

Mechanical and Thermal Transmission Properties of Carbon Nanofiber-Dispersed Carbon/Phenolic Multiscale Composites

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ABSTRACT: The present article reports the development and characterization of carbon nanofiber (CNF)-incorporated carbon/phenolic multiscale composites. Vapor-grown CNFs were dispersed homogeneously in to phenolic resin using an effective dispersion route, and carbon fabrics were subsequently impregnated with the CNF-dispersed resin to develop carbon fiber/CNF/phenolic resin multiscale composites. Mechanical and thermal transmission properties of multiscale composites were characterized. Elastic modulus and thermal conductivity of neat carbon/phenolic and multiscale composites were predicted and compared with the experimental results. It was observed that incorporation of only 1.5 wt % CNF resulted in 10% improvement in Young's modulus, 12% increase in tensile strength, and 36% increase in thermal conductivity of carbon/phenolic composites. Fracture surface of composite samples revealed the formation of stronger fiber/matrix interface in case of multiscale composites than neat carbon/phenolic composites. Enhancement of above properties through CNF addition has been explained, and the difference between the predicted values and experimental results has been discussed. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2383–2392, 2013

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INTRODUCTION

Multiscale nanocomposites have been developed recently to enhance various properties of conventional fiber-reinforced composites. Two different strategies have been employed for the manufacturing of these composites: (1) dispersion of nanomaterials within the matrix^{1–19} and (2) incorporation of nanomaterials on the surface of conventional fibers by depositing, growing, or grafting, prior to their use in composites.^{20–24} It is obvious that the matrix-dominated properties of composites are more influenced by the incorporation of nanomaterials in the first case due to the presence of nanomaterials throughout the matrix. Problem of nanomaterial dispersion in the matrix, however, is the main difficulty in developing multiscale composites using the first route, especially in case of nanomaterials having very high aspect ratio such as carbon nanofiber (CNF) and nanotube (CNT). Moreover, these nanomaterials (CNF and CNT) may show considerable reagglomeration during processing, if the composite manufacturing process allows sufficient resin flow, as in case of vacuum-assisted resin infusion molding (VARIM). At high concentrations, these nanomaterials can be trapped in the

intertow regions within the fiber preform mesh leading to nanomaterial filtering.⁹ Reagglomeration of CNF and CNT can be minimized using the prepreg technique of composite fabrication, which allows less resin flow during processing. Improvement in composite properties such as modulus and strength, which strongly depend on the nanomaterial dispersion, is therefore difficult to achieve by dispersing CNFs and CNTs within the matrix due to their dispersion problem. As a result, although the existing research studies on CNF- and CNT-based multiscale composites reported improvement in various matrix-dominated properties such as fracture toughness, interfacial shear strength, and coefficient of thermal expansion, no major improvement was observed in the in-plane mechanical properties of composites.

Carbon nanomaterial-based multiscale composites using epoxy resin have been widely studied and reported. However, only a few research studies have been carried out for developing multiscale composites using phenolic resins.^{25–27} Also, the dispersion behavior of carbon nanomaterials in phenolic resin has been seldom studied. Because of its highest carbon yield after

Table I. Properties of CNF

Properties	Values ^a
Fiber diameter	60–150 nm
Length	30,000–100,000 nm
Modulus	400 GPa
Tensile strength	2.7 GPa
Strain to break	1.5%
Density	1.95 g cc ⁻¹
Thermal conductivity	20 W m ⁻¹ K ⁻¹

^a Source: Applied Sciences, Inc.

carbonizing, phenolic resins are widely used for fabric-reinforced carbon–carbon composites, which find applications in many high-end sectors such as spacecraft reentry frames, and aircraft brakes.²⁸ There are a few reports on the improvement of mechanical properties and thermal conductivity of carbon fiber/phenolic resin composites using CNTs and CNFs. For example, Mathur et al.²⁵ have grown multiwalled CNTs (MWCNTs) on different carbon fiber substrates (unidirectional fiber tows, bidirectional cloth, and three-dimensional felt) and fabricated multiscale phenolic composites. Flexural modulus and strength improvements of 28% and 20%, 54% and 75%, and 46% and 66% were achieved for these three types of carbon substrates, respectively. Mechanical properties of multiscale phenolic composites reinforced with short carbon fibers and MWCNTs have been investigated by Yeh et al.²⁶ According to their study, MWCNTs showed much better interface and reinforcing effect in phenolic matrix as compared to short carbon fibers and the combination of MWCNTs and short carbon fibers, which showed the lowest reinforcing effect. On the other hand, significant improvement of thermal conductivity (from 250 to 393 W m⁻¹ K⁻¹) of carbon/phenolic composites using highly crystalline MWCNTs (7 wt %) has been reported by Kim et al.²⁷ CNT incorporated carbon–carbon composites have also been developed through carbonization of multiscale phenolic

resin composites and reported better mechanical and wear performance than pure carbon–carbon composites.²⁹

In our recent studies on epoxy-based multiscale composites,^{18,19} it was observed that a homogeneous dispersion of CNF/CNT can ensure strong improvements in the in-plane mechanical, thermal, and electrical properties at much lower nanomaterial concentrations than used in the previous studies. In the present study, the dispersion of vapor-grown CNFs in phenolic resin has been thoroughly investigated and the best dispersion route has been used to develop carbon/phenolic multiscale composites with low CNF loading (0.5–1.5 wt %). The developed multiscale composites have been characterized for in-plane mechanical (tensile) and thermal transmission properties.

EXPERIMENTAL

Raw Material

Carbon fabric with plain weave pattern (areal density of 195 g m⁻²) was supplied by Surabhi International, Kanpur, India. CNF (Pyrograf PR24AGLD) was procured from Applied Sciences, Inc. (Ohio, USA). Properties of these CNFs are listed in Table I and their morphology is provided in Figure 1. Nonionic surfactant, polyoxyethylene 8 lauryl ether (30% w/v) was purchased from Loba Chemie Pvt. Ltd. (India) and AR grade methanol supplied by SRL Pvt. Ltd. (India) was used as a solvent for phenolic resin. AR grade phenol, formaldehyde (40% water solution), and ammonium hydroxide purchased from Qualigens Fine Chemicals (India) were used for the preparation of phenolic resin.

Preparation of Phenolic Resin

Phenol formaldehyde resin was prepared through condensation reaction between phenol and formaldehyde in the presence of ammonium hydroxide catalyst, through refluxing at 70°C for 1.5 h. Based on some initial experiments, raw material proportion (ammonium hydroxide : phenol : formaldehyde) selected to prepare phenolic resin was 1 : 10 : 10 (by volume). Subsequently, methanol was added as a solvent in the ratio of 1 : 3 (methanol : phenolic resin, by volume) to adjust the prepared resin viscosity (2800–3000 cP, as measured in a viscometer from

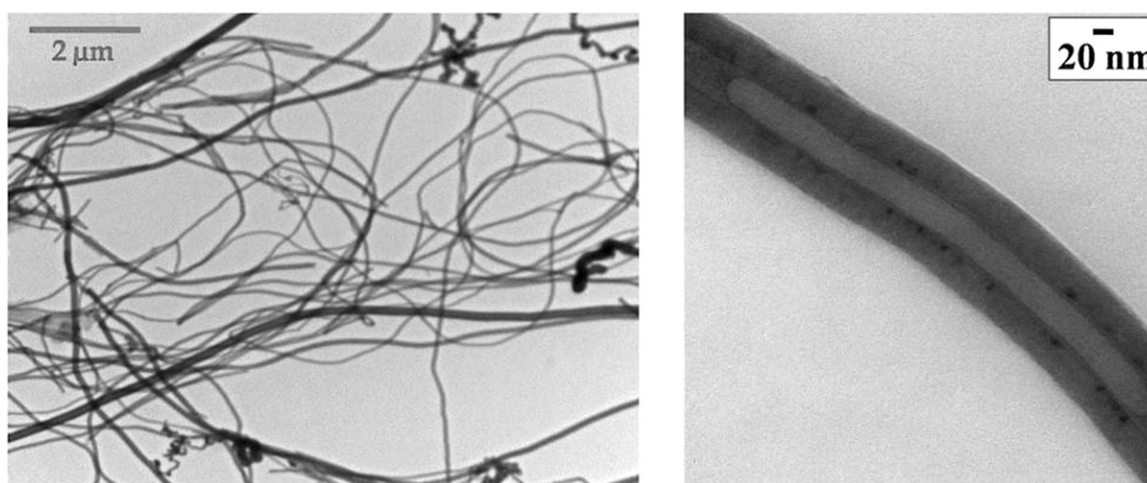


Figure 1. Morphology of CNFs as observed by TEM at different magnifications.

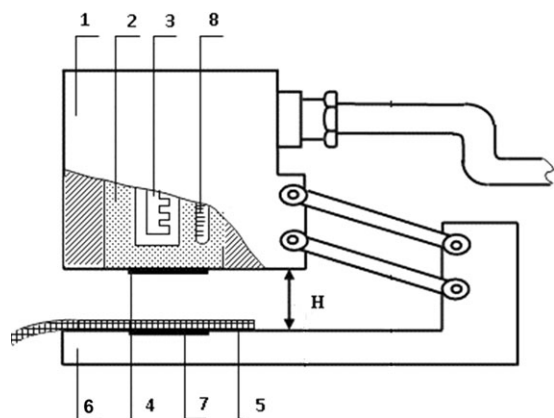


Figure 2. Schematic diagram of thermal conductivity measuring instrument (Alambeta) showing various parts: 1, measuring head; 2, metal block; 3, heater; 4, heat flow sensor; 5, composite sample; 6, instrument base; 7, sample holder; 8, thermometer.

Brookfield Engineering, USA with spindle RV 6 at $38^{\circ}\text{C} \pm 1^{\circ}\text{C}$).

Dispersion of CNF

CNFs were dispersed into the phenolic resin using three different routes: (1) ultrasonication: CNFs (0.5, 1, and 1.5 wt % of resin) were dispersed into phenolic resin through a ultrasonication treatment at 20 kHz frequency for 2 h. Ultrasonication was carried out in a bath sonicator (Elma, Transonic Digital S) at a temperature maintained below 40°C using ice. (2) Using surfactant: in this route, CNFs (0.5, 1, and 1.5 wt %) were dispersed into the phenolic resin using 0.2 vol % (of resin) of nonionic surfactant through mechanical stirring at 1000 rpm for 2 h. (3) Combination of ultrasonication, stirring, and surfactant: in this case, CNFs (0.5, 1, and 1.5 wt %) were dispersed into the phenolic resin using 0.2 vol % of nonionic surfactant through mechanical stirring for 1 h, followed by an ultrasonication treatment at 20 kHz for 1 h.

Fabrication of Composites

To characterize the level of dispersion achieved through the used dispersion routes, thin films were prepared using CNF dispersion resin, dried overnight at room temperature, and then cured at 150°C for 2 h. Carbon fabrics, cut in to specific dimensions, were impregnated by the CNF dispersed resin 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 150°C for 2 h. The average fiber content after curing was calculated as 41% by volume with an average void content of 2% determined by the density measurements.

Characterization

Dispersion of CNF within cured resin was studied using an optical microscope (Leica DMLP) in the transmission mode. Tensile tests were carried out in Zwick Z010 Universal Testing Machine according to ASTM D3039-76 standard using 5 mm/min crosshead speed. Fracture surface of composites after tensile test was studied with the help of optical microscope (Leica DMLP) in both reflection and transmission modes.

Thermal conductivities were measured in Alambeta instrument (Czech Republic). The composite samples were placed between two plates (Figure 2), one of which was kept at ambient temperature and the other one was heated to a constant temperature (40°C) above the ambient temperature. The heat fluxes crossing between the two faces of sample were recorded to evaluate the thermal parameters.

Elastic Modulus Prediction

A simplified approach has been employed in this article to predict Young's modulus of neat carbon/phenolic and multiscale composites. The composite can be thought as a laminate consisting of two plies or layers, a and b as can be seen in Figure 3. The layers a and b are placed perpendicular to each other and consists of warp (or longitudinal yarns) and matrix and weft (or transverse yarns) and matrix, respectively.

As the used carbon fabric had very low crimp level which can be neglected and the fibers were nontwisted, the effect of wave was neglected and the carbon fibers in each section were considered to be straight and parallel. Considering x as the tensile loading direction (warp direction), the modulus of layer a can be predicted using equal strain condition (Rule of Mixture) according to the following equation³⁰:

$$E_a = E_{f\parallel} V_{fa} + E_m V_{ma} \quad (1)$$

where $E_{f\parallel}$ is the axial modulus of warp fibers, V_{fa} is the volume fraction of warp fibers, E_m is the matrix modulus, and V_{ma} is the volume fraction of matrix in layer a. The modulus of layer b can be predicted according to Halpin and Tsai equation,³⁰

$$E_b = \frac{E_m(1 + \xi\eta V_{fb})}{(1 - \eta V_{fb})} \quad (2)$$

in which,

$$\eta = \frac{\left(\frac{E_{f\perp}}{E_m} - 1\right)}{\left(\frac{E_{f\perp}}{E_m} + \xi\right)} \quad (3)$$

$E_{f\perp}$ is the transverse modulus of weft fibers, V_{fb} is the volume fraction of weft fibers, and ξ is the shape factor which depends

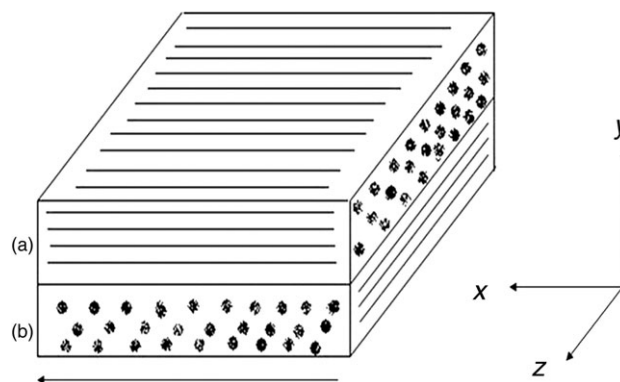


Figure 3. Schematic diagram of carbon fabric composite showing layer (a) that represents combination of warp yarns and matrix and layer (b) representing combination of weft yarns and matrix.

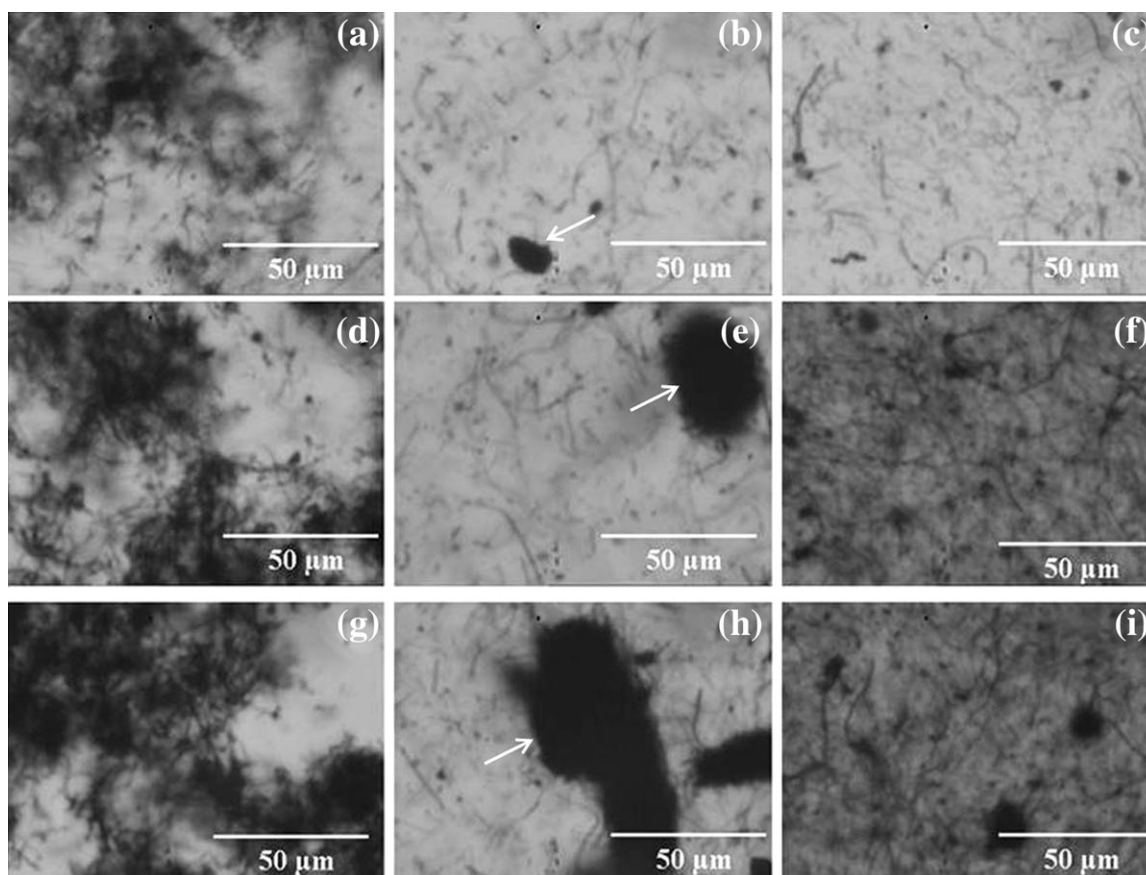


Figure 4. Dispersion of CNF using different routes at different concentrations: (a) 0.5%, route 1; (b) 0.5%, route 2; (c) 0.5%, route 3; (d) 1.0%, route 1; (e) 1.0%, route 2; (f) 1.0%, route 3; (g) 1.5%, route 1; (h) 1.5%, route 2; and (i) 1.5%, route 3.

on the geometrical parameters of the reinforcement and was determined to be ~ 2 in our case. For this purpose, transverse modulus of unidirectional carbon fiber/phenolic resin composites (using same carbon fiber and resin) was measured and the value of ξ was adjusted to fit the experimental values as per eq. (2). The overall modulus of composite can therefore be predicted using the following equation:

$$E = E_a V_a + E_b V_b \quad (4)$$

As the used fabric is a balanced square sett fabric having same carbon fibers in both longitudinal and transverse directions and their numbers are equal,

$$V_a = V_b = 0.5 \quad (5)$$

$$V_{fa} = V_{fb} = 0.5 V_f \quad (6)$$

$$V_{ma} = V_{mb} = 0.5 V_m \quad (7)$$

where V_f and V_m are the volume fractions of fiber and matrix in composite, respectively.

Using eqs. (5)–(7) and , eqs. (1)–(4) can be simplified as:

$$E_a = 0.5(E_{f||} V_f + E_m V_m) \quad (8)$$

$$E_b = \frac{E_m(1 + \eta V_f)}{(1 - \eta V_f)} \quad (9)$$

$$\eta = \frac{\left(\frac{E_{f\perp}}{E_m} - 1\right)}{\left(\frac{E_{f\perp}}{E_m} + 2\right)} \quad (10)$$

$$E = \llbracket 0.5(E) \rrbracket_a + E_b \quad (11)$$

According to the supplier's data, $E_{f||}$ is 230 GPa, $E_{f\perp}$ is 20 GPa. V_f was calculated from the density of fiber, matrix, and composite and was ~ 0.41 . The matrix modulus E_m can be calculated depending on the concentration of CNF dispersed within the matrix, according to the following equation³¹:

$$E_m = \beta E_{nf} V_{nf} + E_r V_r \quad (12)$$

where E_{nf} and V_{nf} are the modulus and volume fraction of CNF, respectively, E_r and V_r are the modulus and volume fractions of resin, β is the CNF orientation factor whose value varies from 0.375 for 2D random orientation to 0.2 for 3D random orientation. In our study, β was determined to be ~ 0.3 . The values of V_{nf} were calculated as 0.4, 0.8, and 1.2 for 0.5, 1.0, and 1.5 wt % of CNF, respectively. The value of E_r was measured as 4 GPa (standard deviation 0.2).

Thermal Conductivity Prediction

Thermal conductivity of carbon/phenolic multiscale composites was predicted using the following model of

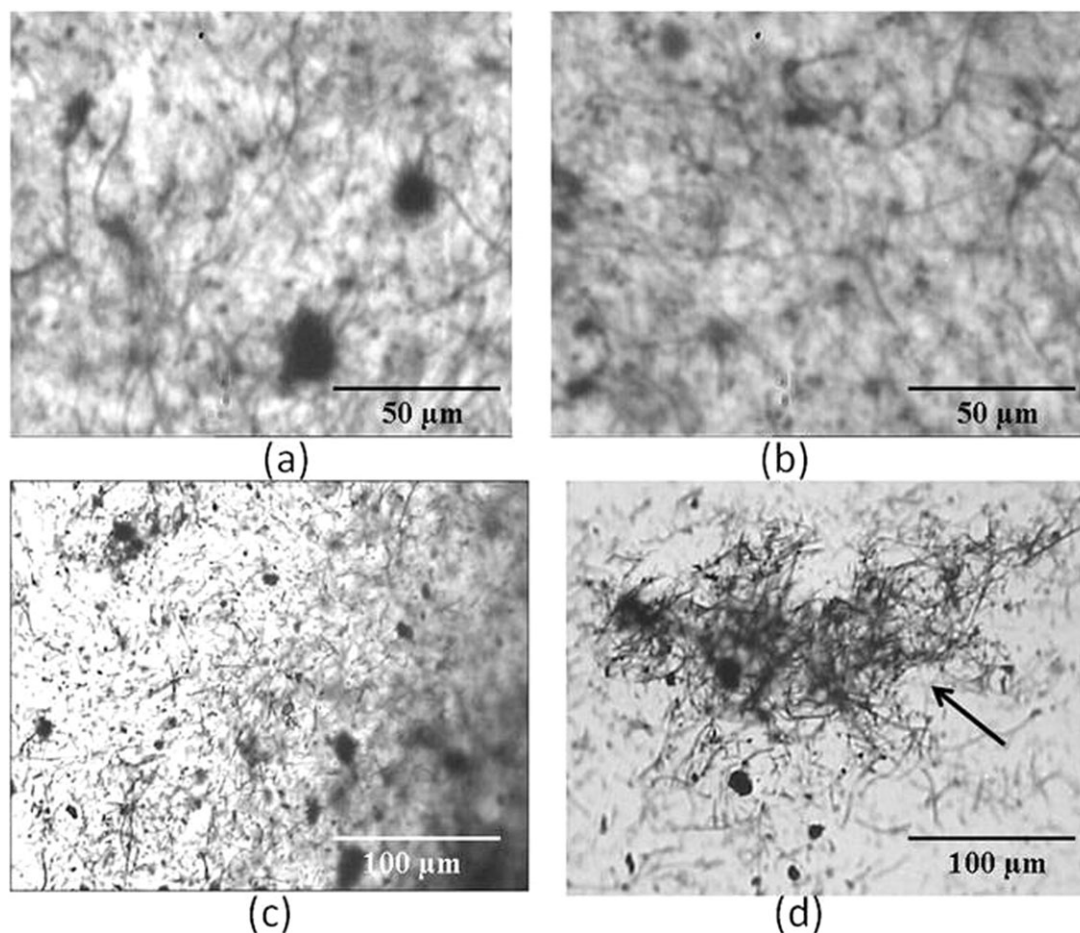


Figure 5. Dispersion of CNF: (a) using route 3, (b) using surfactant (0.1%), stirring (1 h), and ultrasonication (1.5 h), (c) using route 3 after 2 h, and (d) using surfactant (0.1%), stirring (1 h), and ultrasonication (1.5 h) after 2 h.

transverse thermal conductivity, proposed by Hatta and Taya³⁰

$$K_c = K_m + \frac{K_m(K_f - K_m)V_f}{K_m + \frac{(1-V_f)(K_f - K_m)}{2}} \quad (13)$$

where K_c is the transverse thermal conductivity of composite, K_m is the matrix conductivity, K_f is the transverse conductivity of fibers, and V_f is the fiber volume fraction. Thermal conductivity of matrix containing CNFs was predicted using the following equation³²:

$$K_m = K_r \left(1 + \frac{V_{nf} K_{nf}}{3K_r} \right) \quad (14)$$

where K_r is the resin conductivity, K_{nf} is the nanofiber conductivity, and V_{nf} is the nanofiber volume fraction. According to manufacturer's data, K_r is $0.15 \text{ W m}^{-1} \text{ K}^{-1}$, K_{nf} is $20 \text{ W m}^{-1} \text{ K}^{-1}$.

RESULTS AND DISCUSSION

Dispersion of CNF

Quality of CNF dispersion depends on a few crucial factors, namely, presence of large and dense CNF clusters, separation of individual CNFs or CNF bundles, homogeneity of dispersion,

i.e., overall distribution of CNFs throughout the resin, stability of dispersed CNFs and re-agglomeration, damage caused to CNFs due to dispersion process, etc. While evaluating the quality of CNF dispersion, these factors should be considered, since they strongly influence the mechanical behavior of nanocomposites. Dispersions of CNF at different concentrations (0.5, 1.0, and 1.5%) using the three dispersion routes are shown in Figure 4. It is clear that CNFs dispersed through the combination of ultrasonication and stirring using surfactant (third route) resulted in the best quality of dispersion in all three studied concentrations. Our previous studies^{33,34} with epoxy resin revealed that ultrasonication in presence of surfactant is an efficient route for dispersing relatively lower CNF concentrations (0.1%), whereas the combination of ultrasonication with stirring can be effectively used for higher CNF concentrations (0.5%). In the present study, a combination of both these approaches have been tried to disperse much higher concentrations of CNF (up to 1.5%) in phenolic resin. The reasons for obtaining much better dispersion using this combination are (a) better wetting and infiltration of CNF clusters with phenolic resin due to surfactant, (b) opening of CNF clusters and separation of CNF bundles due to ultrasonication, and (c) improvement of dispersion homogeneity due to mechanical stirring. Therefore, using this route, a good state of

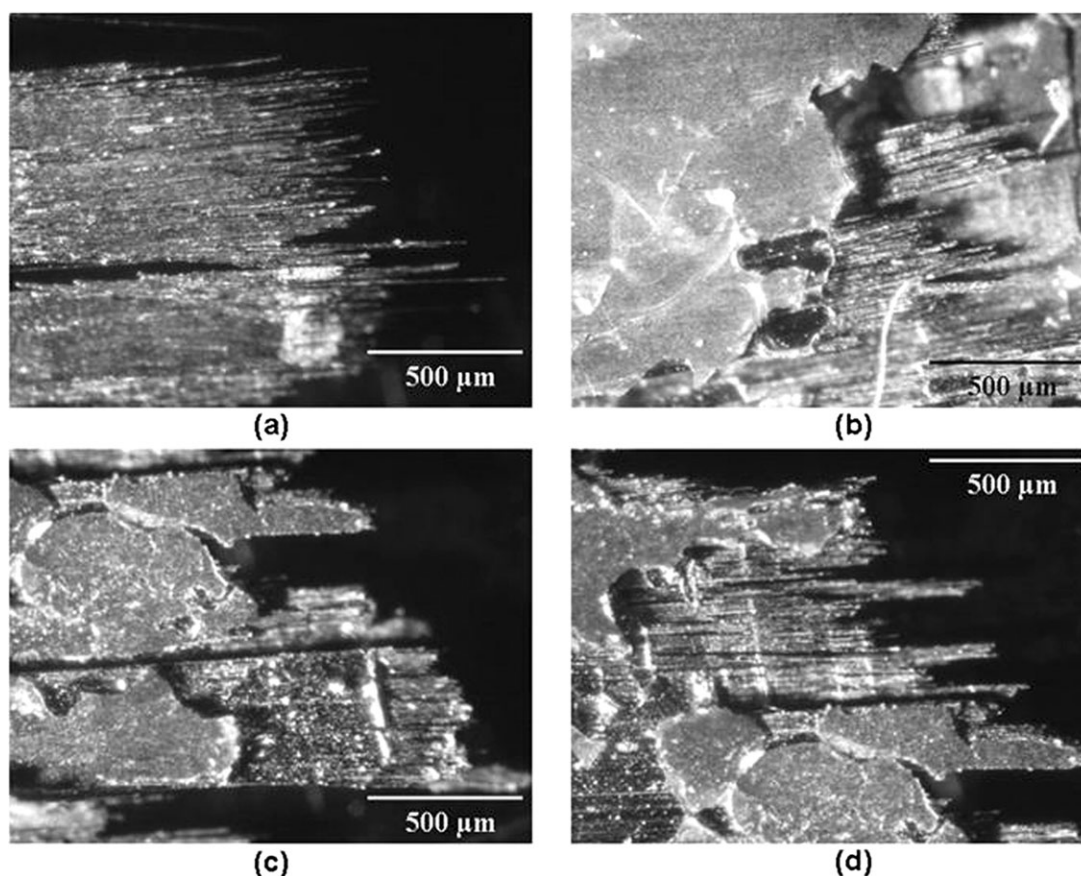
Table II. Tensile Properties of Carbon/Phenolic and Multiscale Composites

Composites	Elastic modulus (GPa)	Predicted modulus (GPa)	Tensile strength (MPa)	% Increase in tensile strength	Elongation (%)
Carbon/phenolic	20.9 ± 0.5	27.4	287 ± 4	-	1.5 ± 0.6
Multiscale with 0.5 wt % CNF	22.0 ± 0.3	27.7	292 ± 5	1.7	1.2 ± 0.5
Multiscale with 1.0 wt % CNF	22.5 ± 0.1	28.1	308 ± 4	7.4	1.2 ± 0.5
Multiscale with 1.5 wt % CNF	23.1 ± 0.2	28.4	321 ± 6	11.8	1.2 ± 0.4

CNF dispersion which was free from large CNF clusters, with separated CNFs and good homogeneity, was achieved. Nevertheless, the quality of CNF dispersion deteriorated with the increase in its concentration.

It is also interesting to note that all dispersions using the second method [Figure 4(b,e,h)] showed two clearly distinct phases: (a) dense CNF clusters, as indicated by arrows and (b) dispersed CNFs. This was attributed to the fact that the stirring process was able to disperse only loose CNFs with the help of surfactant, whereas large and dense CNF clusters remained intact and clearly visible among the dispersed CNFs. Introducing another ultrasonication step (third route) helped in loosening the CNF clusters and in their subsequent homogeneous dispersion in to the phenolic resin, also assisted by the stirring process.

The concentration of surfactant (0.2%) and treatment duration of ultrasonication and stirring (1 h for each treatment) was decided based on our previous study with epoxy resin.^{29,30} Although surfactant helps in CNF wetting and dispersion, it remains in the final composite as an impurity and, therefore, higher surfactant concentrations deteriorate composite's mechanical properties. On the other hand, longer ultrasonic or stirring treatment durations (more than 2 h) lead to significant damage to CNFs and curtailment of their aspect ratios. Besides a good level of dispersion was achieved using route 3, the stability of prepared dispersion was also good. As seen in Figure 5, the dispersed CNFs do not reaggregate after 2 h indicating good dispersion stability, whereas a considerable CNF reagglomeration was observed [Figure 5(d), reagglomerated CNFs are indicated by an arrow] when the dispersion was prepared using 0.1% of surfactant.

**Figure 6.** Fracture surface of composites with (a) 0 wt % nanofiber, (b) 0.5 wt % nanofiber, (c) 1.0 wt % nanofiber, and (d) 1.5 wt % nanofiber.

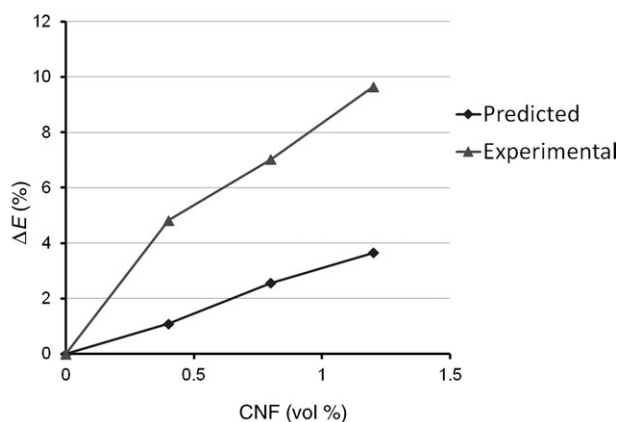


Figure 7. Comparison of experimental and predicted increase in elastic modulus of multiscale composites.

Tensile Properties

Tensile properties of produced composites are listed in Table II. The addition of CNF improved the tensile properties significantly, as can be seen from the improvement in elastic modulus and strength. 1.5 wt % nanofiber dispersion into the matrix resulted in 10% increase in elastic modulus and 12% increase in breaking strength of carbon fiber/phenolic resin composites. The improvement of elastic modulus and breaking strength were associated with the reduction in the breaking strain of composites.

It can be noted from Table II that the predicted modulus of carbon/phenolic composites are higher as compared to the experimental values. This may be attributed to the poor interfacial interactions between carbon fibers and phenolic matrix in case of pure carbon/phenolic composites, impairing proper load transfer between the fiber and matrix. The fracture surface presented in Figure 6(a) showed very less adherence of matrix to the carbon fibers due to weak interface formed between them. The problem of interface between carbon fibers and phenolic matrix has also been reported by other authors.²⁶

The comparison between the predicted increase in modulus after CNF addition and the experimental values are presented in Figure 7. The improvement in tensile modulus of multiscale composites due to CNF dispersion can be attributed to several reasons. Firstly, the modulus of matrix improved with the increase in CNF addition due to very high modulus of CNF, and the modulus of multiscale composites improved due to improved modulus of nanodispersed matrix. The improvement of modulus due to this reinforcing effect of CNF has been predicted in this article and it can be seen from Figure 7 that the experimental increase in modulus is significantly higher than the predicted increase. Therefore, reinforcing effect cannot be the only reason for modulus improvement and it could be due to the improvement in carbon fiber/phenolic matrix interface in the presence of CNFs. Figure 6(b,d) shows the fracture surface of multiscale composites, indicating good adherence of matrix with fibers and much stronger interface as compared to neat carbon/epoxy composites. Although improved interface will have more effect on the tensile strength of composites, the

authors believe that it will also have some contribution toward better load bearing capability of composites during the initial deformation and, therefore, will improve the modulus as well. The improvement in modulus of multiscale composites due to CNF/CNT addition has also been reported by other researchers and as well as in our previous studies with epoxy resin.^{19,20} In most of these cases, the concentration of CNF/CNT was too low to have significant reinforcing effect and the modulus improved due to other reasons which are not so clear till date and needs further investigation. In case of tensile strength, however, the reason for improvement (up to 12%) is mainly the reinforcing effect as well as good interface of multiscale composites. The reinforcing role of CNF/CNT to improve mechanical strength and toughness has been explained by various mechanisms which impose restriction to crack propagation, such as crack-bridging, crack deflection, and crack-tip blunting.³⁵ These mechanisms can play a major role in a textile fabric-reinforced composite having weak interlacing zones [as indicated by arrows in Figure 8(a,c)], which are mainly occupied by the matrix. Crack propagations in these interlacing regions of multiscale composites could be arrested by the presence of CNFs, as shown by arrows in Figure 8(b,d) and, therefore, could result in better tensile strength.

As mentioned earlier, apart from the reinforcing effect, the tensile strength of multiscale composites could also improve due to improved interface between carbon fiber and phenolic matrix. The improved interface originated due to the increased residual stresses or interface pressure of phenolic matrix on carbon fiber surface, owing to different thermal expansion and shrinkage behavior of CNF and phenolic resin during composite curing. Additionally, due to their higher surface area, CNFs formed better interface with phenolic matrix and acted as couplings between the carbon fibers and matrix as can be seen from Figure 9. Higher density of CNFs toward carbon fiber surface, as can be observed, was due to more affinity of CNFs for carbon fibers than phenolic matrix. Because of the presence of these CNF couplings, debonding between fiber and matrix became difficult in case of multiscale composites, as also noted by An et al.²⁰ and resulted in better tensile strength.

Breaking strain of carbon/phenolic composites decreased due to more restriction in matrix extension by the improved interface between CNF dispersed matrix and relatively low extension (1.8%) carbon fibers. Moreover, presence of CNFs with lower elongation (1.5%) than phenolic matrix may also have restricted the matrix movement leading to lower breaking strain of composites.

The improvement of mechanical properties obtained in our research can be compared with that obtained in similar studies conducted without focusing much on the dispersion issues. For example, in a study conducted by Tzeng and Lin,³⁶ CNFs were dispersed within the matrix of carbon fiber/phenolic resin composites using only ultrasonication, and improvements of 21% and 15.5% were achieved in flexural modulus and strength, respectively, using 0.1 wt % CNF. However, dispersion of higher CNF concentrations led to dramatic reduction in the flexural properties due to nonhomogeneous dispersion and with 1 wt % CNF, flexural strength became even lower than the base carbon/

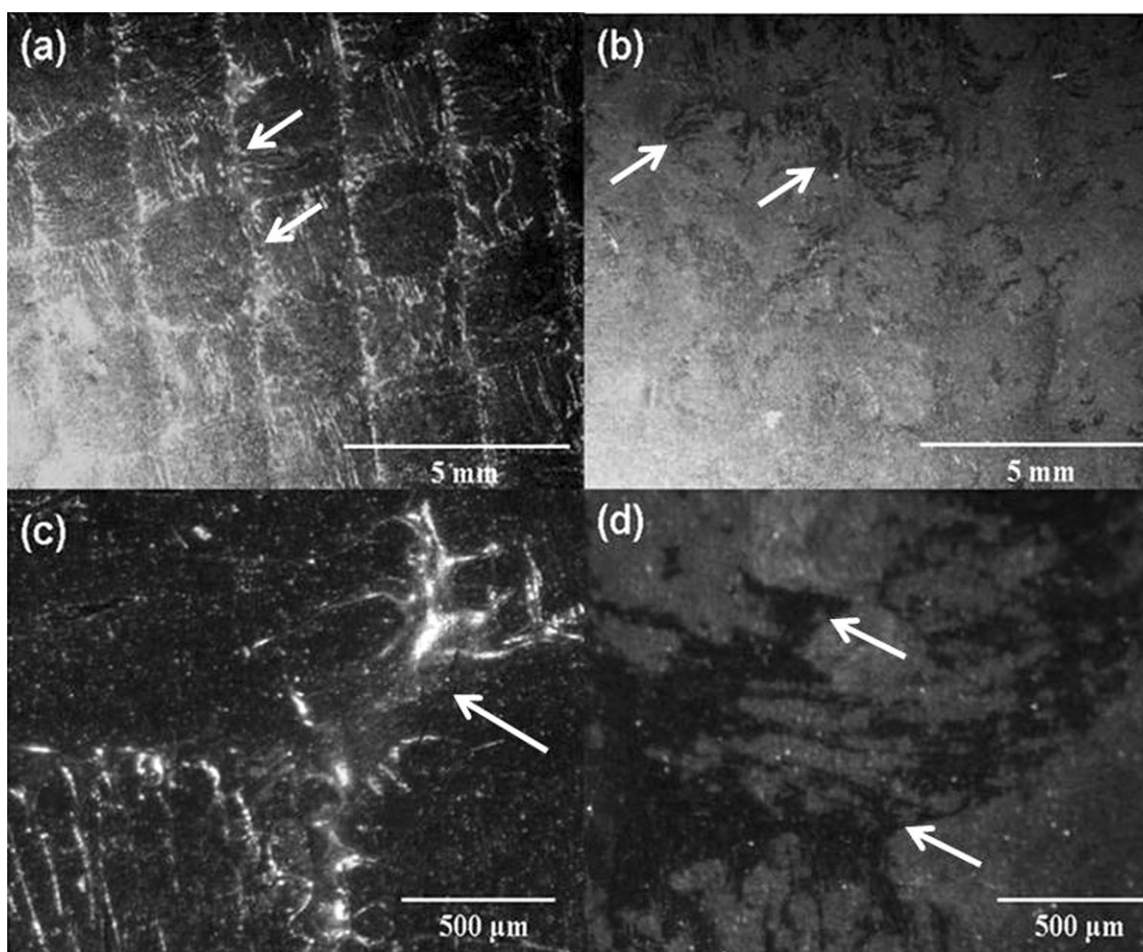


Figure 8. Optical micrographs under reflection mode at two different magnifications: (a) and (c) pure carbon/phenolic composite showing matrix rich interlacing zones, (b) and (d) multiscale composite with 1 wt % CNF, showing presence of nanofibers in the interlacing regions.

phenolic composites. This fact shows the need for a detailed study on the dispersion behavior and finding an efficient dispersion route, as done in our research.

Thermal Conductivity

Table III lists various thermal parameters obtained from Alembeta instrument. It can be noted that the transverse thermal conductivity of carbon/phenolic composite increased significantly (up to 36% using 1.2 vol % CNF) with the increase of nanofiber content within the matrix. Also, the addition of CNF resulted in considerable decrease in diffusivity and resistivity and increase in absorptivity.

However, it can be noted that thermal conductivity values predicted using eq. (13) was much higher than the experimental ones. This could be attributed to the artifact of measurement technique using Alembeta, which is developed and calibrated mainly for the compressible textile materials. For rigid composite samples, there could be problems in ensuring proper contacts between the measuring plates and samples, leading to significant heat loss. This was also observed in case of epoxy-based multiscale composites, developed in our previous research.^{19,20} Moreover, in the prediction, the model used in this article does not take into account the interfacial thermal resistance, which

occurs due to an interfacial layer or voids or cracks in the vicinity of interface³⁰ and may lead to reduced thermal conductivity. Nevertheless, as the authors were more interested to investigate the influence of CNF addition on thermal conductivity and, all the samples have the same dimension and geometry, the effect of heat loss has been neglected, while comparing the conductivities of various samples. The increase in thermal conductivity after CNF addition has been compared with the predicted increase and shown in Figure 10. One of the reasons for improvement in thermal conductivity of carbon/phenolic composites with CNF addition is the improvement of matrix conductivity. This is attributed to much higher conductivity of CNF ($20 \text{ W m}^{-1} \text{ K}^{-1}$) as compared to phenolic matrix ($0.15 \text{ W m}^{-1} \text{ K}^{-1}$). The improvement in matrix conductivity due to CNF addition has been predicted using eq. (14) and the overall improvement of composite's conductivity has been predicted using eq. (13). The dispersed CNFs within the matrix may also form links between the adjacent carbon fibers and improves thermal conduction through formation of conducting network throughout the composite. This mechanism was also believed by other researchers²⁷ to be the main reason for very high improvement in thermal conductivity of carbon/phenolic composites and can be responsible for much higher increase in

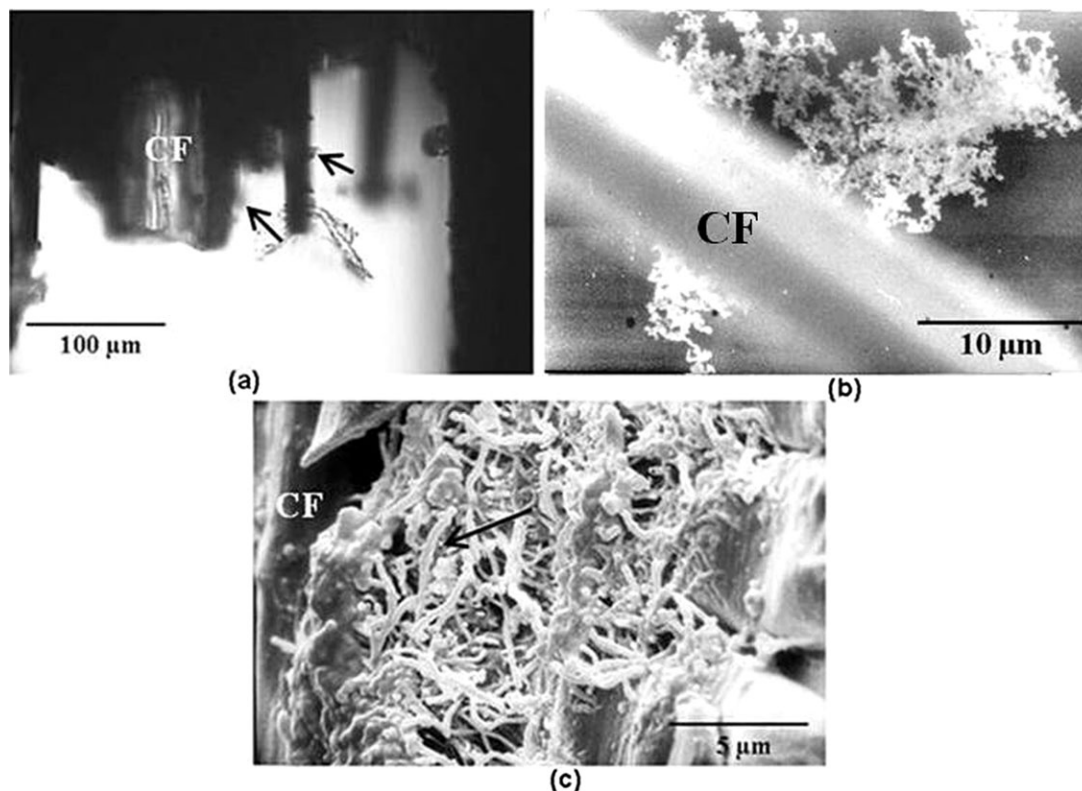


Figure 9. Coupling of carbon fiber (CF) and phenolic matrix through CNFs shown at different magnifications: (a) under optical microscope, (b) and (c) under scanning electron microscope.

thermal conductivity than predicted. Another probable reason for higher increase in thermal conductivity than the predicted values could be explained from Figure 8. As mentioned before, the impregnation of carbon fabric with phenolic resin led to formation of matrix-rich areas in the carbon fiber interlacing zones, and the presence of CNFs in the resin formed conducting networks parallel to the direction of heat flow. Therefore, the transverse thermal conductivity of composites was significantly influenced due to the presence of these parallel conducting networks and probably led to much higher increase in thermal conductivity than the predicted values. The improvement of thermal conductivity achieved in our research was much higher than that (~17%) obtained in a recent study performed by Tzeng and Lin.³⁷ It is interesting to observe in their research that thermal conductivity improved up to this maximum extent through dispersion of only 0.1 wt % CNF, and further increase in CNF content drastically deteriorated the conductivity, probably due

to improper CNF dispersion and agglomeration. On the contrary, the use of an efficient dispersion technique made it possible in our research to properly disperse CNF up to 1.5 wt % and to achieve much higher improvement in thermal conductivity.

CONCLUSIONS

In the present work, low concentrations of CNF (up to 1.5 wt %) were homogeneously dispersed within phenolic resin and, subsequently, the CNF-dispersed resin was used to impregnate carbon fabrics for developing multiscale composites. Following conclusions can be drawn from this study:

- A combination of mechanical stirring (1 h) with ultrasonication (1 h) in the presence of nonionic surfactant (0.2 wt %) was found to be the effective route for dispersing up to 1.5 wt % CNFs in phenolic resin. The obtained dispersion

Table III. Thermal Transmission Properties of Carbon/Phenolic and Multiscale Composites

Parameters	CNF (wt %)			
	0	0.5	1.0	1.5
Thermal conductivity ($W m^{-1} K^{-1}$)	0.052 ± 0.002	0.056 ± 0.001	0.067 ± 0.003	0.071 ± 0.002
Predicted thermal conductivity ($W m^{-1} K^{-1}$)	0.133	0.135	0.137	0.139
Diffusivity ($m^2 s^{-1} \times 10^{-6}$)	0.053	0.045	0.037	0.036
Absorptivity ($W m^{-2} s^{1/2} K^{-1}$)	226	249	358	372
Resistivity ($K m^2 W^{-1}$)	0.031	0.029	0.018	0.017

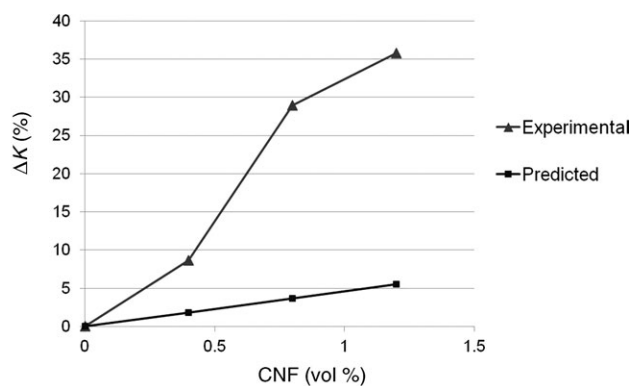


Figure 10. Comparison of experimental and predicted increase in thermal conductivity due to CNF incorporation.

showed good homogeneity as well as stability.

- Significant improvements were obtained in elastic modulus (10%) and tensile strength (12%) of carbon/phenolic composites through dispersion of CNFs (1.5 wt %) within the matrix. The improvement in elastic modulus was much higher than that predicted using a simple micromechanical approach. The improvement of tensile properties was not due to the reinforcing effect of CNFs but mainly due to the improved interface between carbon fibers and phenolic matrix in the presence of CNFs, which acted as coupling agents between them.
- Multiscale composites showed much better thermal transmission properties as compared to neat carbon/phenolic composites. The improvement in transverse thermal conductivity was much higher than the predicted increase, due to the formation of conducting CNF-dispersed matrix regions parallel to the heat flow.

The developed multiscale composites are presently being investigated for other important properties including fracture toughness, dynamic mechanical behavior, thermal expansion, and electrical conductivity in order to know their application potential in several high-end sectors as replacements of existing carbon/phenolic composites.

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