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Experimental study of mechanical and electrical properties of carbon nanofiber/ epoxy composites

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Abstract

Epoxy nanocomposites of different content of carbon nanofibers upto 1 wt% have been fabricated under room temperature and refrigerated curing conditions. The composites were studied in terms of mechanical and electrical properties. Flexural modulus and hardness were found to increase significantly in refrigerated samples due to prevention of aggregates of nanofibers during cure condition. Increase and shifting in G-band by Raman spectra of these samples confirmed stress transfer and reinforcement between epoxy matrix and carbon nanofiber. Electrical conductivity improved by 3-6 orders after infusing carbon nanofibers in insulating epoxy. Room temperature samples acquired higher conductivity that was attributed to network formation by aggregates of nanofibers along the fiber alignment direction as revealed by electron microscopic studies.

Key words: Epoxy matrix; Carbon nanofiber; Mechanical & electrical properties; Raman spectroscopy.

1. INTRODUCTION

Carbon nanofibres (CNF) are hollow cylinders with diameters typically in the range 50-500 nm and lengths of a few tens of microns giving high aspect ratios (length/diameter > 100) with parallel and homogeneous alignment of nanoscopic graphene layers along the axis. They are expected to be promising nanofiller in polymers for the preparation of composites because of their mechanical and physical properties (Young’s Modulus ~500 GPa, tensile strength ~3 GPa, electrical conductivity ~10^3 S/cm, thermal conductivity ~1900 $W.m^{-1}.K^{-1}$) [1]. In the polymer field, epoxy resins are well established thermosetting matrices of advanced composites, displaying a series of interesting characteristics like good stiffness and specific strength, dimensional stability, chemical resistance and also strong adhesion to the embedded reinforcement [2]. They are used as high grade synthetic resins, for example, in the electronics, aeronautics, and astronautics industries.

Studies related to the enhancement of the mechanical properties of epoxy matrix by the introduction of CNF have been conducted [3-6]. To achieve maximum utilization of the properties of nanofibers, uniform dispersion and good wetting of the nanofibers within the matrix must be ensured [7–9]. It has been extensively reported that dry nanofibers often agglomerate, and thereby greatly reduce their ability to bond with the matrix. All these local interfacial properties will affect the macro-level material behavior [10, 11]. For example, distinct dispersion behavior of CNFs in polymers had a profound effect on the physical properties of the nanocomposites investigated [12]. Investigations specific to the electrical properties of CNF/epoxy composites [13-18] and general review of the properties of CNF-based composites [19] are available in the literature. Most of the research work reported so far on the electrical properties of CNF-based composites focused on relatively high contents of CNFs, usually higher than 2 wt %, and aimed to obtain a high conductivity without determination of the critical weight fraction at which the system becomes conductive.

The present work aims to study the influence of reinforcing strategies of CNF/ epoxy composites of different wt% (up to a maximum 1%) of CNFs in the epoxy matrix. To optimize reinforcement of these nanofillers in matrix, a new approach in the form of curing of composite specimens at refrigerated temperature was adopted. Moreover, Raman study supplementing the mechanical properties of CNF/ epoxy nanocomposites is yet to be reported in the literature. Macroscopic and microscopic properties of refrigerated nanocomposites have been analysed and compared with room temperature cured samples. Investigating dispersion strategies and final properties of these nanocomposites will thus help to elucidate the mechanism favoring or hindering synthesis of superior novel materials.

2. Materials and methods

2.1 Materials

Epoxy polymer matrix in the current study was prepared by mixing epoxy resin (araldite LY-556 based on Bisphenol A) and hardener HY-951 (aliphatic primary amine) in wt. ratio 100/12. Epoxy resin and hardener were procured from CIBA-GEIGY, INDIA. This resin (5.3-5.4 equiv/kg) was of low processing viscosity and good overall mechanical properties. Carbon nanofibers (CNFs) used for experimental study were procured from Nanostructured & Amorphous Materials Inc. (NanoAmour), USA. They are 200 nm to 500 nm in diameter, 10 µm to 50 µm long and >95% purity. SEM of nanofibers (Fig.1a) reveals that they are randomly oriented, curved and entangled. Figure 1(b) shows the Raman scattering spectra of CNF in the regions of 100- 2000 cm^{-1}. The ratio (I_D/I_G) of the Raman intensities of the disordered band (D-band) at around 1367 cm^{-1} to that of graphite band at around 1600 cm^{-1} can be taken as a measure of the crystalline order in graphitic systems. Here, smaller I_D/I_G ratio suggests fewer defects, less amorphous carbon and higher graphitic order [20, 21].

2.2 Preparation of composites

The Carbon nanofibers (0.5 wt%. 0.75 wt% and 1 wt %) were first dispersed in acetone by sonication for 2 hours. This condition was optimized to be best dispersion after performing several experiments and confirmed through optical microscope. The process helped to deagglomerate or debundle the entangled nanofibers. These nanofibers were mixed to epoxy resin and sonicated at controlled power levels for 2 hours. Then the CNF and epoxy resin mixture were kept in vacuum oven for 24 hours to eliminate air bubbles and moisture. The hardener was added to the mixture with manual stirring for 10 minutes inside a water bath to avoid further reaction. Another degassing process was conducted to the mixture in vacuum oven for 15 mins. After this the mixture was injected into two molds one of which was kept in room temperature atmosphere (23^0C) and other was in refrigerated temperature (4^0C). Processing time for complete settlement was 3 days for samples under room temperature conditioning and 8 days for samples inside refrigerator. Pure resin samples without adding carbon nanofiber were also fabricated in the same method as above for comparison purpose. These prepared samples were then post cured at 90^0C for 6 hours. The nomenclature of the samples is given in Table1.

Table1: Identification of resin as well as composite specimens

Sample Description	**Sample Identification**	
	Cured at Room temperature	*Cured at Refrigerated temperature*
Epoxy resin	**E**	**RE**
Nanocomposite with 0.5% of carbon nanofiber	$\mathbf{C_{0.5}}$	$\mathbf{RC_{0.5}}$
Nanocomposite with 0.75% of carbon nanofiber	$\mathbf{C_{0.75}}$	$\mathbf{RC_{0.75}}$
Nanocomposite with 1.0% of carbon nanofiber	$\mathbf{C_{1.0}}$	$\mathbf{RC_{1.0}}$

2.3 Mechanical testing

The nanofiber composites in this investigation contain randomly distributed nanofibers with small dimension and volume. So the macro-scale mechanical properties of the nanocomposites are effectively isotropic. Hence, a test standard for polymeric materials was used to evaluate the mechanical properties of nanocomposite materials.

Flexural testing

Bending tests were conducted according to ASTM D790-00 ‘‘Standard Test Methods for Flexural Properties of Un-reinforced and Reinforced Plastics and Electrical Insulating Materials’’ on an Instron 1195 testing machine. The loading rate was 2.0

mm/min. The span between two supports in a three-point-bending fixture was 60mm as shown in specimen geometry in Fig. 2. Five bending specimens in each group and 8 groups in all were tested for different fiber contents.

Hardness test

The hardness of all composite specimens was measured using a micro-hardness tester. A total of 10 points on each of the specimens were measured in order to get average readings. The unit and magnitude of the hardness are defined by Vickers hardness and determined by measuring the average diagonal length of the indentation. The Vickers hardness test method [22] consists of indenting the test material with a diamond indenter as shown in Fig.3.

Vickers hardness (HV) was calculated using equation (1)

$$HV = \frac{2F\, sin\frac{136^0}{2}}{d^2} \quad \text{or} \quad HV = 1.854\ \frac{F}{d^2} \quad \text{(Approximately) …….. (1)}$$

where,

F = Load in kgf
d = Arithmetic mean of the two diagonals, $d1$ and $d2$ in mm

2.4 Electrical testing

The electrical properties of the pure and reinforced epoxy were measured by using an Keithley Electrometer – 617 having maximum input resistance ~10^{17} Ω. The composites were cut into rectangular bars with dimension of 8 mm × 4 mm × 5 mm (length, width and thickness) by a diamond saw. The two end surfaces were coated with silver for ohmic contact. For a comparison purpose, measurement of the resistance of each nanocomposite sample was carried out in three different directions as shown in the Fig.4 and recorded. Electrical resistivity and the respective conductivity were calculated using the measured resistance and the geometry of the sample.

2.5 Raman spectroscopy

All Raman scattering spectra were recorded by using a Renishaw plc in Via MicroRaman spectrometer equipped with 514 nm green laser having 2 cm^{-1} spectral resolution of Raman shift, X-Y step resolution of 0.1 μm and confocal resolution of 2.5 μm.

2.6 Electron microscope (SEM &TEM) study

Scanning electron microscope (Jeol JSM-6480 LV) was used to conduct the dispersion behaviour and fracture surface topography characterization. The composite samples were fractured and the fracture surfaces were coated with a thin platinum layer. Cross section of composite sample was analysed using Trasmission Electron Microscope (FEI, TECHNAI G2).

3. RESULTS AND DISCUSSION

3.1 Bending Experiments

Composites of neat epoxy and nanocomposites with 0.5, 0.75 & 1.0 wt% nanofibers in the epoxy resin were prepared for bending tests. Fig. 5 shows the elastic moduli measured from the flexural test of resin as well as nanocomposites. It was found that the addition of the CNFs is able to raise the bending property of the resin substrate. This result agrees with the previous fact that addition of small amount of CNFs (< 3%) to a matrix system can increase mechanical properties without compromising the processability of the composite [23]. The refrigerated nanocomposites exhibited a higher modulus than their room-temperature counterparts over the whole CNF contents studied. This result confirms the low temperature curing of specimens at the time of fabrication has some effect on the improvement of their mechanical properties. For the room temperature nanocomposites, the bending modulus increases from 1682 MPa of the pure substrate to 2249 MPa for $C_{0.5}$, a rise scope of 33%. With the increase of the CNFs to 0.75%, the bending property is the best (2694 MPa, a rise scope of 60%). However, it was observed that when the wt% was increased to 1%, there was a fall in the value of bending modulus (2521 MPa, a rise scope of 49%) compared to the previous value. Because of their high aspect ratio and of vanderWaals attractive interactions, CNFs may tangle and produce agglomeration at higher concentration thus by reducing the bending property. But the bending property is still better than that of the substrate. With the refrigerated nanocomposites, with the content of CNF to be 1%, the bending modulus of the substrate increased significantly from 1682 to 3343 Mpa, a rise scope of 98%.

3.2 Hardness results

The hardness of the epoxy matrix increases continuously with higher CNF content (Fig.6). The hardness of value of E improved by 53 % with 0.5 weight percentage, 62 % with 0.75 weight percentage and 2 times with 1.0 weight percentage infusion of CNFs. The high aspect ratio, high modulus, strength of CNFs contributed to the reinforcement thus by improving hardness value. However, the hardness value of room temperature samples are little lower than their refrigerated counterparts. Also the refrigerated epoxy sample RE showed greater value than E. These results indicated relatively better curing of epoxy resin at low temperature that allows more interaction with hardener. It was observed that $RC_{0.75}$ and $C_{1.0}$ have the same hardness value of 18MPa. Moreover, $C_{0.75}$ has lower value than $RC_{0.5.}$ In room temperature samples, voids may be created at the time of fabrication of composites and some amount of unreacted resin may be left due to faster curing that could be the reason for the reduced value of hardness. It was reported that few voids were produced during the fabrication process and that voids increased with the higher nanoparticle contents [24, 25].

Hardness results agreed well with flexural test results with the finding that refrigerated samples have improved mechanical properties than room temperature settled samples. This indicates variation in polymerization process under the action of refrigeration temperature. At low temperatures, polymeric chains get frozen and thermal vibrations and mechanical deformations (moduli) are controlled mainly by the weak interatomic bonding (Van der Waals) forces [26]. Therefore after infusing the dispersion of CNFs that restricts the mobility of polymer chains under loading improved the flexural modulus as well as hardness in refrigerated samples.

3.3 Electrical measurement

The conductivity of epoxy resin used in this work was determined to be 2.8×10^{-9} S/cm. No significant variation in the conductivity of the refrigerated resin sample was found. Fig.7 presents the electrical conductivity of all nanocomposites in three different directions as explained in section 2.4. Conductivity was found to be maximum in x-direction in comparison to y & z-directions. Though nanofibers were randomly distributed, it was expected that most of them would be aligned in the direction showing maximum conductivity value. Because even if the nanofibers do not touch each other directly, conductivity of the nanocomposites is achieved as long as the distances between them are lower than the hopping distances of the conducting electrons [27]. This fact was further confirmed by examining the microstructures of sample in different directions that is being presented later in this paper in section 3.5. The conductivity of nanocomposites of different contents was in the range of 2×10^{-6} S/cm to 4×10^{-3} S/cm (Fig.7) i.e. 3 – 6 orders of magnitude greater than that of neat epoxy. Sharp increases in conductivity of this order of magnitude have been associated to percolation [28]. The percolation limit for most polymers filled with carbon black is typically found between 5% and 20% [28], but the amount of CNFs utilized here is only 0.5 – 1%. According to the common used classification of the electrical conducting materials, the materials with electrical conductivity lower than 10^{-6} S/cm are treated as insulators, with electrical conductivity between 10^{-6} S/cm and 10^{-2} S/cm as semiconductors, and consequently with greater than 10^{-2} S/cm as metals. Thus, the nanocomposites of epoxy with CNF presented in this work belong to materials characterized as semiconductors. This finding indicates that the epoxy nanocomposites with (0.5 - 1) wt% of carbon nanofibers can be utilized for electrostatic discharge application. This is a significant result considering earlier literature that indicated for obtaining similar level of conductivity 7-8 % of CNF need to be added [29].

Further Fig.7 shows an increase of the CNF content leads to a significant improvement of electrical properties of the investigated nanocomposites. From $C_{0.5}$ to

$C_{0.75}$, conductivity seems to rise by one order. Similar trend is observed when CNF content was increased from 0.75% to 1.0%. Room temperature and refrigerated samples of same content showed very little variation in the conductivity for higher loadings. Even in some cases refrigerated samples showed little lower value than its room temperature counterpart. Only in 0.5% case, 3 to 4 times enhancement was observed in $RC_{0.5}$ with respect to $C_{0.5}$. This implies that for the same content, low temperature brings improvement in electrical conductivity in a better way to the nanocomposites having less loading of nanofibers. Among the nanocomposites of this work, conductivity was found to be best for $C_{1.0}$. This result is a contrast to the flexural test where increase in modulus was found to be low for the same sample.

3.4 Raman Spectroscopy

Fig.8(a&b) shows Raman scattering spectra of both types of nanocomposites in high frequency regions. A strong peak around 1600 cm^{-1} can be assigned to the G-band due to tangential C—C bond stretching motions generically stem from the E_{2g2} mode in graphite. The weak peak around 1450 cm^{-1} was assigned to D-band arising from disorder induced $A_{(g1)}$ mode and corresponds to the amorphous carbon [30]. The peak observed at 1367 cm^{-1} for neat CNFs (Fig.1b) decreases in intensity in all the composite specimens, indicating a dilution effect of the CNFs when blended with epoxy. In case of room-temperature samples, D-band was seen to increase with order $C_{0.5} < C_{0.75} < C_{1.0}$ i.e. maximum in $C_{1.0}$. This indicates more no. of carbon fibers are converted into amorphous carbons in these samples thus by increasing defect sites. Here, the graphite like G modes exhibits a definite upward shift with increase in nanofiber content from 0.5% to 1 %. In all refrigerated nanocomposites smaller disorder D-band was observed in comparison to the room temperature ones. Increase in peak intensity and a little shift in G-band were found in refrigerated samples as infusion of CNFs increased. The feature around 1605 cm^{-1} of $RC_{0.5}$ is shifted to 1667 cm^{-1} in case of $RC_{1.0}$. G-band shifting confirms good stress transfer from matrix to fiber [31]. This result is supporting flexural test where improvement in modulus was observed in refrigerated case. It implies that low temperature curing facilitates effective reinforcement of matrix and nanofiber that may be possible due to stretching of network. As delay in the settling procedure in these has an impact on the matrix structure and crosslinking ratio and by this way the molecular motions inside the polymer.

3.5 Electron microscopic study

Dispersion behavior of carbon nanofibers in both room temperature and refrigerated composite samples were compared using the micrographs. Study of fracture behavior was also done to obtain the information of the cause and location of failure of the composite specimens. More agglomerates of large size were found in room temperature samples (Fig.9a). This may be the reason for the obtained low flexural modulus value of $C_{1.0}$ sample. Although efforts were made to achieve good dispersion of nanofibers, such as sonication and use of solvent, it was very difficult to prevent aggregation of nanofibers during specimen preparation and curing [4]. However, in the present investigation relative uniform distribution of CNFs was found in refrigerated specimens even if in the higher contents like $RC_{1.0}$ (Fig.9b). Reagglomeration of nanofillers generally occurs during pre curing condition in the conventional room temperature approach. In the present work at the time of fabrication, one part of composite sample was pre cured inside a refrigerator that took longer duration for settlement. Flexibility of movement of nanofillers inside a stretched matrix in a lower temperature in this case facilitates reduction of agglomerates. Through the microscopic observations, it is inferred that refrigeration of samples prevented formation of further agglomeration of nanofibers that ultimately resulted better dispersion.

In Fig. 10a, fracture surface of $C_{1.0}$ reveals the brittle or glassy nature of the composite surface as well as the presence of aggregates of CNFs near void regions. These aggregations are responsible for creating voids or damage sites in nanocomposites [4]. Compared to this a micro rough surface was observed in $RC_{1.0}$ (Fig.10b) confirming the claim that refrigeration helps to reduce void formation even at higher nanofiber content. Fracture surfaces of epoxy resin composite (E) and nanocomposite ($C_{1.0}$) were analysed (Fig.11). Though both of them possess fractographic behavior, different types of interactions were found in latter case (Fig.11b). Some fibers were half pulled out of the matrix but few still embedded inside matrix. Some fibers were broken, but some were bridging microvoids inside the matrix. Therefore $C_{1.0}$ was showing higher flexural modulus and hardness value than pure resin sample. From this observation it can be concluded that use of acetone to disperse nanofibers and then sonication is improving the mechanical properties of composite specimen to some extent, but significant enhancement can be achieved by refrigeration process. Low modulus increase measured as a function of fiber content in room temperature composites may be due to high rigidity of glassy matrix hindering the flexibility of nanofibers [32].

Microstructures of fracture surface of $C_{1.0}$ sample (along x & z directions) are presented in Fig.12. In x-direction, fibers are found to align in the direction of cutting (Fig.12a). This alignment certainly facilitated increase in electrical conductivity in the specified x-direction and the finding supplemented the electrical conductivity result in section 3.3. In z-direction (Fig.12b), the fibers aligned perpendicularly and breaking of nanofibers are prominent (inset of Fig.12b shown by arrow); that might be the reason for lower value of conductivity. By analyzing microstructure of $C_{1.0}$ along x-direction at higher magnification (Fig.13a), it was observed that the aggregate phases of fibers formed a network inside the matrix. TEM of the same sample (Fig.13b) revealed the interaction of fiber with epoxy matrix at the interface along with network formation. For this reason room temperature composite with 1 wt% CNF ($C_{1.0}$) was showing higher conductivity than its refrigerated counterpart $RC_{1.0}$. From electrical testing, maximum conductivity was observed in $C_{1.0}$ (room temperature composites with 1 wt% of CNFs). SEM observation revealed the presence of agglomerates of CNFs in this sample which also the cause for low modulus increase described in flexural test. These findings infer that, agglomerates can be hindrance to get a stronger composite but it can facilitate to acquire good electrical conductivity for desired components. Again, as the conductivity was higher in the direction of fiber alignment, future works can be aimed to carried out with aligned nanoparticles or by aligning fibers by different techniques.

4. Conclusions

Addition of very low (up to 1 wt %) amount of CNFs brought improvement in mechanical and electrical properties of epoxy composite. The curing of nanocomposites at refrigerated temperature facilitated better dispersion by optimizing adhesion between epoxy and CNF. These samples cured at low temperature showed significant enhancement in flexural modulus and hardness that is attributed to flexibility of CNFs inside a stretched matrix. Raman spectra of these refrigerated samples compared to room temperature samples clearly indicated shifting and increasing of G-band that confirmed better reinforcement and stress transfer from matrix to fiber. Insulator epoxy behaved like a semiconductor with very low infusion of CNFs that was confirmed from electrical measurement. Electrical conductivity was found to be best at higher content of CNF in room temperature sample and in the direction of fiber alignment. However, in case of refrigerated sample electrical conductivity was better for low content of CNFs.

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Figure Captions

Fig.1. (a) SEM and (b) Raman spectra of Carbon nanofibers

Fig.2. Flexural testing specimen configuration showing thickness=B, width=W, span length=S and applied force=P

Fig.3. Indentation geometry of hardness test

Fig.4. Measurement of resistances of composite sample along (a) x-direction, (b) y-direction & (c) z-direction

Fig.5. Flexural modulus of resin and CNF/ epoxy nanocomposite samples

Fig.6. Hardness values of epoxy and nanophased epoxy samples

Fig.7 Electrical conductivity of CNF/ epoxy nanocomposites in three different directions along with schematic of the sample indicating directions

Fig.8 Raman spectra of (a) Room temperature (b) Refrigerated nanocomposites

Fig.9 Dispersion of CNFs in epoxy matrix (inside arrows indicate agglomeration)

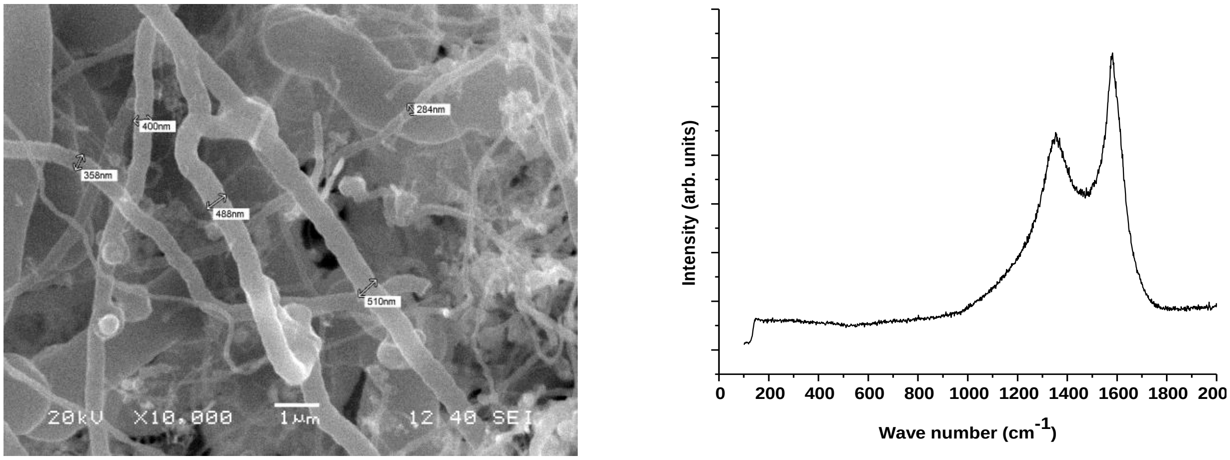
in (a) $C_{1.0}$ (b) $RC_{1.0}$

Fig.10 Fracture surface of CNF/ epoxy composites of (a) $C_{1.0}$ (b) $RC_{1.0}$

Fig.11 (a) Fracture surface of epoxy matrix E (b) Interaction between matrix and carbon nanofiber in nanocomposite $C_{1.0}$

Fig.12 Fracture surface of $C_{1.0}$ sample (a) along x direction showing horizontal alignment of fibers (b) along z direction showing vertical alignment of fibers

Fig.13 Network formation (inside arrow pointing the region) of sample $C_{1.0}$ observed by (a) SEM and (b) TEM


400nm
358nm
284nm
488nm
510nm
20kV X10,000 1μm 12 40 SEI
Intensity (arb. units)
0
200
400
600
800
1000
1200
1400
1600
1800
200
Wave number (cm^{-1})

(a) (b)

Fig.1.

Figure

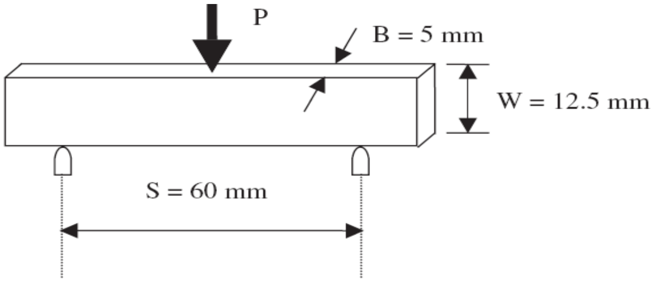


Fig.2

Figure

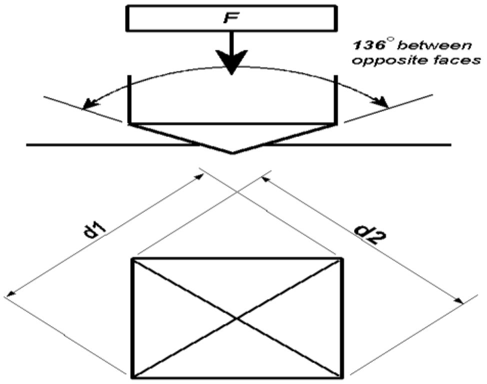


Fig.3

Figure

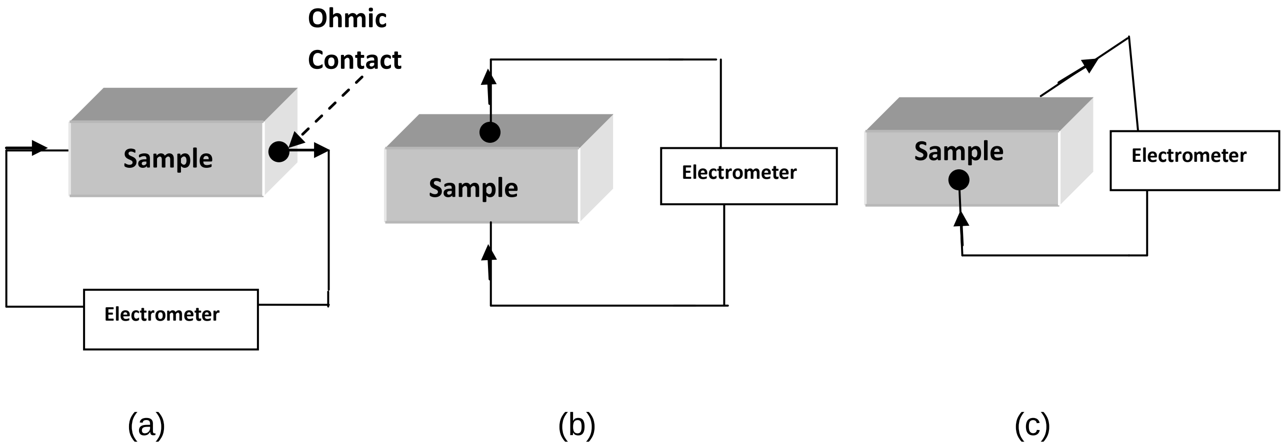
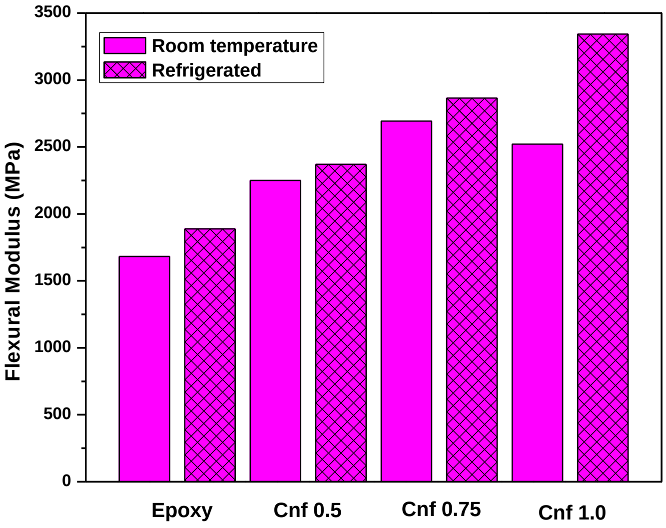

Ohmic
Contact
Sample
Electrometer
(a)
Sample
Electrometer
(b)
Sample
Electrometer
(c)

Fig. 4

Figure



Flexural Modulus (MPa)
3500
3000
2500
2000
1500
1000
500
0
Room temperature
Refrigerated
Epoxy
Cnf 0.5
Cnf 0.75
Cnf 1.0

Fig.5

Figure

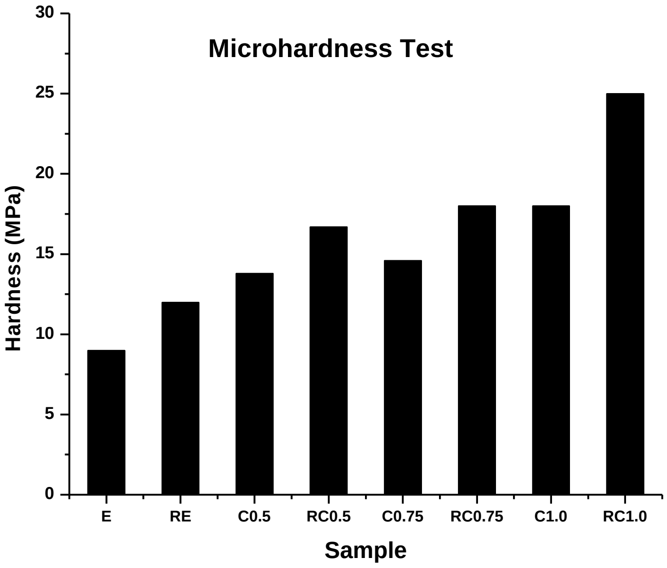

Microhardness Test
Hardness (MPa)
30
25
20
15
10
5
0
E
RE
C0.5
RC0.5
C0.75
RC0.75
C1.0
RC1.0
Sample

Fig.6

Figure

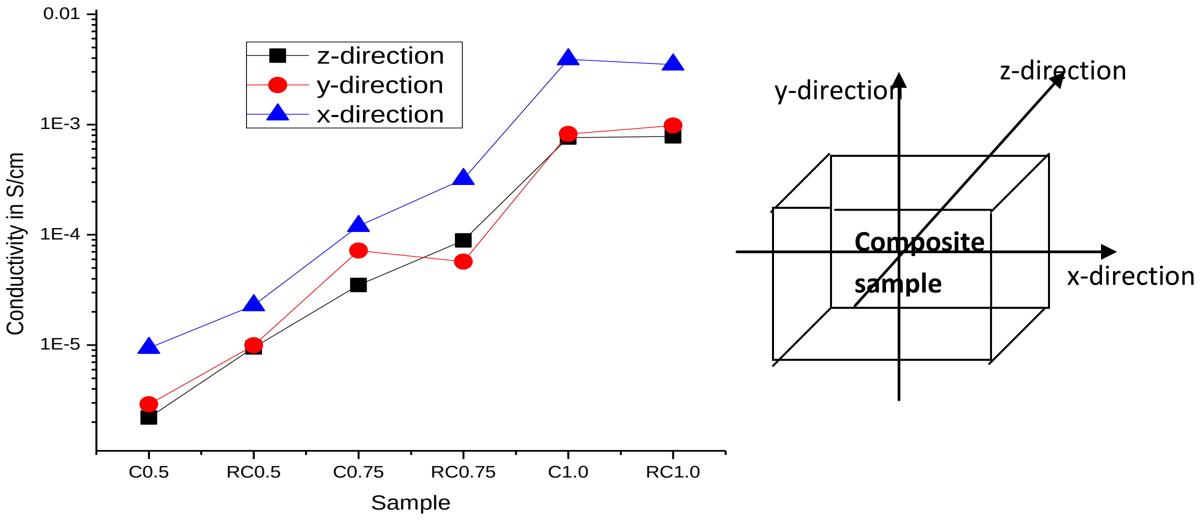
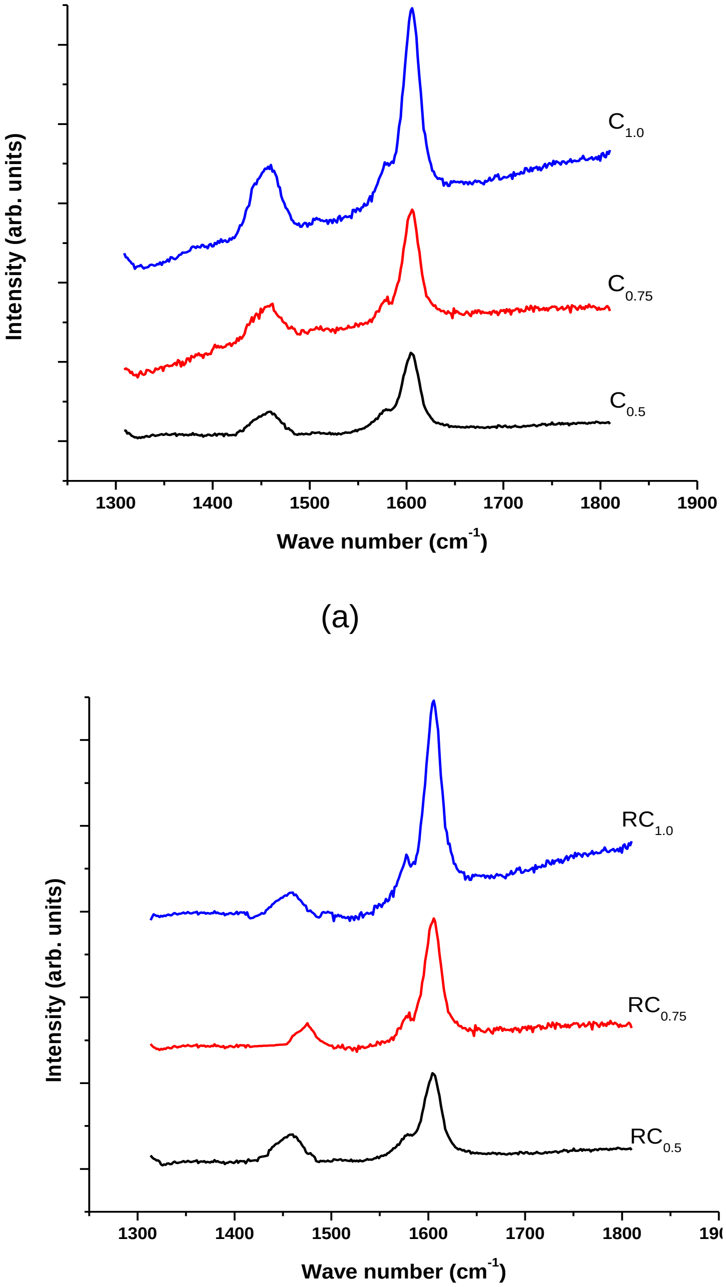

0.01
1E-3
1E-4
1E-5
Conductivity in S/cm
C0.5
RC0.5
C0.75
RC0.75
C1.0
RC1.0
Sample
■ z-direction
● y-direction
▲ x-direction
y-direction
z-direction
x-direction
Composite sample

Fig.7

Figure

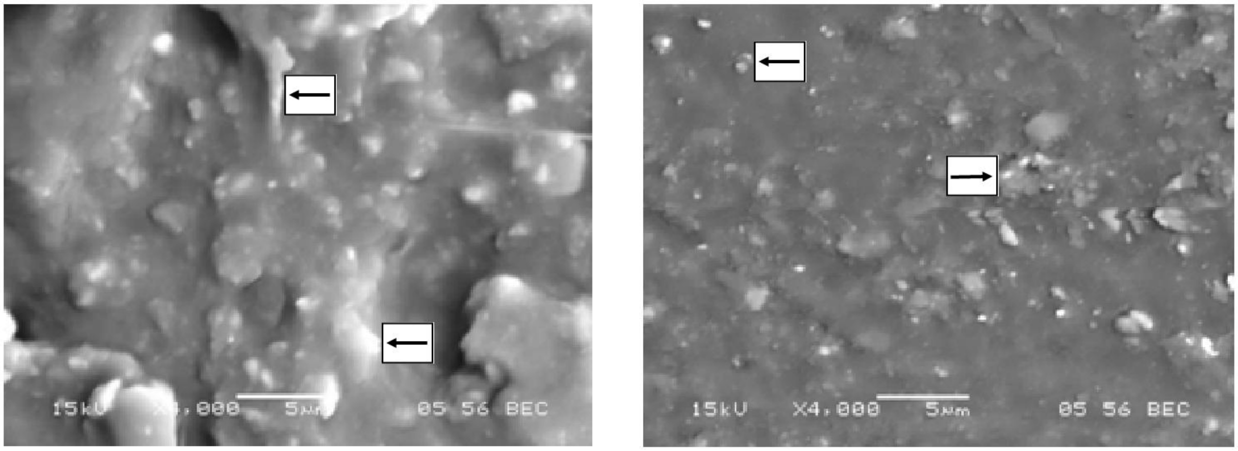


(a)

(b)

Fig.8

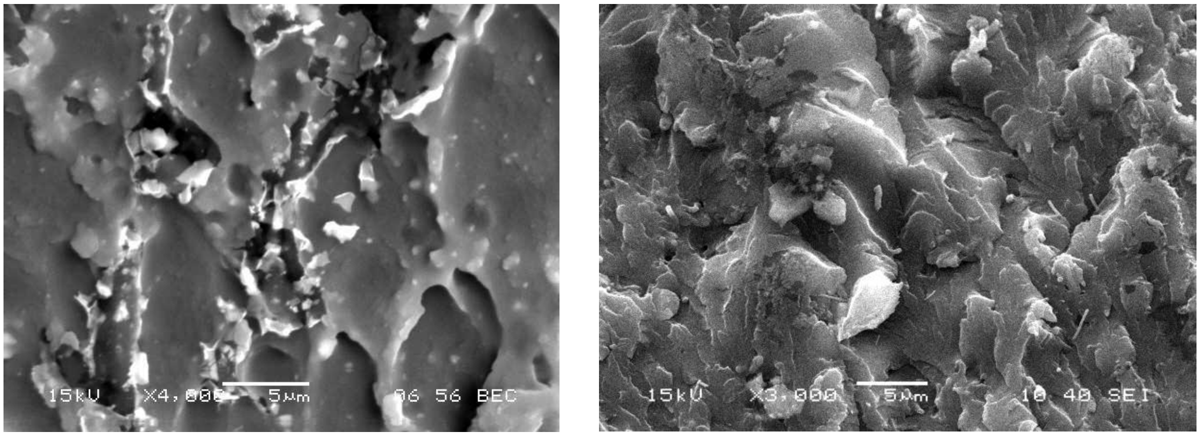
Figure



(a) (b)

Fig. 9

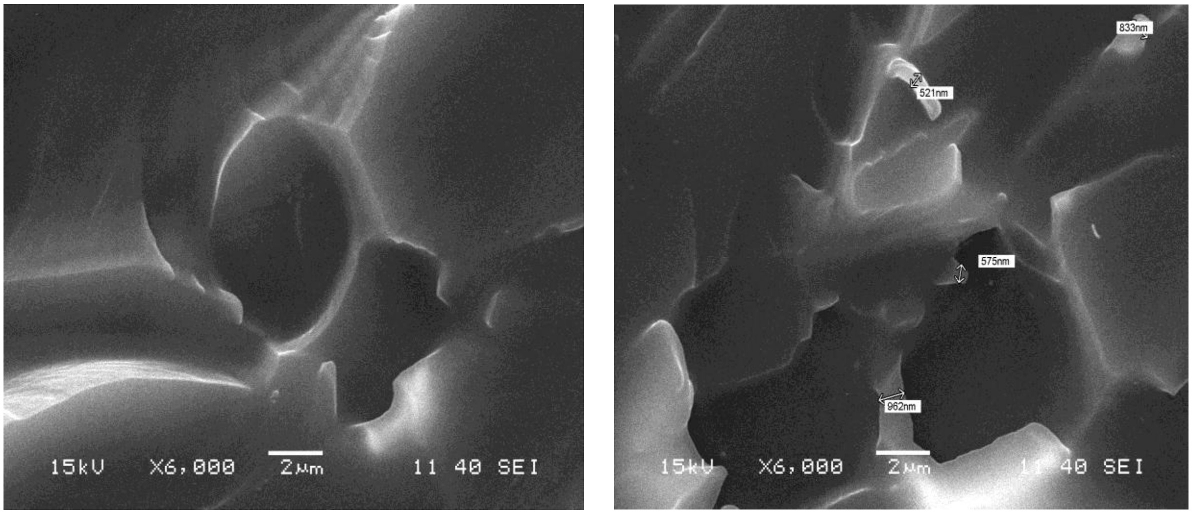
Figure



(a) (b)

Fig.10

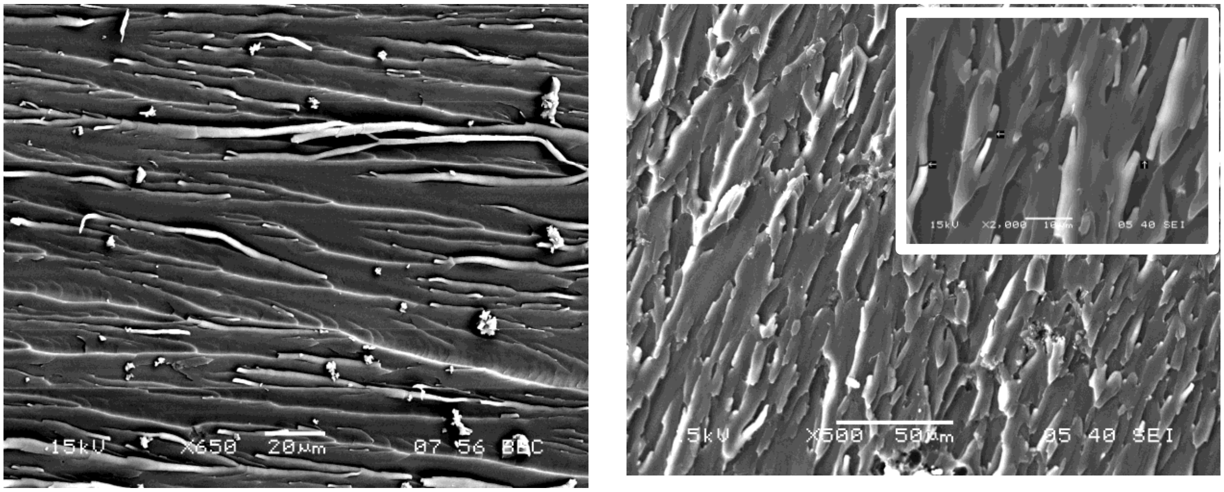
Figure



(a) (b)

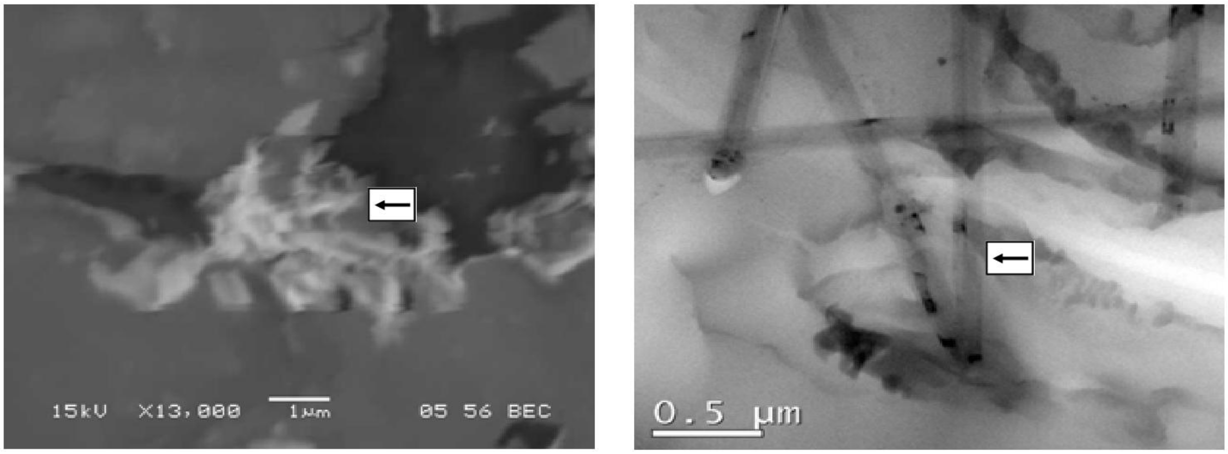
Fig.11

Figure



(a) (b)

Fig. 12



(a) (b)

Fig. 13