COMPARATIVE STUDIES ON THE PROCESSING AND PERFORMANCE OF CARBON NANOTUBE AND NANOFIBRE BASED MULTI-SCALE COMPOSITES

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Keywords: Multi-scale composites, carbon nanotube, mechanical properties, thermal properties, wear performance.

Abstract

The present research compares the processing and various properties of carbon/epoxy multi-scale composites developed incorporating vapor-grown carbon nanofibres (VCNFs) and single-walled carbon nanotubes (SWCNTs). CNFs and SWCNTs (0.5-1.5 wt. %) were dispersed within epoxy resin using a combination of ultrasonication and mechanical stirring in the presence of a non-ionic surfactant and the nanomaterial/resin dispersions were used to impregnate carbon fabrics in order to develop multi-scale composites. It was observed from the experimental results that SWCNTs needed much longer dispersion treatment as compared to CNFs; however, the improvement in properties in case of CNT based multi-scale composites was also much higher. Incorporation of up to 1.5 wt.% of CNT within carbon/epoxy composites led to improvements of 46% in elastic modulus, 9% in tensile strength, 150% in breaking strain, 170% in toughness, 95% in storage modulus (at 25°C), 167% in thermal conductivity and also significant improvements in the wear performance of composites. Additionally, the modeling approach showed that the multi-scale composites, especially containing SWCNTs, presented elastic modulus very close to the predicted values.

1. Introduction

Carbon nanofibres (CNFs) and nanotubes (CNTs) are being widely researched for use as reinforcements of composite materials due to their outstanding physical properties.[1-7] Reinforcement of various matrices with these nanomaterials proved very effective to enhance their mechanical and thermo-mechanical performance and also to introduce many attractive properties such as excellent thermal and electrical conductivity, electromagnetic shielding, strain and damage sensing, etc. [1-7] More recently, attempts are being directed to improve the performance of conventional fibre reinforced composites using CNFs and CNTs. In these composites, as the matrix is reinforced both by conventional fibres (such as glass or carbon) as well as reinforcements with nano-scale dimensions (CNF, CNT or other nanomaterials), the resulting composites are known as multi-scale composites [8-28]. Till date, multi-scale composites have been fabricated using two different approaches, either (a) incorporating the nanomaterials within the conventional fibres by directing growing, spraying, coating or depositing through electrophoresis, before impregnation with the matrix systems or (b) dispersing within the matrix systems. Although the problematic step of nanomaterial

dispersion within matrix is eliminated in the first approach, the matrix dominated properties are more likely to improve using the second approach in which nanomaterials are distributed all over the matrix and therefore, have been studied more frequently. Multi-scale composites with improved properties such as in-plane mechanical behaviour, fracture toughness, inter-laminar shear strength, thermo-mechanical properties, electrical and thermal conductivity and wear performance have been reported in the literature. Various types of nano-reinforcements such as CNF, types of CNT (single walled, multi-walled, double-walled), nano clay, nano graphite, etc. have been used in these composites and the extent of property enhancement was also different depending on the type and concentration of nanomaterials, functionalization and processing conditions. Dispersion of nanomaterials, especially for the nanomaterials having high surface area like CNF and CNT, was reported as one of the key parameters in these various studies influencing the results, even more than the inherent properties of the nanomaterials, and therefore, the use of different dispersion techniques by different researchers made it impossible to compare the performance of multi-scale composites developed using different nanomaterials. For example, use of an efficient dispersion route (combination of ultrasonication with high speed mechanical stirring at 2000 rpm) in our previous studies [27] led to development of CNF based multi-scale composites having much higher mechanical properties than previously reported CNT based multi-scale composites [23-25], although CNT has much better mechanical properties as compared to CNF. However, when we fabricated SWCNT based multi-scale composites using the same dispersion approach, the CNT based composites showed much higher in-plane mechanical properties at much lower concentrations as compared to CNF based multi-scale composites [28]. This indicates that if properly dispersed, CNT has much higher potential to improve mechanical properties of composite materials. However, in the above mentioned studies, we focused only on the mechanical properties which strongly depend of nanomaterial dispersion. Therefore, we tried to achieve excellent dispersion of very low concentrations of nanomaterials (CNF up to 0.5 wt. % and CNT up to 0.1 wt. %) using a lengthy and intensive dispersion technique which significantly reduced the aspect ratio of nanomaterials. Therefore, in the present research, VCNFs and SWCNTs were dispersed using a milder dispersion route (combination of ultrasonication with low speed mechanical stirring in the presence of surfactant) and at much higher concentrations (up to 1.5 wt.%) to achieve considerable improvements in other important properties as well, such as thermal and electrical conductivity, thermo-mechanical properties and abrasion and wear behaviors. Moreover, an attempt has been made in this research to compare the processability and performance of CNF and CNT based multi-scale composites prepared using same concentrations of nanomaterials and using the same processing conditions.

2. Materials and methods

Plain weave carbon fabric (RY90-16, 3k x 3k, 668 g/m^2) was supplied by Cixi Sealing Spacer Material Factory, China. CNF (Pyrograf PR24AGLD) was purchased from Applied Sciences Inc. (Ohio, USA) and SWCNT was supplied by Carbolex Inc. (Pennsylvania, USA). The epoxy resin (DGEBA type) was supplied by Sigma Aldrich (India) and a polyamine type hardener (diethylenetriamine, DEH 20) purchased from Dow Chemicals (India) was used in the ratio of 1:4 (hardener: epoxy) to cure the epoxy resin. Non-ionic surfactant Polyoxyethylene 8 lauryl ether (30% w/v, purchased from Loba Chemie Pvt. Ltd, India) was used for the dispersion of carbon nanomaterials and, AR grade acetone supplied by Qualigens Fine Chemicals (India) was used in ratio of 1:3 (acetone: epoxy) to dilute the epoxy resin in order to get required viscosity.

2.1 Dispersion of CNF and SWCNT

CNFs and SWCNTs (0.5 wt.% to 1.5 wt.%) were dispersed into the epoxy resin (mixed with acetone and hardener) using a combination of mechanical stirring and ultrasonication in the presence of non-ionic surfactant. Ultrasonication was carried out at 20 kHz frequency in a bath sonicator (Elma, Transonic Digital S) at a temperature maintained below 40°C using ice. Mechanical stirring was carried out at a speed of 1000 rpm using a mechanical stirrer with specially designed blades. Surfactant was used at concentration of 0.2%, decided based on our previous studies.[26, 30] The period of mechanical stirring and ultrasonication treatment were varied and their effect on the nanomaterial dispersion was studied using Optical microscopy (Leica DMLP) in cured thin films, in order to find the most suitable dispersion route for achieving homogeneous dispersion.

2.2 Fabrication of composites

In order to characterize the level of dispersion achieved through the used dispersion routes, thin films were prepared using CNF and CNT dispersed resins and then dried overnight at room temperature, followed by curing at 150°C for 2h. Carbon fabrics, cut in to rectangular pieces, were impregnated by the CNF and CNT suspensions and stacked in the form of laminates (0/0/0). After drying, the samples were cured in a compression molding machine (Carver Laboratory Press, Fred C. Carver Inc., Model No. 2627) at 80°C for 2 hours, followed by post curing at 150°C for 2h. The average fiber content after curing was calculated as 41% by volume with an average void content of 2 % determined by the density measurements.

2.3 Characterization

Dispersion of CNF and SWCNT within cured resin was studied using an optical microscope (Leica DMLP) in transmission mode. Tensile tests were carried out in Zwick Z010 UTM according to ASTM D3039-76 standard. Fracture surface of composites after tensile test was studied with the help of Scanning electron microscope (Stereoscan D360, Cambridge Instruments). Dynamic mechanical analysis (DMA, 3-point bending configuration) was carried out in Perkin-Elmer DMA7 instrument in the temperature range of -30°C to 200°C using a static load of 200 mN, dynamic load of 160 mN, frequency of 1Hz and at a scanning rate of 10°C/min. Thermal conductivities were measured in Alambeta instrument (Czech Republic). Abrasion resistance of the carbon/epoxy composites was measured in Linear Abrasive Wear Tester (Magnum Engineers, India). The coefficient of friction, weight loss and thickness loss were calculated after the test to find the wear properties of the prepared composites.

3. Results and discussions

3.1 Dispersion of carbon nanofibre and carbon nanotube

It was observed from the analysis of optical micrographs of CNT suspensions that a dispersion path involving 1h mechanical stirring followed by 2 h ultrasonication and 1 h mechanical stirring was enough to achieve a good quality dispersion and therefore, used for fabrication of multi-scale composites. However, as compared to CNFs, the dispersion of CNT was extremely difficult and good quality dispersion was achieved only after a long treatment period, i.e. 4 h stirring followed by 6 h ultrasonication and 5h mechanical stirring.

3.2 Tensile properties

The tensile test results of neat carbon/epoxy and multi-scale composites are listed in Table 1 and 2. It can be observed that the elastic modulus improved significantly (up to 34%) with addition of CNF. However, the improvement in the tensile strength was only marginal (3.6%), whereas breaking strain decreased considerably (up to 53%). On the other hand, the addition of CNT led to much higher improvement in elastic modulus (46%) as compared to CNF. The improvement in tensile strength was also higher (9%) in this case. Also, it was very interesting to note that addition of CNT resulted in strong improvement (up to 150%) in the breaking strain of the composites unlike CNFs which led to significant reduction of breaking strain. This was attributed to the to the fact that CNTs have much higher flexibility and breaking elongation (5 %) as compared to CNFs (only 1.5%). Moreover, the improvements in elastic modulus and tensile strength were also higher in case of CNT due to much better mechanical properties and reinforcing capability of CNTs when dispersed homogeneously within the matrix.

Samples	Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
Carbon/epoxy composite	33.2	253.2	1.46
Multi-scale with 0.5% CNF	39.2	257.7	1.15
Multi-scale with 1.0% CNF	42.1	259.9	0.85
Multi-scale with 1.5% CNF	44.5	262.3	0.69

Table 1. Tensile properties of CNF based multi-scale composites.

Samples	Elastic Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
Neat carbon/epoxy composite	33.0	254.0	1.52
Multi-scale with 0.5% CNT	40.4	268.5	2.14
Multi-scale with 1.0% CNT	46.3	274.2	3.16
Multi-scale with 1.5% CNT	48.1	277.8	3.80

Table 2. Tensile properties of CNT based multi-scale composites.

One important benefit of dispersing CNTs within the matrix, as observed in the present study, was the improvement in breaking strain along with modulus and strength. This resulted in strong improvement in the toughness of the composites. As compared to the neat carbon/epoxy composites, toughness improved by 170%, while a decrease in toughness was observed in case of CNF based multi-scale composites. A simplified approach [27], for predicting elastic modulus of woven composites showed that the neat carbon epoxy composites had much lower elastic modulus than the predicted values and the incorporation of nanomaterials, especially CNTs, led to strong rise in the composite modulus reaching very close to the predicted values. It is also worth mentioning that predicted modulus calculated using the above approach based on the reinforcing effects of CNF and CNT did not show much change with the increasing nanomaterial content, but the experimental modulus was strongly influenced by the incorporation of nanomaterials. This indicates that some other factors (besides the reinforcing effect of nanomaterials) were also responsible for such strong improvement in elastic modulus such as the improved fibre/matrix interface in the presence of nanomaterials or any other phenomenon which has not been explored till now.

3.3 Dynamic mechanical analysis (DMA)

The storage modulus curves for neat carbon/epoxy and multi-scale composites are provided in Fig. 1 (a). It can be observed that incorporation of CNF led to increase in the storage modulus both in the glassy and rubbery state. A strong improvement in the storage modulus can be observed in glassy state below the glass transition temperature (T_g). Storage modulus improved by 30% at 25°C with addition of 1.5% CNF. The loss modulus of neat carbon/epoxy and multi-scale composites is shown in Fig. 1(b). It can be observed that loss modulus also increased with increase in nanofiber content. Loss modulus represents the damping characteristics of the composites and is a measurement of unrecoverable oscillation energy dissipation per cycle. Presence of CNFs, however, resulted in slight decrease in the T_g of the composites, as can be seen from Tan delta curves presented in Fig. 1(c).
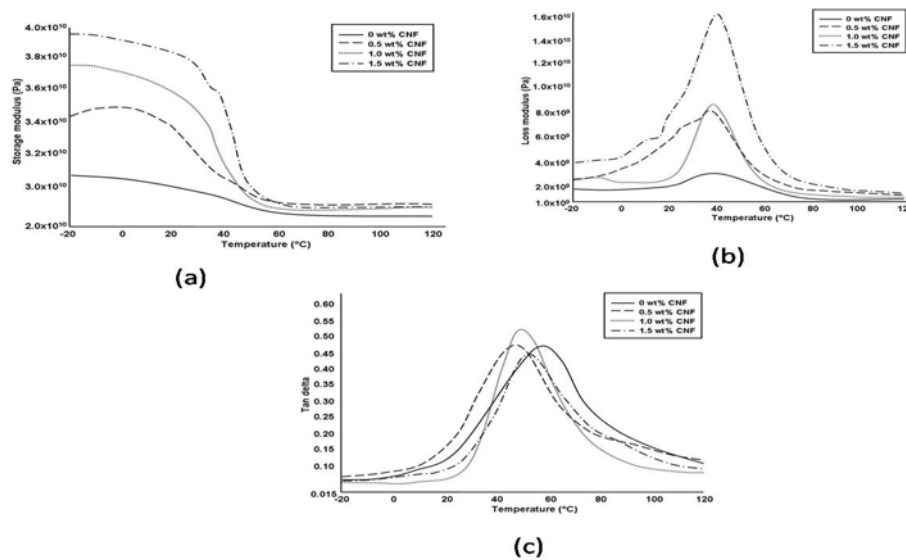

Figure 1. Dynamic mechanical properties of carbon/epoxy composites containing different CNF%: (a) storage modulus, (b) loss modulus and (c) tan-delta curves.

It can observed from Fig. 2(b) that similar to the case of CNF based multi-scale composites, the addition of CNT within epoxy matrix led to strong improvement in the storage modulus of carbon/epoxy composites. However, the improvement in storage modulus due to addition of CNT was much higher as compared to CNFs. At 25°C, storage modulus improved by 95% through addition of 1.5 wt. % CNT. The higher improvement in case of SWCNTs was attributed to their higher surface area and better mechanical properties as compared to the CNFs. Moreover, the loss modulus of carbon/epoxy composites also increased strongly with the addition of CNTs and the increase was more as compared to the case of CNFs (Fig. 2b). Therefore, CNT based multi-scale composites exhibited better energy dissipation and damping behaviour as compared to the neat carbon/epoxy and CNF based multi-scale composites. Similar to CNF addition, the addition of CNT also led to slight decrease in T_g due to reduction in epoxy cross-linking density, as can be noticed from the Tan delta curves presented in Fig. 2c. However, in case of very low concentration of CNT (0.5 wt.%), probably the CNTs were dispersed individually and therefore, could impose much higher restrictions to the segmental movements of epoxy molecular chains and therefore, raised the T_g of the matrix. In case of higher concentrations, although dispersion was homogeneous, it was not possible to disperse CNTs individually and therefore, T_g of the composites decreased due to reduced cross-linking.
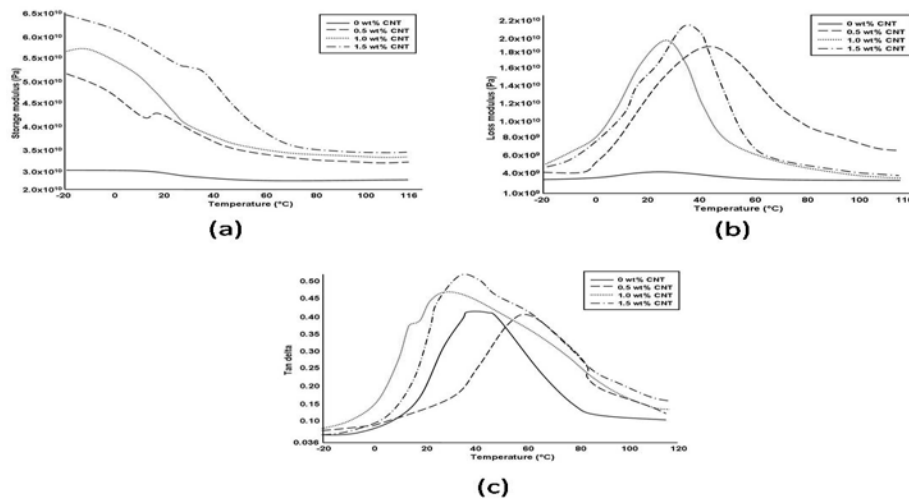
Figure 2. Dynamic mechanical properties of carbon/epoxy composites containing different SWCNT%: (a) storage modulus, (b) loss modulus and (c) tan-delta curves.

3.4 Thermal transmission properties

The thermal transmission parameters of neat carbon/epoxy and multi-scale composites are provided in Table 3 and 4. It can be observed that incorporation of both CNF and CNT within epoxy matrix resulted in improved thermal conductivity and absorptivity and reduced thermal resistance and diffusivity. Thermal conductivity improved by 35% and 167% due to addition of 1.5% CNF and CNT respectively. One principal reason for improvement of thermal conductivity due to addition of CNF or CNT is the improvement of epoxy matrix conductivity. This is obvious as the thermal conductivity of CNF (20 W m^{-1}K^{-1}) and CNT (1200 W m^{-1}K^{-1}) is much higher than the epoxy matrix (0.1 W m^{-1}K^{-1}) and therefore, their dispersion within epoxy matrix brings down the thermal resistance of the matrix. Another reason for improvement of thermal conductivity in multi-scale composites can be the formation of a three dimensional conducting network of carbon fibres which are linked in the matrix by the CNFs or CNTs. The improvement in thermal conductivity in case of CNT addition was much higher due to much higher thermal conductivity of SWCNTs as compared to CNFs.

Parameters	0% CNF	0.5% CNF	1.0% CNF	1.5% CNF
Thermal conductivity (λ) Wm^{-1}K^{-1}	56.5 x 10^{-3}	66.0 x 10^{-3}	71.9 x 10^{-3}	76.4 x 10^{-3}
Diffusivity (a) m^{2}s^{-1}	0.045 x 10^{-6}	0.038 x 10^{-6}	0.035 x 10^{-6}	0.032 x 10^{-6}
Absorptivity (b) Wm^{-2} s$^{1/2}$K^{-1}	249	359	373	381
Resistivity (r) Km^{2}W^{-1}	28.8 x 10^{-3}	18.1 x 10^{-3}	14.8 x 10^{-3}	12.2 x 10^{-3}
Thickness (h) mm	1.65	1.59	1.78	1.22

Table 3. Thermal transmission parameters of CNF based multi-scale composites.

3.5 Abrasion and wear performance

The wear properties of neat carbon/epoxy and multi-scale composites are listed in Table 5. It can be observed from Table 5 that the incorporation of carbon nanomaterials into the carbon/epoxy composites resulted in significant reduction in weight and thickness losses with respect to neat carbon/epoxy composites. Additionally, the wear performance was better in case of CNT based multi-scale composites.

Parameters	0% CNT	0.5% CNT	1.0% CNT	1.5% CNT
Thermal conductivity (λ) Wm^{-1}K^{-1}	56.5 x 10^{-3}	96.6 x 10^{-3}	130 x 10^{-3}	151 x 10^{-3}
Diffusivity (a) m^{2}s^{-1}	0.045 x 10^{-6}	0.028 x 10^{-6}	0.015 x 10^{-6}	0.008 x 10^{-6}
Absorptivity (b) Wm^{-2} s$^{1/2}$K^{-1}	249	408	470	487
Resistivity (r) Km^{2}W^{-1}	28.8 x 10^{-3}	11.3 x 10^{-3}	8.7 x 10^{-3}	6.3 x 10^{-3}
Thickness (h) mm	1.65	1.12	1.12	0.95

Table 4. Thermal transmission parameters of CNT based multi-scale composites.

Composites	Weight loss (%)	Thickness loss (%)	Coefficient of friction
Carbon/epoxy	4.6	3	2.8
Multi-scale with 1% CNF	3.1	1.1	4.4
Multi-scale with 1% CNT	1.3	0.5	3.3

Table 5. Wear performances of carbon/epoxy and multi-scale composites.

4. Conclusions

In conclusion, it can be said that the processing of SWCNT based multi-scale composites is more difficult as compared to CNF based composites due to the lengthy dispersion process of CNT; however, SWCNTs were found much more effective in enhancing various properties of conventional composites. Therefore, a choice has to be made to select either CNF or SWCNT for fabrication of multi-scale composites, considering the cost of raw materials, processability and performance.

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