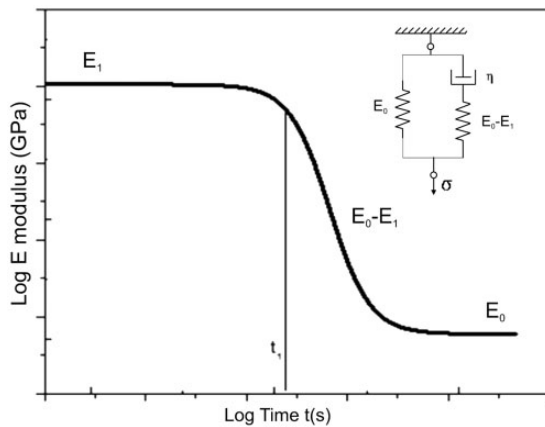
$$E(t) = E_0 \exp\left(-\left(\frac{t}{\tau_1}\right)^{m_1}\right) \tag{4}$$

where  $T_1$  is the temperature characteristic of the considered region and  $E_0$  a reference value for the considered region. If there are different mechanisms of relaxation, we can sum the different components (equation (5))

$$E = \sum_{i=1}^N E_i * \exp\left(-\left(\frac{T_i}{T_{ri}}\right)^{m_i}\right) \tag{5}$$

The general equation can represent different values, for example  $1 \leq N \leq 3$ . The coefficients  $E_i$  can be obtained by different means, experimental or analytical. For the case of a material that does not undergo any relaxation, before reaching the rubbery state, its behaviour is described by equation (6); for a material with two relaxation, it is represented by equation (7); and a case in which the material undergoes three relaxations uses equation (8).<sup>10</sup>

$$E = E_3 * \exp\left(-\left(\frac{T}{T_1}\right)^{m_3}\right) \tag{6}$$



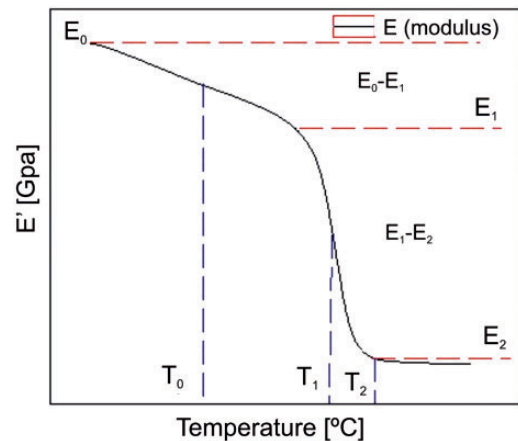
**Figure 3.** Behavior of the standard model for a constant force ( $n = 1$ ).

$$E = (E_2 - E_3) * \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 * \exp\left(-\left(\frac{T}{T_1}\right)^{m_3}\right) \tag{7}$$

$$E = (E_1 - E_2) * \exp\left(-\left(\frac{T}{T_2}\right)^{m_1}\right) + (E_2 - E_3) * \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 * \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \tag{8}$$

Three relaxation processes were considered, so the curve can be divided in three sections (Figure 4). Each section has associated a Weibull parameter  $m_i$  (equation (8)). The reference temperatures and modules can be independently measured or calculated.  $T_i$  corresponds to the inflection point of the relaxations and  $E_i$  is the modulus at the beginning of each section. In the Figure 4,  $E_0$  is the instantaneous relaxation module at a very low temperature,  $E_1$  is the instantaneous relaxation module at the beginning of the glass transition and  $E_2$  is the instantaneous relaxation module at the beginning of the rubbery region.

From the glassy state to the rubbery region, the primary links of the molecule remain intact. However, the secondary bonds (hydrogen, dipole, Van der Waals) will be altered by the molecular movements during temperature increase. The segmental mobility of the chains is possible at the rubbery state. If the temperature is still raised, degradation of polymer will occur. Figure 5 shows a scheme of the primary and secondary links within a polymeric matrix.



**Figure 4.** Different sections for the applied model.



**Figure 5.** Representation of primary and secondary bonds in a polymeric matrix.

## Experimental

### Materials

The matrix was an epoxy resin diglycidyl ether of bisphenol-A (DGEBA), an aliphatic amine, tris-triaethyleneamine (TETA, 70%) was used as curing agent, the density of the matrix is 1.65 gr/cc and was provided by Distraltec S.R.L. Multi-walled carbon nanotubes (MWCNTs) (diameter = 9.5 nm, length = 1.5  $\mu\text{m}$ , surface area = 250–300, purity = 90%) were provided by Arkema S.R.L. (NC7000). Resol phenol-formaldehyde (Formaldehyde free 1.1, pH 8.8) was provided by Atanor S.A. (Liquid Resin RL478).

### Fabrication of the composite

DGEBA was heated at 80°C to decrease the viscosity and the required amount of MWCNTs was added. The suspension was sonicated for 10 min in order to break the bundles of MWCNTs. Then, it was homogenized (Bio-Homogenizer Pro 200Gen) at 30,000 rpm for 10 min to break the remaining bundles. A vacuum pump was applied for 30 min to remove the air bubbles, and the curing agent was added and mixed for 3 min. The material was poured in the mould and was cured with the following schedule: 40°C for 2 h, 80°C for 8 h, 120°C for 2 h and 140°C for 2 h. In the case of epoxy-resol composite, the resol was first mixed with TETA and the same schedule described earlier was followed. In the case of oxidized MWCNTs, they were heated at 400°C for 4 h in an oven in the presence of oxygen.

### Methods

In order to characterize the mechanical properties of the nanocomposites, a Perkin Elmer DMA 8000 was used. The test was made on rectangular specimens (30  $\times$  8  $\times$  2.5 mm). The temperature scanning was from room temperature to 180°C at 2°C/min. The oscillation amplitude was 0.05  $\mu\text{m}$  at 1 Hz. Fourier transform infrared (FTIR) spectrum (FTIR-Shimadzu IRAffinity-1) was used to characterize the oxidized MWCNTs (KBr pellets).

An analysis of voids content was carried out through a quantitative optical method with a camera and *Hokern* microscope. The pictures were analyzed using image analysis software to calculate the voids content according to the following equation:

$$\text{Voids} = \frac{\text{Area of void}}{\text{Area total}} * 100 \quad (9)$$

Ten frames per sample were taken and the reported results are the average value of all measurements.

## Results

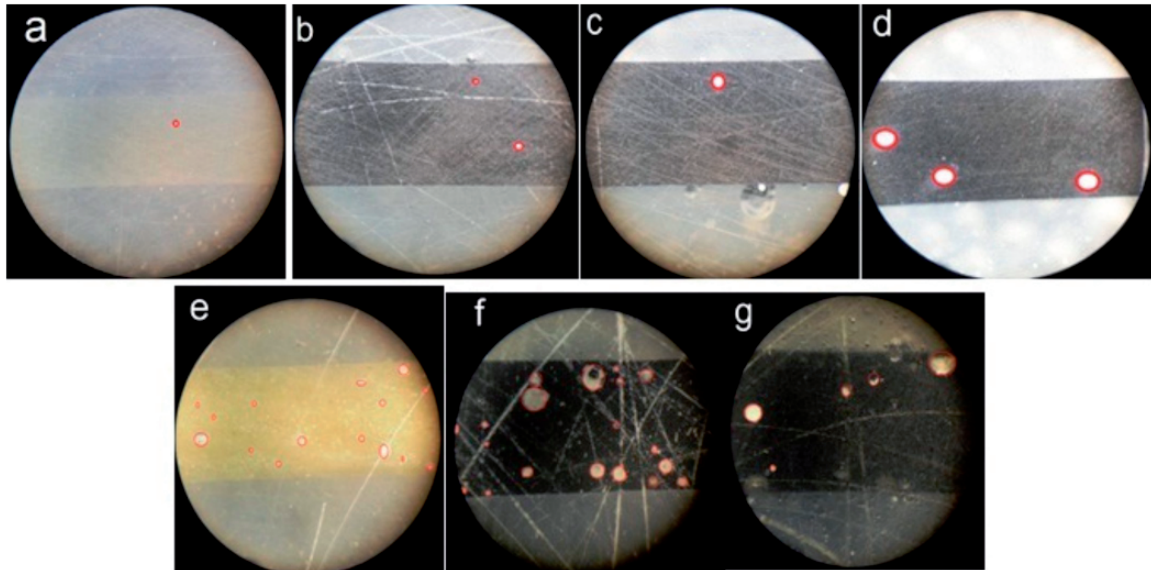
### Void content

Figure 6 shows the optical images of the different specimens. The present voids are highlighted on the images. The quantitative results are showed in Table 1. An increase in the void content was observed with the amount of CNT. It is probably because (i) MWCNT can act as a nucleating agent for the void and (ii) there is an increase in the viscosity when MWCNTs are present, which can difficult the diffusion of air bubbles from the inner to the outside of the nanocomposite. In the case of epoxy-phenolic nanocomposites, the void content is even higher. It is because the phenolic resin produces either water or formaldehyde (volatile) during the curing process and they could be retained within the composite due to increase of the viscosity.

### Epoxy/MWCNT nanocomposites

Figure 7 shows the relaxation modulus and  $\tan \delta$  vs. temperature curves for the different samples. The curve *a* corresponds to the net matrix and curves *b* and *c* correspond to the samples containing 0.2 and 0.5 wt.% of MWCNTs. An increase in the modulus at the glassy state was observed with the amount of CNT (Table 1). It is interesting to note that the highest modulus corresponds to the sample containing 0.5 wt.%. At the same time, it was estimated as the highest void content for this sample. For the composites with 0.5 wt.% of MWCNTs, the  $T_g$  value (measured as the maximum of the  $\tan \delta$  curve) increase some degrees due to the immobilization of the resin chains. Probably, the polymer chains are impeded in their movement by the presence of MWCNTs.<sup>4,11</sup>

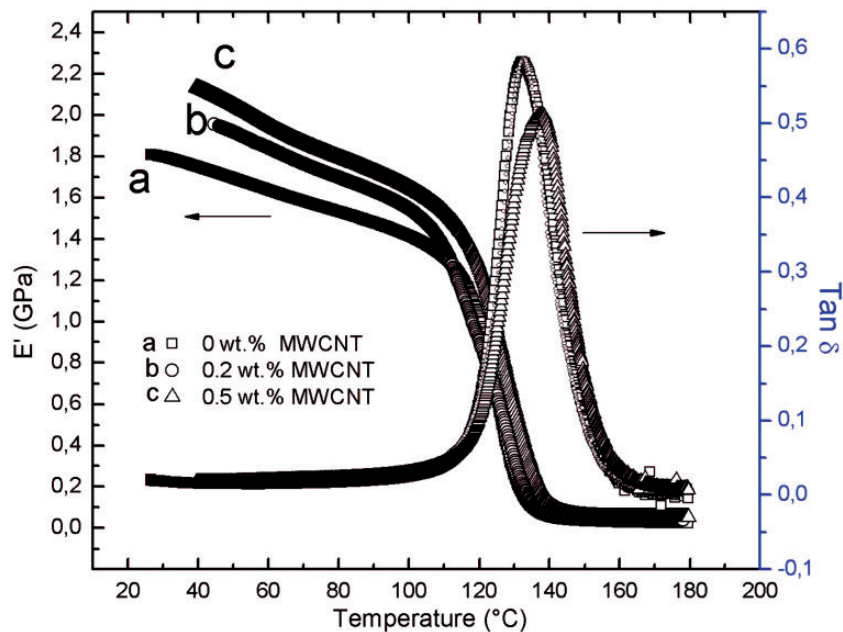
Figure 8 shows the result of the experimental measures and the modeling of the behavior of epoxy/MWCNT nanocomposites according to equation (8). The results of the model are summarized in Table 1. The Weibull parameters ( $m_i$ ) are continuous probability distributions corresponding to the behaviour of the



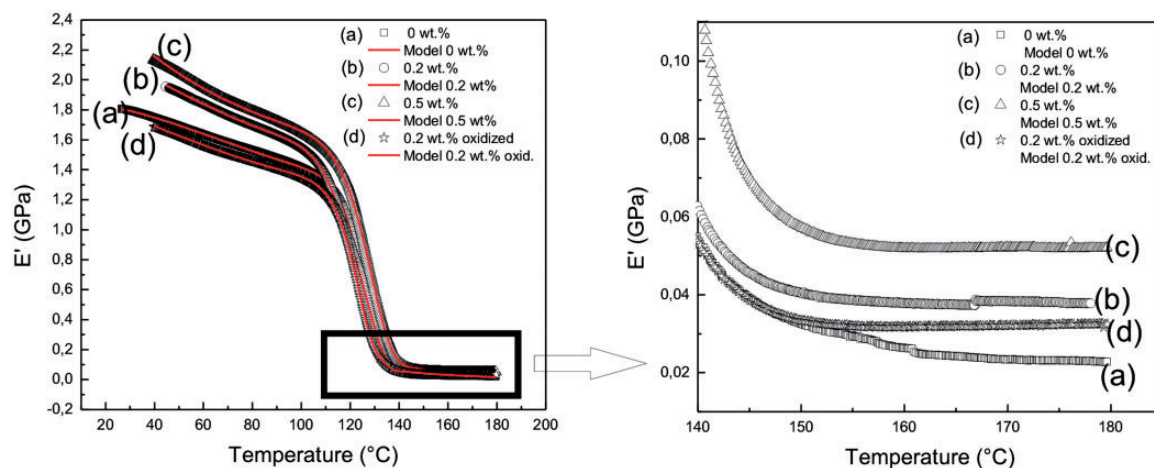
**Figure 6.** Optical images of samples containing different amount of MWCNTs in epoxy matrix: (a) 0 wt.%, (b) 0.2 wt.%, (c) 0.2 wt.% oxidized, (d) 0.5 wt.%; and resol/epoxy: (e) 0 wt.%, (f) 0.2 wt.%, (g) 0.2 wt.% oxidized.

**Table I.** Weibull parameters ( $m_1$ ,  $m_2$  and  $m_3$ ),  $T_g$ , relaxation modulus and void content of epoxy/MWCNT nanocomposites.

Content of MWCNT epoxy/MWCNT nanocomposites	$m_1$	$m_2$	$m_3$	$T_g$ ( $^{\circ}C$ )	$\dot{\epsilon}$ (GPa) $T = 50^{\circ}C$	$\dot{\epsilon}_{rubber}$ (MPa) $T = 180^{\circ}C$	%Void content
0 wt.%	2.03	22.68	121.06	132.2	1.63	53.0	0.009
0.2 wt.%	1.39	19.44	21.74	132.8	1.92	72.0	0.052
0.2 wt.% oxidized	1.61	20.46	64.54	132.8	1.62	66.4	0.013
0.5 wt.%	1.17	16.73	17.86	137.8	2.06	88.0	0.221



**Figure 7.** Relaxation modulus and  $\tan \delta$  of: (a) 0 wt.%, (b) 0.2 wt.% and (c) 0.5 wt.% of MWCNTs.



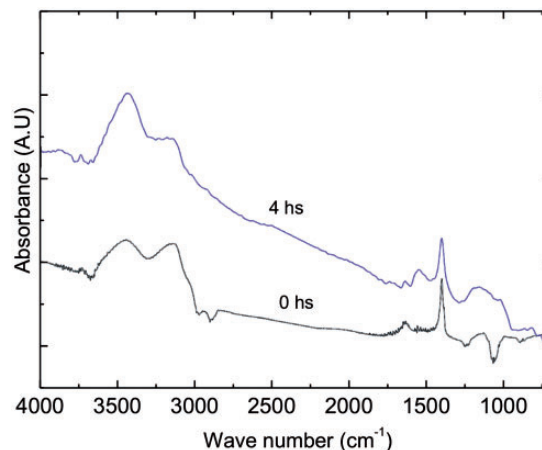
**Figure 8.** Modeling of the relaxation modulus. Points are experimental results and lines are the fitting model: (a) 0 wt.%, (b) 0.2 wt.%, (c) 0.5 wt.%, (d) 0.2 wt.% oxidized.

breaking of bonds in the material.<sup>9</sup> However, this parameter will depend on the degree of impairment of molecular motion (crosslinking, molecular weight, side chains, etc.). If the movement of the molecular chains is severely restricted in determined locations (i.e. for crosslinking), we expect  $m$  value will be very low (approaching a Boltzmann distribution). But if mobility becomes more appreciable, the value of  $m_i$  will increase.<sup>9</sup>

After the  $T_g$ , the mobility of the polymer chains increase and the system reach the “rubbery” state. Within this region, the modulus ( $E'_{\text{rubber}}$ ) increase with the quantity of pristine MWCNTs due to their higher modulus in comparison with that of the matrix (reinforcing effect). If we compare the  $E'_{\text{rubber}}$  of the nanocomposites containing the same quantity of CNT (0.2 wt.%), the lowest value correspond to the sample containing oxidized MWCNTs (Table 1). The rubber elasticity theory predicts the molecular weight between crosslinking points taking into account the module at the rubber state of polymers. In the case of nanocomposites, it can be compared if they have the same quantity of MWCNT. In the present case, the matrix of the sample containing the pristine CNT would have a higher rigidity of the material due to a more crosslinked network.

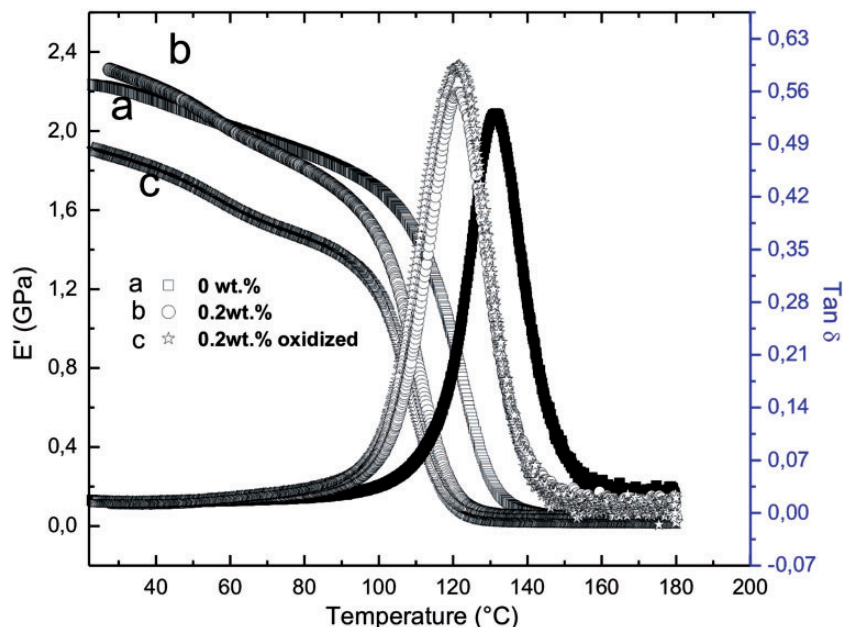
The oxidized MWCNTs have the surface activated and the carboxylic groups on its surface could consume part of the epoxy by the reactions between the epoxy with the acid, so it would lead to an opened network. For this reason, the molecular weight between crosslinking points would be lower for the sample containing oxidized MWCNTs.

Figure 9 shows the FTIR of pristine and oxidized MWCNTs. The pristine sample shows two band around  $1405\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  related to the



**Figure 9.** FTIR of pristine and oxidized MWCNTs.

stretching of the backbone of CNT. Furthermore, it is observed that the band at  $3450\text{ cm}^{-1}$  is associated to the  $\text{OH}^-$  groups from room humidity (KBr is highly hydrophilic). The oxidation process promotes the formation of surface-functional groups at defect sites along the tube sidewalls.<sup>12</sup> These functional groups increase the surface polarity and further alter the surface charges.<sup>13</sup> It can provide a large number of chemical adsorption sites and thereby can increase the adsorption capacity of oxidized MWCNTs.<sup>14</sup> The spectra of oxidized samples present features at  $1560\text{ cm}^{-1}$  and  $1733\text{ cm}^{-1}$  that can be attributed at stretching of  $\text{C}=\text{O}$  and bending of  $\text{OH}^-$  of the  $\text{COOH}^-$  group. Furthermore, the relative intensity of the band at  $3450\text{ cm}^{-1}$  increases with respect to the intensity of that at  $3150\text{ cm}^{-1}$  indicating the presence of a higher concentration of OH groups.



**Figure 10.** Relaxation modulus and tan  $\delta$  of phenolic/epoxy containing MWCNTs: (a) 0 wt.%, (b) 0.2 wt.%, (c) 0.2 wt.% oxidized.

**Table 2.** Weibull parameters ( $m_1$ ,  $m_2$  and  $m_3$ ),  $T_g$ , relaxation modulus and void content of epoxy-phenolic/MWCNT nanocomposites.

Content of MWCNT epoxy-phenolic/MWCNT nanocomposites	$m_1$	$m_2$	$m_3$	$T_g$ ( $^{\circ}\text{C}$ )	$\dot{E}$ (GPa) $T = 50^{\circ}\text{C}$	$\dot{E}_{\text{rubber}}$ (MPa) $T = 180^{\circ}\text{C}$	%Void content
0 wt.%	0.971	3.19	16.06	131.37	2.08	52.8	1.084
0.2 wt.%	1.56	2.24	16.30	121.7	2.11	46.1	2.438
0.2 wt.% oxidized	1.11	4.25	15.61	121.7	1.72	22.4	3.446

### Epoxy-phenolic/MWCNT nanocomposite

A 10 wt.% of phenolic resin was incorporated to the epoxy nanocomposite in order to improve the mechanical properties of the epoxy-based nanocomposites.

Figure 10 shows the relaxation modulus and tan  $\delta$  vs. temperature curves for the different samples. Table 2 present values of relaxation modulus at  $50^{\circ}\text{C}$ . It is observed that nanocomposites containing phenolic resin have a greater relaxation modulus than that containing only epoxy matrix.

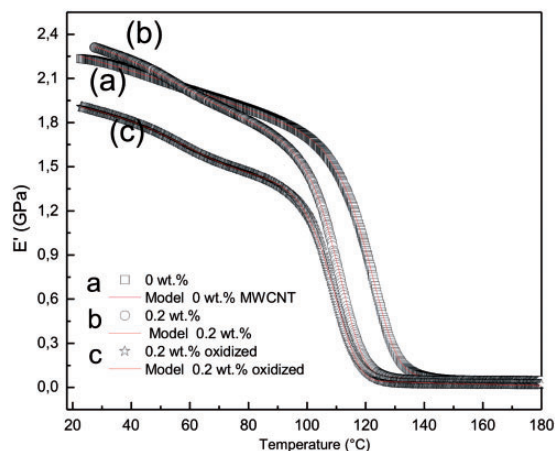
The relaxation modulus at glassy state is not changed with the inclusion of 0.2 wt.% of MWCNTs. When the added MWCNTs are oxidized, the modulus drops. This is due to the interaction of the methylene bridges of the resol and epoxy groups with the carboxylic groups present at the surface of nanotubes. During the crosslinking reaction of the phenolic resin, the formation of the bridges is easier when the resol is alone than in the presence of the epoxy-amine system

or oxidized CNT, leading to a lower crosslinked network.<sup>15</sup>

The glass transition temperature of the epoxy-phenolic nanocomposites decrease when it is incorporated CNT, independently of its state (pristine or oxidized). The tendency of the  $T_g$  behavior is opposite to that found for epoxy/MWCNT nanocomposites. It can be explained taking into account the reactions between epoxy and resol resin. Sturiale et al.<sup>7</sup> also showed that the incorporation of phenolic resin to an epoxy matrix lead to a reduction in glass transition temperature. It was suggested that this is a consequence of the reaction between the methylene bridges of the resol and epoxy groups. The height of the tan  $\delta$  (damping) decreased as consequence of the reduction of the rigidity of the composite due to the interaction between the phenol rings and the CNT.

Figure 11 shows the modeling of the experimental data for the epoxy-phenolic/MWCNT nanocomposites and the results are summarized in Table 2. The values





**Figure 11.** Modelling of the relaxation modulus of resol/epoxy containing MWCNTs: (a) 0 wt.%, (b) 0.2 wt.%, (c) 0.2 wt.% oxidized.

of  $m_1$  are slightly similar to that obtained for epoxy-based nanocomposites. However,  $m_2$  and  $m_3$  values are higher than that obtained for epoxy-based nanocomposites. It is due to the higher degree of crosslinking. It is a consequence of the interaction between the phenol rings and the CNT. Table 2 also includes the relaxation modulus at rubbery state. The most important feature is that the oxidized MWCNTs lead to a very open network, indicating that the carboxylic group in its surface influence on the reaction between the epoxy and methylene groups of the phenolic resin. It is clear that the value of rubbery plateau is related to the nature of the molecular structure and to the density of entanglements for the same quantity of MWCNTs.

## Conclusion

The viscoelastic properties of epoxy and epoxy-phenolic reinforced with MWCNTs were studied. Also, Weibull statistics are used to represent the failure of secondary bonds during the relaxation processes that lead to stiffness change over the full range of use temperatures.

Considering the epoxy-based nanocomposites, an increase in the modulus at the glassy state was observed with the amount of CNT. The incorporation of oxidized MWCNTs lead to an opened network of the polymer matrix due to the carboxylic groups on its surface consumes some of the epoxy groups available to react with the amine.

The incorporation of phenolic resin leads to an increase of the relaxation modulus. The glass transition temperature of the epoxy-phenolic nanocomposites decrease when it is incorporated CNT, independently of its state (pristine or oxidized).

Regarding the Weibull parameters, the values of  $m_1$  are slightly similar to that obtained for epoxy-based nanocomposites. However,  $m_2$  and  $m_3$  values are higher than that obtained for epoxy-based nanocomposites. It is due to the higher degree of crosslinking. It is a consequence of the interaction between the phenol rings and the CNT.

## Conflict of interest

None declared.

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