JOURNAL OF Applied Polymer SCIENCE

Resin Film Infusion: Toward Structural Composites with Nanofillers

Anoop Anand, Rahul Harshe, Makarand Joshi
Composites Research Center, Research and Development Establishment (Engineers), Defense Research and Development Organisation - Ministry of Defense, Pune 411 015, Maharashtra, India
Correspondence to: A. Anand (E-mail: aanand@rde.drdo.in)

ABSTRACT: Resin Film Infusion (RFI) has been used to fabricate composites with continuous unidirectional E-glass and epoxy with low weight fractions of carbon nanotubes (CNTs) in matrix. An ultrasound-assisted dissolution-evaporation method with thermoplastics or block copolymers as dispersing agents for nanoparticles enabled uniform dispersion of CNTs in the resin. Rheological characterization of CNT-filled epoxy revealed that viscosity, and hence processing of the resin remains unaffected as compared to pristine resin at elevated temperatures of subsequent composite manufacturing. Local flow of the modified resin through the sandwiched fabric plies in RFI process as against the global flow in traditional liquid composite molding processes, made sure that uniform distribution of nanoparticles is accomplished throughout the composite. Compressive properties of hybrid composites improved considerably with CNTs at loading fractions as low as 0.2 wt %. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1618–1624, 2013

KEYWORDS: composites; mechanical properties; properties and characterization

Received 9 August 2012; accepted 19 November 2012; published online 18 December 2012
DOI: 10.1002/app.38855

INTRODUCTION

Continuous fiber reinforced thermoset composites have been widely commercialized for load bearing structural applications in virtually all sectors of engineering. Manufacturing processes for such advanced composites include methods such as hand lay-up, resin transfer molding (RTM), compression molding, filament winding, autoclave curing, vacuum-assisted resin transfer molding (VARTM), etc.[1] Some of these advanced fabrication techniques enable structural composites to be manufactured with better compaction and low void fractions, and in turn superior mechanical properties. Nevertheless, manufacture of high performance composites using prepregs with autoclave curing has been the gold standard established by aerospace industry. In the current work, Resin Film Infusion (RFI) process has been used for realizing load bearing composites. RFI is one of the most promising methods for composites in aerospace, automotive and military applications. It has been developed as a cost-effective technique for the fabrication of complex shaped parts resolving several critical concerns of conventional liquid composite molding methods. RFI also ensures near zero void fractions because of better compaction and local flow of the polymer resin.

Regardless of these features of composites manufactured through RFI, relatively weak compression and interlaminar properties of laminated structures as compared to their excellent in-plane properties remains a major challenge.[2] Because of their outstanding mechanical properties, carbon nanotubes (CNTs) could be promising candidates to modify the matrices of composites and to enhance the matrix dominated properties of composites. In recent years, it was demonstrated that the addition of CNTs in epoxy can increase the toughness and improve the interface properties of CNT-composites.[3] Additionally, the development of epoxy/CNT based composites opens new perspectives for multifunctional materials, e.g., conductive composites with improved mechanical performance and with a possibility of damage sensing and life-monitoring.

In the present investigation, an attempt has been made to improve the matrix dominated properties of epoxy composites reinforced with unidirectional E-glass. Hybrid composites with nanofillers viz. multi walled carbon nanotubes (MWCNTs), dispersed in the matrix component has been developed. In fact, limited attempts have been made in the past to hybridize structural composites with nanoparticles, which otherwise paved the way for numerous polymer based nanocomposites for over a decade.[4,5] The concept of hybridising structural composites with nanomaterials can benefit from the macroscale reinforcement provided by traditional fibers and from the complimentary reinforcement on nanoscale offered by the nanomaterials.

Attempts to develop effective methods to de-bundle and discretely disperse CNTs (which are agglomerated in their as-prepared form), mostly use surfactants.[6,7] In general, a medium for the dispersion of CNTs should be capable of both wetting the

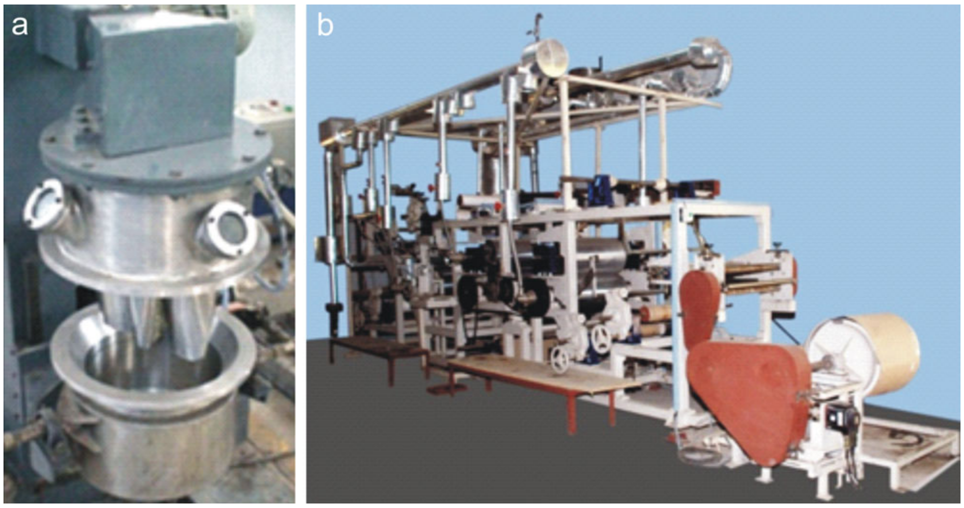

Figure 1. (a) Planetary Mixer, (b) Casting machine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrophobic tube surfaces and then modifying these surfaces to decrease the interaction between tubes. Polymers are appealing candidates for this since; given an appropriate structure, they can wrap themselves around CNTs. Indeed, such cases have been reported in literature.[8,9]

In this article, effect of CNTs on the mechanical properties of unidirectional E-glass/epoxy hybrid composites is reported. In order to achieve a proper dispersion in epoxy resin, CNTs have been dispersed in solutions of thermoplastics or block copolymers through ultrasonication followed by mixing with epoxy and subsequent solvent removal. Polymers are optimised to disperse the nanotube bundles. Solutions with dispersed CNTs can be effectively mixed with the epoxy resin for subsequent composite fabrication.

Polyethylene terephthallate, Polycarbonate and a commercially available block copolymer Disperbyk 2150 have been used as dispersing agents for MWCNTs and RFI has been used to fabricate composite laminates. Prior to making composites, effect of nanofiller loading on the processing aspects and thermal properties of epoxy resin has also been studied.

EXPERIMENTAL

Materials

The matrix system used in composites of the present study consists of a proprietary epoxy resin formulation developed inhouse. This resin system consists of diglycidyl ether of bisphenol A (DGEBA)-based solid and liquid epoxy components, the ratio of which has been optimized to result in sufficient tackiness in order for the resin films to stick to the dry fabric during the composite manufacturing, in addition to appropriate rheological, thermal, and mechanical properties. This formulation has a shelf life of 2 years when stored at subzero temperatures.

Unidirectional E-glass fabric (Chomarat Ruban 8033/1F) of 500 gsm areal density with >99% fibers oriented in warp direction was used as reinforcement. Multi walled CNTs of ~ 25 nm diameter, ~ 3 μm length and >99% purity have been supplied by Chemapol Industries, India. Polyethylene Terephthalate, and Polycarbonate pellets (characteristic cylindrical diameter ~ 2.5 mm, length ~ 3 mm) used were of commercial grade. Mixture of 1,1,1,3,3,3-hexafluro-2-propanol (HFIP) and chloroform was used as solvent for PET and dichloromethane was used to dissolve Polycarbonate. The block co polymer (BCP) solution, Disperbyk-2150 was procured from BYK-Chemie, Germany.

Dispersing Carbon Nanotubes in Epoxy

Solutions of thermoplastics were made by dissolving their pellets in respective solvents. Their concentrations were optimised to result in optimum viscosity so as to suspend the nanoparticles as stable dispersions. Weighed amount of MWCNTs were mixed with the solutions and ultrasonicated with a mechanical probe sonicator (13 mm, VibraCell Processor VCX 750, operating at 40% of the maximum power 750 W) over an ice bath. The ratio of MWCNTs to thermoplastics was optimized as 1 : 5 by weight. Ultrasonication for 15 min dispersed CNTs well in solutions which were then mixed with liquid component of the epoxy resin formulation using a thorough mechanical mixing followed by subsequent removal of solvent. Further, this was mixed with the rest of the ingredients in a planetary mixer (3 kg capacity, three blades counter rotating at 10 rpm) [Figure 1(a)] so as to result epoxy composition with CNTs at a loading fraction of 0.5 wt %. A proper uniform mix is facilitated by a reduced viscosity of the resin being mixed at 120°C prior to the addition of accelerator and hardener, followed by mixing at 60°C for 2 h of the final formulation under vacuum. A control formulation containing no nanofillers was also prepared under identical conditions. The epoxy resin formulations are made in to films (Figure 2) of thickness 300 μm using a casting machine [Figure 1(b)] and subsequently used for RFI process.

Rheological Characterization

Rheological characteristics and in turn processing aspects of filled epoxy resin, (in comparison to the pristine formulation) to be used in RFI process have been studied using a Modular Compact Rheometer, Anton Paar (Physica MCR 101). Plate–plate geometry with a plate diameter of 75 mm was used for measurements. Variation of viscosity with temperature of the

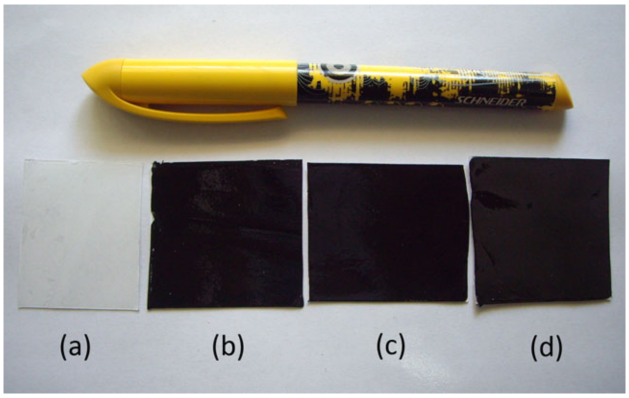

Figure 2. Photograph of calendared epoxy resin films (300 μm thick) (a): Pristine resin film, (b): MWCNTs/PET/Epoxy, (c): MWCNTs/PC/Epoxy, (d): MWCNTs/BCP/Epoxy, on a siliconised paper. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

control and modified epoxy systems has been studied in a range of 60–90°C at a ramp of 2°C/min. Shear rate was maintained at 25/sec throughout the experiment while a pre-shear of 5/sec for one min was given at 60°C while equilibrating.

Dynamic Mechanical Analysis

Dynamic mechanical analyzer (DMA Q-800, TA Instruments) was used to study the effect of MWCNTs on the glass transition temperature of epoxy. Rectangular shaped specimens of dimensions 35 × 12.5 × 2.5 mm were exposed from ambient temperature to 180°C at a ramp of 3°C/min using a single cantilever clamp. The amplitude used was 30 microns, and the frequency of oscillation was maintained at 1 Hz.

The Resin Film Infusion Process

Hybrid composite laminates were fabricated through RFI; the methodology involved is as follows. Cast epoxy resin film is cut to the desired dimension and transferred to a fabric layer (placed over a metallic mould plate) ensuring that the film just sticks to the fabric. The process is repeated to yield sandwiches of resin films with two fabric layers on both sides. Such sandwiches are placed on one another to build desired thickness. The sandwich stack over the mould is then cured by vacuum bagging technique inside an oven (Figure 3). A thermocouple is placed on top of the job to continuously monitor the temperature. Vacuum is applied to the job and measured via digital sensor. The job is heated at 2°C/min up to 80°C, held at this temperature for 30 min while the resin films melt and infuse amidst the fabric plies. Curing process takes place with subsequent heating to 120°C and holding for 60 min. After completing the heating cycle, oven is switched off and the job is allowed to cool slowly to room temperature before demolding.

Hybrid composites of unidirectional E-glass/epoxy containing MWCNTs were made with thermoplastics or block copolymers as dispersing agents for the latter. Their properties have been evaluated in comparison to a control composite specimen prepared with pristine epoxy resin formulation containing no nanofillers.

Determination of Constituent Volume Fractions

Volume fractions of constituents of composites were determined as per ASTM D3171 as follows. The matrix portion of the composite specimen of known mass is removed in a furnace (combustion at 600°C for 6 h). The remaining residue, of reinforcement, is then cooled and weighed. The weight percent of the reinforcement is calculated. From this value, and using densities of the composite (1.85 g/cm^3) and the reinforcement (2.54 g/cm^3), the volume percent is calculated. This method also estimates void volume in the composite.

Mechanical Properties of Composites

Mechanical properties of hybrid composite laminates were determined using a Servo Hydraulic Universal Testing Machine (BiSS India) with a load cell of 10 kN capacity. Specimens used for compressive strength measurements were rectangular strips of dimensions 140 × 10 × 2 mm with end tabs as per ASTM D3410. The gauge length between the jaws at the start of each test was adjusted to 20 mm and measurements were carried out at a cross-head speed of 1 mm/min. Specimens used for tensile strength measurements were rectangular strips of dimensions 250 × 15 × 1 mm with end tabs as per ASTM D3039. The gauge length between the jaws at the start of each test was adjusted to 138 mm and the measurements were carried out at a cross-head speed of 2 mm/min. An extensometer attached (Averaging Axial model from Epsilon Technology Corp.) on the specimens recorded the strain data and was used for Young's modulus determination. Average of at-least eight sample measurements was taken to represent each data point.

RESULTS AND DISCUSSION

Mixing of CNTs with polymers to produce composite materials has been practiced for more than a decade.[10–13] Research programs to engineer materials that combine the desirable properties of nanofillers and polymers are on the verge of maturity. Nevertheless, the greatest stumbling block to the large-scale production and commercialization of these composites is the lack of cost-

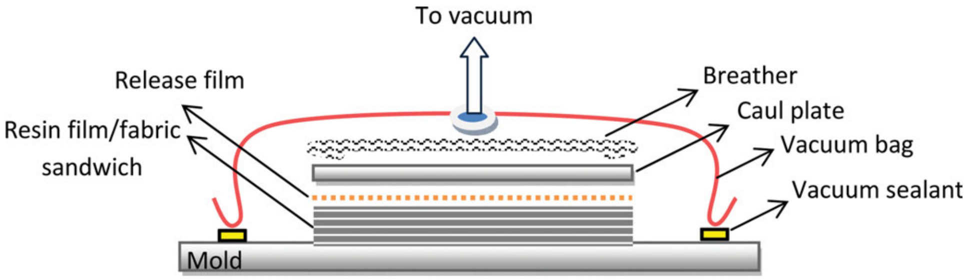

Figure 3. Schematic of the RFI process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

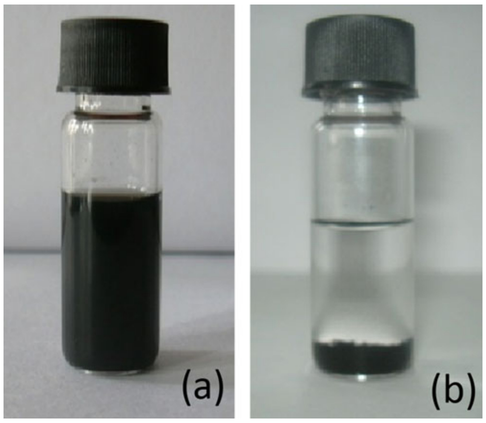

Figure 4. Photographs of representative vials containing (a): dispersed MWCNTs in solution of dispersing aid, (b): settled nanotubes in solvent without any dispersing aid.

effective methods for controlling the dispersion of nanoparticles in polymeric hosts. The nanoscale particles typically aggregate into bundles by Van der Waals interactions, which negates any benefits associated with the nanoscopic dimension. Establishing processing techniques that are effective on the nanoscale, yet applicable to macroscopic processing warrant more focussed research.

On adopting a solvent assisted route in combination with suitable surfactants via noncovalent functionalization, for the preparation of composites, CNTs have been shown to result in stable dispersions in polymer solutions made from selective solvents.[14] In this frame, the tube surface can be modified via Van der Waals forces and π–π interactions, by adsorption or wrapping of polynuclear aromatic compounds, surfactants, or polymers. The advantage of supramolecular functionalization is reflected in the preservation of intrinsic physical properties of CNTs as the carbon π-network is not destroyed by noncovalent interaction. The main area of noncovalent, supramolecular functionalization comprises the exohedral decoration of CNTs for example, wrapping of CNTs by polymers is widely used for the integration of CNTs into different matrices of other substance classes. In attempts to disperse nanotubes through solvent assisted routes; use of block copolymers in selected solvents has also been attempted. The idea here is modifying the short-range attraction among CNTs to long-range repulsion by tethering block copolymers on the nanotubes in a selected solvent.

Hybrid composites with thermoplastics or block copolymers as dispersing agents for nanoparticles (in solvents compatible with the matrix resin) have been developed.

MWCNTs have been dispersed by ultrasonication of its suspension in the solvent containing dissolved surfactants. Figure 4 shows that the solution containing CNTs remained stable for at least 6 weeks. On the other hand, CNTs have been ultrasonicated in each solvent system but without any dispersing aids and it was observed that they settle immediately after ultrasonication. This indicates that thermoplastics and block copolymers act as effective surfactants for MWCNTs. They tend to disperse CNTs by wrapping around them and avoiding individual CNTs to come in contact with each other, thus avoiding agglomerates and forming a stable suspension in the solvent medium. Ultrasonication conditions were optimised to result in stable dispersions of CNTs in solutions. Further, they were mixed with epoxy to result in a loading fraction of 0.5 wt % of CNTs. Solvent was subsequently removed and hybrid composites were fabricated through RFI process.

Attempts in hybridising structural composites with nanomaterials, so far have been limited to a few publications with academic interests. To our knowledge, there have been no reports in literature that addressed the issues related to development of hybrid composites through RFI. Indeed, the process of sandwiching a fabric assembly over a mould with nanofillers in the matrix component through the RFI process offers a good deal of scope for focussed research and subsequent practical applications on a larger scale. This process is also indentified as the only viable route for scale up of advanced composites that contain nanofillers. In the present work, hybrid composite laminates of continuous unidirectional E-glass/epoxy reinforced with multiwalled CNTs have been fabricated. Local flow of the resin through the sandwiched fabric layers in RFI process (Figure 3) ensures that proper nanofiller distribution has been achieved in hybrid composites, which is substantiated with the consistently improved mechanical properties of the resulting composites as reported in subsequent sections. Determination of constituent volume and void fractions has revealed that this process resulted in composite laminates with void fractions, lower than 0.5%. Prior to making laminates, the effect of nanofillers on rheological characteristics and in turn the processing aspects of matrix epoxy resin has also been studied. Photograph of a representative E-glass/epoxy composite laminate containing MWCNTs, fabricated through RFI process is shown in Figure 5.

Rheological Characterization

Rheological properties and in turn the processability of polymer matrix materials has been a subject of several studies. In the case of a hybrid composite system containing nanofillers in matrix, these properties are more sensitive and are highly dependent on the dispersion state of the latter.

In order to understand the effect of nanofillers on the processing of matrix, rheological characterisation of epoxy filled with

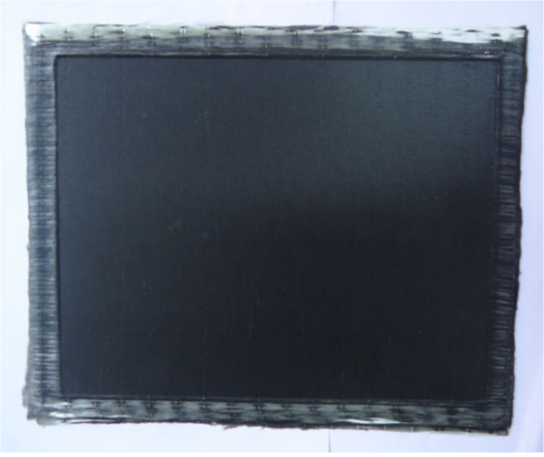

Figure 5. Representative hybrid composite laminate with carbon nanotubes, fabricated through Resin Film Infusion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

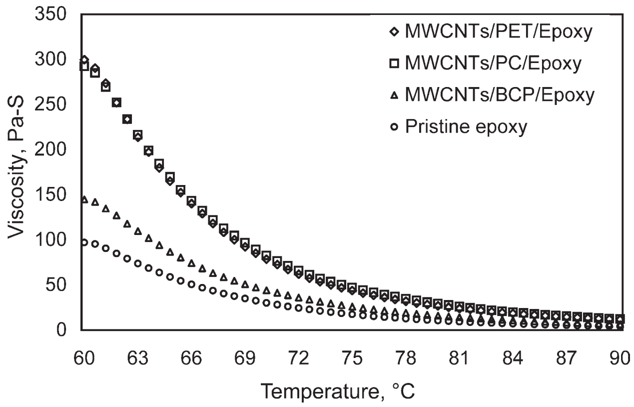

Figure 6. Viscosity vs. temperature plots of reinforced epoxy in comparison to pristine epoxy resin.

CNTs at a concentration of 0.5 wt % dispersed with thermoplastics or block copolymers, has been carried out. The results are compared with that of a control sample subjected to identical conditions of preparation, but containing no nanofillers. As depicted in Figure 6, viscosity of epoxy with nanofillers increases with concentration at 60°C (lowest possible temperature at which the resin melts and starts flowing for rheometry). Dispersed CNTs offer resistance to deformation and in turn hindered flow, and contribute to increase in viscosity of modified polymer resins, as expected. It is also noted that the liquid block copolymer owing to their plasticizing effect, limits the increase in viscosity as compared to that with thermoplastics. Rheology of epoxy with nanofillers has been a subject of interest in several other literature reports as well. For example, Wang et al. has reported increase in viscosity of epoxy with nanosilica.[15] Variation of viscosity of epoxy with CNTs has been reported by Rahatekar et al. also.[16] Nevertheless, the increase of viscosity at 60°C in the present system is not of concern and is well within the processability limits and tackiness requirements. Additionally at the processing temperature range of 80–90°C, viscosities of modified systems become comparable to that of the pristine one. It is evident that, at low loading fractions, MWCNTs has little effect on rheology and processing parameters of composites with modified matrix can be retained the same.

Effect of Carbon Nanotubes on Glass Transition Temperature of Epoxy

Thermal endurance is one of the critical aspects of composites, especially for military applications. Matrix component of composites contribute to the overall thermal properties to a considerable extent. In this context, effect of nanofillers on the glass transition temperature of epoxy has been investigated, using a Dynamic Mechanical Analyzer. Table I shows the DMA-determined T_g values of MWCNTs-filled epoxy resin in comparison to that of the pristine resin. Data indicates that the glass transition temperature of epoxy is improved considerably. Increase in glass transition temperature is attributed to the increase in density and reduction in the mobility of epoxy chains around the nanofillers due to the strong interfacial interactions existing between MWNTs itself and epoxy chains. This is also an indication of the effective dispersion of CNTs that corresponds to a large amount of interfacial area with altered polymer chain mobility throughout the matrix resulting in a local carbon nanotube and epoxy network organization, i.e. formation of crystalline regions within epoxy. Effect of nanofillers on glass transition temperature has also been reported by several other researchers though it depends, on the processing methods and in turn the dispersion state of nanofillers, to a great extent.[17,18]

Mechanical Properties

Although the high strength of CNTs is derived from the strong in-plane graphitic bonds, their weak interlayer interactions may cause problems. MWCNTs appear to fall victim to their own in-plane structural perfection which minimises load transfer to the inner shells when the outermost shell is strained in tension. This problem remains to be seen whether the end effects, or high aspect ratios, or modest defect concentrations can alleviate. Experimentally, these ideas are supported by the failure mechanisms observed in individual CNT tensile tests and by some composite data. For example, macroscopic epoxy samples containing 5 wt % of dispersed MWCNTs subjected to tensile and compressive loads showed a more pronounced property enhancement in compression; the result is consistent with the idea that only the outer nanotube layers are stressed in tension, whereas all layers contribute under compression.

In order to address the critical matrix dominated failure mechanisms such as compression and interlaminar properties, nanomaterials could be incorporated into the matrices of conventional fiber reinforced composites.[19–21] Indeed, the effect of nanoparticles in improving the mechanical properties of polymers has been thoroughly investigated during the last two decades.[22,23] Several articles have demonstrated the influence of very low weight fractions of nanofillers on the tensile and compressive properties of thermoset resins.[24–27] However there have been only limited attempts in the past that addressed the effect of nanoparticles in hybrid composite systems.[28,29] For example, Gojny et al. reported an increase of 19% in interlaminar shear strength of glass fabric reinforced composites with a weight fraction as low as 0.3 % of CNTs in epoxy.[30,31]

Several reports have mentioned ultrasound assisted dissolution evaporation methods as effective routes for the preparation of polymer nanocomposites with CNTs. For example S. Bal et al. fabricated CNT based epoxy composites by sonicating CNTs in ethanol without any surfactant and reported improved flexural moduli, electrical conductivity and glass transition temperature.[32] A. Herna'ndez-Pe'rez et al. reported on nanocomposites

Table I. Glass Transition Temperature of Epoxy with 0.5 wt % MWCNTs Dispersed with Various Dispersive Aids

Specimen	Glass transition temperature, T_g , (°C)
Pristine epoxy resin	118.0
Epoxy/MWCNTs with PET	128.4
Epoxy/MWCNTs with PC	129.1
Epoxy/MWCNTs with BCP	130.0

prepared with two different nanotubes of different aspect ratios using sonication method and reported that nanotube morphology and impurity content can significantly affect the properties of resulting composites.[33] J. Cho et al. modified epoxy matrix with CNTs by debundling via sonicating in ethanol and mixing with epoxy resin.[34] They reported an increase of compressive and interlaminar shear strengths by 39% and 15%, respectively. Successful dispersion of CNTs in selected solvents using block copolymers has also been reported.[35,36] Using the same block copolymer in ethanol, Li et al. reported a significant increase in tensile strength of CNT/epoxy nanocomposites.[37]

In this investigation, composite laminates of glass-epoxy have been prepared through RFI. The infusion has been carried out at 80°C, which made sure that the flow of nano modified matrix resin through the fabric stack is comparable to that of the pristine resin system.

When subjected to tensile and compressive loads the composites showed a more pronounced enhancement in compression properties, as would be expected considering the fiber dominated nature of the tensile properties.[38] Data in Figure 7 depicts that the compressive strength of hybrid composites with CNTs improved considerably with respect to that of the control glass/epoxy composites. At a loading fraction of 0.2 wt % CNTs, compressive strength of the hybrid composite increased by 14% and 17% with the use of PET and PC respectively as a dispersing aid, and upto 25 % with block copolymer. Loading fractions of CNTs in composites have been calculated from the fraction of epoxy which is experimentally determined as per ASTM D3171. Concentration of MWCNTs is 0.5 wt % with respect to epoxy and the composite laminates are made with a fiber volume fraction of 60%.

It has been proposed that only the outermost layer of multi walled CNTs is loaded during tensile loading, since the relatively weak (Van der Waals) bonding between the concentric layers causes slippage of the inner layers, reducing its load bearing capacity.[39,40] This is evident from the data reported in Figure 8. This slippage, however, seems to provide an extraordinary elastic deformation capability to multi walled CNTs when loaded in compression.[41]

CONCLUSIONS

Hybrid composites of continuous unidirectional E-glass and epoxy with CNTs have been fabricated through RFI. Thermoplastics such as PET and PC and block copolymers were found to effectively disperse MWCNTs in solution; their mixing and subsequent solvent removal resulted in reinforced epoxy resin. This modification of the matrix component with low weight fractions of CNTs is found to have negligible effect on the processing parameters of composites. CNTs also improved the glass transition of matrix epoxy resin. While tensile strength and modulus of composites remain unaffected, compressive strength of hybrid composite was improved considerably at low loading fractions of nanotubes. These attempts on improving the matrix dominated properties of structural composites by modifying their matrices with nanoparticles are considered promising toward developing light weight, yet stronger products for both civilian and defence engineering sectors.

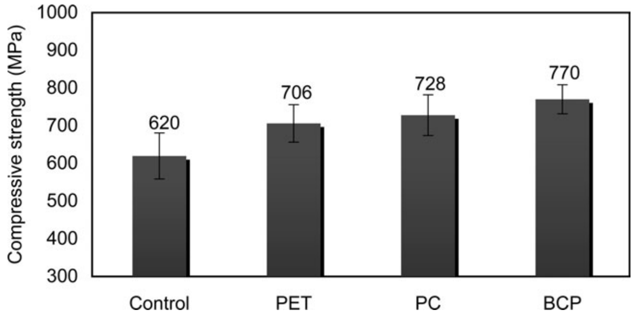

Figure 7. Compressive strength of UD E-glass based composites with MWCNTs-dispersed epoxy using PET, PC, and block copolymer as dispersing agents.

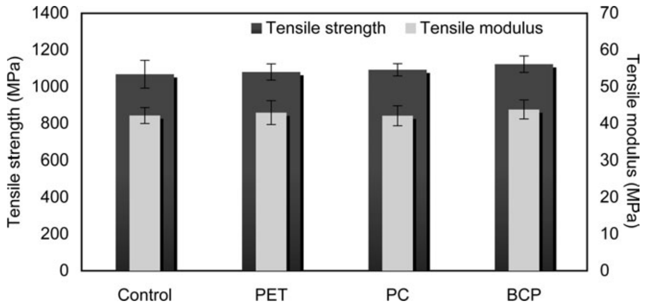

Figure 8. Tensile properties of hybrid composites in comparison to that of control composite.

ACKNOWLEDGMENTS

The authors are thankful to: Saket Lakhotia (NIT C), Praveen Kumar (ARDE), and Samudra Dasgupta (ADE) for their support with evaluation of properties of composites.

REFERENCES

1. Leslie, J. C.; Beardmore, P.; Borstell, H. In Engineered Materials Handbook; Reinhart, T. J. Ed.; ASM International: Ohio, **1987**; Vol.*1*, Chapter 8, p 497.
2. Schwartz, M. M. In Composite Materials: Properties, Nondestructive Testing and Repair; Prentice Hall PTR: New Jersey, **1996**; Vol.*1*, Chapter 4, p 90.
3. Thostenson, E. T.; Ren, Z.; Chou, T. W. *Compos. Sci. Technol.* **2001**, *61*, 1899.
4. Breuer, O.; Sundararaj, U. *Polym. Compos.* **2004**, *25*, 630.
5. Maruyama, B.; Alam, K. *SAMPE J.* **2002**, *38*, 59.
6. Anand, A.; Jose, S.; Alex, R.; Joseph, R. *Inter. J. Polym. Mater.* **2010**, *59*, 33.
7. Bandyopadhyay, R.; Roth, E. N.; Regev, O; Rozen, R. Y. *Nano Lett.* **2002**, *2*, 25.
8. Star, A.; Stoddart, J. F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X.; Chung, S. W.; Choi, H.; Heath J. R. *Angewandte Chemie Int. Ed.* **2001**, *40*, 1721.
9. Yudasaka, M.; Zhang, M.; Jabs, C.; Iijima, S. *Appl. Phys. A Mater. Sci. Process.* **2000**, *71*, 449.

10. Anand, A.; Agarwal, U. S.; Joeseh, R. *Polymer* **2006**, *47*, 3976.
11. Bhattacharyya, A. R.; Sreekumar, T. V.; Liu, T.; Kumar, S.; Ericson, L. M.; Hauge, R. H.; Smalley, R. E. *Polymer* **2003**, *44*, 2373.
12. Pötschke, P.; Bhattacharyya, A. R.; Janke, A. *Polymer* **2003**, *44*, 8061.
13. Anand, A.; Agarwal, U. S.; Joseph, R. *J. Appl. Polym. Sci.* **2007**, *104*, 3090.
14. Anand, A.; Agarwal, U. S.; Nisal, A.; Joseph, R. *Euro. Polym. J.* **2007**, *43*, 2279.
15. Xia, W.; Jiang, L.; Cheng, F. L.; Yun-Zhao, Y. *Chinese J. Polym. Sci.* **1999**, *17*, 253.
16. Rahatekar, S. S.; Koziol, K. K. K.; Butler, S. A.; Elliott, J. A.; Shaffer, M. S. P.; Mackley, M. R.; Windle, A. H. *J. Rheol.* **2006**, *50*, 599.
17. Karippal, J. J.; Murthy, H. N. N.; Rai, K. S.; Krishna, M.; Sreejith, M. *Polym.-Plast. Technol. Eng.* **2010**, *49*, 1207.
18. Ramanathan, T.; Stankovich, S.; Dikin, D. A.; Liu, H.; Shen, H.; Nguyen, S. T.; Brinson, L. C. *J. Polym. Sci.: Part B: Polym. Phys.* **2007**, *45*, 2097.
19. Godara, A.; Mezzo, L.; Luizi, F.; Warrier, A.; Lomov, S. V.; Van Vuure, A. W; Gorbatikh, L.; Moldenaers, P. Verpoest, I. *Carbon* **2009**, *47*, 2914.
20. Romhany, G.; Szebenyi, G. *eXPRESS Polym. Lett.* **2009**, *3*, 145.
21. Tan, P.; Tong, L.; Sun, X. *Comp. Struct.* **2008**, *84*, 1.
22. Schadler, L. S. Polymer based and polymer filled nanocomposites. In: Nanocomposite Science and Technology; Ajayan, P. M.; Schadler, L. S.; Braun, P. V., Eds.; Wiley: Weinheim, **2003**; p 77.
23. Ajayan, P. M.; Stephan, O.; Colliex, C.; Trauth, D. *Science* **1994**, *265*, 1212.
24. Coleman, J. N.; Khan, U.; Blau, W. J.; Gun'ko, Y. K. *Carbon* **2006**, *44*, 1624.
25. De Villoria, R. G; Miravete, A.; Cuartero, J.; Chiminelli, A.; Tolosana, N. *Comp.: Part B, Eng.* **2006**, *37*, 273.
26. Allaoui, A.; Bai, S.; Cheng, H. M.; Bai, J. B. *Compos. Sci. Technol.* **2002**, *62*, 1993.
27. Gojny, F. H.; Wichmann, M. H. G.; Kopke, U.; Fiedler, B.; Schulte, K. *Compos. Sci. Technol.* **2004**, *64*, 2363.
28. Iwahori, Y.; Ishiwata, S.; Sumizawa, T.; Ishikawa, T. *Comp.: Part A, Appl. Sci. Manufact.* **2005**, *36*, 1430.
29. Siddiqui, N. A.; Woo, R. S. C.; Kim, J. K.; Leung, C. C. K.; Munir, A. *Comp.: Part A, Appl. Sci. Manufact.* **2007**, *38*, 449.
30. Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Schulte, K. *Compos. Sci. Technol.* **2005**, *65*, 2300.
31. Wichmann, M. H. G.; Sumfleth, J.; Gojny, F. H.; Quaresimin, M.; Fiedler, B.; Schulte, K. *Eng. Fract. Mech.* **2006**, *73*, 2346.
32. Bal, S. *Bull. Mater. Sci.* **2010**, *33*, 27.
33. Herna'ndez-Pe'rez, A.; Avile's, F.; May-Pat, A.; Valadez-Gonzalez, A.; Herrera-Franco, P. J.; Bartolo-Pe'rez, P. *Compos. Sci. Technol.* **2008**, *68*, 1422.
34. Cho, J.; Daniel, I. M. *Scripta Materialia*, **2008**, *58*, 533.
35. Shvartzman-Cohen, R.; Nativ-Roth, E.; Baskaran, E.; Levi-Kalisman, Y.; Szleifer, I.; Yerushalmi-Rozen, R. *J. Am. Chem. Soc*, **2004**, *126*, 14850.
36. Zhao, L.; Gao, L. *Coll. Surf. A Physicochem. Eng. Asp.* **2003**, *224*, 127.
37. Li, Q.; Zaiser, M.; Koutsos, V.; Koutsos, V. *Phys. Status Sol. A* **2004**, *201*, R89.
38. Quaresimin, M.; Varley, R. J. *Compos. Sci. Technol.* **2008**, *68*, 718.
39. Schadler, L. S.; Giannaris, S. C.; Ajayan, P. M. *Appl. Phys. Lett.* **1998**, *73*, 3842
40. Wagner, H. D.; Lourie, O.; Feldman, Y.; Tenne, R. *Appl. Phys. Lett.* **1998**, *72*, 188.
41. Bower, C.; Rosen, R.; Jin, L.; Han, J.; Zhou, O. *Appl. Phys. Lett.* **1999**, *74*, 3317.