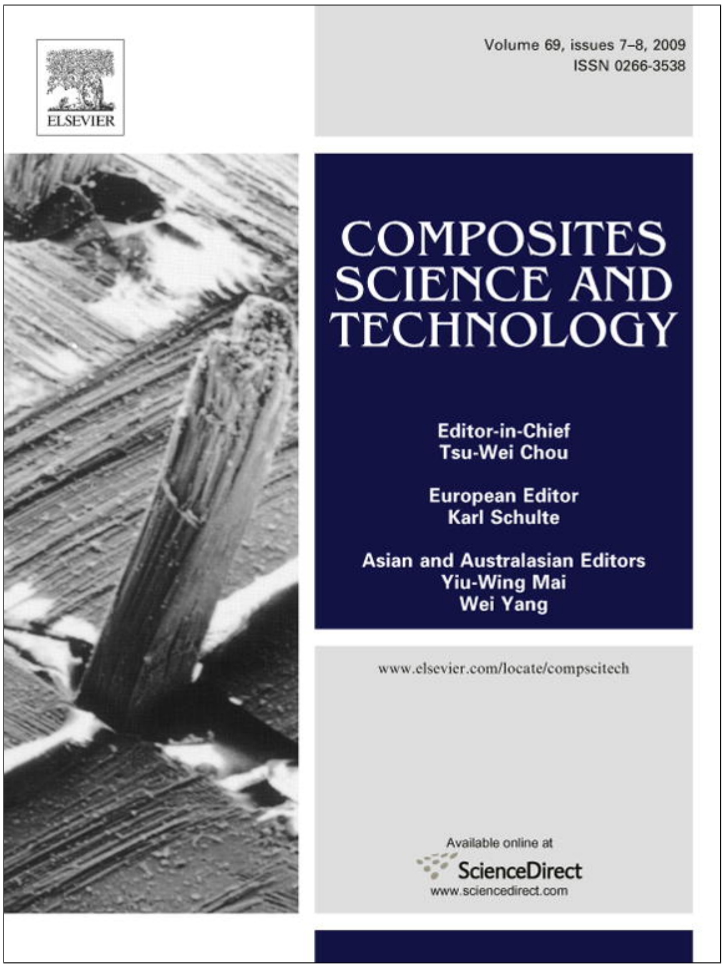

Volume 69, issues 7–8, 2009
ISSN 0266-3538

COMPOSITES SCIENCE AND TECHNOLOGY

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Composites Science and Technology 69 (2009) 1088–1092

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Single-wall carbon nanotubes/epoxy elastomers exhibiting high damping capacity in an extended temperature range

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ARTICLE INFO

Article history:
Received 23 September 2008
Received in revised form 8 December 2008
Accepted 21 January 2009
Available online 31 January 2009

Keywords:
A. Carbon nanotubes
A. Nanocomposites
A. Functional composites
B. Mechanical properties
B. Interfacial strength

ABSTRACT

In nanocomposites containing single-wall or multi-wall carbon nanotubes (SWCNT and MWCNT) high damping can be achieved by taking advantage of the weak bonding and interfacial friction between individual nanotubes and the matrix. The increase in damping capacity has already been proved for stiff epoxies and in this study it is extended to epoxy elastomers. Variable amounts (0.5–3 wt%) of oxidized SWCNT were dispersed by ultrasonication in precursors of an epoxy elastomer based on the reaction of diglycidylether of bisphenol A (DGEBA) and a polyoxypropylene with average molar mass of 2000, end-capped with primary amine groups. The quality of the initial dispersion was assessed by the constancy of the storage modulus with frequency in the low-frequency range. A rheological percolation threshold of 0.41 wt% SWCNT was found. Cured elastomers exhibited a large increase of the loss modulus with increasing amounts of SWCNT. For 3 wt% SWCNT, the increase in loss modulus was 1400% at room temperature. When temperature was increased up to 140 °C the loss modulus of the nanocomposite was practically constant while the one of the matrix dropped to a negligible value. The damping capacity at high temperatures opens important practical applications.

1. Introduction

Noise reduction and attenuation of vibration have become important technological issues associated to the application of structures and machines. Consequently, the demand of materials with high structural damping capacity is growing in a variety of sectors (aerospace, transport, construction and machinery) [1–3].

In general, rubber-like polymers have been used as damper and isolator materials in metallic and composite structures to mitigate mechanical vibration, noise, shock and impact [4]. In the design of metallic structures, the incorporation of damping is often through the use of dampers or damping layers, whereas in the case of composites, the desired structural damping is obtained by modifying the damping capacity of the different components (polymeric resin and reinforcement) [5]. However, attempts to apply viscoelastic materials for the solution of practical engineering vibration and noise control problems, comes with a detrimental effect to the stiffness of the material. In general, current technological requirements necessitate a good balance between stiffness and loss characteristics (damping characteristics) [5,6]. For more effective design of high performance structures, there is a particularly strong need for lightweight and high stiffness structural materials with the ability to absorb vibration energy by damping.

Carbon nanotubes are believed to be the ultimate low-density high-modulus fibers [7]. All of the benefits associated with composite design could thus be implemented on the nanoscale. Studies have shown that nanocomposites containing single-wall or multi-wall carbon nanotubes (SWCNT and MWCNT) can achieve high damping capacity by taking advantage of the weak bonding and interfacial friction between individual nanotubes and the matrix. This concept was proved by dispersing carbon nanotubes in stiff polymer matrices (epoxies and polycarbonate) [3,8–10]. On the other hand, the effects of carbon nanotubes on the mechanical behavior of elastomeric materials have been recently reviewed [11]. But, to the best of our knowledge, the effect of carbon nanotubes on the damping of elastomeric materials has not been specifically addressed. The aim of this study is to show the effect of SWCNT dispersed in an epoxy elastomer on the damping capacity of the material in an extended temperature range.

2. Experimental

2.1. Materials

SWCNT were purchased from NTP (Nanotech Port, Shenzhen, China). Technical specifications were a diameter < 2 nm, length < 20 μm, purity of CNTs > 90%, amorphous carbon < 5%.

The elastomeric epoxy/amine matrix was formulated using stoichiometric amounts of an epoxy monomer based on diglycidylether

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0266-3538/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2009.01.030

of bisphenol A (DGEBA, Epon 828, Miller-Stephenson), and a polyoxypropylene with average molar mass of 2000, end-capped with primary amine groups (Jeffamine D-2000, Huntsman), as hardener. The cured product had a glass transition temperature located below room temperature implying that the matrix behaved as a cross-linked elastomer at room temperature.

2.2. Oxidation of SWCNT

A conventional process based on the one developed by Liu et al. [12], was used. Basically, 1 g of SWCNT was dispersed in 250 ml of 3:1 H_2SO_4 (98%)/HNO_3 (70%) and submitted to 1 h of sonication followed by 3 h of stirring at room temperature. These conditions were selected to achieve moderate oxidation and maintain a high aspect ratio [13]. After exhaustive washes with deionized water, HCl was added to facilitate the formation of carboxylic acid groups, rather than carboxylate groups [14]. The solution was extensively washed again with deionized water until a constant pH value in the range 5–6 was attained. The acid-treated nanotubes (denoted as SWCNT-COOH) were obtained after centrifugation of the aqueous suspensions and dried overnight in a vacuum oven at 90 °C.

2.3. Synthesis of nanocomposites

Epoxy nanocomposites were synthesized employing 1 wt% pristine SWCNT or 0.5–3 wt% of SWCNT-COOH (the weight refers to the neat mass of carbon nanotubes discounting the mass of organic material lost at 600 °C under nitrogen, calculated from thermal gravimetric analysis). THF was selected as an intermediate solvent for the dispersion of SWCNT because it is a good solvent for DGEBA (the final solvent) and it can be easily eliminated at 50 °C under vacuum. Direct dispersion in DGEBA was not performed because of its high viscosity. SWCNT were dispersed in THF sonicating for 5 min. Following DGEBA addition, the dispersion was sonicated for 20 min and placed overnight in a vacuum oven at 50 °C to allow solvent evaporation. Finally, a stoichiometric amount of hardener was added, followed by further mixing (2 min) and degasification (10 min). The solution was cast into a PTFE mold and cure was performed at 75°C for 3 h, with a subsequent step at 125°C for 3 h.

2.4. Characterization techniques

Thermal gravimetric analysis of unmodified and oxidized SWCNT was performed with a TGA Q500 device (TA Instruments). Samples were heated to 800 °C at 10 °C/min under nitrogen.

The rheological properties of the dispersions of SWCNT-COOH in epoxy/D-2000 precursors were determined at room temperature using an AR-G2 rheometer (TA Instruments). Parallel plate geometry (diameter 25 mm) was used to monitor the viscoelastic response of the suspensions. A linear viscoelastic response characterized the entire range of strain amplitudes used in this work (0.01–100%). A 0.01% strain was used to determine the storage modulus as a function of frequency for the different formulations.

The glass transition temperature of the neat epoxy matrix was determined by differential scanning calorimetry (DSC Q2000, TA Instruments). Samples were heated from −80 °C to 100 °C at 5 °C/min under nitrogen atmosphere.

Dynamic mechanical analysis was performed with a RSA III device (TA Instruments), using a film testing tool. Samples were subjected to sinusoidal displacement of 1% strain at a frequency of 1 Hz, from 25 °C to 200 °C at a heating rate of 5 °C/min.

Scanning electron microscopy (SEM, Zeiss EVO 50) was used to observe the fractured surfaces of the nanocomposites pre-chilled in liquid nitrogen. Samples were sputter-coated with gold prior to SEM observation.

3. Results and discussion

3.1. Oxidation of SWCNT

Fig. 1 shows the weight loss vs. temperature, under nitrogen, for unmodified and oxidized carbon nanotubes. Taking the difference between both curves in the temperature range where they have similar slopes (e.g., from 500 °C to 600 °C), leads to a mass fraction of neat carbon nanotubes equal to 91.4% in the oxidized samples. This value was taken into account to prepare dispersions containing different mass fractions of neat carbon nanotubes. The selected conditions for chemical modification did not produce significant changes in the aspect ratio of the modified nanofibers. Similar results were also reported in the literature [15].

3.2. Rheological and morphological characterization of dispersions of unmodified and oxidized SWCNT in the epoxy precursors

The reaction between DGEBA and Jeffamine D-2000 is very slow at room temperature enabling to perform a frequency sweep without and significant advance in conversion (as assessed by monitoring the viscosity before and after the rheological characterization). Fig. 2 shows the frequency dependence of the storage modulus for dispersions containing 1 wt% SWCNT-unmodified or SWCNT-COOH in the epoxy precursors. In both cases, the solid-like behavior related to the constancy of G' in the low-frequency range, indicates a good dispersion of carbon nanotubes in the epoxy precursors characterized by the rheological percolation of the nanofillers [16,17]. The higher storage modulus observed for SWCNT-COOH implies that the oxidation procedure led to a better dispersion of carbon nanotubes [18]. This may be explained by the decrease in the average size of bundles of carbon nanotubes produced by the acid treatment.

The effect of SWCNT-COOH concentration on the storage modulus is shown in Fig. 3. For concentrations comprised between 0.5 and 3 wt%, a solid-like behavior was observed. A power law relation can be used to determine the threshold of rheological percolation [16]:

$$G' \sim (\text{wt\%} - \text{wt\%}_{\text{crit}})^{\beta} \quad (1)$$

where $\text{wt\%}_{\text{crit}}$ is the rheological percolation threshold and β is the critical percolation exponent.

Fig. 4 shows an excellent regression obtained for a critical percolation threshold equal to 0.41 wt%. The percolation threshold depends on several parameters such as the selected source and

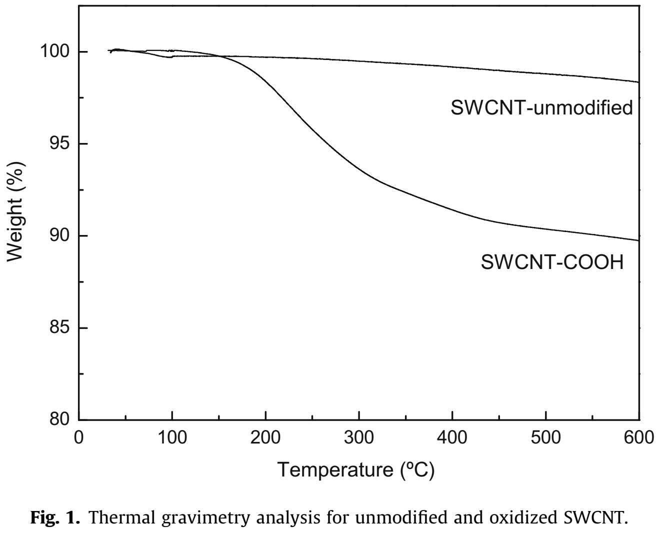

Fig. 1. Thermal gravimetry analysis for unmodified and oxidized SWCNT.

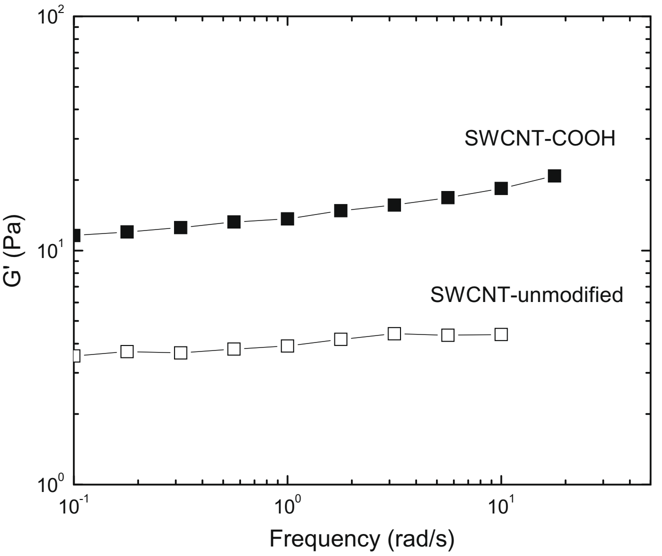

Fig. 2. Frequency response of the storage modulus for dispersions containing 1 wt% SWCNT-unmodified or SWCNT-COOH in epoxy precursors.

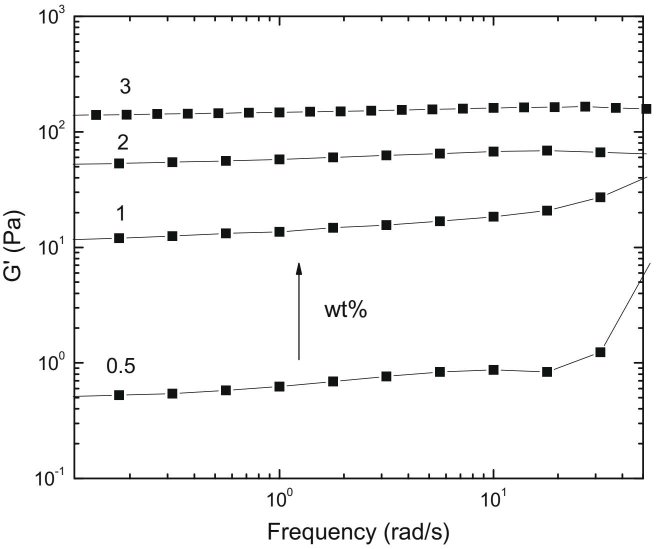

Fig. 3. Frequency response of the storage modulus for dispersions of SWCNT-COOH in epoxy precursors containing different mass fractions of carbon nanotubes.

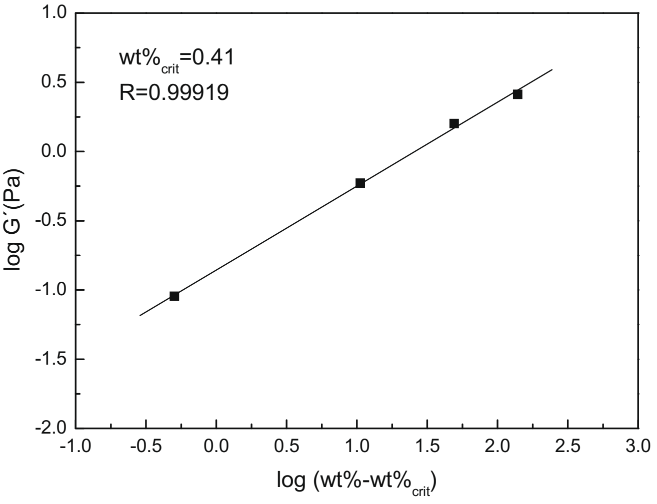

Fig. 4. Power law plot of G' vs. reduced weight percent on a logarithmic scale.

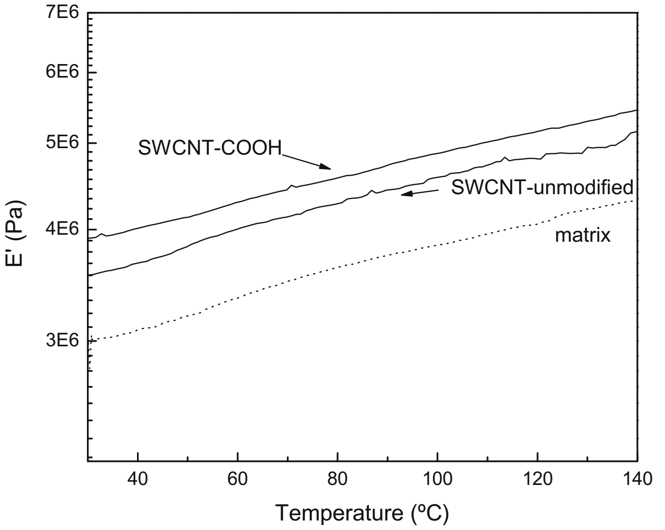

Fig. 5. Storage modulus as a function of temperature for the neat epoxy elastomer (matrix) and nanocomposites containing 1 wt% SWCNT-unmodified or SWCNT-COOH.

aspect ratio of the SWCNTs, the chemical modifications carried out and the method and nature of the solvent used to produce the dispersion. The critical exponent found in our case lies in the range of values reported in the literature for dispersions containing small bundles of SWCNT with a modest aspect ratio [9,19,20]. The experimental value found for the critical exponent was $\beta = 1.65$. For aqueous suspensions of SWCNT, Hough et al. [21] and Islam et al. [22] reported a percolation exponent equal to 2.3 that could be compared with the value of 2.1 reported for simulations of percolating bonds that resist stretching but are free to rotate [23]. A lower value of the critical exponent, $\beta = 0.70$, was reported for dispersions of SWCNT in poly(methyl methacrylate) [16].

3.3. Viscoelastic properties of epoxy elastomers containing unmodified and oxidized SWCNT

The neat epoxy matrix was characterized by DSC. The glass transition temperature was $T_g = -46$ °C implying that the material behaves as a cross-linked elastomer at room temperature.

The effect of the oxidation procedure was assessed by comparing viscoelastic properties of elastomers containing 1 wt% unmodified SWCNT or SWCNT-COOH. Fig. 5 shows the storage modulus as a function of temperature in the 30–140 °C range, for the neat epoxy elastomer (matrix) and nanocomposites containing 1 wt% SWCNT-unmodified or SWCNT-COOH. For the three samples the elastic modulus increased with temperature indicating the dominant entropic contribution to the elastic behavior. Modification with both types of carbon nanotubes led to an increase in the elastic modulus. This is explained by the strain energy contribution due to the bending/unbending of the initial waviness of carbon nanotubes [11]. The increase in modulus was larger for SWCNT-COOH (about 30% at room temperature), possibly reflecting the better quality of the dispersion of oxidized nanotubes in the final material.

The damping capacity of the nanocomposites is usually measured by the increase in the loss modulus with respect to the one of the matrix [3,9,10]. Fig. 6 shows the loss modulus as a function of temperature for the neat epoxy elastomer (matrix) and nanocomposites containing 1 wt% SWCNT-unmodified or SWCNT-COOH. The addition of carbon nanotubes produced a significant increase in the damping capacity of the cross-linked elastomer in the investigated temperature range. The relative increase is higher

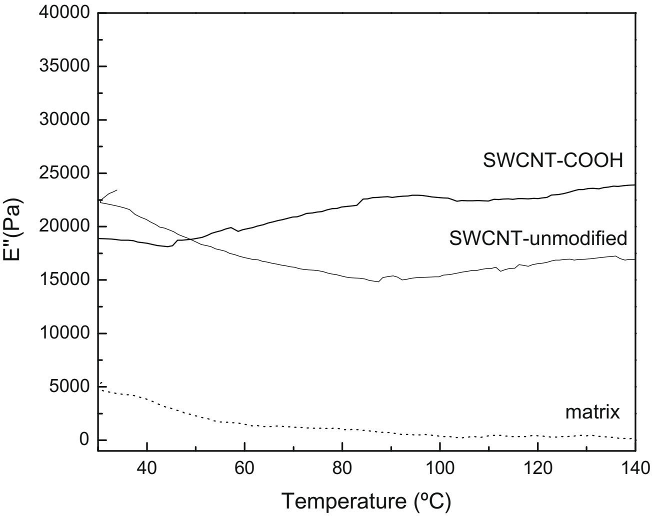

Fig. 6. Loss modulus as a function of temperature for the neat epoxy elastomer (matrix) and nanocomposites containing 1 wt% SWCNT-unmodified or SWCNT-COOH.

at high temperatures where the matrix exhibited a very low value of the loss modulus. It is significant that the better dispersion of oxidized nanotubes, reflected in the higher value of the storage modulus, did not improve the loss modulus (at room temperature the loss modulus was higher for pristine nanotubes than for the oxidized ones). Considering the mechanism of energy dissipation derived from frictional sliding at the nanotube polymer interface [9], adhesion of nanotubes to the polymer matrix should produce a deleterious effect on the damping capacity. Functionalization of carbon nanotubes with COOH groups might produce covalent bonding to the matrix by reaction with epoxy groups [13], although in the absence of a catalyst this reaction should occur at a slower rate than the epoxy-amine reaction. Even in the absence of covalent bonds, H-bonding between COOH groups attached to carbon nanotubes and hydroxyl, ether or tertiary amine groups of the cross-linked network can explain the adhesion increase with a corresponding decrease of the damping capacity. An alternative explanation is that an additional damping mechanism based on tube–tube sliding in bundles, contributes significantly to the overall energy dissipation [1,2].

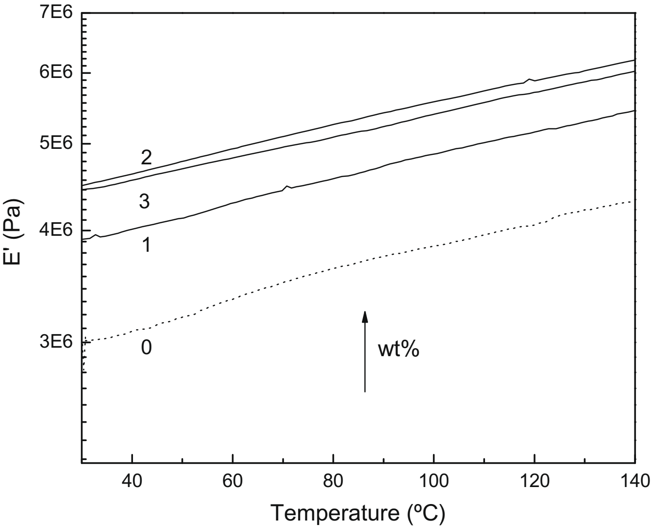

Fig. 7. Storage modulus as a function of temperature for the neat epoxy elastomer (matrix) and nanocomposites containing 1–3 wt% SWCNT-COOH.

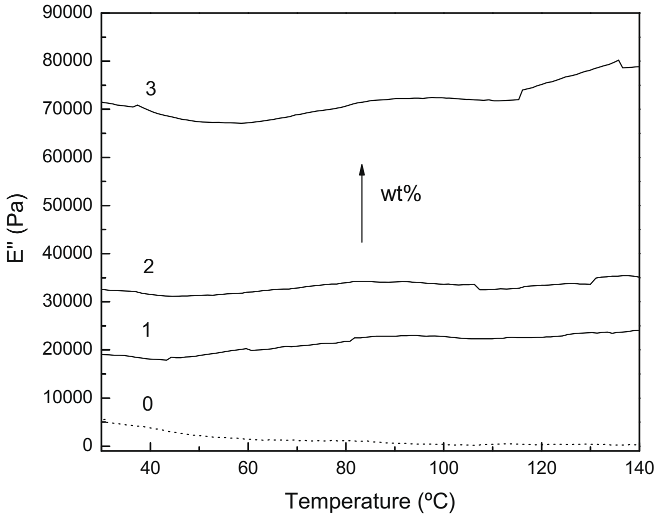

Fig. 8. Loss modulus as a function of temperature for the neat epoxy elastomer (matrix) and nanocomposites containing 1–3 wt% SWCNT-COOH.

Increasing the concentration of SWCNT-COOH in the cross-linked elastomer increases the storage modulus as is shown in Fig. 7. However, in the range of 2–3 wt% no variation of the storage modulus was observed, possibly due to the decrease in the quality of the dispersion (e.g., increase in the bundling of nanotubes when increasing their concentration). But what is relevant is the fact that this effect is not present in the loss modulus, as shown in Fig. 8. A 14-times increase in the loss modulus at room temperature was observed for the elastomer containing 3 wt% SWCNT-COOH, compared with a 6.5-times increase for the material with 2 wt% of oxidized nanotubes. Therefore, it may be inferred that the presence of a nanotube–nanotube sliding mechanism contributes significantly to the loss modulus of the material with 3 wt% SWCNT-COOH.

The state of the dispersion of the SWCNT-COOH in the epoxy nanocomposites was corroborated by SEM micrographs (Fig. 9). Although it is difficult to analyze the quality of dispersion from these images, they clearly show the degree of agglomeration obtained with samples containing 2 wt% and 3 wt% of SWCNT-COOH (bundles are indicated with arrows), which justify the results obtained during the viscoelastic experiments. In general, the average size of bundles was larger for 3wt% SWCNT-COOH (Fig. 9c) than for 2 wt% SWCNT-COOH (Fig. 9b).

As shown in Figs. 6 and 8, the loss modulus of the nanocomposites is practically independent of temperature meaning that mechanisms contributing to energy dissipation keep their activity in the whole temperature range. This is to be compared with the loss modulus of the matrix that exhibits a continuous decrease with temperature. Therefore, the dispersion of carbon nanotubes in the cross-linked elastomer produced materials exhibiting damping capacity at high temperatures, a fact that can find several practical applications as light-weight and robust damping components that can be easily integrated into the heterogeneous composite structures.

4. Conclusions

Epoxy elastomers containing oxidized single-wall carbon nanotubes exhibited a high damping capacity in an extended temperature range. Mechanisms contributing to energy dissipation kept their activity when increasing temperature while the matrix showed no intrinsic mechanism at high temperatures. A significant finding was that an increase in nanotube concentration from 2 wt% to 3 wt% did not improve the storage modulus but produced a

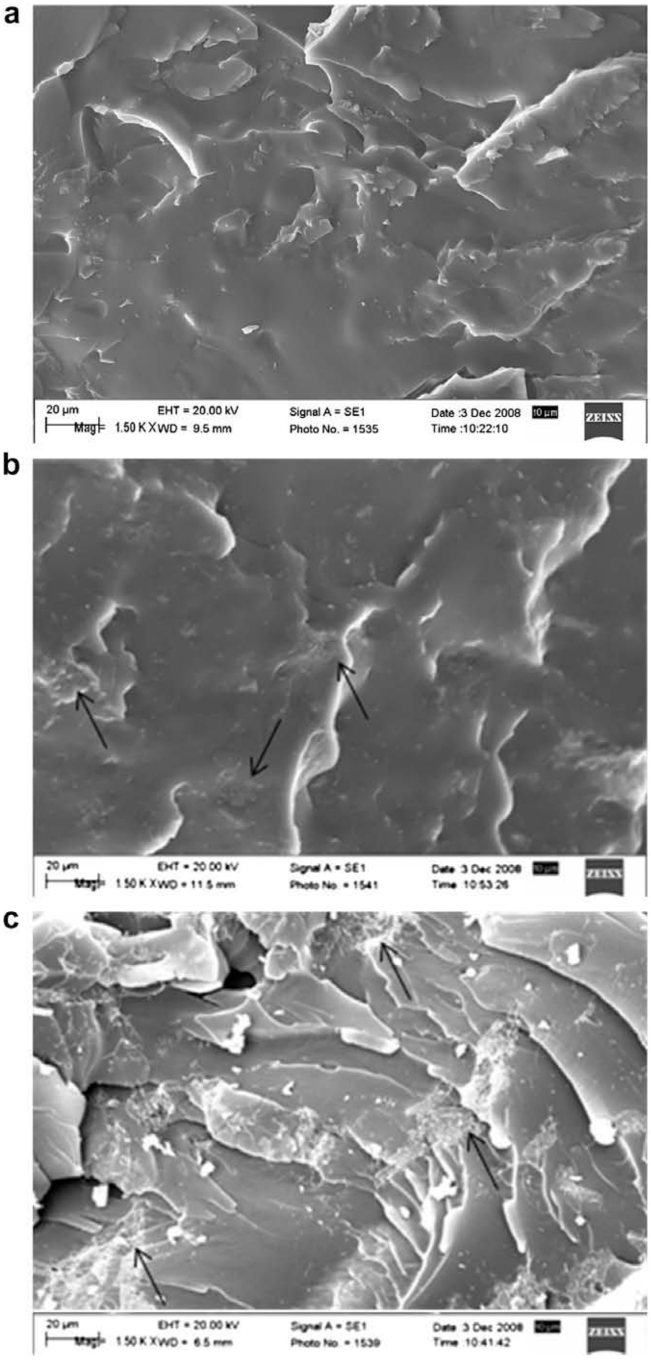

Fig. 9. SEM micrographs of fracture surfaces of nanocomposites containing (a) 1 wt% SWCNT-COOH, (b) 2 wt% SWCNT-COOH and (c) 3 wt% SWCNT-COOH. Bundles are indicated with arrows.

significant increase in the loss modulus. The lack of improvement of the elastic modulus was explained by the bundling of nanotubes and the effect on the loss modulus by the significant contribution of nanotube–nanotube sliding to energy dissipation (additional to the nanotube–matrix sliding).

Acknowledgements

Prof. Maria L. Auad acknowledges the support of the Polymer and Fiber Eng. Department and Department of Commerce. The financial support of University of Mar del Plata, Research Council of Argentina (CONICET) and ANPCyT (Argentina) is gratefully acknowledged.

References

[1] Koratkar N, Wei B, Ajayan PM. Carbon nanotubes films for damping applications. Adv Mater 2002;14(13):997–1000.
[2] Suhr J, Zhang W, Ajayan PM, Koratkar N. Viscoelasticity in carbon nanotube composites. Nat Mater 2005;4:134–7.
[3] Suhr J, Zhang W, Ajayan PM, Koratkar NA. Temperature-activated interfacial friction damping in carbon nanotube polymer composites. Nano Lett 2006;6:219.
[4] Zinoviev PA, Ermakov YN. Energy dissipation in composite materials. PA: Technomic Publishing Company; 1994.
[5] Jones DG. Handbook of viscoelastic vibration damping. New York: J. Wiley; 2001.
[6] Brodt M, Lakes RS. Composite-materials which exhibit high stiffness and high viscoelastic damping. J Compos Mater 1995;14:1823–33.
[7] Krishnan A, Dujardin E, Ebbesen TW, et al. Young modulus of single-walled nanotubes. Phys Rev B. 1998;58(20):14013–9.
[8] Zhou X, Shin E, Wang KW, Bakis CE. Interfacial damping characteristics of carbon nanotube-based composites. Compos Sci Technol 2004;64:2425.
[9] Koratkar NA, Sur J, Joshi A, Kane RS, Schadler LS, Ajayan PM, et al. Characterizing energy dissipation in single-walled carbon nanotube polycarbonate composites. Appl Phys Lett 2005;87:63102.
[10] Rajoria H, Jalili N. Passive vibration damping enhancement using carbon nanotube-epoxy reinforced composites. Compos Sci Technol 2005;65:2079–93.
[11] Cantournet S, Boyce MC, Tsou AH. Micromechanics and macromechanics of carbon nanotube-enhanced elastomers. J Mech Phys Solids 2007;55:1321–39.
[12] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, et al. Fullerene Pipes. Science 1998;280:1253–6.
[13] Zhu J, Kim J, Peng H, Margrave JL, Khabashesku VN, Barrera EV. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. Nano Lett 2003;3:1107–13.
[14] Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, et al. Solution properties of single-walled carbon nanotubes. Science 1998;282:95.
[15] McIntosh D, Khabashesku VN, Barrera EV. Benzoyl peroxide initiated in situ functionalization, processing, and mechanical properties of single-walled carbon nanotube-polypropylene composite fibers. J Phys Chem C 2007;111:1592–600.
[16] Du F, Scogna RC, Zhou W, Brand S, Fischer JE, Winey KI. Nanotube networks in polymer nanocomposites: rheology and electrical conductivity. Macromolecules 2004;37:9048–55.
[17] Fan Z, Advani SG. Rheology of multiwall carbon nanotube suspension. J Rheol 2007;51(4):585–604.
[18] Moniruzzaman M, Winey KI. Polymer nanocomposites containing carbon nanotubes. Macromolecules 2006;39:5194–205.
[19] Shaffer MSP, Fan X, Windle AH. Dispersion and packing of carbon nanotubes. Carbon 1998;36(11):1603–12.
[20] Kinloch IA, Roberts SA, Windle AH. A rheological study of concentrated aqueous nanotube dispersions. Polymer 2002;43(26):7483–91.
[21] Hough LA, Islam MF, Janmey PA, Yodh AG. Viscoelasticity of single wall carbon nanotube suspensions. Phys Rev Lett 2004;93:168102–4.
[22] Islam MF, Rojas E, Bergey DM, Johnson AT, Yodh AG. High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. Nano Lett 2003;3:269–73.
[23] Sahimi M, Arbabi S. Mechanics of disordered solids II. Percolation on elastic networks with bond-bending forces. Phys Rev B 1993;47:703–12.