

REVIEW ON MECHANICAL BEHAVIOR OF (CNTs) REINFORCED EPOXY-BASED NANOCOMPOSITE MATERIALS

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ABSTRACT

A number of experiments have already shown that CNTs are integrally multifunctional and the addition of these substantially improves the mechanical, thermal, optical and electrical properties of low concentrations nanocomposites. CNTs possess unique electrical, mechanical and surface properties and utilization as filler for epoxy-based composites finds application in electronics, automobile, aircraft and numerous other industrial fields. The current challenges exist in sense of the processing technique for materials, owing to the typical small size and high specific surface area associated with CNTs. Upon mixing CNT into epoxy, entangled aggregates of CNTs are generate, leading to increased viscosity of CNT-epoxy system and thereby difficult processing. Another existing challenge involves the attainment of strong interface for effective load transfer between nanotubes and matrix because the transfer of load not only depends upon the interfacial shear stress acting between the matrix and the fibre but also between the matrix and CNTs. This assessment focuses over the techniques to overcome the above-mentioned oppositions, primarily utilizing the functionalization of CNTs because it would alter the CNT surface characteristics along with increasing its polarity, leading to covalent bond formation with epoxy matrix and thereby enhancing load-transfer efficiency. The fabrication routes have been established for achieving higher shear forces during fabrication of CNT filled epoxy composites and thereby ensuring uniform dispersion of nanotubes throughout the matrix along with acid treatments of reinforcing fibers for achieving quality interfacial adhesion.

Keywords: Epoxy; carbon nanotubes; mechanical behavior; functionalization; silanized

1. Introduction

Polymer-matrix composites (PMCs) have attracted huge interests of industries and research laboratories because of their excellent mechanical behavior involving high modulus of elasticity, increased mechanical strength, flame retardancy and barrier properties [1]. The most commonly utilized matrix in many advanced versatile applications of PMCs is epoxy [2]. The carbon nanotubes (CNTs) are the one-dimensional carbon nanomaterials possessing

excellent mechanical properties involving ultra-high Young's modulus (nearly 1 TPa) and high tensile strengths (11–63 GPa), thereby behaving as an ultra-high-strength reinforcement for polymer based composites [3, 4]. Their excellent attributes involving excellent aspect ratio, very low density, small size and superior physical properties involves extremely high mechanical stiffness and strength along with high thermal and electrical conductance), thereby making them as ideal reinforcement fillers for elevated strength, light weight polymer-based nanocomposites. But the challenges involved in the fabrication of excellent performance CNT filled polymer-based composites include (a). Uniform distribution of CNTs in polymeric matrix along with (b). High interfacial interactions for effective transfer of load between polymeric matrix and the CNT reinforcement. The chemical interactions between functionalized CNTs and polymeric matrix could achieve much efficiency of load transfer whereas in the absence of chemical interactions, transfer of load between polymer and CNTs (i.e. crosswise the polymeric matrix and CNT interface because of the chemically smoothened CNT surfaces) occurs because of van der Waals along with electrostatic interactions [5, 6]. The epoxy resin possesses superior resistance towards heat and chemical attacks, high adhesion, high impact strength, excellent electrical insulation along with high strength and hardness. It displays good temperature performance due to high cross-linking density but lack the required toughness and are very brittle. It is characterized by a group involving three membered ring called epoxy, oxirane, epoxide and ethoxyline or glycidyl and has been depicted in Fig. 1 [7]. Moreover, the epoxy maintains minimum shrinkage during curing, absenteeism of byproducts and volatiles associated with curing, wide temperature ranges of curing along with superb adherence to various collection of fibers, fillers and other substrates [8].

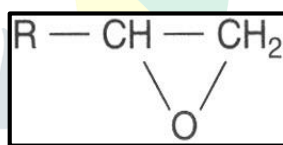


Fig. 1. Epoxy or oxirane group [7].

The chemical functionalization of CNTs is amongst the most successful methods for inhibiting CNT aggregation in polymeric matrix through either direct covalently functionalization of sidewall or defect functionalization. The direct covalently functionalization of sidewall involve reaction between reactive molecules such as fluorine with CNT, followed by replacement of fluorine with hydroxyl, amino and alkyl groups whereas the defect functionalization involves oxidative process for creating defects on sidewalls or at the CNTs open ends and includes the utilization of strong acids like HNO_3 and H_2SO_4 for oxidative process. The defect sites could further bond with carboxylic acid or hydroxyl groups and the modification processes involving silanation, polymer grafting, esterification, thiolation, arylation along with alkylation could be implected over these functionalized CNTs. Moreover, the amine-functionalized CNTs shows enhanced CNT dispersion and interfacial interactions with the epoxy matrix due to covalent bonding formation between epoxy and CNTs but this reaction rate is limited due to steric hindrance and high activation energy required and therefore functionalization of CNT with epoxy

chains act as an alternative for achieving several covalent bondings, with the curing agent inside the matrix [10]. The epoxy matrix reinforced with carbon fibers and glass fibers have been widely utilized in packaging, coating, electronics, hulls of ship, structural parts of wind turbine, piping associated with corrosive chemicals, automobile and aerospace applications because of superior stiffness-to-weight and strength-to-weight ratios along with long fatigue life, corrosion resistance, low density, wear resistance and environmental stability [11, 12]. This paper reviews the mechanical behavior of epoxy composites reinforced with CNT and a few researches involving CNT filled fiber (pristine and functionalized) reinforced epoxy composites have also been covered at elevated temperatures and cryogenic conditions.

2.Literature Review

A lot of work has been done where Husaen [15] reported the mechanical behavior of CNT reinforced with epoxy resin composites and observed that the flexural and tensile properties along with Shore D hardness values showed an increasing trend with increasing CNT amounts (0.01, 0.05 and 0.1 wt. %), with the maximum values being observed corresponding to 0.1 wt. % CNT. Sapiai et al. [16] reported the mechanical behavior of epoxy composites reinforced with kenaf and filled with CNT in pristine (PCNT), acid-treated (ACNT) and acid-silane treated (SCNT) states, involving 0.5, 0.75 and 1.0 wt. % contents. It was observed that the SCNT filled kenaf reinforced epoxy composites shown excellent mechanical properties (flexural, tensile and impact behavior) in comparison with PCNT along with ACNT filled kenaf reinforced epoxy composites, with maximum improvement for 1.0 wt. % reinforcement and this enhancement was attributed to the hindered molecular mobility of CNT, its better dispersion along with strong crosslinking with epoxy due to the combined effect of acid and silane treatment. Yang et al. [17] studied the influence of strain rate on the mechanical behavior and fracture mechanism of multi-walled carbon nanotube (MWCNT) (0.0, 0.1, 0.3 and 0.5 wt. %) reinforced epoxy composites and it was observed that for constant true strain values, the true stress increased linearly with strain rate increase in 10^{-3} – 10^{-1} s^{-1} range whereas the fractographic studies recognized the MWCNT as obstacle to slip bands motion in epoxy and thereby increasing flow resistance, as shown in Fig. 2.

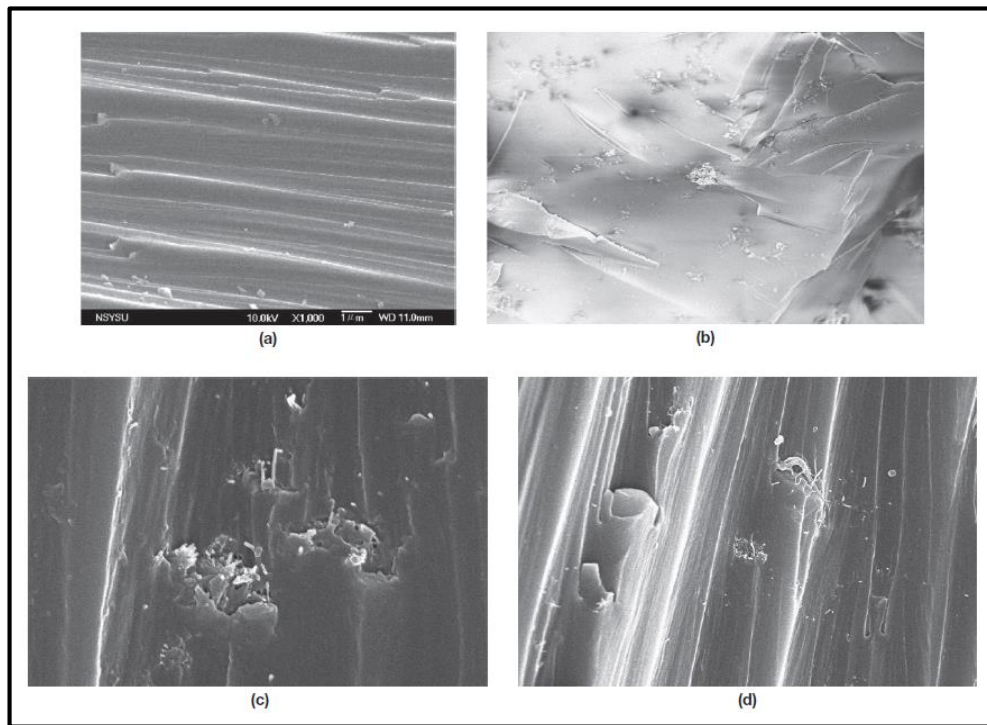


Fig.2. Fracture surface features at different MWCNT contents (a) 0 wt. %; (b) 0.1 wt. %; (c) 0.3 wt. %; (d) 0.5 wt. % [17].

Moumen et al. [18] studied the impact of CNT (0.0, 0.5, 1.0, 2.0 and 4.0 wt. %) on the impact strength and damage evaluation of epoxy composites reinforced with laminated carbon fibers using Taylor impact loading (the setup is shown in Fig. 3), with three impact velocities ranges as 3 m/s (no damage on composite surface), 7 m/s (with damaged surface) as well as 12 m/s (total fracture and rupture of plies). It was observed that the impact resistance decreased by 13 % for 4 wt. % CNT due to improper dispersion and agglomeration at higher percentages whereas the fractography revealed surface and bulk fractures for pristine composite along with large energy absorption during presence of CNT between plies.

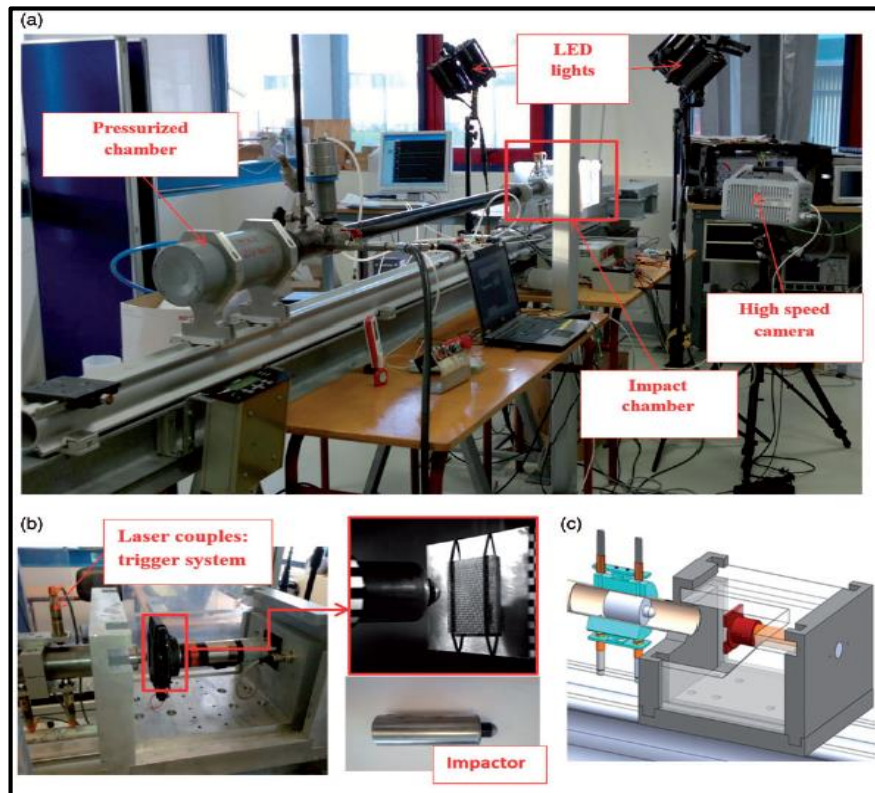


Fig. 3. ENSTA Bretagne Taylor gun system (a) experimental setup and Taylor gun; (b) impact chamber with fixture system; (c) schematic presentation of the impact chamber [18].

Ramana et al. [19] reported the impact of the surface modification regarding MWCNT (0.2–1.0 wt. %) on the mechanical behaviour and matrix-reinforcement interface generation in epoxy-based composites. The enhancement of 100 % in bending strength for acid treated MWCNT was reported and attributed to the attachment of functional groups in the CNTs surface, which reacted with epoxy matrix while curing occurred and thereby built covalently linkages. Moreover, the fractography revealed that for functionalized CNTs, the failure cracks occurred more on the interface between CNTs along with fiber pull-out, which absorbed energy before fracture as shown in Fig. 4 whereas thermogravimetric analysis (TGA) results concluded the enhancement of thermal decomposing temperatures because of strong interactions between the epoxy and functionalized CNTs.

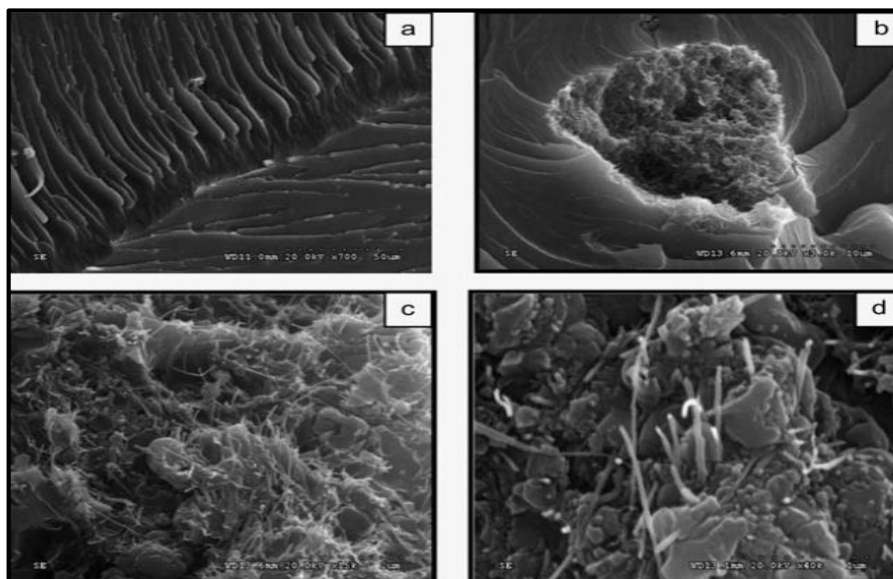


Fig. 4. Fracture surface of (a–b) pristine epoxy; (c–d) 1 wt. % CNT-epoxy composites [19].

Moreover CNT bridging mechanism in crack propagation regions, as observed in fractographic studies, confirmed the strong interfacial adhesion between amino CNT, glass fiber and epoxy. Rathore et al. [24] evaluated the mechanical properties of CNT (0.0, 0.1, 0.3 and 0.5 wt. %) filled glass fiber reinforced epoxy (GE) composites under in-situ high temperature environments (20 °C, 70 °C, 90 °C and 110 °C) and it was observed that at room temperature, the 0.1 wt. % CNT reinforced GE composites showed 32.8 % and 11.5 % enhancement in flexural strength along with modulus, respectively as compared to pristine GE whereas at elevated temperatures, 0.1 wt. % CNT reinforced GE composites showed degraded properties due to the thermal differential expansion at the interface, leading to the formation of micro-cracks at large interfacial area present. Scanning electron microscopy (SEM) analysis, as shown in Fig. 6, depicted heavy matrix deformation for 0.5 wt. % CNT reinforced GE composites at 110 °C, thereby indicating relatively ductile failure. Wang et al. [25] observed the fracture and mechanical properties of epoxy based composites reinforced with hyperbranched polymer (HBPs) covalent functionalized MWCNT (0.2–0.8 phr), owing to the fact that HBPs possess unique highly branched structures and available surface multifunctionalities, thereby leading to enhanced uniform distribution and interfacial interactivity of CNTs during processing with epoxy.

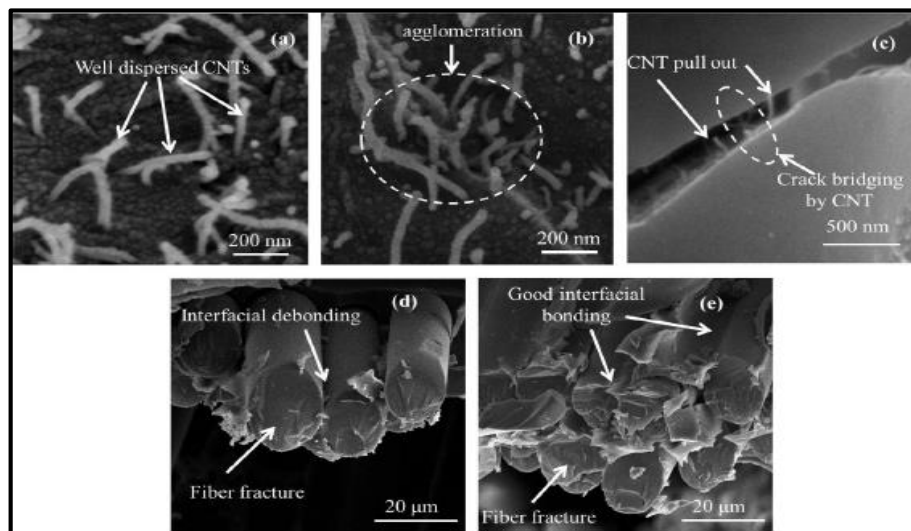


Fig. 6. Dispersion of (a) 0.1 wt. %; (b) 0.5 wt. % MWCNT in GE composite; (c) CNT pullout and crack bridging by CNT in 0.1 wt. % MWCNT-GE composite after room temperature testing; (d) glass fiber bundle in GE; (e) glass fiber bundle in 0.1 wt. % MWCNT-GE composite [24].

It was concluded that the 0.6 phr loaded functionalized MWCNT composites showed 12 %, 107.6 % and 34 % and improvements in tensile strength, critical energy release rate (G_{IC}) and fracture toughness (K_{IC}) respectively, whereas major toughening mechanisms reported, as shown in Fig. 7, were nanotubes breakage and their bridging phenomenon in wake of propagating crack along with shear failure in epoxy resin. Kara et al. [26] studied the impact behavior of carbon fiber-epoxy composites reinforced with MWCNT (0.3 wt. %) at cryogenic temperatures (0 °C, -50 °C, -100 °C and -196 °C) and the initial damage to the samples during immersion in liquid nitrogen was reported. Increase in the damages on the specimens with decreasing temperatures was observed for all the samples and moreover higher contact force values were concluded upon nanoparticles addition, for the similar temperatures, and little damaged sample sections. Xiao et al. [27] coated the carbon fibers with MWCNTs using aqueous suspension deposition method and studied the improvement in mechanical properties upon composite preparation with epoxy. 15.1 %, 17.6 % and 12.6 % improvement in flexural strength, tensile strength and interlaminar shear strength was observed as compared to pristine composite whereas fractographic studies confirmed the mechanical interlocking of MWCNTs, as shown in Fig. 8, as the major toughening mechanism. Prusty et al. [28] studied the flexural behavior of CNT (0.3 wt. %) filled glass reinforced epoxy (GE) composites during in situ elevated (70 °C and 110 °C) and low (-80 °C, -40 °C) temperature conditions and reported 67 % along with 81 % decrease in bending strength of GE and CNT-GE composites, respectively at 110 °C, in comparison to their strength at -80 °C, owing to matrix softening, microvoids formation and their coalescence upon load application. It was concluded that the properties deteriorated with increasing service temperature and this degradation was larger for CNT-GE composites as compared to GE composites.

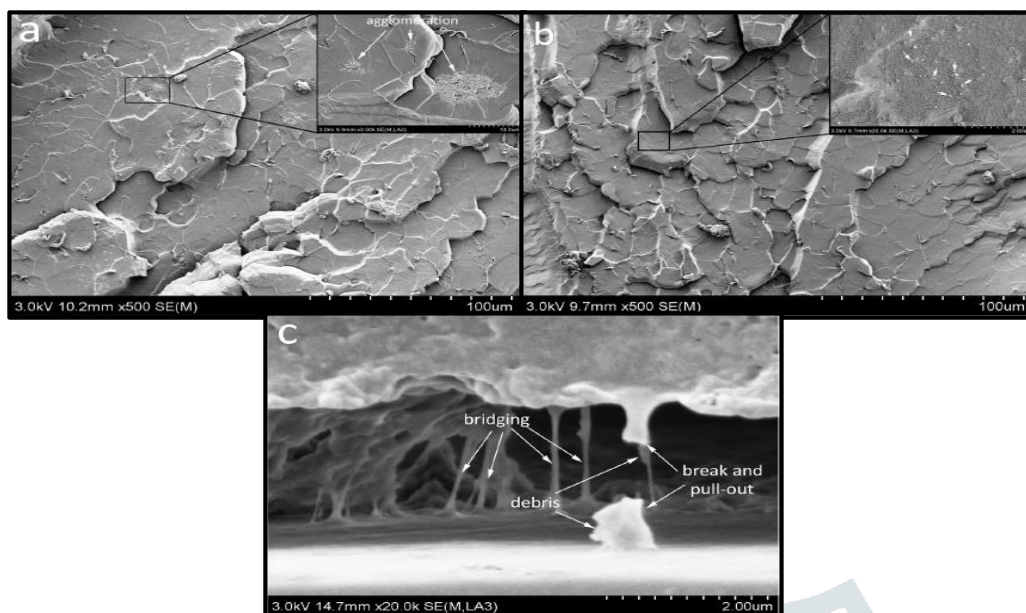


Fig. 7. SEM micrographs of fracture surfaces for (a) MWCNT-epoxy composite; (b) 0.6 phr MWCNT-epoxy composite; (c) crack in 0.6 phr MWCNT-epoxy composite [25].

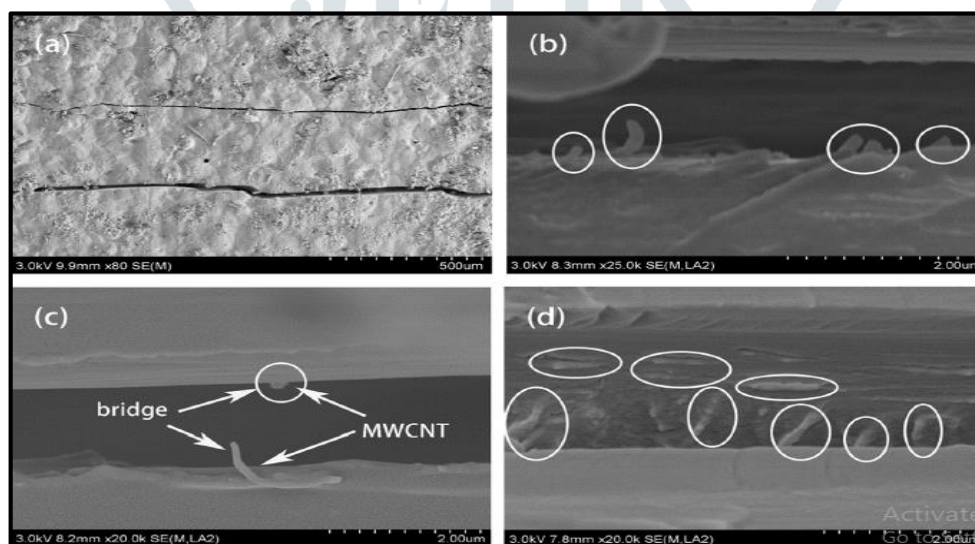


Fig. 8. Interfacial strengthening using MWCNTs; (b); (c); (d) are partially magnified SEM images of (a) [27].

Lee et al. [29] studied tensile and thermal behavior of modified (oxidized and silanized) CNT (1 wt. %) filled basalt reinforced epoxy composites, thereby reporting 34 % along with 60 % improvement for silanized CNT composites, as compared to unmodified CNT composites. Moreover higher T_g values for silanized CNT composites was obtained as compared to the unmodified CNT and oxidized CNT filled composites and was attributed to the effective dispersion and increased interfacial interactions in silanized CNT composites. Laurenzi et al. [30] investigated the failure modes of MWCNT (0.5 and 1.0 wt. %) reinforced aerospace grade epoxy using microscopy and reported decrement in mechanical properties in 0.5–1.0 wt. %, owing to clustering of nanotubes due to van der Waals forces. The nanotubes oriented orthogonal to the applied load direction exhibited pullout caused by interfacial debonding whereas nanotubes oriented parallel to the loading direction showed complete rupture as well as telescopic pull outs. Mei et al. [31] reported the impact of nanotubes reinforcement on interfacial reinforcing mechanisms of carbon fiber reinforced epoxy based composites and 9.86 %, 44.01 % along

with 12.40 % enhancement in tensile strength, failure strain and modulus of elasticity respectively was reported for CNT filled carbon fiber-epoxy composites. Further the nitric acid treatment of fibers activated the potential of reinforcement for CNTs, thereby leading to 35.7 %, 21.7 % and 70.0 % increase in tensile strength, failure strain and Young's modulus respectively, attributed to chemical and physical modification of fiber surfaces involving enhanced roughness, changes in functional groups along with wettability of fiber surfaces. Kharitonov et al. [32] studied the influence of fluorinated (gaseous fluorine treatment at elevated temperatures) CNT (0.01, 0.1 and 0.5 wt. %) on the mechanical behavior of bisphenol-F epoxy and observed higher degree of improvement in mechanical behavior of fluorinated 0.1 wt. % CNT composites (fluorinated at 150 °C), as compared to pristine CNT composites, with 50 %, 74 %, 60 % and 66 % increase in tensile strength, tensile modulus, flexural strength and flexural modulus, respectively. Moreover SEM analysis reported the absence of CNT on surface of both pristine and fluorinated CNT composites, thereby confirming good adhesion of CNT with epoxy matrix.

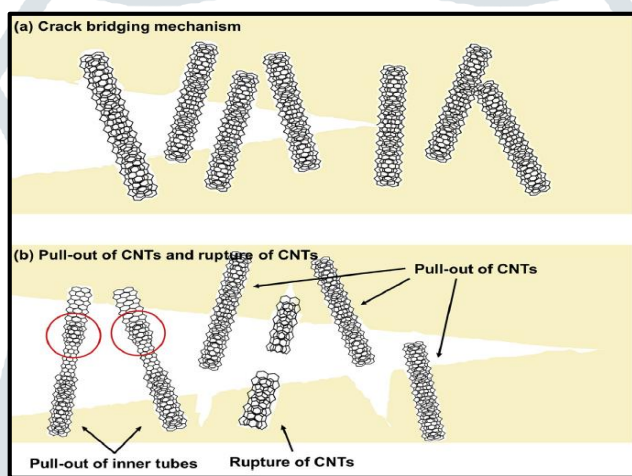


Fig. 9. Schematic representation of propagating crack (a) crack bridging mechanism in CNTs; (b) rupture of CNTs along with CNTs pull-out and inner tubes [33].

Cha et al. [33] studied the impact of non-covalently functionalized (using melamine) CNTs (i.e. M-CNT in 0.1, 0.5, 1.0, 2.0, 3.0 and 5.0 wt. % amounts) on the mechanical behavior of epoxy composites. Non-covalent functionalization maintained the properties and pristine structure of CNTs by not destroying the CNT sidewalls. The 2 wt. % M-CNT reinforced epoxy composites showed improvements by 64 %, 22 % and 95 % in Young's modulus, tensile strength and fracture toughness, respectively. Moreover fractographic analysis confirmed the crack bridging mechanism involving rupture and pullout of CNTs responsible for toughening in 2 wt. % M-CNT reinforced epoxy composites, as shown in Fig. 9. Hong et al. [34] reported the impact of nanotubes (0, 1, 2 and 5 wt. %) reinforcement over the thermal and mechanical behavior of epoxy resin, utilizing functionalized CNTs-reactive polymer linkages (for enhanced nanotube polymer interface bonding) and three-roll milling (involving shear forces generated by three rolls positioned horizontally, rotating in opposite directions and at different velocities, thereby detangling the heavy bundles of CNT). Elastic modulus was reported to improve by 100 % for functionalized CNT composites, as compared to pristine CNT composites, owing to the covalent bonding leading to van der Waals interactions between the functional molecules present on the CNT surface. Moreover, onset

temperature of degradation and the endset temperature of decomposition were higher for functionalized CNT composites, with the highest for 5 wt. % functionalized CNT-epoxy composites. Rahaman and Imran [35] utilized the vacuum-assisted resin infusion molding (VARIM) for fabricating MWCNTs (0.5 wt. %) reinforced glass fiber-epoxy (GF-Epo) composites and no significant variation was observed between the thermal stabilities of the GF-Epo and MWCNT-GF-Epo composites, owing to very less concentration of MWCNT along with increase in both flexural modulus and strength because of better dispersion of MWCNT in epoxy matrix. Moreover, the SEM analysis reported brittle to ductile transformation of composite upon incorporation of MWCNT in the composite.

3. Conclusion and Scope of Future Study

It was concluded that at the ambient temperature, the mechanical properties of epoxy composites improved with increasing CNT contents in the range of 0.5–1.0 wt. %, owing to the high aspect ratio being responsible for the increased interfacial adhesion between nanotubes and epoxy resin along with excellent mechanical behavior of CNTs. However the mechanical behavior deteriorated at higher CNT concentrations because of the agglomeration of nanotubes, leading to stress concentration effects along with decrease in the availability of interface for load transfer between epoxy resin and CNTs. Moreover the researchers had also performed the functionalization of CNTs for further improving the mechanical behavior associated with CNT filled epoxy based composites and it possesses advantages involving (a). Better dispersion of CNT, (b). Reaction between functional groups attached on CNT and epoxy during curing and building covalent bonds, leading to van der Waals interactions between the functional molecules present on the CNT surface, along with (c). Prevention of CNT agglomeration. However, the elastic modulus was an exception because higher elastic modulus were achieved for the pristine CNT filled epoxy composites owing to higher crystallinity and integrity of structure in pristine nanotubes whereas functionalized CNT filled epoxy composites involves defect formation and shortening in CNTs during chemical functionalization. Various processing techniques involving homogenization and ultrasonication along with three-roll milling were successful in breaking nanotube agglomerates due to high shear forces and thereby achieving fine CNT dispersions. Acidic treatment of reinforcing fibers initiated physical and chemical modifications over fiber surfaces involving enhanced roughness and thereby improving interfacial interactions. The researchers also concluded that the performance of CNT filled epoxy composites showed deteriorated performance at elevated temperatures as compared to performances at room and cryogenic temperatures, owing to thermal differential expansion at the interface, thereby leading to microvoids generation and their coalescence during loading. The major toughening mechanisms involved for CNT filled epoxy composites, as noticed from the fractographic studies, were nanotube pullout and nanotube breakage (leading to interfacial debonding), nanotube bridging effect to the propagating crack, MWCNT obstacles to slip bands motion in epoxy along with mechanical interlocking of MWCNTs. However the effective distribution of CNTs into the polymer based matrix along with addition of CNTs into metal matrix still poses as a scope of future

studies in sense of optimizing the processing parameters for achieving maximum enhancement of mechanical as well as physical properties.

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