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Effect of dispersion conditions on the thermo-mechanical and toughness properties of multi walled carbon nanotubes-reinforced epoxy

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ABSTRACT

In this work, multi wall carbon nanotubes (MWCNTs) dispersed in a polymer matrix have been used to enhance the thermo-mechanical and toughness properties of the resulting nanocomposites. Dynamic mechanical analysis (DMA), tensile tests and single edge notch 3-point bending tests were performed on unfilled, 0.5 and 1 wt.% carbon nanotube (CNT)-filled epoxy to identify the effect of loading on the aforementioned properties. The effect of the dispersion conditions has been thoroughly investigated with regard to the CNT content, the sonication time and the total sonication energy input. The CNT dispersion conditions were of key importance for both the thermo-mechanical and toughness properties of the modified systems. Sonication duration of 1 h was the most effective for the storage modulus and glass transition temperature (T_g) enhancement for both 0.5 and 1 wt.% CNT loadings. The significant increase of the storage modulus and T_g under specific sonication conditions was associated with the improved dispersion and interfacial bonding between the CNTs and the epoxy matrix. Sonication energy was the influencing parameter for the toughness properties. Best results were obtained for 2 h of sonication and 50% sonication amplitude. It was suggested that this level of sonication allowed appropriate dispersion of the CNTs to the epoxy matrices without destroying the CNT's structure.

1. Introduction

Epoxy resins are commonly used with reinforcing fibers and fillers for advanced composite applications [1]. The resins of this class have good stiffness, specific strength, dimensional stability, and chemical resistance, and exhibit good stress transfer properties for a variety of reinforcements [2]. The use of an additional phase, such as fibers and fillers aims in improving further the properties of the epoxy resins and tailor them for specific applications. Further to the successful incorporation of micro-scale fillers to epoxy resin [3–6], nanoparticles, nanotubes, and nanofibers are now in the forefront of material research as filler material to produce high performance composite structures with enhanced properties [7–9].

CNTs are known as materials with very remarkable electronic, thermal, optical, mechanical, spectroscopic and chemical properties, which have been attributed to the bonding structure of the CNTs [10–13]. These properties imply the huge potential applications of CNT/polymer nanocomposites. The significant enhancement in the polymer/CNT composites are generally related to the degree of dispersion, impregnation, and interfacial adhesion [14–18].

Epoxy resins are inherently brittle and hence have reduced damage tolerance. Additionally, in reinforced plastics, damping is governed by the matrix properties and consequently the research effort has been oriented towards the modification of matrix resin systems (matrix additives, interleaves, etc.). During the past decade, techniques that allow the tailoring of the resin properties are in the forefront of scientific research. These techniques target in maximizing the dissipated energy through either the plastic deformation of the matrix, e.g. the inclusion of elastomers which increase the resin toughness [19], or the modification of the crack initiation and propagation process e.g. ceramic modified polymers that inhibit interlaminar crack propagation [20]. Other techniques include interleaving [21,22] or toughening with the inclusion of thermoplastic fibers [23,24]. An interesting scenario is the use of CNTs as an additive [25]. Due to their nanoscale size and huge aspect ratio and free surface, CNTs are expected to increase by several orders of magnitude the interfacial area in a polymer composite system. Moreover, a minimum addition of the order of few percent may potentially dramatically modify the properties of the matrix material [26]. The use of CNT in resin systems has been the basis of the development of new technologies, which explore the compatibility of matrices and CNT tubes and lead to spectacular improvement in structural material properties [27,28] and additional functionalities [29,30].

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Although of key importance, the CNT dispersion remains an issue, and one of the limitations to the utilization of the CNTs in a polymer matrix. This occurs mainly due to the CNTs tendency to agglomerate and entangle together because of strong Van der Waals bonds which become predominate as the CNTs length increases [31]. Next to that, the lack of functional sites on the surface of the CNTs is also complicating the dispersion issue [31]. Many researchers have experimentally investigated effective methods to disperse CNTs homogeneously within a matrix and improve the interfacial bonding between CNTs and the matrix. In terms of nanotube dispersion the two main approaches followed are categorized as mechanical/physical and chemical. Under chemical methods are considered the techniques affecting the chemical structure of CNTs (e.g. functionalisation, covalent bonding, and incorporation of other atoms in the carbon lattice) and are not the focus of this paper. The physical dispersion routes on the other hand include the ultrasonication, high-shear and high-impact mixing [32–37].

Modeling work has been conducted addressing the effects of nanotube clustering and curvature on the ensuing mechanical properties [38]. According to an idealized two-scale model that have developed to capture the overall elastoplastic response of carbon nanotube reinforced composites in which CNT agglomeration and interface conditions can play the key role, the calculated results indicated that the formation of CNT agglomeration can seriously reduce the elastic stiffness and yield strength of the nanocomposite [38]. At the nanoscale, the structure of the carbon nanotube strongly influences the overall properties of the composite. Thostenson and Chou [39] focused on developing a fundamental understanding of the structure/size influence of carbon nanotubes on the elastic properties of nanotube-based composites. They developed a model composite system where they found that the nanocomposite elastic properties are particularly sensitive to the nanotube diameter, since larger diameter nanotubes show a lower effective modulus and occupy a greater volume fraction in the composite relative to smaller-diameter nanotubes [39].

Ultrasonication is the act of applying ultrasound energy to agitate particles in a solution for various purposes. In the laboratory, it is usually achieved using an ultrasonic bath or an ultrasonic probe/horn, known as a sonicator. It is the most frequently used method for nanoparticle dispersion. The principle of this technique is that when ultrasound propagates via compression, attenuated waves are induced in the molecules of the medium through which it passes. The production of these shock waves promotes the “peeling off” of individual nanoparticles located at the outer part of the nanoparticle bundles, or agglomerates, and thus results in the separation of individualized nanoparticles from the bundles. Ultrasonication is an effective method to disperse CNTs in liquids having low viscosity, such as water, acetone and ethanol. However, most polymers are either in a solid or viscous liquid state, which requires the polymer to be dissolved or diluted using a solvent to reduce the viscosity before dispersion of CNTs. Commercial probe sonicators have an adjustable amplitude ranging from 20% to 70% and a power of 100–1500 W. The probe is usually made of an inert metal such as titanium. Most probes are attached with a base unit and then tapered down to a tip with a diameter from 1.6 to 12.7 mm. This means that the energy from the wide base is focused on the tip, thus giving the probe high intensity. The application of this configuration is that sonication can generate heat rapidly. Therefore, for the CNTs dispersed in volatile solvents, such as ethanol and acetone, the samples should be kept cold (e.g. using an ice bath) and the sonication must be done in short intervals. If the sonication treatment is too aggressive and/or too long, CNTs can be easily and seriously damaged, especially when a probe sonicator is employed, suggesting the generation of defects on CNT surface [40]. In extreme cases, the graphene layers of CNTs are completely destroyed and the nanotubes are converted into amorphous carbon nanofibers [41]. The localized damage to CNTs deteriorates both the electrical and mechanical properties of the CNT/polymer composites.

Ultrasonication has been used to disperse CNTs in epoxy matrices. The results have shown enhanced mechanical properties as compared to the neat epoxy. Special emphasis has been placed on composite toughness and the opening-mode stress intensity factor K_{IC}, which was found to increase by 20–75% [13,42].

Although the sonication process has been used in the past to disperse CNTs in the epoxy matrix, this process has not been optimized. According to our knowledge there has not been a thorough investigation of the effect of sonication condition, i.e. duration and amplitude on the dispersion. Therefore the purpose of the present study was to systematically investigate the effect of sonication on the thermo-mechanical and toughness properties of the CNT modified epoxies. Two sets of experiments were carried out. In the initial experiments the sonication duration varied between 0.5 and 4 h while the sonication amplitude was kept constant at 100%. Based on thermo-mechanical and toughness properties obtained through the initial experiments, a second, optimization stage, was followed in order to identify best conditions for enhanced toughness properties. In the second stage the amplitude of the sonotrode and the duration of sonication were the varying parameters.

2. Experimental

2.1. Materials

MWCNTs supplied by ARKEMA, France were used as reinforcement in this study. The tube diameter ranged from 10 to 15 nm, the tube length was more than 500 nm and the production method was Catalyzed Chemical Vapor Deposition (CVD).

A two part low viscosity epoxy resin, i.e. Araldite LY 564 and Aradur 2954, supplied by Huntsman Advanced Materials, Switzerland at a mix ratio of 100:35 by weight was used as matrix material.

2.2. Specimen preparation

An ultrasonic mixer (UP400S, Hielscher) was used to disperse the CNTs into the epoxy resin. CNTs and Araldite LY 564 resin were carefully weighed and mixed together in a beaker. A high intensity, ultrasonic probe was employed for the mixing process. In order to avoid overheating and induction of defects on the CNTs surface the temperature of the mixture was kept low by submerging the container in an ice bath [40], as shown in Fig. 1.

As discussed in the introduction, two sets of specimen series were prepared in the current study. Initial experiments were carried out as seen in Table 1 at two CNT contents (i.e. 0.5 and 1 wt.%) and four sonication durations (i.e. 0.5, 1, 2 and 4 h) in order to thoroughly investigate the effect of sonication conditions, at maximum sonicator amplitude (100%) which corresponds to the maximum sonotrode power or 400 W and a frequency of 24 kHz. Based on the thermo-mechanical and toughness results obtained from the initial experiments, an optimization stage was followed according to the conditions seen in Table 1. The key parameters varied in this stage were the sonication duration and the sonication amplitude. The dispersion power is given as a fraction of the full power, which is defined by the manufacturer at 400 W.

Table 1 summarizes all the configurations and the sonication conditions. All sonication protocols were performed at 100% amplitude.

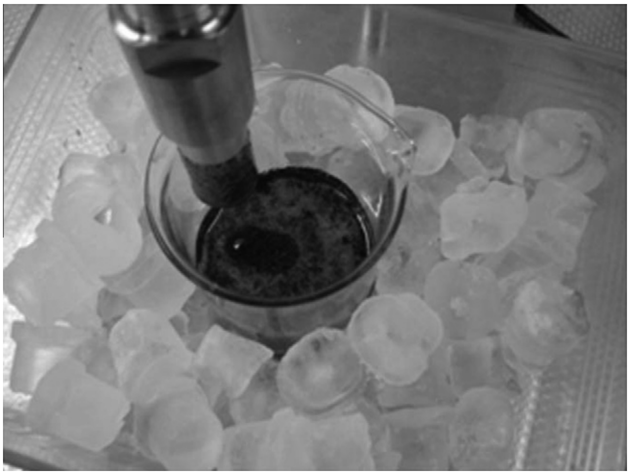

Fig. 1. Sonication process.

Once the sonication was complete, the hardener was added to the modified resin and mixed using a mechanical agitator for about 10 min. To remove entrapped air and voids induced during mixing [16], the mixture was degassed in vacuum for 10 min. Finally, the mixture was transferred to silicon rubber molds and cured for 2 h at 60 °C. All specimens were post-cured at 120 °C for 4 h. The test specimens were cut in appropriate dimensions for the Dynamic Mechanical Analysis (DMA), the tensile and the Single Edge Notch 3-point Bending (SENB) characterization. The dimensions of the specimens are shown in Fig. 2.

2.3. Testing procedure

2.3.1. Tensile tests

Tensile tests were performed to evaluate the mechanical performance of the unmodified and modified systems. The tests were performed according to the ASTM 638-03 [43].

The specimens were loaded to failure in displacement control mode at a crosshead speed of 0.5 mm/min (corresponding to a strain rate of app. 80 μs^{-1}). A video extensometer was used to measure the axial strain of the specimens. For all configurations five specimens were tested.

2.3.2. Dynamic mechanical analysis (DMA)

DMA was performed to evaluate the thermo-mechanical performance of the epoxy resin and that of the nano-modified composites. A dynamic mechanical analyzer DMA 242 C (Netzsch) was used, operating in three-point bending mode (the support span was 30 mm). Rectangular specimens with dimensions of $50 \times 10 \times 3$ mm^3 were tested at an oscillation frequency of 1 Hz and constant amplitude (30 μm) (corresponding to a mean strain rate of app. 800 μs^{-1}). Thermal scans from 20 °C to 220 °C were performed at a scanning rate of 1 °C/min.

2.3.3. Single edge notch 3-point bending (SENB)

The toughness properties of the composites were examined using notched prismatic specimens in single edge notch 3-point bending configuration. Tests were performed according to ASTM D 5045-99 [44].

A 3 mm notch was generated mechanically and a natural crack was created by tapping on a razor blade placed in the notch. The crosshead speed was 10 mm/min. Five specimens were tested for every one of the configurations. The experimental configuration is shown in Fig. 3.

The critical stress intensity, factor, K_{IC}, and fracture toughness, G_{IC}, were calculated according to Eqs. (1) and (2), respectively, as described in ASTM D 5045.

$$K_{1C} = f(\alpha/w)\frac{F_Q}{h\sqrt{w}} \tag{1}$$

$$G_{1C} = \frac{W_B}{h * w * \varphi(\alpha/w)} \tag{2}$$

where W_B is the energy to break, h is the test specimen thickness, w is the test specimen width, $\varphi(\alpha/w)$ is the energy calibration factor, depending on the crack length α, $f(\alpha/w)$ is the geometric calibration factor, depending on the crack length α.

3. Results and discussion

In Fig. 4 typical stress–strain curves for the neat and doped nanocomposites are presented. Due to the nature of the epoxy resin both neat and nanomodified systems behave in a typical brittle manner, where plastic deformation before failure is absent. Based on these graphs it can be noted that the addition of CNTs resulted in an increase of the tensile strength and the axial strain at failure. Based on the linear part of the stress–strain curves the tensile modulus of the neat and CNT modified epoxy systems was calculated and plotted as a function of CNTs loading and duration of sonication in Fig. 5.

As can be seen from the obtained results the addition of a small amount of CNTs did not significantly influence the tensile modulus. The average value of the tensile modulus of the modified systems remained almost unaffected being close to that of the neat resin. A slight improvement can be documented for the system with 1 wt.% CNT reinforcement at 4 h of sonication. It should be noted though that this system is the one with the highest variation in values between the different specimens tested. The lack or marginal improvement in stiffness with the addition of a small amount of CNTs has been documented in the past [45,46]. In theory, the reinforcement potential of the CNTs can only be activated if there is an effective load transfer from the surrounding epoxy matrix into the CNTs. Therefore, a good dispersion into the matrix, together with a strong interfacial adhesion has to be ensured. However, the larger the provided interface, the more difficult it is to efficiently disperse the reinforcing phase [47]. The key issue in exploiting the remarkable properties of CNTs lies in exploiting the increase in interface created by the introduction of the nanophase [6,48]. Thus, load transfer by shear at the locus of discontinuities or when the load is at different orientation relative to that of the nanotube may contribute to the enhancement of properties [49]. The marginal improvement in elastic properties may be attributed to the difficulty of securing uniform dispersion. It is interesting to note, however, that recent research work claims an opposite mechanism where poorly dispersed CNT result in better Young modulus values compared to those obtained when good dispersion is achieved [50]. This was explained based on the fact that when CNTs are poorly dispersed the agglomerates trap polymer resin in the voids between the tubes and effectively reduce the volume fraction [50]. The incorporation of CNTs may lead to the improvement of other properties which are more related to the damage tolerance of the nanocomposite or its resistance to crack initiation and propagation [49]. This is achieved via the crack deflection and bifurcation mechanisms which are instigated by the presence of the nanophase. These effects are expected to indirectly affect the viscoelastic properties of the nanocomposite.

Fig. 6 presents the effect of CNT addition and sonication duration on the tensile strength of the neat and CNT modified epoxy systems. An enhancement in the tensile strength can be observed

Table 1
Configurations and sonication conditions.

Stage	Abbreviation	CNT level (wt.%)	Sonication amplitude (%)	Duration of sonication (h)
	Neat epoxy	0	–	–
Initial experiments	0.5% – 0.5 h	0.5	100	0.5
	0.5% – 1 h	0.5	100	1
	0.5% – 2 h	0.5	100	2
	0.5% – 4 h	0.5	100	4
	1% – 0.5 h	1	100	0.5
	1% – 1 h	1	100	1
	1% – 2 h	1	100	2
	1% – 4 h	1	100	4
Optimization stage	0.5% – 1.5 h – 100%	0.5	100	1.3
	0.5% – 2 h – 50%	0.5	50	2
	0.5% – 1.3 h – 75%	0.5	75	80
	0.5% – 5 h – 100%	1	100	5

in the modified systems compared to the neat resin dependent on the sonication conditions. This suggests that the sonication parameters highly affect the dispersion of CNTs in the epoxy resin. Better results are obtained at intermediate levels of sonication duration (between 1 and 2 h of sonication). It is suggested that small durations are not sufficient for good CNT dispersion, while very high durations may lead to breakage of the CNTs. These two conflicting mechanisms may also explain the quite big scatter that can be observed between specimens with the same CNT loadings and sonication duration. These results are in agreement with those recently published on the effect of sonication [50] on the mechanical properties of CNT modified epoxy systems, where it was shown that improvement was achieved when sonication time increased from 0.5 to 1 h. Further increase in the sonication time let to deterioration in the mechanical properties which was linked to possible nanotube damage.

As already mentioned in the introduction section, resin modification with CNTs is expected to change the dynamic properties of the resulted materials. Figs. 7–9 show the results of dynamic mechanical analysis of the neat and the CNT modified epoxies obtained through the initial sonication experiments. The elastic part of the complex modulus (storage modulus) is plotted in Fig. 7, and the loss factor ($\tan\delta$), measured by the ratio of storage to loss modulus, is plotted in Fig. 8. It is evident in Fig. 7 that the addition of CNTs led to a significant increase of the modulus values both in the glassy and in the rubbery state. If the slope of the storage modulus values in the glass transition zone is used to estimate the glass transition temperature (T_g) of the neat and the CNT modified systems, then it can be stated that similarly to the storage modulus the addition of CNTs led to an increase of the T_g up to app. 15 °C for the case of 1 wt.% CNT content and 1 h of sonication. The thermal stability of the CNT modified samples was also increased, based on the increase of the T_g. Fig. 8 presents the curves of the loss factor of the neat epoxy and its composites versus temperature. The height of the $\tan\delta$ peaks of the modified systems remained unaffected or slightly decreased compared to that of the neat epoxy. The decrease of the loss factor can be attributed to the stiffening effect due to the CNT inclusion. However, since this is not the only mechanism that in influencing the way energy is dissipated in the modified systems, some discrepancies can be seen in the $\tan\delta$ peak with the CNT contents and sonication durations. Again if the T_g is associated with the temperature where the $\tan\delta$ peak is observed, a clear increase of the T_g can be observed for the optimum sonication conditions.

While the increase of the storage modulus at the glassy state with the addition of CNTs is a quite common observation due to the reinforcing effect of the CNTs and the restricted mobility of the epoxy chains, most studies do not report rubbery modulus enhancements [7,16,51–53], and in some instances a drop in the T_g has been observed due to agglomeration of the CNTs and interference with the polymer structure and curing process of the resin [54]. In previous studies, [55–57], an increase in the rubbery modulus (between 150 °C and 200 °C) was also observed, which was attributed to the reinforcing effect by the CNTs, the increased crosslink density and restricted mobility from enhanced polymer – CNT interactions. The restricted mobility of the polymer chains around the nanotubes and the interfacial bond between them are also explaining the increase in T_g.

The plots presented in Figs. 7 and 8 are characteristic curves from one specimen per sample series. The DMA measurements were performed on 4–5 specimens for the same sample series in order to verify the uniformity of dispersion of CNTs into the epoxy matrix within the same batch. As in the case of the static results a variation has been observed between the dynamic properties of the different specimens. In order to illustrates the aforementioned variation, the average storage modulus of all tested specimen along with the standard deviation was recorded at the glassy region (30 °C) and plotted as a function of the CNT loading and sonication duration in Fig. 9. Based on this graph the upper and lower limits of the obtained storage modulus can be obtained. Similar trends to those observed in Fig. 9 can be observed also based on the average values. The storage modulus steadily increased with higher CNT contents. The addition of 1 wt.% CNT at 1 h of sonication yielded to an average increase of 25% of the storage modulus at 30 °C. The quite high variation between the lower and upper limits obtained at 1 and 2 h of sonication indicate that there is room for further optimization of the sonication process in order to achieve optimum dispersion in a stable manner. Although the results from the static tests did not illustrate a clear enhancement in terms of modulus values due to the CNT addition, those from the DMA suggest clearly that when appropriate dispersion of nanoparticles is achieved a clear increase in modulus is also present. The discrepancy between the two methods is quite common for polymer composites. This can be explained based on the fact that the strain rate used during DMA is one order of magnitude higher than that during the static testing. Next to that the predetermined displacements during DMA are within the elastic limits of the materials tested. Therefore these tests have far greater sensitivity to both macroscopic and molecular relaxation processes than static techniques.

In Fig. 10 typical load–displacement curves for the neat and doped nanocomposites are presented. As can be seen from both curves, for approximately the same displacement the doped systems demonstrate higher load values compared to the neat epoxy. Based on the maximum peak of the load and the area below the curve the critical stress intensity factor and the fracture toughness of the tested materials were calculated.

Fig. 11 shows the critical stress intensity factor and the fracture toughness of the tested materials based on the initial set of experiments. The CNT addition exhibits adverse effects with different

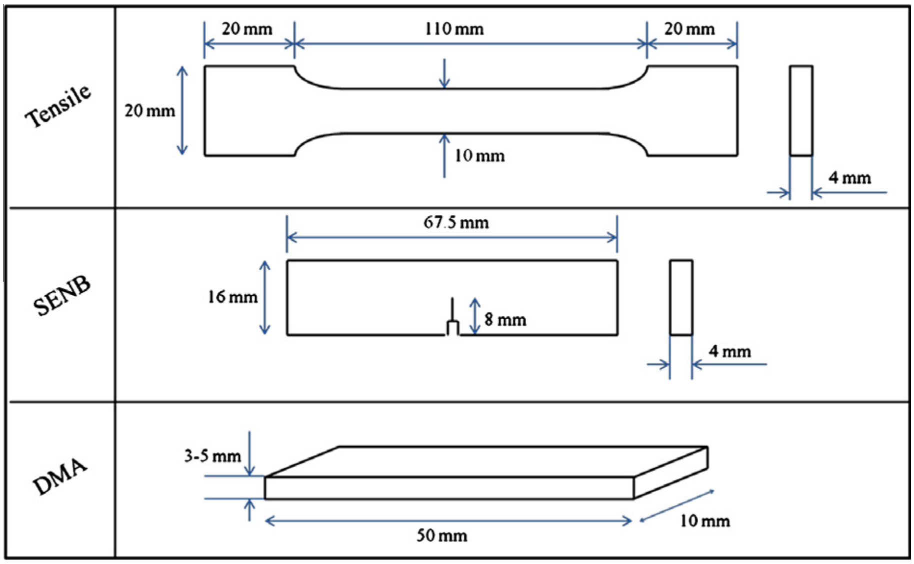

Fig. 2. Specimens configuration and dimensions.

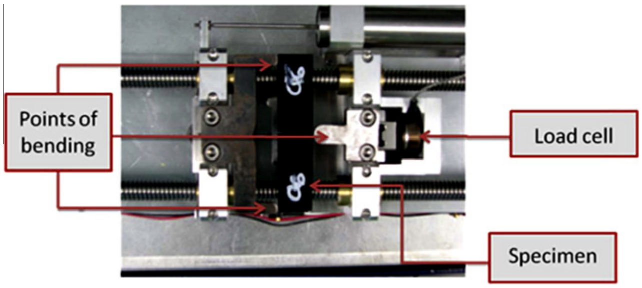

Fig. 3. SENB experimental setup.

dispersion parameters as far as the nanocomposite toughness is concerned. As can be seen, in the case of 0.5% per weight CNT content, the toughness of the nanocomposite is initially improving with sonication to reach a maximum at 1 h at full sonication amplitude, where a spectacular improvement of approximately 80% is observed for both K_{IC} and G_{IC}. Further sonication at 2 h is only reducing the toughness of the nanocomposite to the levels of the pure resin. Finally, sonication at 4 h is significantly improving the resin toughness to almost the levels of the 1 h sonication but with considerably higher scatter in the experimental data. Interestingly enough, increasing the CNT content to 1% does not have the same effect in the toughness of the nano composite. The initial sonication stage results in a marginal increase of the stress intensity factor and the toughness which is accompanied by a substantial increase in the experimental scatter. The best results are exhibited for 2 h of sonication with an increase of the stress intensity factor and the fracture toughness of about 40%. This increase although substantial enough is by far less spectacular than the increase noted for the 0.5% reinforced nanocomposite. For the case of 1% reinforcement, further sonication led to the deterioration of the toughness properties to approximately the levels of the neat epoxy.

The aforementioned behavior of the nanoreinforced composite suggests that there are more than one mechanisms that are active during dispersion. Moreover, these mechanisms are competitive and interdependent. As is obvious from the above, the increase in sonication time does not necessarily involve a respective increase in the toughness properties. The primary effect of sonication is the breaking of the CNT agglomerates which leads to the efficient dispersion of the reinforcing phase [58] However, sonication is also responsible for the deterioration of the CNTs which may be manifested either by reduction of the CNT aspect ratio, a direct effect of the brakage of the agglomerates or by the cleavage of surface graphene layers of the MWCNTs [40,41]. CNT breakage and aspect ratio reduction is limiting the reinforcing efficiency of the nanotubes. Graphene cleavage on the other hand may also enhance stress transfer between the nanotubes and the matrix which means better reinforcing efficiency, but at the same time may also introduce defects that deteriorate the strength of the CNTs and

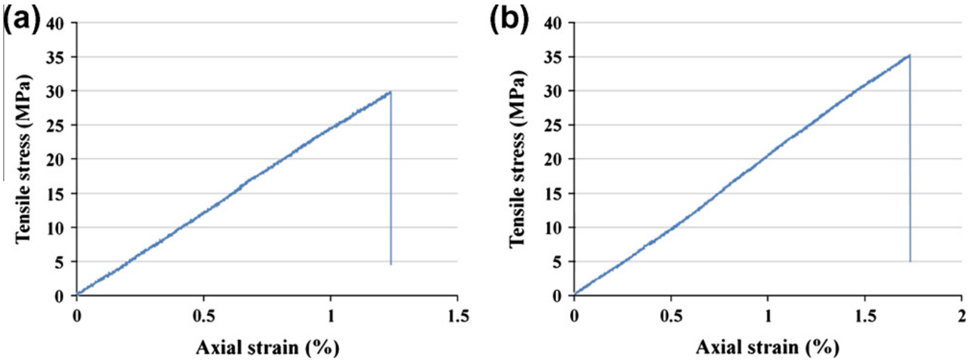

Fig. 4. Typical plots of the tensile stress versus axial strain (a) for neat and (b) doped epoxy (0.5% – 2 h) nanocomposite.

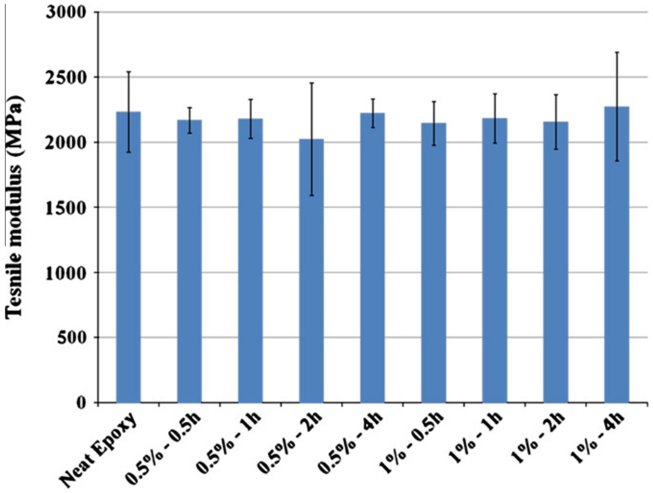

Fig. 5. Tensile modulus of the neat epoxy and the various nanocomposite samples as a function of the CNT loading and the sonication duration.

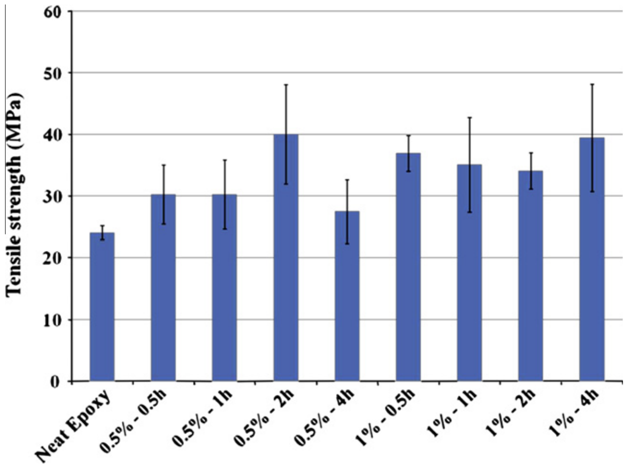

Fig. 6. Tensile strength of the neat epoxy and the various nanocomposite samples as a function of the CNT loading and the sonication duration.

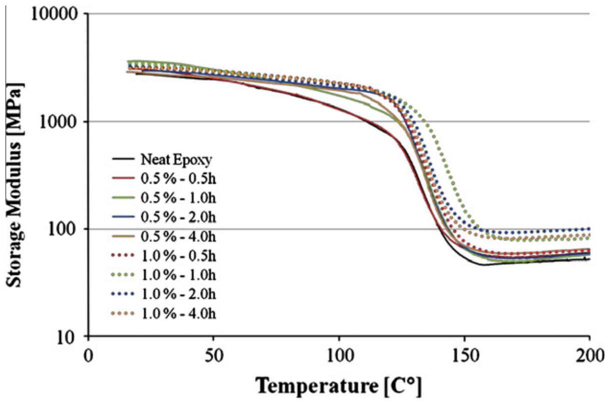

Fig. 7. Plot of the storage modulus versus temperature of the neat epoxy and the various nanocomposite samples.

therefore deteriorate the composite properties. Such effects have been thoroughly studied in the case of oxidative treatment for carbon fibers [59].

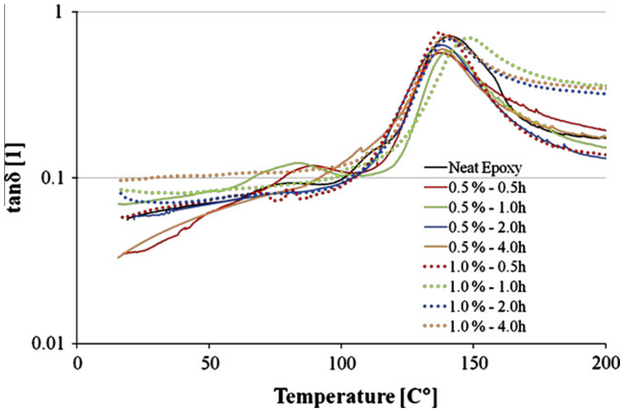

Fig. 8. Plot of the tan δ versus temperature of the neat epoxy and the various nanocomposite samples.

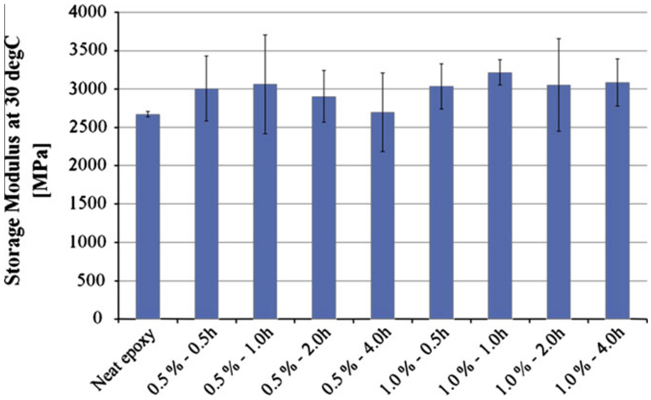

Fig. 9. Plot of the storage modulus at 30 °C of the neat epoxy and the various nanocomposite samples.

The experimental data that relate to the dispersion process also reveal that the increase in CNT content does not involve the respective increase in toughness. This finding suggests either that the sonication power that is required to efficiently disperse the CNTs is not enough, or that the aforementioned degradation mechanisms of the CNTs become dominant for higher CNT contents. Last but not least, the effect of sonication time is not monotonic, at least in the case of 0.5% reinforcement (Fig. 11). This implies that different reinforcing mechanisms become dominant at different stages of the dispersion process.

In view of the above and as the requirement is maximum improvement in properties via efficient dispersion, the mechanisms can be assumed (i) to be interdependent and (ii) to possess an energy influx threshold above which they are triggered. It may be postulated that de-agglomerate breakage requires less energy density than the CNT breakage. This postulation can also be based on the fact that CNT strength is a length dependent property [60] – even if deagglomeration involves CNT breakage, as CNT length is reduced their respective strength is enhanced and therefore the energy density required to break them is increasing. In other words, the optimization of the properties of the nanocomposite may be achieved via the modification of the sonication power input for total input energies that indicate property improvement, as indicated by the power times time product. Such an optimization would involve the examination of the optimal total energy throughput, as well as the examination of different power inputs for protocols that yielded the best fracture properties.

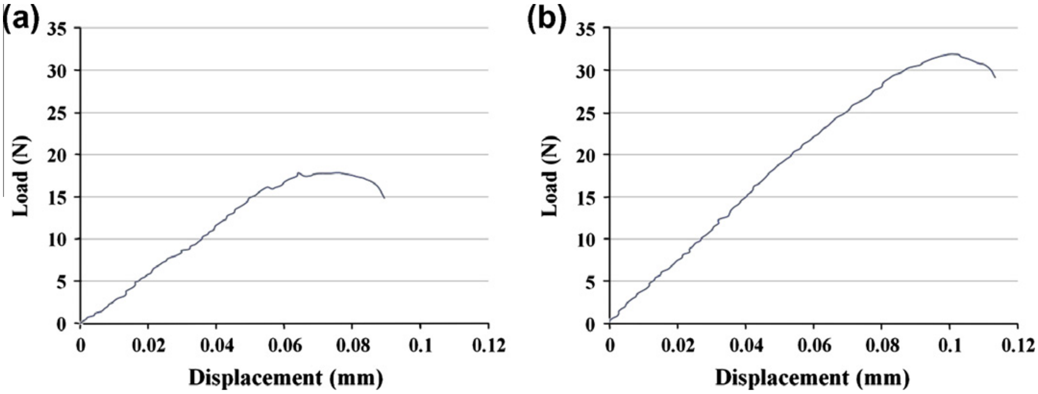

Fig. 10. Typical plots of load versus displacement curve (a) for neat and (b) for doped epoxy resin (1% – 2 h) nanocomposite.

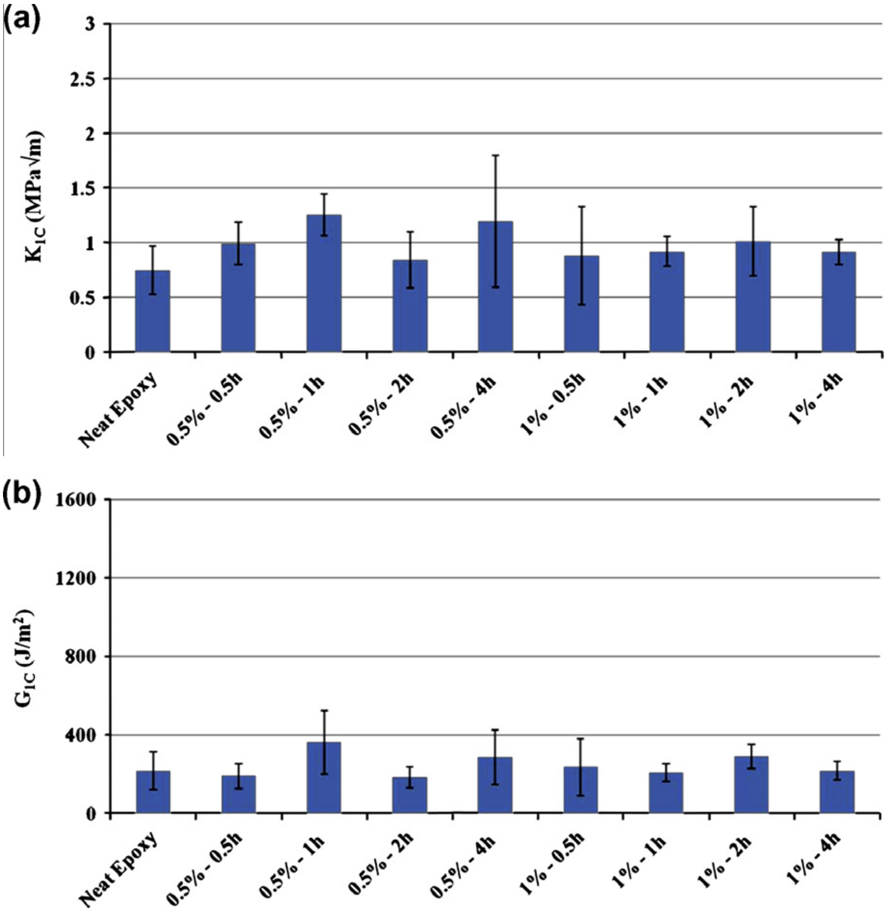

Fig. 11. Plot of (a) the critical stress intensity factor and (b) the fracture toughness of the neat epoxy and the various nanocomposite samples during the initial experiments.

To this end, the following additional dispersion protocols were further applied:

(i) Sonication for 1.3 h at 75% amplitude and sonication for 2 h at 50% amplitude for 0.5% CNT content. This protocol aimed at defining the optimization window for the optimum properties achieved for 1 h sonication at 100% amplitude for 0.5% CNT content.

(ii) Sonication for 1.5 h at 100% amplitude for 0.5% CNT content. This protocol aimed at confirming the reproducibility of the effect of reduced fracture properties with a view to confirming that competitive mechanisms are active throughout the dispersion process.

(iii) Sonication for 5 h at 100% amplitude for 0.5% CNT content. This protocol was chosen in order to explore the possibility of further improvement via the increase in the total energy input which was observed for the sonication protocol of 4 h at 100% amplitude for 0.5% CNT content.

Fig. 12 depicts the fracture properties for the nanocomposites manufactured via the aforementioned sonication protocols as determined by the SENB test. The achieved properties for the initial protocols are also depicted for comparison purposes. As can be seen, the intermediate (1.5 h) and prolonged (5 h) dispersion times rather reduced than improved the toughness properties to a level similar or less than that of the unreinforced epoxy. However the

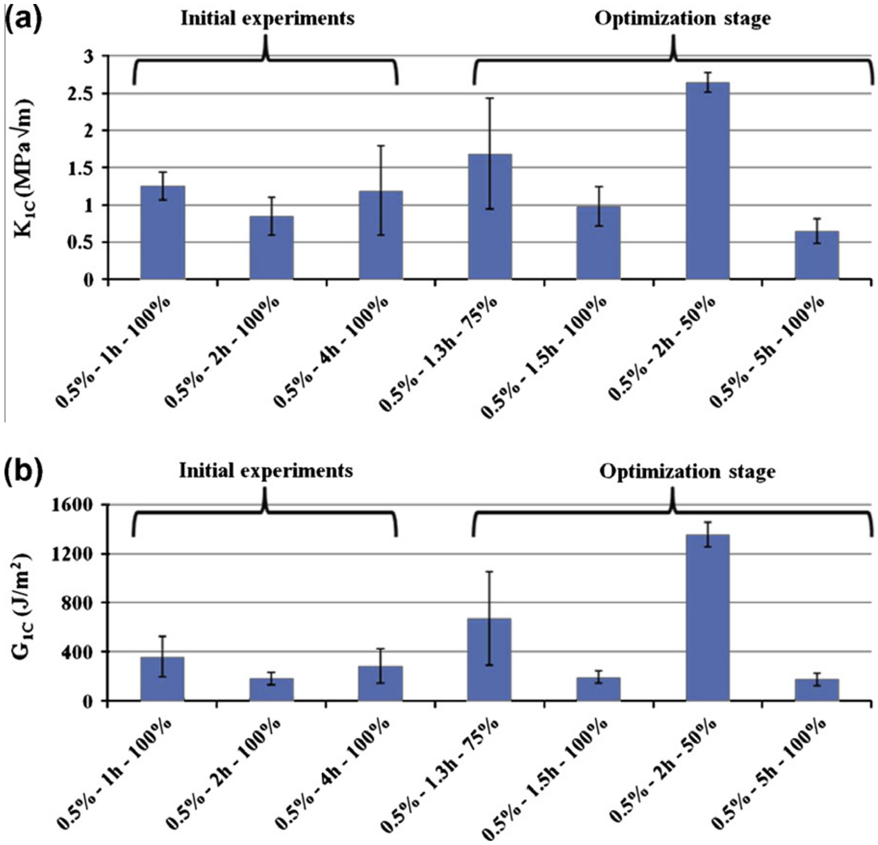

Fig. 12. Plot of (a) the critical stress intensity factor and (b) the fracture toughness of the neat epoxy and the dopped with 0.5 wt.% CNTs nanocomposite samples during the optimization stage and correlation with the initial experiments.

situation is not the same for the dispersion protocols with reduced ultrasonic power. Both at 75% and at 50% the fracture properties are substantially improved. Particularly in the latter case, a further improvement of approximately 170% is obtained compared to the initial protocol with the same energy input or a total of 250% compared to the unreinforced matrix. This outcome verified the postulations that (i) different CNT dispersion mechanisms in epoxy are triggered at different powers and (ii) dispersion may be optimized when only "favorable" dispersion mechanisms are active which may be saturated (or optimized) at a given energy input.

4. Conclusions

In the current study MWCNTs have been dispersed in epoxy using an ultrasonic mixer. The scope of the study was to verify the effect of ultrasonic dispersion on the thermo-mechanical and toughness properties of the CNT modified systems with the ultimate goal to optimize this process. Based on the thermo-mechanical and toughness results, the following conclusions can be drawn:

(1) Sonication duration of 1 h was found to be the most effective for the storage modulus and T_g enhancement for both 0.5 and 1 wt.% CNT loadings. The significant increase of the storage modulus and T_g under specific sonication conditions is linked with the improved dispersion and interfacial bonding between the CNTs and the epoxy matrix, which allows sufficient load transfer and therefore enhances the reinforcement effect of the CNTs.

(2) The duration and amplitude of the sonication process is of key importance for the dispersion of the CNTs in the epoxy resin. Best results are obtained for intermediate levels of duration and amplitude, which allow appropriate dispersion without damaging the CNTs structure.

(3) The increase in dispersion time of CNT content only may have adverse effects in the properties of the nanocomposite.

(4) Fracture toughness and critical stress intensity factor are sensitive to both the amplitude and the duration of the sonicator. The optimization factor by keeping the energy input steady and varying the ultrasonic power is more than three when fracture properties are concerned. This observation is attributed to the fact that lower ultrasonic power favors deagglomeration to degradation of the reinforcing phase or the CNTs and is suggesting that different active mechanisms during dispersion are triggered when power thresholds are exceeded.

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