

Degradation in Mechanical and Thermal Properties of Partially Aligned CNT/Epoxy Composites due to Seawater Absorption

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Abstract

This literature gives an overview of the effect of water uptake on the mechanical and thermal performances of partially aligned carbon nanotube (CNT)/ epoxy (having CNTs wt.%: 0.5, 0.75 and 1) along with pure epoxy composites. Weight change behaviour of all the composites immersed in seawater for a period of six months has been recorded. The state of CNT/matrix interface is believed to be influenced due to water absorption. Reduction in flexural modulus, strength, hardness and glass transition temperature (T_g) of the specimens have been evaluated as compared to their unexposed counterparts due to adverse effect of water absorption. Results demonstrated 35-46% reduction in flexural modulus, 43-56% decrement in flexural strength, 4-7 MPa reduction in hardness and minor deterioration in T_g values for all the composites. However, the specimen having 0.75 wt.% CNT loading, exhibited minimum reduction in properties in all aspects compared to others. Scanning electron microscopy (SEM) has been employed to study the failure mechanism of the specimens after performing the mechanical tests.

Keywords

Moisture absorption, flexural properties, hardness, glass transition temperature (T_g)

1. Introduction

Carbon nanotube (CNTs) exhibits a series of excellent properties such as high elastic modulus, strength, electrical and thermal conductivities [1-3]. CNTs are thereby being used as promising reinforcing fillers in the polymer composites over a few decades for developing high-performance multifunctional composites. However, due to the low volume fraction, poor dispersion and random orientation of the CNTs in matrices, most resultant CNT-based composites can only receive limited enhancements and exhibit properties much lower than expected [4]. To overcome these challenges, various CNT preforms such as CNT arrays, CNT yarns, functionalized CNTs have been developed to pre-arrange as well as modify the CNTs in a pre-forming structure before preparing composites [5-7]. However, as surfactants and sonication are commonly involved to achieve a good dispersion of CNTs, the CNTs dispersed would usually suffer from inevitable damages or shortenings during this process, and the CNT orientation is also uncontrollable [8]. Hence, for the purpose of getting full advantages of the anisotropic properties of individual CNTs, a number of studies focused on the developments



of aligned CNT architectures and aligned CNT polymer composites. It is also well established that the well-aligned CNTs could facilitate higher CNT packing densities and yield greater property enhancements in the composites than their entangled configurations [9-11].

Evaluation of the environmental performance of polymer matrix composites on the other hand is very much essential for marine and aerospace applications [12, 13]. These composite specimens are exposed to various harsh environments which include different level of humidity, different temperatures, and immersion in several types of water etc. for a certain period of time. Depending on the type and level of exposure as well as the time exposed, the magnitude of the degrading effects on exposed composites can vary significantly. Periodic weight change of the specimens can be frequently measured to quantify the level of moisture absorption over time. Instead of extensive microscopy and measurement of weight change residual mechanical and thermal properties are often measured to determine the extent of damage occurred in the exposed specimens. Some previous researches have been reported that water absorption would cause numerous unwanted effects, such as swelling, plasticization and in certain cases degradation that may significantly affect the major properties of the composites [14, 15].

However, the trend of seawater absorption and its impact on overall properties of partially aligned CNT/epoxy composites is yet to be published that is essential for marine applications. So the main objective of this work is to explore the adverse effect of moisture absorption on the overall mechanical and thermal performances of the mentioned composites. Seawater absorption is correlated with the failure mode of the nanocomposites explaining the severe effect of water on the nanotube-matrix interfacial region with the help of microscopes. It is expected that, the adoption of CNT based epoxy composites for marine applications can be accelerated by determining the effect of seawater absorption on the overall properties of this composite for prolonged immersion in sea water.

2. Experimental details

2.1 Materials

In this investigation for fabricating the composites, epoxy resin (Ciba-Geigy, araldite LY-556 based on bisphenol A) was used as a matrix material and partially aligned CNTs as reinforcement. In particular this epoxy resin (5.3-5.4 equiv/kg) was cured with an aliphatic primary amine hardener (HY-951) in the wt. ratio 100/12. As-received CNTs were purchased from NanoAmour, USA. Here the CNTs have the diameter of 10-20 nm and their lengths varying from 5–15 μm with a carbon purity of > 95%.

2.2 Nanocomposite preparation

A schematic representation of nanocomposite presentation has been shown in Figure 1. A detailed description on the processing of the nanocomposites is given in our earlier work [16].

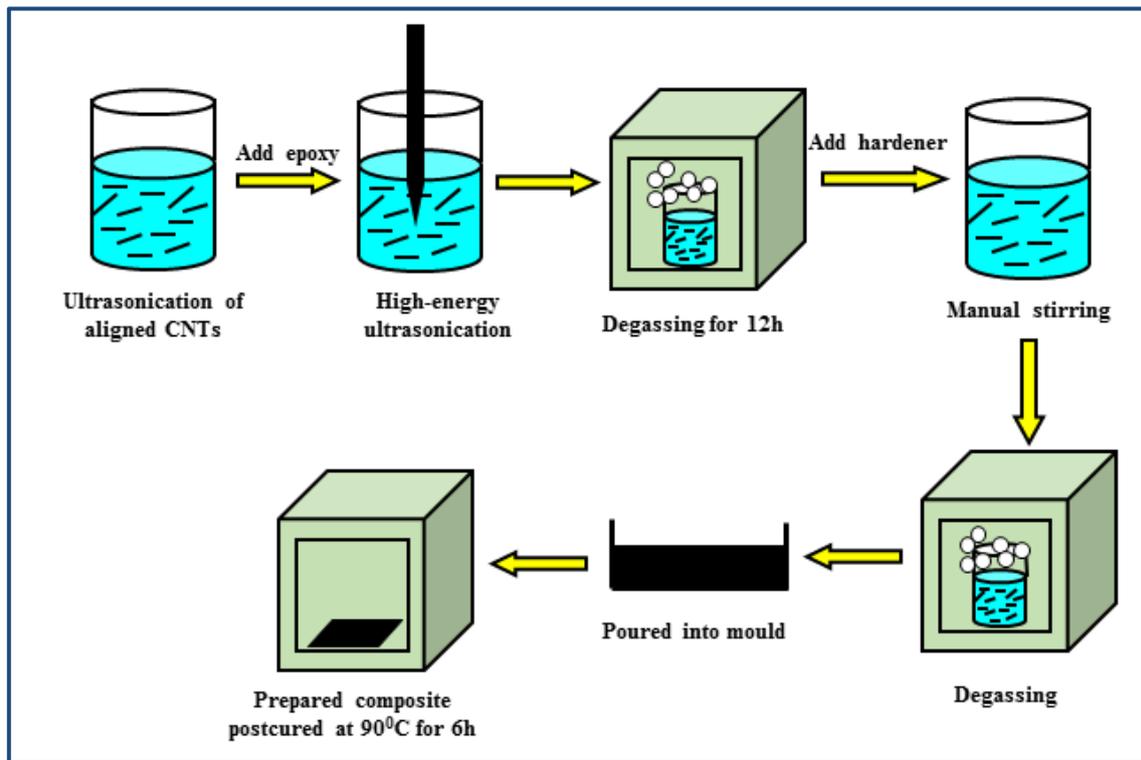


Figure 1. Schematic of nanocomposite preparation

2.3 Water absorption Tests

The moisture absorption trend of all the edge sealed specimens of dimensions 127 mm × 12.5 mm × 5 mm were studied via immersing the specimens separately into sea water up to six months. The weight gain of the samples was measured periodically using an electronic balance with an accuracy of 0.001 g after the removal of only the traveller samples from beaker. Prior to weighing, the surface of the wet samples was wiped with tissue papers. Percentage of weight gain by the samples was calculated using the formula:

$$M\% = \frac{M_t - M_0}{M_0} \times 100$$

where, M_t is the mass of the specimen after a given immersion time and M_0 is the mass of the dry specimen (before immersion). Then specimens were removed from the water bath and dried in an oven before conducting the required tests.

2.4 Characterization techniques

2.4.1 Flexural test

Flexural test was carried out according to ASTM D790–02 “Standard Test Methods for Flexural Properties of Un-reinforced and Reinforced Plastics and Electrical Insulating Materials” using universal testing machine Instron-5967 [16]. The testing mode was three

point bending having a loading rate 2.0 mm/min. The dimension of the sample was 60 mm × 12.5 mm × 5 mm (span length × width × thickness) respectively.

2.4.2 Hardness test

The hardness of all the composites is studied using a micro hardness tester. The hardness value is calculated using the Vickers hardness (HV) method is given by:

$$HV = 2 F \sin\left(\frac{136^\circ}{2}\right) / d^2 \text{ (approximately)}$$

where, F = Load in kgf and d = average length of the diagonal left by the indenter in millimetres (mm). A total of 10 points on each of the specimens were measured in order to get the average readings.

2.4.3 Thermal analysis

Differential scanning calorimetry (DSC) of all the samples had been studied to estimate the glass transition temperatures (T_g) using mettler Toledo DSC822° differential thermal analyser; each of the sample of around 10 mg were heated from 40-150 °C with a heating rate of 5 °C/minute in nitrogen at a flow rate of 30 ml/min.

2.4.4 Microscopic study

The surface morphology and fracture surfaces of the unexposed and seawater exposed specimens after performing the flexural test have been investigated using field emission scanning electron microscope (FESEM, Nova NANOSEM 450). The fractured surface was sputter coated with a thin gold layer in vacuum chamber for conductivity before test.

3. Results and discussion

The samples under present investigation are designated as follows: E_p - Pristine epoxy; $AC_{0.5}$ - Epoxy composite with 0.5 wt.% CNTs; $AC_{0.75}$ -Epoxy composite with 0.75 wt.% CNTs; and AC_1 - Epoxy composite with 1 wt.% CNTs.

3.1 Moisture absorption

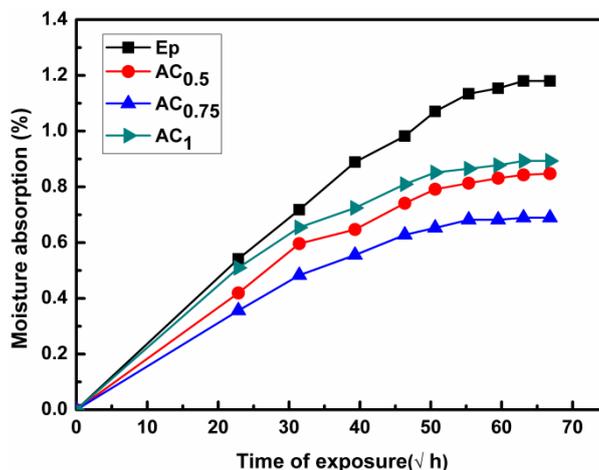


Figure 2. Moisture absorption behaviour of composites as a function of square root of time

In order to investigate the absorption behaviour of the specimens, percentage of moisture gain is plotted in Figure 2 against square root of time. The moisture absorption curves for neat epoxy and nanocomposites follow slightly different trends providing relatively lower weight gain in case of nanocomposites. Greater moisture absorption by epoxy is due to presence of hydroxyl group in it which is hydrophilic in nature and thereby very prone to water absorption. This sample gained moisture linearly and reached their saturation with equilibrium moisture content of 1.18% after 180 days of immersion in seawater. While for the nanocomposites, a mild linear increase in the moisture absorption curves was observed as compared to the pure epoxy specimens. After that, the nanocomposite specimens reached their equilibrium moisture content slowly after 110 days (approximately). The percentage of moisture absorption was 0.85%, 0.68% and 0.89% respectively for AC_{0.5}, AC_{0.75} and AC₁ specimens.

As mentioned, the maximum water content absorbed for CNT composites is lower than that absorbed by neat epoxy resin. Present observation is well matched with some previous research reports [17-18]. The phenomenon of reduced water uptake in nanocomposites is due to the excellent barrier properties of these nano-fillers [19-20]. The presence of high aspect ratio of nano-fillers can create a tortuous pathway for water molecules to diffuse into the composites [20]. Further, when compared with other nanocomposites, AC_{0.75} showed least water absorption. Indeed, nanofillers occupy either additional volume or the free volume depending on dispersion quality of the nanofillers within epoxy system. When nanofillers are homogeneously distributed in the epoxy then number of nanofillers in the free volume got enhanced. These accumulated nanofillers in turn reduce the ultimate water uptake [21]. This may happen in AC_{0.75} specimen and hence water penetration through the surface of this sample got seriously disturbed.

The water diffusion occurring in a material can be classified as Fickian [22], if (a) the moisture absorption graph shows an initially linear behavior with the square root of exposure time, (b) glass transition temperature (T_g) of the material is higher than the test temperature, and (c) the overall water uptake is low. Present case satisfies all the mentioned conditions; that is why the moisture absorption behaviour by the composites in this study can be categorised as Fickian nature. Similar kind of absorption phenomena also have been reported earlier by the other researchers [23, 24].

3.2 Flexural properties

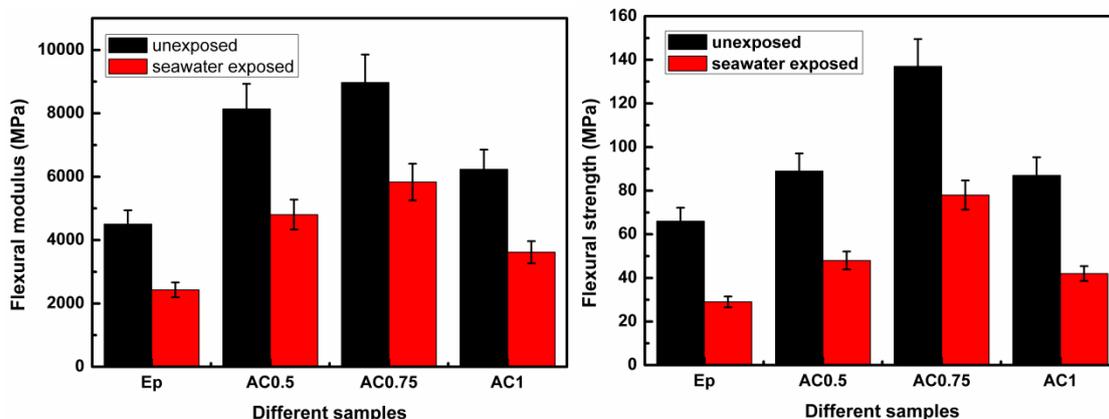


Figure 3. (a) Flexural modulus of unexposed and exposed specimens, (b) flexural strength of unexposed and exposed specimens

Among the unexposed specimens, flexural modulus & flexural strength of nanocomposites have been found to be enhanced with respect to that of neat epoxy specimen (Figure 3). The increment in modulus values were 81%, 99% and 39% respectively for AC_{0.5}, AC_{0.75} and AC₁ specimens as compared to epoxy composite is shown in Figure 3 (a). Further, a significant amount of improvement has been noticed in the strength values also. Flexural strength of neat epoxy was 66 MPa while; the nanocomposites AC_{0.5}, AC_{0.75} and AC₁ demonstrate the values around 89, 137 and 87 MPa respectively is shown in Figure 3 (b). This significant increase in strength & modulus of the nanocomposites compared to the neat epoxy counterparts is due to the addition of partially aligned CNTs that reinforces the performances of epoxy matrix [25]. Further, enhance effectiveness of the reinforcement and hence local stiffening occurs due to the aligned CNTs at the CNT/epoxy interface which may facilitate efficient load transfer from matrix to aligned CNTs in axial direction [26, 27]. It has been noticed that in case of higher loading of CNTs (AC₁) the increment in modulus and strength is relatively poorer as compared to others. This is probably due to the formation of CNTs' agglomeration into epoxy which causes weak bonding and thereby affecting the interfacial region [28]. However, major increment in flexural properties in case of AC_{0.5} and AC_{0.75} specimens are may be due to the good dispersion and occurrence of effective interfacial interaction of nanotubes into epoxy, will be further confirmed in microscopic study [29]. Obtained flexural properties were well matched with results obtained by other reports [30-31].

Flexural behaviour of all the seawater exposed specimens is shown in Figure 3. Results demonstrate that all the exposed specimens are showing reduction in flexural modulus & strength due to penetration of water molecules through the specimen. The modulus and strength values of the neat epoxy are deteriorated by 46% and 56% respectively under the action of water conditioning. It is observed that for the nanocomposites the reduction is relatively lesser as compared to neat epoxy. The decrement of moduli is 41%, 35% and 42% respectively for AC_{0.5}, AC_{0.75} and AC₁ specimens as compared to their unexposed counterparts. Further, the reduction in strength values while comparing to non-exposed samples is 46%, 43% and 51% respectively for AC_{0.5}, AC_{0.75} and AC₁ specimens. This

reduction in flexural modulus and strength values can be attributed to the swelling and plasticization effect of water absorption in epoxy matrix [32]. Water acts as an effective plasticizer and can diffuse through the CNT-epoxy interface and weaken the bonding between them [33]. As a result, the stress transfer capability of the composites got seriously affected causing drop in flexural properties.

Apart from these, higher void content in the composites may cause degradation of composites due to higher absorption of moisture/ water and also can create poor interfacial bonding. This trapped water damaged the interface region that penetrated through the microvoids and microcracks. However, it is interesting to note that compared to neat epoxy the reduction in flexural properties is lesser in case of nanocomposites. This is due to less water absorption by the nanocomposites when compared to neat epoxy. The reason for the reduced water permeability in nanocomposites is that the nanotubes restricted the molecular dynamics of the epoxy polymer chain surrounding them by not allowing the diffusion of small molecules [34]. In addition, it is observed that reduction in properties is least in AC_{0.75}. Because, at this wt.% the water absorption was also minimum among all that may be due to the achievement of strong bonding between fillers and matrix as a result of good dispersion.

3.3 Hardness

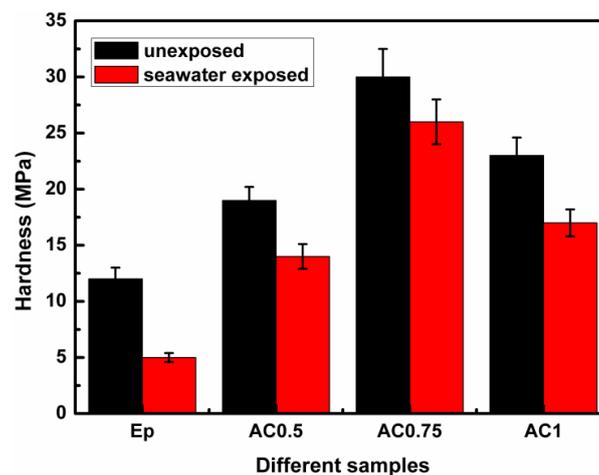


Figure 4. Hardness of unexposed and exposed specimens

In Figure 4 it has been observed that all the nanocomposite specimens demonstrated increase in hardness values as compared to the neat epoxy sample. In addition, hardness of the nanocomposites increases due to the addition of partially aligned CNTs into the epoxy matrix. An increment of 59%, 150% and 91% respectively for AC_{0.5}, AC_{0.75} and AC₁ specimens is recorded as compared to epoxy composite. The increment in hardness value of the epoxy after the incorporation of CNTs is due to the addition of high aspect ratio, high modulus, and high strength aligned CNTs. Further, as the hardness of the composite is a localized property so that may at the point of indentation very high resistance is realized by the indenter due to the achievement strong adhesion between partially CNTs and epoxy that will be further confirmed by the micrographs.

After the water absorption test the hardness values of all the specimens got deteriorated. After the complete time of exposure to seawater (6 months) a reduction of 4-7 MPa in hardness is observed than that of unexposed one. Neat epoxy sample showed maximum decrement in hardness. The lessening of the hardness value is mainly due to the moisture absorption that causes plasticization, swelling and interfacial damages of the composite materials. Due to absorption of water molecules by the specimen, the connection between molecules of polymer may disrupt and the composite specimens become so soft that the grasp between CNT and epoxy polymer got weakened [35]. Another possible reason for the reduced hardness is the generation of pressure on CNTs. Indeed, compared to CNTs the epoxy matrix got swelled to a larger extent and thereby exerts pressure to CNTs that may sometimes breaks the nanotubes and assists in pulling out of CNTs from the matrix. These combine affects not only reduces the material properties but also generates micro cracks inside the specimen that apparently diminishes the strength and hardness of the composite material.

3.4 Glass transition temperature (T_g)

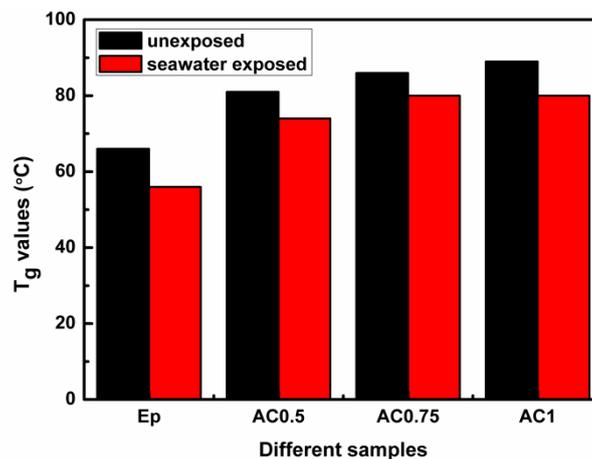


Figure 5. T_g values of unexposed and exposed specimens

Glass transition temperature (T_g) of a material is that critical temperature region in which material undergoes a transition from glassy to rubbery region, exhibiting a drastic change in the properties of the specimen. Below this temperature the material under consideration can be extensively used. Results shown in Figure 5 demonstrated an increment of around 15-23 °C in T_g value for the nanocomposites compared to neat epoxy specimen. Further T_g of the nanocomposites got slightly increased with the positive gradient of loading wt.% of CNTs. Increased values of T_g compared to neat epoxy is attributing to the cross linking reaction between epoxy and aligned CNTs [32]. Further addition of CNTs makes the epoxy matrix stiffer by restricting the mobility of chain segments of polymer and hence T_g increases [36].

T_g values of all the seawater exposed specimens are represented in Figure 5. All the specimens show reduction in T_g values (6-10 °C) after water exposure as compared to their unexposed counterparts. However, decrement of T_g value was greater in neat epoxy compared to nanocomposites. Though for the nanocomposites T_g values decreased to some extent still their values are higher than neat epoxy even after water absorption. Water exposure to these samples causes swelling (volumetric expansion) of both the matrix and fillers. Now the coefficient of volumetric expansion is higher in case of matrix rather than fillers. This

difference in expansion in turn induces residual stresses at the interface. Development of residual stresses in this manner may weaken the brittle epoxy, degrade the interfacial properties, leads to generation of osmotic pressure which further creates microvoids and microcracks in the composite. This combine effects reduce the stiffness, strength and T_g of the composite [37].

3.5 Microscopical analysis

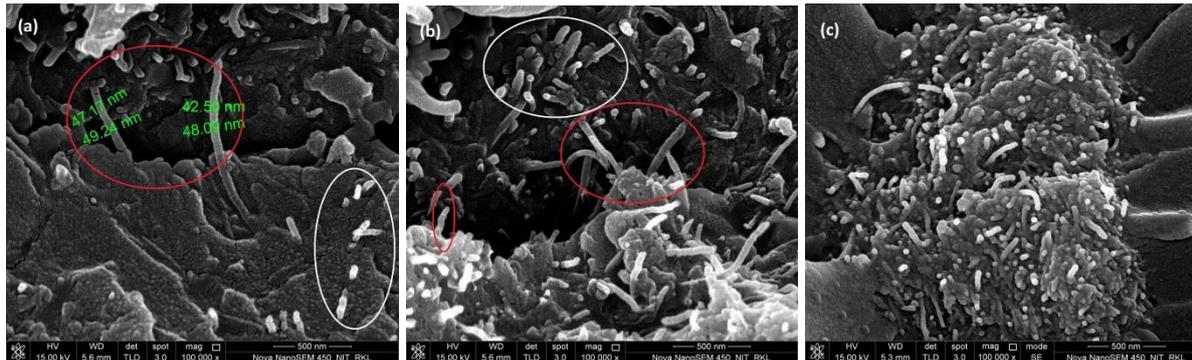


Figure 6. Fracture surface of unexposed nanocomposites showing (a) bridge formation across the crack in $AC_{0.5}$, (b) partial pull out of nanotubes in $AC_{0.75}$ and (c) agglomeration of nanotubes and weak interface in AC_1 specimen

Figure 6 (a) and (b) indicate good dispersion of CNTs in the epoxy matrix. Careful observation revealed that a major fraction of nanotubes which are in axial direction along the load got completely ruptured and partial pull out (shown by white circles) of CNTs has been noticed due to the application of load. This means that strong bonding occurs between the aligned nanotubes and host matrix. While, some of the nanotubes that are placed orthogonal to the direction of applied load try to resist the crack induced in the matrix by bridge formation (shown in red circles). The propagation of cracks are obstructed by the nanotubes is reported here which is the cause behind the increment in mechanical properties of the nanocomposites with respect to the neat epoxy resin. On the other hand, for higher wt.% (Figure 6 (c)) voids and agglomeration of nanotubes have been noticed. Due to the presence of voids moisture absorption at this wt.% was higher among the nanocomposites. Both the voids and agglomeration of CNTs are responsible for not forming good interfacial region resulting minimum values of flexural modulus and strength when compared with the other nanocomposites.

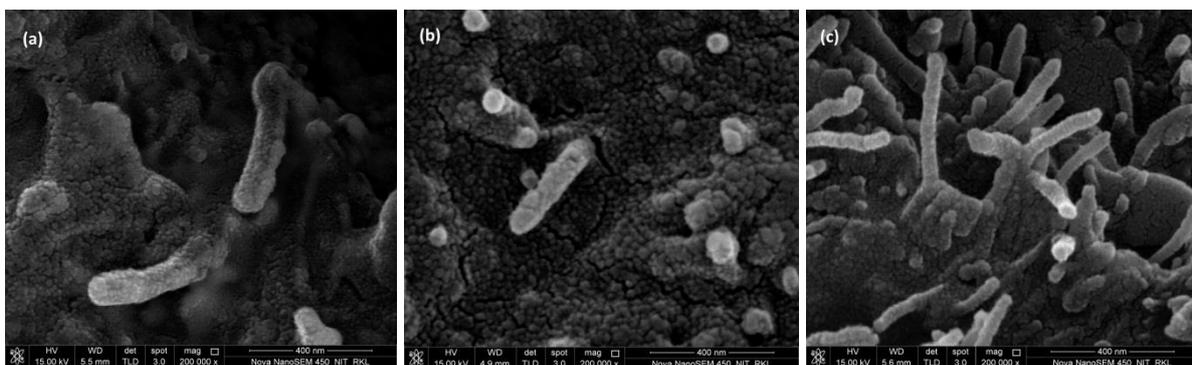


Figure 7. Fracture surface of moisture absorbed nanocomposites showing swelling of epoxy matrix and CNTs as well as partial and complete pull out of CNTs in (a) AC_{0.5}, (b) AC_{0.75}, and (c) AC₁ specimen.

Fracture surfaces of water absorbed nanocomposites are shown in Figure 7. Water absorption reduces the compatibility between the matrix and CNTs which contributes to debonding and weakening the interfacial adhesion. Matrix cracking is clearly observed in all the micrographs due to the generation of internal stresses as a result of water absorption. Further, swelling of both the matrix as well as nanotubes damages the interfacial region and hence load bearing capacity by the interface got reduced. CNTs pull out is clearly visible in the micrographs Figure 7 (a), (b) and (c) which is a clear evidence of interfacial debonding phenomena are very much responsible for the deterioration in mechanical properties. However, the degree of pull out is relatively less in AC_{0.75} specimen (Figure 7 (b)) compared to others. This is why at this wt.% lesser degradation in properties has been noticed as compared to others.

4. Conclusions

- ❖ Flexural modulus, strength, hardness and T_g of the unexposed specimens were enhanced compared to neat epoxy specimens.
- ❖ In seawater exposed case, weight gain of neat epoxy was 1.18% while for AC_{0.5}, AC_{0.75}, and AC₁ it was 0.85%, 0.68% and 0.895 respectively i.e., inclusion of nanotubes reduced the water uptake of epoxy polymer.
- ❖ Degradation in properties of all the composites to some extent were realised due to after effects of moisture absorption. However, deterioration in properties was more pronounced in neat epoxy compared to nanocomposites. Further, among the nanocomposites AC_{0.5} showed lesser degradation in all aspects.
- ❖ Enhancement in mechanical properties in nanocomposites as compared to neat epoxy was found to be dependent on the quality of dispersion of nanotubes in epoxy for the unexposed specimens. While, swelling of the matrix and fillers as well as CNT pull out were marked to be responsible for the reduction in mechanical and thermal performance of the water exposed specimens.

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