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Effect of dispersion of MWCNTs on the static and dynamic mechanical behavior of epoxy matrix nanocomposites

G. C. Papanicolaou · K. P. Papaefthymiou ·
A. F. Koutsomitopoulou · D. V. Portan ·
S. P. Zaoutsos

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Abstract In this investigation, specimens of MWCNT-epoxy nanocomposites were prepared by two different dispersion methods including the use of ultrasonication, and high speed shear mixing. The dispersion degree between MWCNT and polymer resin was analyzed after completing the curing reaction, by scanning electron microscopy. The effect of the nanotubes dispersion achieved on the properties of the manufactured nanocomposite was analyzed through static three point bending tests and dynamic mechanical thermal analysis. Interesting results concerning the dispersion effect of MWCNTs added to the polymer matrix on the storage and loss moduli as well as on tanδ and T_g values of the specimens manufactured by the sonication and high speed shear mixing methods were derived.

Introduction

In order to make much stiffer, light weight and high performance material products, polymer nanocomposites play an emerging role in the material innovation. Unlike other plastics, polymer nanocomposites are fabricated by introducing a small amount of solid nano-scale fillers (normally less than 5 wt%) such as nano-clay, carbon nanotubes or nanofibers into a plastic resin to dramatically enhance its stiffness, strength, and thermal properties [1, 2]. The difference between nanocomposites and conventional fiber composites is that the added fillers are extremely small, only one-millionth of a millimeter thick, and provide a much larger interface area per unit volume for greatly improving the interfacial bonding effect between nanofillers and the polymer matrix [3, 4]. As it has been reported by Eitan et al. [5], the large nanotube surface area in a nanotube-polymer composite results in a significantly thick interphase region of immobilized polymer which contributes as a supplementary reinforcement mechanism for the composite.

Some recent investigations show that the length of nanofibers/nanotubes plays an important role in the toughening mechanism of nanocomposites [6, 7]. Therefore, in this study, long MWCNT, whose length reaches 1–25 μm, have been added as reinforcement on epoxy resins. However, these large lengths difficult the MWCNTs separation necessary to reach a homogeneous distribution in the matrix, avoiding entanglement, and clustering effects.

The dispersion of the CNTs in the matrix system is a main problem to be solved for nanotube-reinforced polymers [8]. Nano-scaled particles exhibit an enormous surface area (1000 m^2/g and more), which is several orders of magnitude larger than the surface of conventional fillers. This surface area acts as interface for a stress transfer, but is also responsible for the strong tendency of the CNTs to form agglomerates. At present, an extended research activity related with carbon nanotubes reinforced polymer

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G. C. Papanicolaou (✉) · K. P. Papaefthymiou ·
A. F. Koutsomitopoulou · D. V. Portan
Composite Materials Group (CMG), Department of Mechanical and Aeronautics Engineering, University of Patras, 26500 Patras, Greece
e-mail: gpapan@mech.upatras.gr

D. V. Portan
Faculty of Applied Chemistry and Materials Science, University Politehnica, Spl. Independentei 313 1, Bucharest, Romania

S. P. Zaoutsos
Laboratory of Advanced Materials and Constructions (LAMCO), Department of Mechanical Engineering, Technological Educational Institute of Larissa, 41110 Larissa, Greece

composites and other possible applications of CNT's is being carried out in an effort to exploit their unique behavior. To a large extent, this can be achieved by improving the dispersion conditions of the nanofillers in the resin which leads to better wetting of the nanotubes and increasing of the surface contact area between the constituent phases [9–13].

The dispersion of nanotubes in the matrix can be enhanced through physical–mechanical or chemical processes. Physical methods involve breaking up the agglomerates through impact (ball milling), shear (high speed shearing), and high frequency oscillation (ultrasonication) or a combination of them. Concerning the chemical methods, purification procedure involves: removal of the metallic catalyst residues, which arise from CNT synthesis and creation of functional groups on the surface or caps of the CNTs. These functional groups are the reactive sites of the CNT surfaces during further chemical modifications. They can also improve the polymer-CNT interfacial interactions. Therefore, results from TGA analysis by Aviles et al. [14] report a compromise between the functionalization parameters (sonication, concentration of acid treatment, etc.) and damage of the graphitic structure of CNT's.

In this study, two different dispersion methods, namely high speed shear mixing and ultrasonication, were applied for the manufacturing of MWCNT-Epoxy nanocomposites. The aim of this study was to investigate the quality of dispersion that can be achieved by the different methods applied for a given filler weight fraction, as well as the efficiency of the dispersion methods applied on the basis of the nanocomposites static and dynamic thermomechanical behavior. Thus, the quality of dispersion of the nanotubes in the cured materials was evaluated through scanning electron microscopy. The materials' static and dynamic thermomechanical response were studied by means of static three-point bending and DMTA tests, respectively. Experimental results indicated that the intensity of ultrasonic dispersion can more efficiently exfoliate the nanotubes in the resin, though is thought to be responsible for shifts in the transition temperature and energy dissipation damage on account of the damage caused in polymer chains and CNTs sidewalls during processing. The quality of dispersion achieved by high speed shearing was inferior leading to limited aggregation of the CNT's; however, the nanocomposites derived presented improved thermostability.

High speed shear mixing

A practical method of producing MWNT/polymer composites is high speed shear mixing. At a given temperature, the dispersion efficiency is related to the exfoliation of agglomerates as a result of the stress fields developed due to the shear flow and also to the diffusion of nanoparticles in the resin [15–17]. Results showed that some breakage of the MWCNT's does occur during processing and that mean tube length decreases with increasing mixing energy input into the system [18, 19]. However, the rate at which mean tube length is reduced diminishes as the material is dispersed through the matrix and tube separation distance increases. Hence, tube breakage may not be a serious problem, and good dispersion can therefore be achieved at the expense of an acceptable reduction in tube length.

Ultrasonication

High intensity ultrasonication is a widespread technique for dispersing nanotubes into polymers or liquids in general [20, 21]. During sonication the sound waves that propagate into a liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. This applies mechanical stress on the attracting electrostatic forces (e.g., van der Waals forces). Ultrasonic cavitation in liquids causes high speed liquid jets of up to 1000 km/h. Such jets press liquid at high pressure between the particles and separate them from each other. This makes ultrasound an effective means for the dispersing and de-agglomeration but also for the milling and fine grinding of micron-size and sub micron-size particles.

Dynamic mechanical thermal analysis (DMTA)

The DMTA imposes a sinusoidal stress on a sample for the determination of the material's storage modulus, E' and loss modulus, E'', as well as the tangent of dissipation coefficient, tanδ, as a function of temperature and/or frequency. As the temperature increases, the deformation frequency reaches the frequency set, leading to a peak on the curve (tanδ). The DMTA is a method with great sensitivity in detecting changes in intrinsic molecular mobility. Moreover, the apparent activation energy can be calculated from the glass transition temperatures (T_g) measured at specific frequencies. Secondary (β-) or tertiary (γ-) relaxations in the glassy state can also be studied as well as the glass transition α-relaxation process.

Dynamic loadings cause a more complex damage in structures than static loadings. High damping structures and high damping materials can effectively attenuate vibration. Damping behavior is a fundamental concept in dynamic analysis. The damping factor is defined as the phase difference between excitation and response and reflects a material's capacity for energy absorption. In fiber-reinforced composites, interfaces between fibers and the matrix play a major role in damping. For polymer materials, DMTA is widely used to obtain the loss factor, which is linked with damping properties [22]. The different sources of energy dissipation in both fiber and nanotube-reinforced composites are [23]:

(a) *Viscoelastic and viscoplastic damping* The major contribution to composite damping is due to matrix. However, the fiber damping must be included in the analysis for fibers having high damping as compared to other types of fiber. At large amplitudes of vibration/high stress levels, especially an evident degree of non-linear damping can exist due to the presence of high stress and strain concentration in local regions between fibers [24].

(b) *Interphasial damping* [25] Interphase, is the region adjacent to fiber surface all along the fiber length containing both areas of adsorption interaction in nanotube surface layers as well as areas of mechanical imperfections such as voids, flaws, impurities, positions of imperfect adhesion, etc. The interphase, having different thermomechanical and viscoelastic behavior than the nanotubes and the bulk matrix, considerably affects the behavior of the entire composite system. The properties of the interphase can be used to describe quantitatively the quality of adhesion between the matrix and the filler particles [26–28].

(c) *Damping due to friction* Frictional damping is due to slip in the unbound regions between fiber and matrix interface or delaminations [29, 30].

(d) *Damping due to internal damage* Damping due to energy dissipation in the area of matrix cracks, broken fibers, etc. [31].

(e) *Thermoelastic damping* It is due to cyclic heat flow from the region of compressive stress to the region of tensile stress in the composite. Thermoplastic composites show high temperature rise which is a function of applied load, frequency, sample thickness and number of cycles [32].

Experimental

Materials

An epoxy system type R921 was used as matrix along with a polyamine curing agent system type 172012, reinforced with Multi-Walled Carbon Nanotubes with diameter 10–40 μm and length 1–25 μm, all provided by Fibermax S.A. Two different methods were applied for the dispersion of the nanofiller particles in the resin, namely ultrasonication and high speed shearing.

Methods applied

SEM microscopy

Scanning electron microscopy (SEM) was applied in order to evaluate the degree of agglomeration of the nanotubes in the resin and accordingly the efficiency of the dispersion methods.

Ultrasonication

The ultrasonication (or sonication) method involved the dispersion of the nanotubes in the epoxy resin in the absence of any organic or inorganic solvents. The ultrasonic homogenizer used was a SONOPULS HD 2200 manufactured by BANDELIN S.A with a maximum power of 200 W. The ultrasonic power was transmitted in the mixture through a probe incorporating a titanium flat tip. The following procedure was adopted for the dispersion of the nanotubes in the resin: the resin was placed in a pot, the nanotubes were added and the mixture was pre-heated at 50 °C in order to achieve a sufficiently low viscosity value and to make the ultrasonication feasible. The ultrasonication time was fixed at 20 min during which the temperature of the mixture was limited to a maximum of 60 °C by circulating cold water circa the pot.

High-speed shearing

High-speed shearing at controlled conditions of temperature and shearing rate was utilized to disperse the nanotubes in the resin. The device used was a high speed dissolver type Dispermat AE, VMA Getzmann GmbH consisting of a dissolver disk and a mixer shaft, powered by an electric motor. As the disk was set to rotation it generated a turbulence free movement of the resin (doughnut effect), through which the powdery component was stirred into the liquid component. After several preliminary tests, the process was optimized as follows: The resin was pre-heated at 50 °C, the nanotubes were added and the mixture was shear-mixed at 1500 rpm for 15 min. Throughout the high-speed shearing process the temperature of the resin was monitored and limited to no more than 60 °C by placing the mixing pot in a bath filled with cold water. After the shearing process was completed, the mixture was finally inserted in a vacuum chamber for 20 min in order for the entrapped air to be released.

After dispersion process of the nanotube was completed the hardener was added at a ratio of 17 P.H.R. The mixture was finally, infused into special moulds having the exact dimensions of the specimens to be used. The material was then cured for 24 h at 80 °C. The fiber loading applied was 0.1 wt% in MWCNT’s. After post-curing for 24 h at room temperature each specimen was polished with two types of sand paper in order to eliminate local surface cracks and surface material heterogeneities.

Three-point bending tests

A series of three point bending tests was performed for the characterization of the material static linear elastic response. All tests were performed at room temperature using an INSTRON 4301 universal testing machine with a constant displacement rate of 1 mm/min. The results obtained represent the mean values from at least five successful tests. In all cases, the specimens' dimensions were $100 \times 12.8 \times 2.2$ mm^3 (±0.2 mm) and the span between the grips was fixed at 63 mm.

DMTA testing

The materials' dynamic thermo-mechanical response was investigated by the means of DMTA tests. All tests were performed in dual cantilever bending mode with maximum amplitude of 35 μm at a constant frequency of 1 Hz using a TA Instruments Q800 dynamic mechanical analyzer. Data were collected from ambient temperature to 160 °C, with a temperature ramp of 3 °C/min. For each condition considered five tests were performed in order to confirm the reliability of experimental results. The specimens' dimensions were $75 \times 10 \times 2$ mm^3 (±0.2 mm) and the span between the grips was fixed at 70 mm.

Results and discussion

SEM fractography

Figure 1a–d shows SEM images of the 0.1 wt% MWCNT-EPOXY nanocomposite prepared by means of the high speed shearing method. Figure 1a illustrates a low magnification-high detail image of an area of several thousand square μm incorporating regions of associated or dispersed nanotubes. As it can be observed, in a composite prepared by shear mixing there can be observed the two possible states (exfoliated and agglomerated) that one can deduce. From these figures it can be seen that individual nanotubes are scattered in the matrix while some aggregation is observed. High magnification images of regions where nanotubes are agglomerated or exfoliated can be observed in Fig. 1b, c, respectively. In both micrographs there can be observed pulled-out nanotubes. As it is indicted by the arrow in Fig. 1b, another existing failure mechanism is the "sword-in-sheath" rapture of CNT's meaning failure of the nanotube's outer one or more graphitic layers. Subsequent relative sliding attributed to weak interlayer Van der Waals bonds. Finally, in Fig. 1d there can be observed a region where no agglomerates of MWCNT's are present.

Figure 2a illustrates a low magnification-high detail SEM image of a 0.1 wt% MWCNT-Epoxy nanocomposite prepared by means of sonication method. A higher magnification image of the same region can be observed in Fig. 2b. From these figures it can be seen that individual nanotubes are scattered in the matrix and no aggregation is observed. However, in this case, nodules up to 10 nm across have been detected which are stated to be volumes of higher cross-link density in a matrix of relatively lower cross-link density. These nodules tend to be aligned in clumps of the order of 100 nm in the direction of fracture propagation and lead to a granular structure.

The aligned nodules and resulting grain are shown in Fig. 2. In addition, in Fig. 2b, it can be seen that the grain produces a feather pattern. The fracture progresses in a finger-like manner on a series of curved fronts. These crack fronts may be initiated and progress on slightly different planes and where they meet the small perturbations of the fracture plane necessary for convergence result in the well-known river markings. As the fracture progresses the planes further converge, the direction of confluence of the rivers thus giving a clear indication of the direction of local crack propagation.

Mechanical characterization

A comparison between flexural properties of the neat resin and the nanocomposites manufactured by the two methods is shown in Table 1. As can be seen, nanocomposites manufactured by the high speed shearing method showed a 3.25% increase in flexural modulus while those prepared by the sonication method showed a respective increase of 26.6% when compared with the neat resin modulus. Concerning the flexural strength, again the addition of nanotubes resulted in an enhancement which in the case of the shearing method was on the order of 8.5% while for the sonication method the respective increase was 19.1%. So, in both methods there is an increase in values of both flexural modulus and strength, in comparison to the respective values for the neat resin, with the sonication method to always be superior. Moreover, in the case of high speed shearing, the deviation from the rule of mixtures confirms the observation of coexistence of CNT's in dispersed and agglomerated states observed through SEM images (Fig. 1). Accordingly, the good quality of dispersion in the case of the ultrasonication method that was evaluated by the SEM micrographs (Fig. 2) is further confirmed by the convergence of the experimental results to the law of mixtures, which among others, assumes perfect dispersion of fillers into the resin.

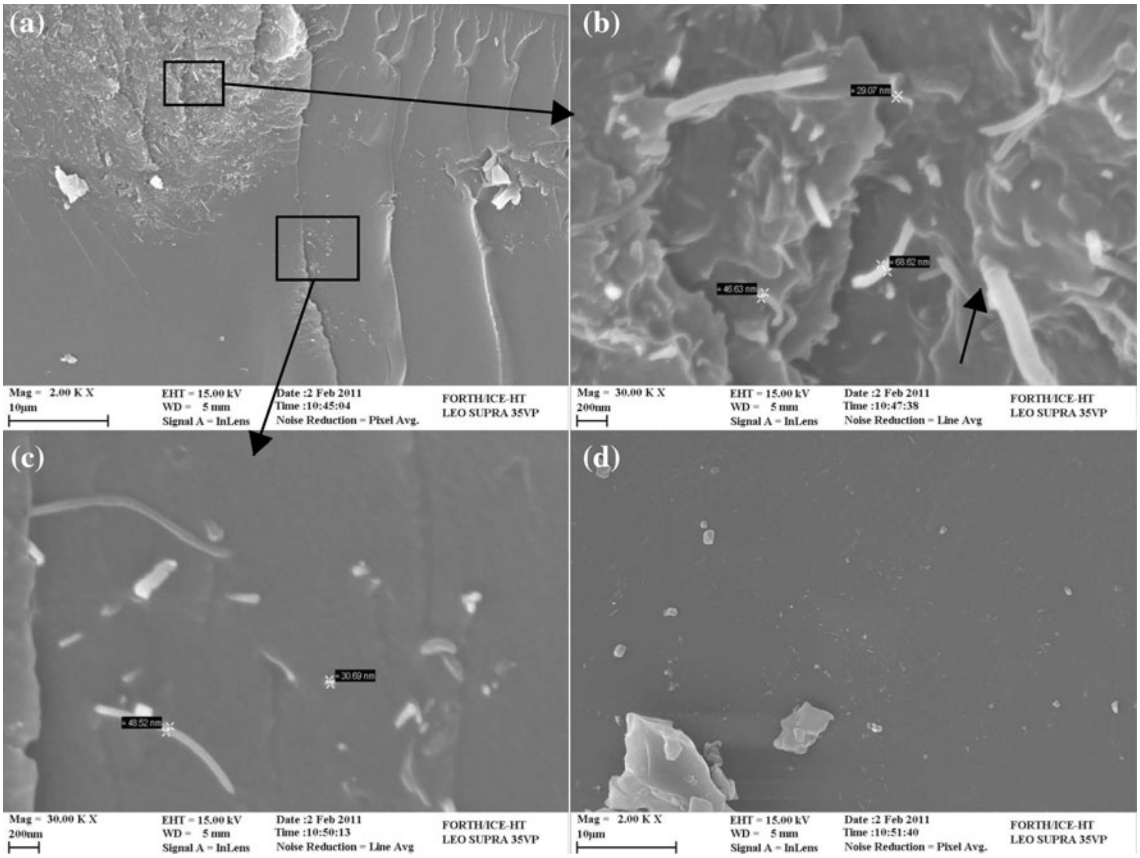

Fig. 1 SEM images at various magnifications of the 0.1 wt% MWCNT-EPOXY nanocomposite manufactured by means of the high speed shearing method. **a** Low magnification-high detail image illustrating regions agglomerated and exfoliated CNT's coexisting. **b** High magnification image of a CNT bundle. The *arrow* indicates "sword-in-sheath" rupture of CNT's. **c** High magnification image of a dispersed pulled out CNT's. **d** Low magnification-high detail image illustrating a region where no agglomeration of CNT's is observed

A possible advantage of the high speed shearing dispersion method is the homogeneous introduction of shear forces over the whole volume of the composite, while the sonication process introduces the energy locally. For this reason we do not expect a significant shortening of the nanotubes caused by the sonication processing. However, on the other hand, sonication results in a decrease of the resin viscosity which, in turn, has a dual effect on the nanocomposite structure. The first, concerns the better wetting and more homogeneous adhesion between matrix and fillers, leading to the superior mechanical properties, while the second one, has to do with the increased kinetics of polymer macromolecules and free volume of the system which, in turn, as it will be shown in the next section, will result in a decrease of the glass transition temperature.

DMTA results

Nanocomposites manufactured by the shearing method

The effect of the incorporation of nanotubes on the dynamic mechanical behavior and the T_g of the produced nanocomposite and the neat epoxy polymer were observed by DMTA analysis at dual cantilever bending mode. The dissipation factor (tanδ) is defined as the ratio of the loss modulus and the storage modulus. Its value at peak shows the glass transition temperature. The T_g can also be determined on the basis of the storage modulus, E' (as the temperature at the midpoint of the descent) and the loss modulus, E'' (as the temperature at peak). However, the T_g derived from the tanδ peak is considered the most reliable since it comprises both the E' and E''. Consequently, the values of T_g discussed hereinafter will correspond to the tanδ, except otherwise stated.

The storage modulus, the loss modulus and tanδ profiles versus temperature for the neat epoxy matrix and the nanocomposite system manufactured by the shearing and sonication methods can be observed in Figs. 3, 4, 5. As it can be observed, the T_g can vary up to 20 °C on the basis of the dynamic property from which it derives regardless of the material considered. The nanocomposites manufactured by the shearing method exhibit a maximum increase by 25 °C in the T_g derived from the tanδ with respect to the neat resin. The nanocomposite exhibited, also, an increase

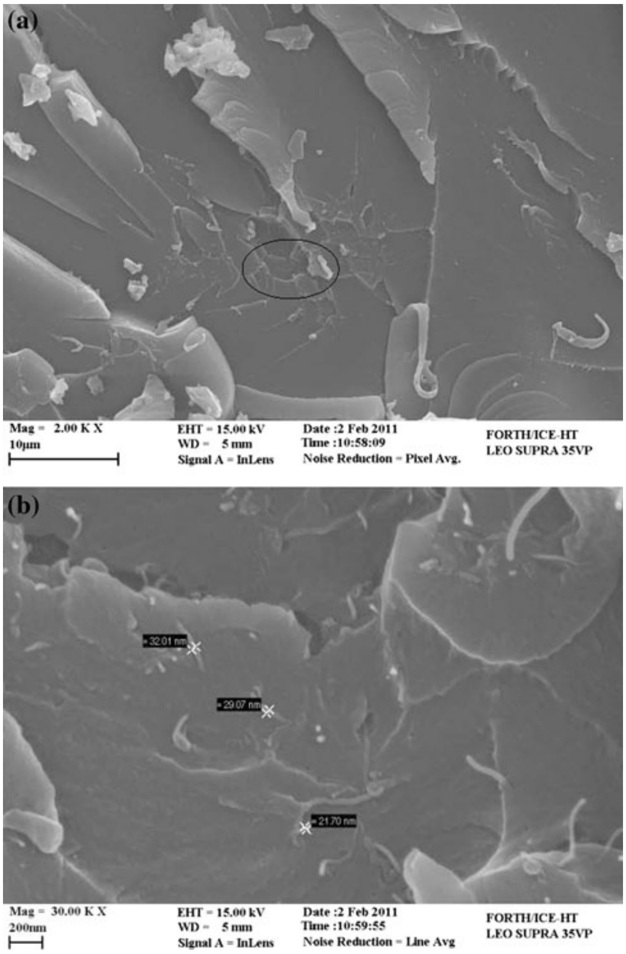

Fig. 2 SEM images of the 0.1 wt% MWCNT-EPOXY nanocomposite manufactured by means of the sonication method at **a** Low magnification-high detail and **b** High magnification-high detail from which no agglomeration of CNT's is observed

Table 1 Flexural properties and glass transition temperatures of the neat resin and the nanocomposites manufactured by the two methods and comparison with the rule of mixtures

Static and transition properties			
Sample	E_{flex} (GPa)	σ_{flex} (MPa)	T_g (°C)[b]
Neat Resin	2.9	85.8	101
0.1 wt% Shearing	3.0	93.0	126
0.1 wt% Sonication	3.7	102.2	85
0.1 wt% Rule of mixtures[a]	3.89	–	–

[a] $E_{\mathrm{CNT}} = 1.3$ [1] [TPa] $\rho_{\mathrm{CNT}} = 1.4$ [1] (g cm^{-3})

[b] Determined from tanδ

in the storage modulus. It might be implied that the used nanofiller increases the glass transition temperature of the soft-phase by restricting segmental chain motion and generating an interphase region.

These restriction effects result in broadening the tanδ peak, decrease in intensity (height) of this peak, and

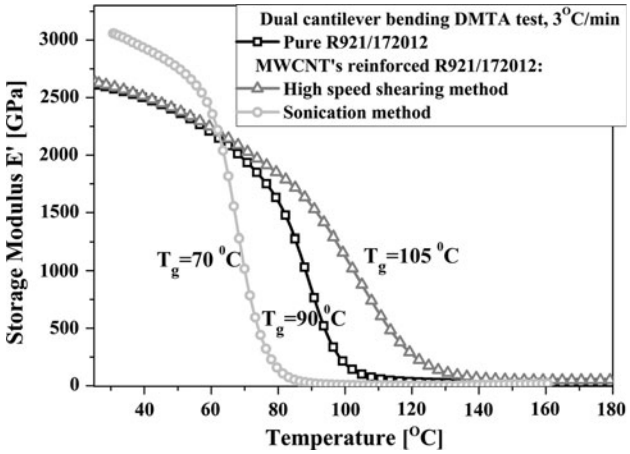

Fig. 3 Comparison of storage modulus, E', profiles versus temperature for the neat resin and the MWCNT-Epoxy nanocomposite manufactured by means of the two methods applied

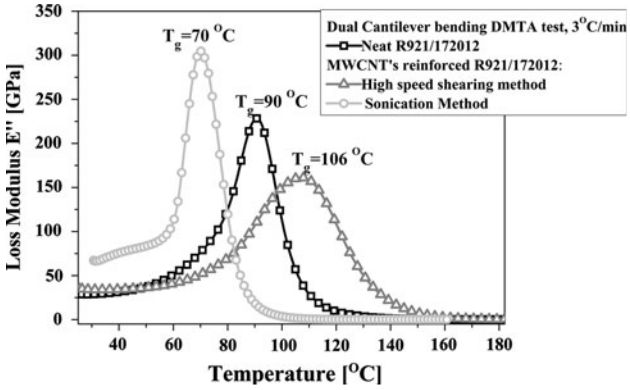

Fig. 4 Comparison of loss modulus, E'', profiles versus temperature for the neat resin and the MWCNT-Epoxy nanocomposite manufactured by means of the two methods applied

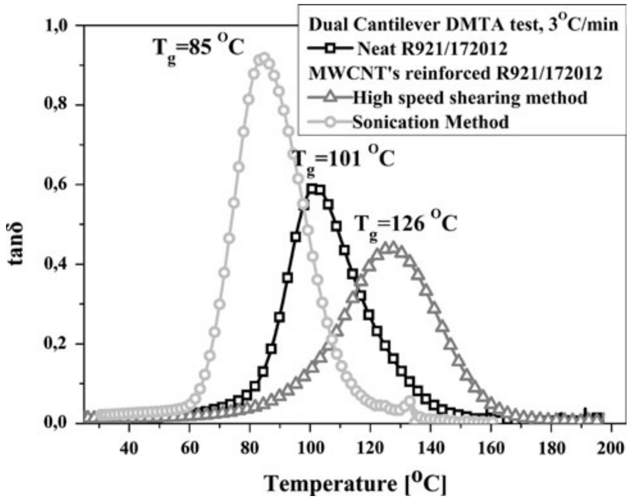

Fig. 5 Comparison of energy dissipation coefficient, tanδ, profiles versus temperature for the neat resin and the MWCNT-Epoxy nanocomposite manufactured by means of the two methods applied

reduction of the damping capacity. At the same time, the storage modulus of the epoxy increased after adding the nanofiller in the whole temperature range. The modulus of the nanocomposite and the temperature at which the modulus begins to decrease are much higher than those of the neat epoxy system demonstrating the strong confinement of nano-dispersed particles on the nanocomposite. The increase in the storage modulus value was significant for both the glassy and the rubbery regions. This observation is most likely related to the interaction between the hydroxyl groups of epoxy and the hydroxyl groups that are known to exist on damaged sites on the nanotubes' surface [33] or as a result of atomic scale defects formed during CNT growth [34–36]. The increase in T_g, also suggests that degree of interaction between the polymer chains and the surface of the nanotubes is increased.

Nanocomposites manufactured by the sonication method

A pulsed ultrasound exfoliates agglomerates and disperses CNTs in the matrix effectively. However, this method is only manageable for small batches due to the extreme reduction of the vibrational energy with increasing distance from the sonic tip. Another detrimental effect of this method, due to the local energy input, is the reported rupture of the CNTs leading to a reduction of the effective length [37, 38]. Retaining a high aspect ratio of the CNTs is of special interest toward an improvement of the mechanical performance of a CNT-reinforced polymer. Ultrasonication is also known to damage the nanotubes walls [39, 40]. So, in the case of multi-walled CNT's, an increase in the surface roughness caused by partial damage of the nanotube's outer layer may act as a mechanism of damping and adhesion enhancement, as a result of boundary friction and slip-stick effects.

As reported by Lu et.al. [41], high energy ultrasound was found to cause more serious damage to carbon nanoparticles than to carbon nanotubes. Significant amounts of dislocation defects are observed in the treated nanoparticles and these may be vulnerable areas toward subsequent attack by ultrasound cavitation. Partially or virtually completely destroyed nanoparticles are observed giving opened bundles of carbon ribbons. Further sonication turned these to amorphous carbon. The damage on these carbon structures clearly appears to progress from the external carbon layers and gradually to the inner layers. This observation suggests that the carbon layers in nanotubes and particles are rather independent and this is consistent with the 'Russian doll' structure.

The dynamic moduli E', E'' as well as the dissipation factor, $\tan\delta$ profiles for the nanocomposite system manufactured by the sonication method can be observed in Figs. 3,4, 5. Although the transition temperature is a subject of variation based on the property from which it is determined, it can be deduced that T_g values of nanocomposite manufactured by sonication method are lower than the respective ones of the neat resin. As a general observation for the dynamic mechanical behavior of the nanocomposite manufactured by the sonication method it can be implied that for temperatures up to 60 °C all the three parameters, E', E'', and $\tan\delta$, remain almost constant having values higher than the respective ones of the neat matrix, while for temperatures higher than 70 °C their values fail to lower levels than those of the matrix. This decline in the elastic properties combined with the increase in damping at higher temperatures is attributed to the damage of the polymer chains' structure. Ultrasonic processing has been reported to reduce the effective length of polymer chains which has a reducing effect on the uncured resin's viscosity [42]. This promotes a more effective exfoliation and wetting of nanofillers in the resin resulting in an improvement of the elastic response of the material when being in the glassy state. However, the reduction in the material's T_g is also attributed to the decrease in the length of polymer chains after the sonication process. For polymer chains with lower molecular weight the α-relaxation is shifted to lower temperatures due to a reduction in inertia and activation energy and increase in the free volume of the system, while the dissipation factor is increased.

Comparison between applied methods

A comparison between storage modulus profiles versus temperature for the neat resin and the MWCNT-Epoxy nanocomposite manufactured by means of the two methods is shown in Fig. 3. As can be seen for temperatures up to 60 °C specimens manufactured by the sonication method show higher E' values from both the neat matrix and the specimens manufactured by the shearing method. Above this temperature, shearing results in specimens with superior dynamic stiffness than the stiffness of both the matrix and the nanocomposite manufactured by the sonication method.

Next, a comparison between loss modulus profiles versus temperature for the neat resin and the MWCNT-Epoxy nanocomposite manufactured by means of the two methods is shown in Fig. 4. As can be seen, the specimens manufactured by the sonication method show a T_g value determined from the E'' being 20 °C lower compared to that of the neat resin, while those manufactured by the shearing method show a T_g of 16 °C higher than the respective one of the neat resin.

Finally, a comparison between $\tan\delta$ profiles versus temperature for the neat resin and the MWCNT-Epoxy nanocomposites manufactured by means of the two methods is shown in Fig. 5. As can be seen, specimens manufactured by the sonication method show a T_g value derived from the tanδ being 16 °C lower compared to that of the neat resin, while those manufactured by the shearing method show a T_g of 25 °C higher than the respective one of the neat resin.

The reduced spectra of nanocomposites prepared by the high speed shearing method normalized with respect to the neat epoxy values are shown in Fig. 6. It becomes evident that for temperatures ranging from room temperature up to 80 °C there is no increase in properties for the nanocomposite when compared to the respective ones of the neat matrix. However, at temperatures higher than 80 °C a tremendous increase is observed. More precisely, a tenfold increase in storage modulus is observed at 110 °C, while the loss modulus is 16 times higher than the respective one of the matrix at 140 °C. Finally, it was observed that values of tanδ show a maximum value of eight times higher than the respective ones of the neat matrix at 150 °C.

Next, for comparison reasons with respective values of the neat resin, the reduced storage modulus, loss modulus and tanδ profiles of the nanocomposites manufactured by applying the ultrasonication method are superimposed in Fig. 7. As shown in Fig. 7, for temperatures up to 60 °C, the storage modulus of the nanocomposite is almost constant having a value of about 10–20% higher than the respective one for the neat resin. However, for temperatures higher than 60 °C, a dramatic decrease of the reduced storage modulus is observed.

Reduced loss modulus variation with temperature is shown in Fig. 7. As can be seen again for temperatures up to 60 °C the loss modulus for the nanocomposite is kept almost constant showing a 230% increase with respect to that of the matrix, while for temperatures higher than 60 °C a further increase is observed showing a maximum at 70 °C the value of which being on the order of 4 (400%).

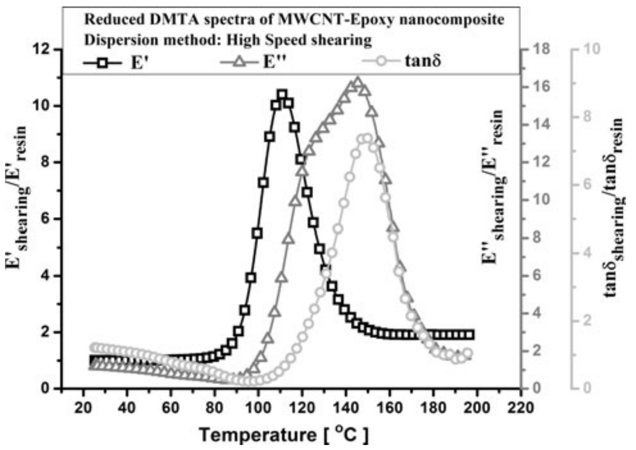

Fig. 6 DMTA spectra of tanδ, storage and loss moduli for the MWCNT-Epoxy nanocomposite manufactured by means of the high speed shearing method normalized with respect to the neat resin

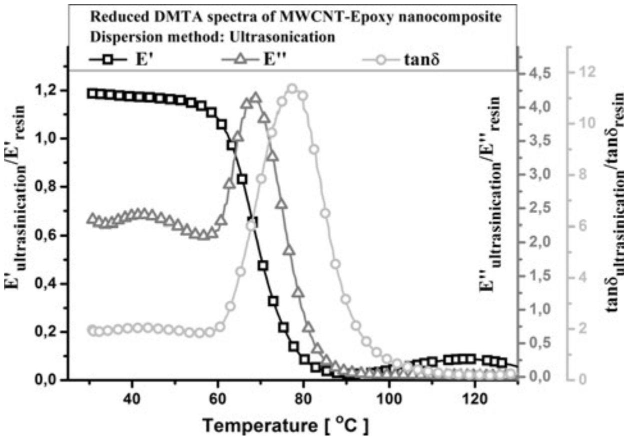

Fig. 7 DMTA spectra of tanδ, storage and loss moduli for the MWCNT-Epoxy nanocomposite manufactured by means of the ultrasonication method normalized with respect to the neat resin

The same behavior is observed in the case of the reduced tanδ variation with temperature. In the latter case, the maximum value of the ratio is equal to 11.5 and is achieved at 78 °C.

The comparison between the applied methods is better shown in Fig. 8. The ratios of the storage moduli, loss moduli, and energy dissipation factors, for the materials manufactured by the sonication method divided by the respective properties of nanocomposites manufactured by the high speed shearing method are plotted against temperature. In the case of the storage moduli of the nanocomposites manufactured by the two different methods, for temperatures up to 60 °C, the ratio remains constant with the sonication method giving nanocomposites with superior E' in comparison to those produced by the shearing method while above this temperature threshold the result is reversed. The same temperature threshold is observed for

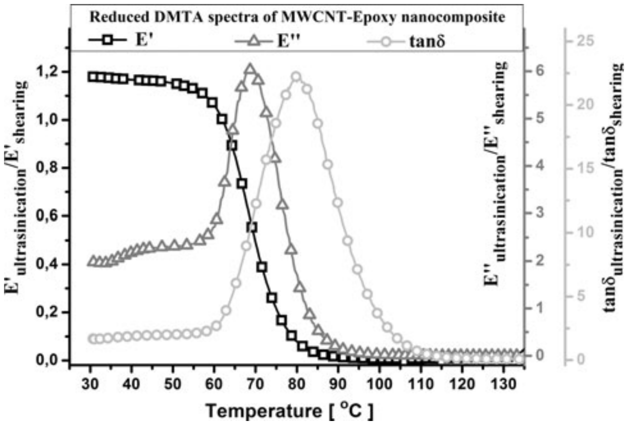

Fig. 8 The reduced DMTA spectra of storage modulus, loss modulus and tanδ of the nanocomposites manufactured by means of sonication method normalized with respective values of the nanocomposites manufactured by the shearing method

the ratio of the loss moduli and tanδ after which they cease from being constant. Concerning the loss modulus ratio, a maximum value of this ratio on the order of 6 is observed at 70 °C while at temperatures above 80 °C this behavior reversed. Accordingly, a maximum of the ratio of tanδ reaches a value on the order of 22 at 80 °C while decreasing for temperatures above 110 °C.

The most important observations from all the above-mentioned results are summarized in Tables 1, 2, 3, 4. A general result is that except for the glass transition temperature, all static, and dynamic properties of nanocomposites manufactured by the sonication method are superior from respective ones of nanocomposites manufactured by the shearing method.

Conclusions

In this investigation, specimens of MWCNT-epoxy nanocomposites were prepared by applying high speed shear mixing and sonication methods and the effect of the dispersion degree between MWCNT and polymer resin was analyzed after completing the curing reaction, by scanning electron microscopy, static and dynamic tests. The main results can be summarized as follows:

- From SEM micrographs observations there was a clear indication that nanocomposites produced by the shearing method, were characterized by a limited aggregation while those manufactured by the sonication method showed that individual nanotubes are scattered in the matrix and no aggregation was observed. In addition, a specific mechanism of crack propagation in the epoxy matrix material was observed having as main characteristics feather-like patterns, crack propagation mode in a finger-like manner, and river markings.
- The evaluation of the dispersion quality made from the photomicrographs obtained was confirmed by the reinforcing efficiency of the nanotubes for each the dispersion method applied. The criterion implemented was the convergence of the nanocomposites' elastic response with ideal case approach of the rule of mixtures.
- In both methods there was an increase in flexural modulus (3.25% for the shearing method and 26.6% for the sonication method), and in flexural strength (8.5% for the shearing method and 19.1% for the sonication method), in comparison to the respective values for the neat resin, with the sonication method being always superior.
- From the comparison made between tanδ profiles versus temperature for the neat resin and the MWCNT-Epoxy nanocomposites manufactured by means of the two methods, it was derived that specimens manufactured by the sonication method showed a T_g value of 16 °C lower as compared to that of the neat resin, while those manufactured by the

Table 2 Comparison between the dynamic mechanical properties of nanocomposites manufactured by the shearing method and those of the neat matrix

Shearing method/matrix					
E'_{sh}/E'_m at 25 °C	E''_{sh}/E''_m at 25 °C	$\tan\delta_{sh}/\tan\delta_m$ at 25 °C	$(E'_{sh}/E'_m)_{max}$ 110 °C	$(E''_{sh}/E''_m)_{max}$ 140 °C	$(\tan\delta_{sh}/\tan\delta_m)_{max}$ 155 °C
1	1	1	10	16	9

Table 3 Comparison between the dynamic mechanical properties of nanocomposites manufactured by the sonication method and those of the neat matrix

Sonication method/matrix					
E'_{so}/E'_m at 25 °C	E''_{so}/E''_m at 25 °C	$\tan\delta_{so}/\tan\delta_m$ at 25 °C	$(E'_{so}/E'_m)_{max}$ at 25 °C	$(E''_{so}/E''_m)_{max}$ at 70 °C	$(\tan\delta_{so}/\tan\delta_m)_{max}$ at 75 °C
1.2	2.3	2.0	1.2	4.3	11.5

Table 4 Comparison between the dynamic mechanical properties of nanocomposites manufactured by the sonication method and those manufactured by the shearing method

Sonication/shearing method					
E'_{so}/E'_{sh} at 25 °C	E''_{so}/E''_{sh} at 25 °C	$\tan\delta_{so}/\tan\delta_{sh}$ at 25 °C	$(E'_{so}/E'_{sh})_{max}$ at 25 °C	$(E''_{so}/E''_{sh})_{max}$ at 70 °C	$(\tan\delta_{so}/\tan\delta_{sh})_{max}$ at 80 °C
1.2	2.3	2.0	1.2	6.0	22.0

shearing method showed a T_g of 25 °C higher than the respective one for the neat resin.

- The nanocomposites manufactured by the sonication method exhibited lower transition temperatures and increased damping capacity. This behavior was partly attributed to the "intensity" of the sonication method, which is known to damage the polymer chains as well the CNT walls' structure.
- A general result that can be derived is that except of the glass transition temperature, all static and dynamic properties of nanocomposites manufactured by the sonication method, are superior when compared to respective ones for nanocomposites manufactured by the shearing method.

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