

Mechanical Behavior of Carbon Nanofibre-Reinforced Epoxy Composites

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Received 13 October 2008; accepted 28 May 2009

DOI 10.1002/app.30861

Published online 22 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Epoxy resins are widely used in a variety of applications because of their high chemical and corrosion resistance and good mechanical properties. But few types of epoxy resins are brittle and possess low toughness which makes them unsuitable for several structural applications. In this work, carbon nanofibres have been dispersed uniformly into the epoxy resin at a very low concentration (0.07 vol. %). Improvement of 98% in Young modulus, 24% in breaking stress and 144% in work of rupture was achieved in the best sample. The emphasis is on achieving uniform dispersion of carbon

nanofibers into epoxy resin using a combination of techniques such as ultrasonication, use of solvent and surfactants. The fracture surfaces of the specimens were studied under scanning electron microscope to see the fracture mechanism of nanocomposites under tensile load and correlate it to the enhancement in their properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2276–2283, 2010

Key words: carbon nanofibre; epoxy; dispersion; nanocomposite; work of rupture

INTRODUCTION

Epoxy resins are quite popular among the family of high performance resins. Their advantageous properties include good mechanical properties, resistance to environmental degradation, good adhesive properties, and low shrinkage during curing, good chemical resistance, high electrical insulation; good wear resistance, good stiffness, and heat resistant properties.^{1–3} These properties make these resins ideal for use in aircraft components, boats and many other applications. But some varieties of epoxy resin suffer from low breaking strain and toughness which creates problems during their applications. Several ways to overcome these problems have been reported.^{4–17} Two major toughened epoxy systems are rubber toughened and particle filled epoxy. Toughening of epoxy resin by liquid rubbers was first investigated by McGarry et al.^{4,5} Carboxyl terminated butadiene-acrylonitrile rubber was used for this purpose as it is soluble in conventional epoxy resin and during curing with amine curing agents produces micro particles of rubber by precipitation. Amino and vinyl-terminated butadiene-acrylonitrile rubbers have also been used for epoxy toughening.⁶ Another approach to improve toughness of epoxy resin is to use rigid inorganic fillers such as silica,

kaolin, alumina, barium titanite, dolomite, glass beads, aluminum hydroxide, and CaCO₃ fillers.^{7–10} The dispersed rigid particles interact with the moving crack front and increase the fracture energy of the matrix. Inorganic fillers can also be used with rubber particles to toughen epoxy resin.¹¹ However, these toughening agents often reduce other important properties such as modulus, strength, and thermo-mechanical properties. Recently high performance engineering thermoplastics having high glass transition temperature (T_g) and toughness such as polysulfone, poly (ether sulfone), poly (ether imide) and polyimide (PI) have been tried by blending for improving the toughness of epoxy resins.^{12–15} But toughness is effectively improved only at high fractions of the engineering thermoplastic polymers making the modified resin difficult to handle due to the high viscosity. Semi-interpenetrating polymer network of linear thermoplastic polymer and epoxy have also been attempted to improve toughness of epoxy resin.^{16,17} The most recent approach to improve the toughness of epoxy is to disperse nanofillers into the resin. Nanofillers have very high surface area and hence provide huge interface. So they interact better with the propagating cracks than the micro particles in arresting them.¹⁸ Also they provide higher probability of micro structural perfection of composites by minimizing the size of defects. So they have higher potential to improve toughness as compared to micro particles. Nanofillers can be nanoparticles or can have very high aspect ratio

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such as nanofibres or nanotubes. Use of Al_2O_3 nanoparticles has been reported by several researchers to improve toughness.¹⁹

Carbon nanofibres (CNF) and carbon nanotubes (CNT) have been widely used in various matrices to improve mechanical, thermal, thermo-mechanical, electrical, and many other properties. A great deal of research has been devoted to improve the toughness of epoxy by dispersing CNT.^{20,21} Due to very high surface area and aspect ratio, CNT have huge potential to improve toughness of brittle matrix by crack bridging and several other mechanisms. However, the problem lies in dispersing CNT uniformly into the matrix because of very strong attractive forces between them. Several methods have been tried to disperse CNT successfully into the matrix such as ultrasonication, mechanical stirring, using solvent and surfactant, functionalization, wrapping organic polymers to CNT, etc.^{22–27} CNF are relatively easy to disperse as compared with nanotubes due to their larger diameter and have been used in various matrices to enhance several properties. Peter et al.²⁸ used CNF into polypropylene single polymer composites produced by hot compaction and achieved improvements in mechanical properties. Effect of CNF incorporation in rubbery epoxy matrix was investigated by Gauthier et al.²⁹ The possibility of carbon nanofibre entanglement can result in network formation in the matrix and hence higher reinforcement efficiency is expected to be visible at large deformation when these CNF networks are stretched. That was the reason for the incorporation of CNF in a rubbery epoxy matrix as it allows relatively large deformation at ambient temperature. CNF were dispersed in the hardener using ultrasonication and then mixed with the epoxy resin. They observed significant improvements in tensile strength and strain (160 and 100%, respectively at 5 wt % of CNF) but increase of modulus with CNF content was low.²⁹ In another study by Patton et al.,³⁰ large improvements in flexural modulus and strength (97 and 37%, respectively) of epoxy matrix were achieved by dispersing carbon nanofibers into the resin. They used acetone/epoxy solution infusion through a mat of CNF under vacuum to prepare the nanocomposites. Choi et al. used a combination of sonication and stirring (at 1000 rpm) to disperse CNF into both high viscosity and low viscosity (obtained by diluting with acetone) epoxy resins.³¹ Maximum tensile strength and Young modulus were observed at 5 wt % CNF content for both types of nanocomposites and at higher contents mechanical properties decreased with filler loading.

In this article, an attempt has been made to study a combination of different dispersion techniques such as ultrasonication, use of surfactants, and solvent for getting homogeneous dispersion of CNF

at relatively very low loading (0.07 vol %) as compared with the much higher loadings used in earlier studies with epoxy matrix systems. The idea is to maximize the CNF reinforcement efficiency in terms of mechanical properties that is, tensile strength, modulus, extension at break, and work of rupture by obtaining a fine and uniform dispersion of CNF in epoxy resin.

EXPERIMENTAL

Materials and methods

Pyrograf III (PR24 AGLD) grade CNF of diameter 60–150 nm and length 30–100 μm was obtained from Applied Sciences, Inc. (USA). Bisphenol A Diglycidyl Ether (DGEBA) type epoxy resin was supplied by Sigma Aldrich (India) with the epoxide equivalent weight of 172–176. Diethylene triamine (DETA) hardener supplied by Sigma Aldrich was used to cure the resin. Polyoxyethylene 4 lauryl ether was used as nonionic surfactant and obtained from Acros Organics (Belgium). AR grade acetone was supplied by Qualigen (India) Fine Chemicals.

Dispersion of CNF

CNF (0.1% on the weight of resin) were dispersed into the epoxy resin using an Ultrasonicator (Elma Transsonic Digital). The temperature was maintained at 40°C. CNF were dispersed using 1 and 2 h of sonication to study the effect of sonication time on the dispersion of CNF. Acetone was used as solvent due to its low boiling point to dilute the epoxy resin and thereby to help the dispersion process. A nonionic surfactant (Polyoxyethylene 4 lauryl ether) was also used to improve the CNF dispersion in the resin. Two concentrations of surfactant were used (0.2 % and 0.4% on the weight of resin) to study the effect of surfactant concentration on the dispersion of CNF.

Preparation of nanocomposites

The prepared CNF/epoxy dispersion was then kept under vacuum at 40°C over night to remove the air bubbles introduced during dispersion process and to remove acetone from the dispersion. High temperature was not used because at elevated temperature, viscosity of epoxy resin reduces considerably and dispersed CNF tend to reaggregate again. DETA hardener (10 phr) was mixed properly with the CNF dispersed resin by mechanical stirring and again kept under vacuum for another 10 min. The nanocomposites were cast in a specially designed metallic mold with a provision to release the sample

TABLE I
Sample Codes Used and Their Descriptions

Sample No.	Sample Code	Description
1	E	Pure Epoxy
2	CNF1So	0.1% CNF dispersed with 1 h sonication
3	CNF2So	0.1% CNF dispersed with 2 h sonication
4	CNF2So2Sf	0.1% CNF dispersed with 2 h sonication & 0.2% surfactant
5	CNF2So4Sf	0.1% CNF dispersed with 2 h sonication & 0.4% surfactant
6	CNF2So2SfAc	0.1% CNF dispersed with 2 h sonication & 0.2% surfactant & acetone

easily after curing. The curing was done at room temperature for 24 h. The amount of hardener used was less than the stoichiometric amount (12 phr) and curing was carried out at room temperature to get a rubbery epoxy matrix. The different samples prepared and their sample codes are listed in Table I.

Characterization of dispersion

The level of CNF dispersion achieved using ultrasonicator was studied using an optical microscope (LEICA DMLP) at different magnifications ($\times 100$ and $\times 200$). Mechanical damage to CNF due to ultrasonication power was studied using transmission electron microscope (TEM, Phillips C M 12, type of filament: Tungsten and accelerating voltage 100 KV).

Characterization of nanocomposites

The pure epoxy and nanocomposite samples were cut to the specific dimensions according to ASTM D638-03 standard and tested for tensile properties in Zwick Universal Testing Machine at 1 mm/min crosshead speed. Five samples were tested from each category. Work of rupture has been calculated from the area under the stress–strain curve and % increase has been reported with respect to pure epoxy sample. Work of rupture has been used to estimate the degree of toughening with the addition of CNF. The fracture surfaces of the nanocomposites after tensile testing were studied under Scanning electron microscope (SEM) (ZEISS, Model: Evo 50, type of filament: Tungsten and accelerating voltage 20 KV). Very thin sections (100 nm) of nanocomposites were prepared by ultra microtome (LEICA EM UC6) and observed under TEM to see the dispersion of CNF in the final composites.

RESULTS AND DISCUSSION

The stress–strain curves of pure epoxy samples and nanocomposites are given in Figure 1, and the results of tensile testing are listed in Table II.

Effect of ultrasonication

It can be seen from Table II that 0.07 vol % of CNF dispersed using 1 h ultrasonication improved the Young modulus and breaking stress by almost 83 and 5% respectively as compared with pure epoxy sample E. Due to their very high modulus (400 GPa), CNF were so effective to improve the matrix modulus. In contrast to that, breaking stress was improved by only 5%. This may be due to the fact that 1 h of ultrasonication was not sufficient to break up CNF agglomerations which lead to the formation of voids and defects in the nanocomposites. Further sonication up to 2 h breaks down the CNF aggregates and improves the dispersion which can be seen from the optical microscope photographs in Figure 2(a–c).

However, ultrasonication energy cannot break all the CNF agglomerations even when ultrasonication is done for longer duration. Figure 2(d) shows the optical micrograph of CNF dispersion in epoxy resin after 10 h of ultrasonication. CNF are uniformly dispersed in the resin but still CNF aggregates are present in the resin even after 10 h of sonication.

Improved dispersion due to 2 h of sonication was reflected in higher breaking stress and strain values of sample 3. Breaking stress was improved from 46.6 to 50.9 MPa and breaking strain was improved from 11.4 to 13.5% with additional 1 h of sonication. But Young modulus decreased from 498.4 to 436.4 MPa. This may be attributed to the mechanical damage

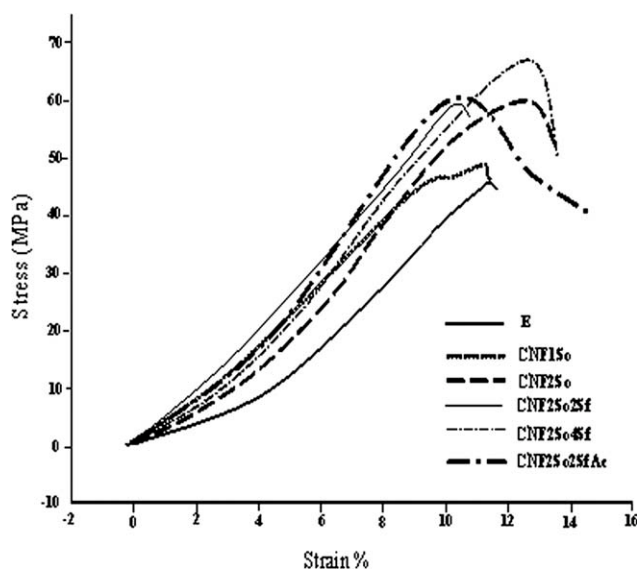


Figure 1 Stress–strain curves of pure epoxy and nanocomposite samples.

TABLE II
Tensile Properties of Pure Epoxy and Epoxy/CNF Nanocomposites

Sample No.	Samples	Young Modulus (MPa)	Stress at break (MPa)	Strain at break (%)	Increase in work of rupture (%)
1	E	272.6	44.5	11.7	–
2	CNF1So	498.4	46.6	11.4	34
3	CNF2So	436.4	50.9	13.5	101
4	CNF2So2Sf	540.5	55.4	11.0	36
5	CNF2So4Sf	473.7	49.9	13.6	104
6	CNF2So2SfAc	493.0	40.7	14.8	144

caused to the CNF by ultrasonication which can cut down the length of CNF leading to low aspect ratio. Figure 3 shows the TEM photograph depicting the mechanical damage to CNF due to 1 h of ultrasonication.

Figure 3(a) is the TEM photograph of a single carbon nanofibre. It has a diameter of 60 nm. Figure 3(b) shows the bundle of three CNF of different

lengths. The upper one has longer length where as the middle and lower one have shorter lengths due to breakage. Similar findings were observed by Gauthier et al.,²⁹ who studied the length distribution of CNF before and after sonication using image analysis. The length distribution after sonication became narrower, and the average length came down to 4 μm from 11 μm .

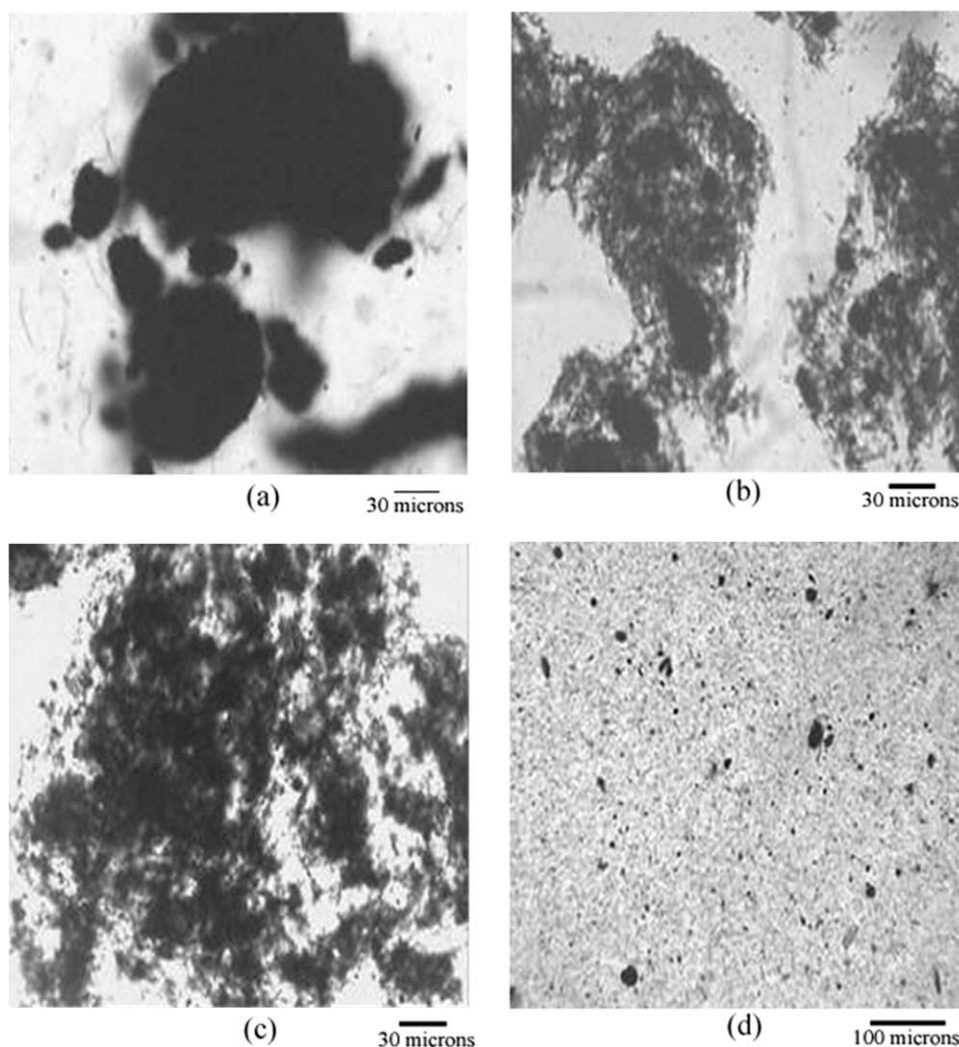


Figure 2 Effect of ultrasonication on dispersion of CNF into Epoxy resin, as observed under Leica optical microscope (a) no treatment (b) 45 min sonication (c) 2 h sonication (d) 10 h sonication.

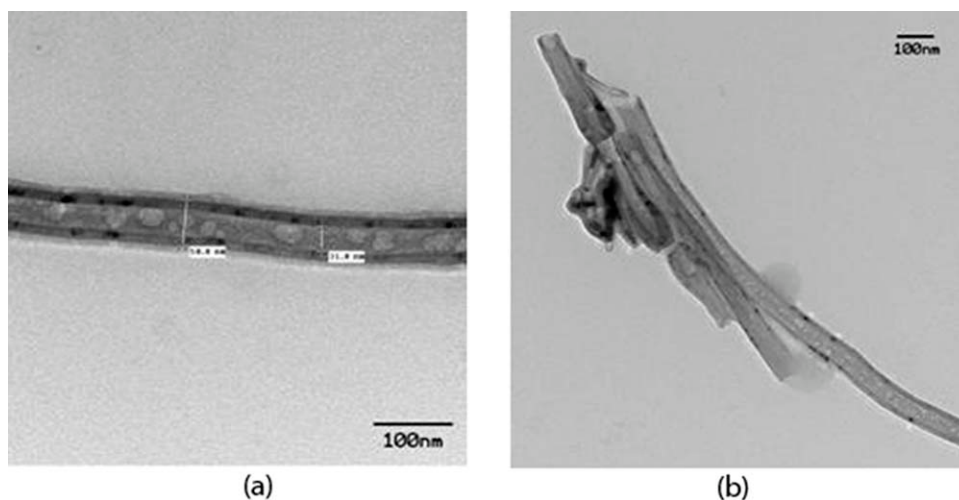


Figure 3 Mechanical damage of CNF due to ultrasonication as observed under TEM (a) single carbon nanofibre (b) a bundle of three CNF of different lengths.

Effect of surfactant

Highest Young Modulus and breaking stress [sample 4 in Figure 4(a,b)] were achieved using 0.2% nonionic surfactant. Young modulus and breaking stress were improved by 98 and 24%, respectively, as compared with pure epoxy sample. Very good dispersion was achieved when nanofibres were

sonicated for 2 h in the presence of surfactant leading to highest Young Modulus and breaking stress. CNF dispersion in sample 4 can be seen in Figure 5(a) which is the TEM photograph of a very thin section (100 nm) prepared by Ultra microtome.

The section shows very good dispersion of carbon nanofibre in epoxy resin, which results in very good

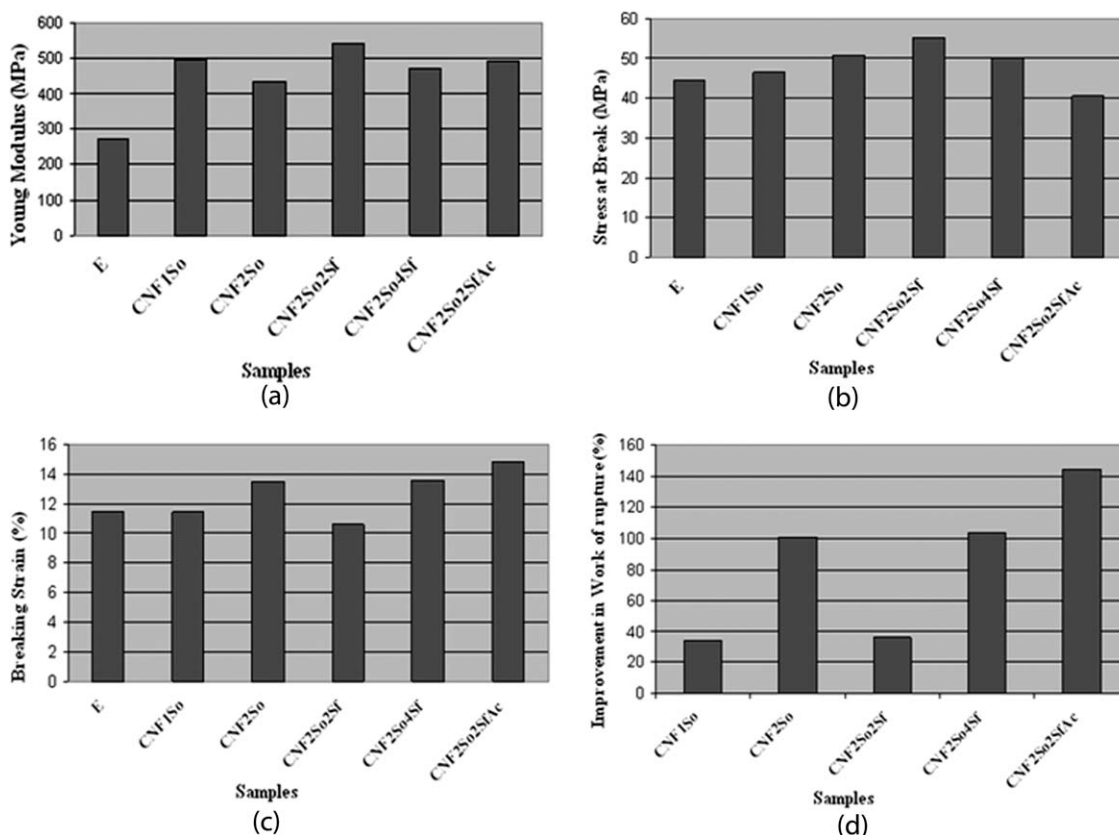


Figure 4 Comparison of mechanical properties (a) Young modulus (b) stress at break (c) breaking strain (d) work of rupture.

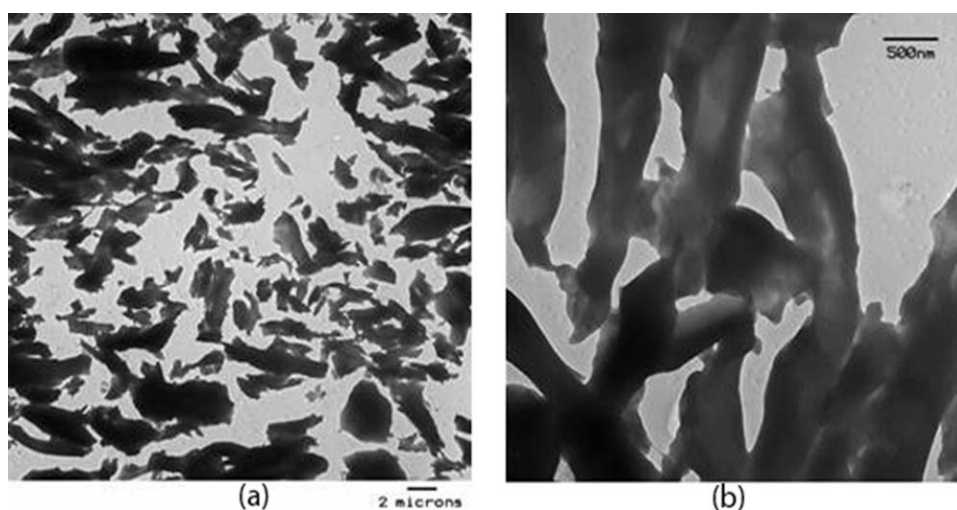


Figure 5 Cross section of sample 4 showing carbon nanofibre dispersion in epoxy resin as observed under TEM (a) lower magnification (b) higher magnification.

Young modulus and breaking stress. Figure 5(b) shows the same section at higher magnification. But higher surfactant concentration (0.4%) [sample 5 in Figure 4(a,b)] was found to have detrimental effect on both Young modulus and breaking stress. Although surfactant molecules help in CNF dispersion, they remain as impurities in the final nanocomposite and have adverse effect on the properties of nanocomposites.

Effect of solvent

Use of acetone (sample 6) makes the matrix ductile thereby reducing the Young modulus and breaking

stress and improves breaking strain (compare sample 4 and 6). Like surfactant acetone also remains as impurity in the final composite since complete acetone removal is extremely difficult at low temperature (40°C) even after applying vacuum.

Work of rupture

All nanocomposite samples showed higher work of rupture than pure epoxy sample [Fig. 4(d)]. Sample 3, 5, and 6 showed 101, 104, and 144% increase in work of rupture with respect to pure epoxy sample. These results clearly indicate that it is possible to prepare nanocomposites with higher fracture energy

TABLE III
Comparison of Tensile Test Results with Other Similar Studies on Epoxy/CNF or CNT Nanocomposites

Serial No.	Researchers	Carbon nanomaterials used	Dispersion technique	Results
1	Gauthier et al. ²⁹	Pyrograf III PR19 AG carbon nanofibre (5 wt %)	Ultrasonication	Breaking stress improved by 160%, strain at break increased by 100% and improvement of Young modulus with CNF content was low
2	Patton et al. ³⁰	Pyrograf III Carbon nanofibre (18.2 vol %)	Using acetone	Flexural modulus and strength increased by 97 and 37%, respectively
3	Choi et al. ³¹	Vapor Grown CNF from Showa Denko Japan company (5 wt %)	Using sonication and stirring at 1000 rpm	Young Modulus increased by ~93%, Tensile strength improved by ~12% and strain at break decreased due to CNF addition
4	Gojny et al. ²⁰	Single walled CNT from Thomas Swan Ltd. & Co., UK. (0.1 wt %)	Using a mini-calendar	Young modulus improved by 3.5%, Tensile strength improved by 4% and fracture toughness increased by 23%
5	Our study	Pyrograf III (PR24 AGLD) carbon nanofibre (0.07 vol %)	Using a combination of ultrasonication and surfactant	Improvements of 98% in Young modulus, 24% in breaking stress and 144% in work of rupture

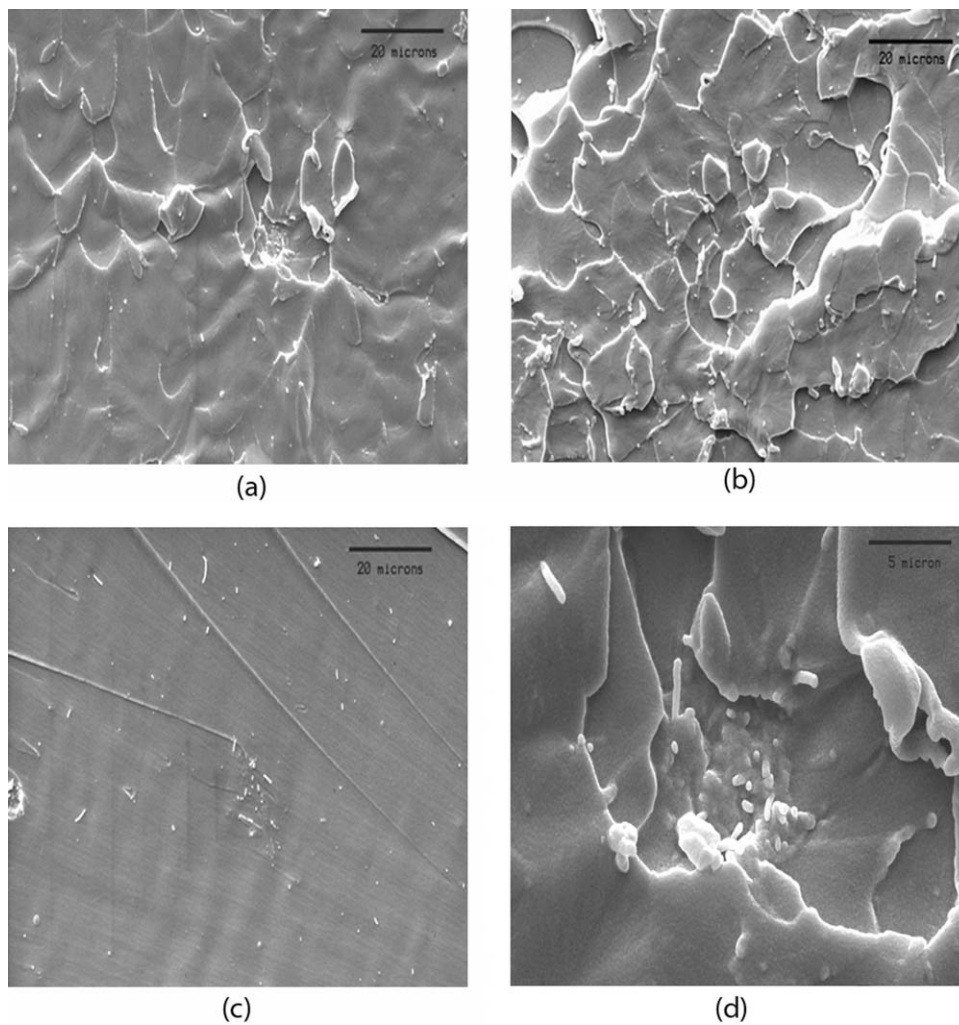


Figure 6 Fracture surfaces of nanocomposites as observed under SEM (a) CNF2So (b) CNF2So2Sf (c) CNF2So2SfAc (d) CNF2So2Sf at higher magnification.

with addition of only 0.07 vol % of CNF. The results of tensile tests have been summarized and compared with the previous studies carried out by other researchers in Table III.

Fracture surface study

Fracture surface of the nanocomposites after tensile test were studied by SEM. Fracture surface of sample 4 [Fig. 6(b)] was extremely rough with lots of ridges and wavy lines. This indicates that ductile fracture occurred during failure of sample 4 which resulted in best tensile properties. In contrast to that, sample 6 [Fig. 6(c)] showed very smooth fracture surface and hence poor tensile properties were achieved due to brittle fracture mechanism. The fracture surface of sample 3 [Fig. 6(a)] is moderately rough resulting in intermediate tensile properties. Figure 6(d) is the fracture surface of sample 4 at higher magnification which shows nanofiber pull-

out from the fracture surface resulting in higher mechanical properties.

CONCLUSIONS

CNF were successfully dispersed into epoxy matrix using a combination of ultrasonication and 0.2% nonionic surfactant. Very low concentration of CNF (0.07 vol %) was found very effective in improving work of rupture as well as tensile modulus and strength of the epoxy nanocomposites. Ultrasonication did help in the CNF dispersion but also led to the low aspect ratio of dispersed nanofibres due to breakage. At this low concentration of CNF, solvent did not help much in the dispersion and rather had detrimental effect on the final composite properties. Although scope is there to use higher concentration of CNF, the major challenge is to disperse them properly into the matrix. Improper dispersion can lead to the deterioration of composite properties.

Fracture surfaces of nanocomposites processed using ultrasonication and surfactant were very rough and showed significant nanofibre pull-outs from the surface during fracture. This resulted in good enhancement in mechanical properties, specially the work of rupture, which indicates an improved toughness of CNF/epoxy nanocomposites at very low levels of properly dispersed CNF. Study of fracture toughness can further help to understand the role of CNF in toughening the epoxy matrix. Further study is underway to explain the reinforcing mechanism of CNF in the epoxy matrix.

The authors would like to acknowledge Prof. A.K. Ghosh (Head, Center for Polymer Science & Engineering, Indian Institute of Technology, Delhi) for his kind support in tensile testing of epoxy nanocomposites.

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