

# Improved mechanical properties of carbon nanotube/polymer composites through the use of carboxyl-epoxide functional group linkages

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## ABSTRACT

Single-walled and multi-walled carbon nanotubes (CNTs) were functionalized with carboxyl groups and dispersed in a polymer containing an epoxide group. We have then observed experimentally that mutual chemical reaction between the functional groups on the CNTs with the polymer epoxide group can enhance, two-fold, both the tensile strength and elastic modulus,  $E$ , of single walled CNT/polymer composites. A simple model was formulated to understand the variation of  $E$  with CNT volume fraction, considering agglomeration effects as well. An increase in the work of fracture, obtained from the experimental stress–strain curves, was seen at low nanotube filling fractions and is presumably due to crack bridging of the polymer matrix by CNTs. The influence of CNT length and geometry on mechanical properties, along with the influences of electrical and mechanical percolation thresholds was considered.

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## 1. Introduction

Polymer composites containing conducting fillers [1] such as carbon black [2], carbon fiber, and metal fiber have been extensively investigated for multi-functional applications incorporating structural reinforcement [3], electromagnetic interference (EMI) shielding [4], electronic packaging [5], radar absorbing materials [6], and high charge storage capacitors [7,8]. A concomitant enhancement in the mechanical properties was also observed in the composites, e.g., facilitated through load transfer from a low elastic modulus ( $E$ ) polymer matrix to a high  $E$  filler [9]. However, there is a limit to the impregnation of polymers with such traditional filler material due to possible embrittlement beyond a certain loading. Consequently, high aspect ratio fillers which favor reinforcement and electrical properties/percolation at lower volume fractions are desirable. Carbon nanotubes (CNTs) offer a most attractive option in this regard, primarily due to their extremely large aspect ratio – which could be as high as  $10^6$  [10] coupled with a large interfacial area  $> 1300 \text{ m}^2/\text{g}$  [11], which implies load transfer over a longer length incorporating superior shear strength. Additionally, the CNT surfaces and interfaces can be functionalized and made to interact suitably with the polymer matrix groups through the use of suitable coupling agents [12].

However, there are still several challenges to the utilization of CNTs, e.g., (a) aggregation and bundling which leads to a non-uniform dispersion, along with (b) poor interfacial bonding of the nanotubes with the polymer matrix, both of which lead to variable composite characteristics, along with the (c) high cost of CNTs. A case in point is that while single walled CNT (SWCNT) and multi-walled CNT (MWCNT) based composites have been reported [13–15] to yield enhanced  $E$  and ultimate tensile strength ( $UTS$ ), the values of these parameters greatly diminishes beyond a certain loading, e.g.,  $\sim 0.6 \text{ vol\%}$  in phenol/SWCNT composites [16] or polypropylene/SWCNT composites [15]. It was also frequently seen that concomitant with an increased  $E$  or  $UTS$  for the composites, a diminished work of fracture and strain to failure [17,18].

In this paper, we suggest a possible method to enhance the mechanical properties of polymer composites comprising homogeneously dispersed CNT and enhanced nanotube–polymer interface bonding, facilitated through mutual localized chemical reactions [19,20] between functional groups on the SWCNTs with groups on the polymer. We then show that  $UTS$  and  $E$  of such functionalized SWCNT/polymer composites, at identical CNT filling fractions, are superior to those using unfunctionalized nanotubes. Additionally, we show that simultaneous toughening and strengthening could be achieved when the average length of the uniformly dispersed SWCNTs was adequate to bridge incipient cracks. We then propose models to explain the observed mechanical characteristics considering the effects of CNT agglomeration, aspect ratio, and the effect of CNT filler interactions in reducing the work of fracture, beyond a certain critical CNT concentration in the matrix.

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## 2. Experimental procedure

### 2.1. Synthesis of functionalized SWCNT/polymer composites

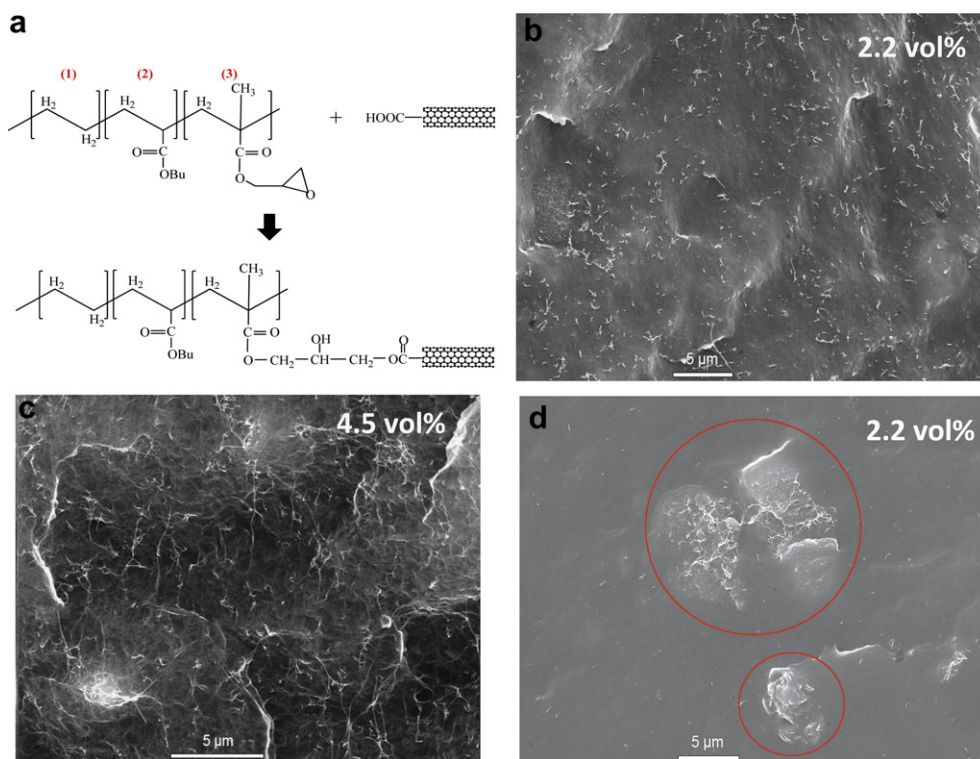
We chose, for proof of principle, a polymer matrix composed of reactive ethylene terpolymer (RET: Elvaloy 4170, density  $0.94 \text{ g cm}^{-3}$ ) constituted of (1) polyethylene, (2) a polar methyl-methacrylate group, and (3) epoxide functional groups – Fig. 1(a). While (1) and (2) contribute to elastomeric characteristics and corrosion resistance and are critical to the utility of RET as a hot-melt adhesive and coating, the epoxide group has high reactivity [21] and is amenable for effective anchoring of the constituent ring bonds with functional groups (e.g.,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$  etc.) on the CNTs [22,23]. The pertinent reaction mechanism is that the epoxide ring rupture could be acid catalyzed [24] through the carboxyl ( $-\text{COOH}$ ) groups on the functionalized CNTs. As the functional groups are associated with defects on the CNTs and are randomly dispersed, isotropic bonding of the nanotubes with the polymer matrix was implied and yields uniform CNT dispersion. A schematic of the chemical reaction between the  $-\text{COOH}$  group of the CNT with the epoxide ring on the RET is illustrated in Fig. 1(a). Both pristine and  $-\text{COOH}$  functionalized SWCNTs (average diameter of  $1.5 \text{ nm}$ , length range  $\sim 5\text{--}20 \text{ }\mu\text{m}$ , 90% purity, with density  $2.1 \text{ g cm}^{-3}$ ) were obtained from Cheap Tubes Inc. Additionally, MWCNTs (average diameter of  $140 \text{ nm}$ , length range  $\sim 5\text{--}9 \text{ }\mu\text{m}$ , 90% purity, and density  $1.7 \text{ g cm}^{-3}$ ) were obtained from Sigma–Aldrich Inc. A mixture of sulfuric and nitric acids (3:1 ratio) was used for CNT surface functionalization [19,21,25] with  $-\text{COOH}$  groups, and for removing impurities. Following oxidation, the CNTs were rinsed with deionized water and then dried at  $60 \text{ }^\circ\text{C}$  for 10 h. We have previously shown that the type, density, and charge of the defects on the CNTs and consequently the placement of the  $-\text{COOH}$  functional groups on

the CNTs could be tailored through exposure to argon irradiation [8,26].

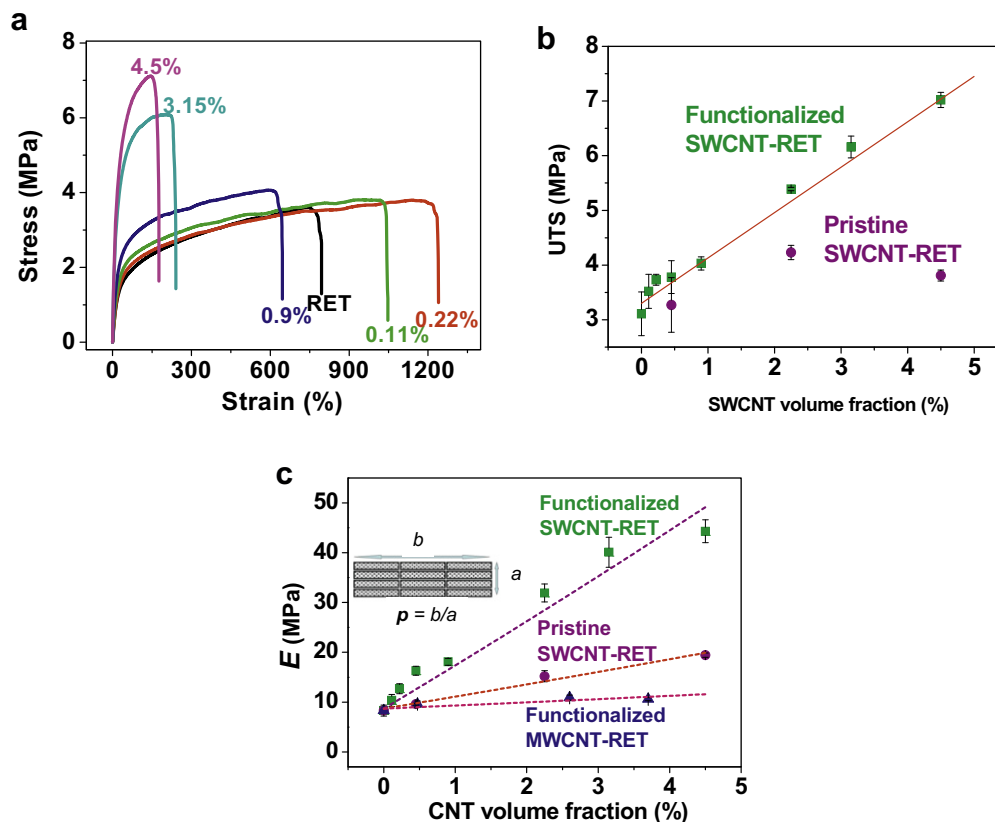
The treated SWCNTs and MWCNTs were first dispersed/solution blended in toluene with sonication (VCX-750, Sonic Materials Inc., 750 W, 42 kHz) for 20 min. The RET was also mixed with toluene and heated to  $\sim 60 \text{ }^\circ\text{C}$  for 2 h. The CNT dispersion was then added to the RET solution and the mixture re-sonicated for  $\sim 50$  min. To remove excess solvent, the mixture was stirred at  $60 \text{ }^\circ\text{C}$  for 3 h and then poured into glass dishes and subsequently degassed (at  $10^{-3}$  Torr) for 12 h. A hot press (Carver M) was then used to press the composites into desired thickness. Atomic Force Microscopy (AFM) characterization determined that, subsequent to sonication, the average length of the SWCNTs is reduced to  $\sim 4.3 \text{ }\mu\text{m}$  with a bundle diameter  $\sim 4.8 \text{ nm}$ , resulting in an aspect ratio of  $\sim 880$ . Concomitantly, the MWCNTs have a reduced average length of  $5.6 \text{ }\mu\text{m}$  with a diameter  $\sim 190 \text{ nm}$ , yielding an aspect ratio of  $\sim 30$ .

### 2.2. Characterization of mechanical properties

The mechanical properties of CNT/RET composites, in the form of  $25 \text{ mm} \times 9 \text{ mm} \times 0.7 \text{ mm}$  test samples, were measured at room temperature using an electro-mechanical testing machine (INSTRON 3342), incorporating a tension/compression transducer (load cell) operated at a crosshead speed of  $30 \text{ mm/min}$ . Isothermal testing conditions were ensured to prevent temperature induced effects [27]. At least five specimens were tested to obtain the averaged values. The average values were used for Figs. 2(b), (c) and 3. It was generally seen that the data scatter/error in the strain values, for given values of stress, was of the order of a few percent, for well dispersed CNT-polymer composites. Scanning electron microscopy (SEM) (Phillips XL30 ESEM) was used to probe the morphology of the CNT/RET composites, prior to and subsequent to mechanical



**Fig. 1.** (a) Schematic of the reaction between  $-\text{COOH}$  functional groups on nanotubes with the epoxy group of a Reactive Ethylene Terpolymer (RET) constituted from (1): polyethylene, (2) methyl-methacrylate, and (3) epoxide groups. Uniform dispersion of functionalized SWCNTs in the polymer as seen through Scanning Electron Microscope (SEM) micrographs, at both (b) 2.2 vol% and (c) 4.5 vol% SWCNTs. (d) When non-functionalized SWCNTs are dispersed into the RET, at  $\sim 2.2$  vol%, severe agglomeration is observed.



**Fig. 2.** (a) Stress–strain curves of functionalized SWCNT–RET composites with varying SWCNT vol%, (b) The ultimate tensile strength (UTS) of functionalized and unfunctionalized (pristine) SWCNT/RET composites with varying SWCNT vol%, (c) Elastic modulus,  $E$ , of functionalized SWCNTs and MWCNT–RET composites and pristine SWCNT–RET composites with varying CNT vol%. The data were fit (dotted lines) through a modified Halpin–Tsai equation. The inset shows a schematic to indicate the defined agglomeration factor  $p$  related to the bundle length ( $b$ ) and diameter ( $a$ ).

measurement, where samples were quenched in liquid nitrogen and broken to achieve a fracture surface. Typically, the surfaces were coated with a thin Au/Pd over layer (5–10 nm in thickness) to increase imaging contrast.

### 3. Results and discussion

#### 3.1. Uniform dispersion of CNTs in polymer matrix

We indeed observed, through SEM, that the general strategy of employing mutual chemical reaction between functional groups on the CNT and the polymer through covalent functionalization of the nanotube surface [20,28] resulted in a more uniform dispersion of the SWCNTs in the polymer, as was seen over a wide range of nanotube volume fractions, *i.e.*, 2.2 vol% – Fig. 1(b) and 4.5 vol% – Fig. 1(c). In contrast, considerable clumping reflective of CNT agglomeration was observed when unfunctionalized CNTs were mixed into the polymer – Fig. 1(d). The covalent bonding between COOH functionalized SWNTs and the RET, which can also contribute to enhanced shear strength of the interface, was confirmed through Fourier Transform Infrared (FT-IR) Spectroscopy, the details of which have been published elsewhere [28].

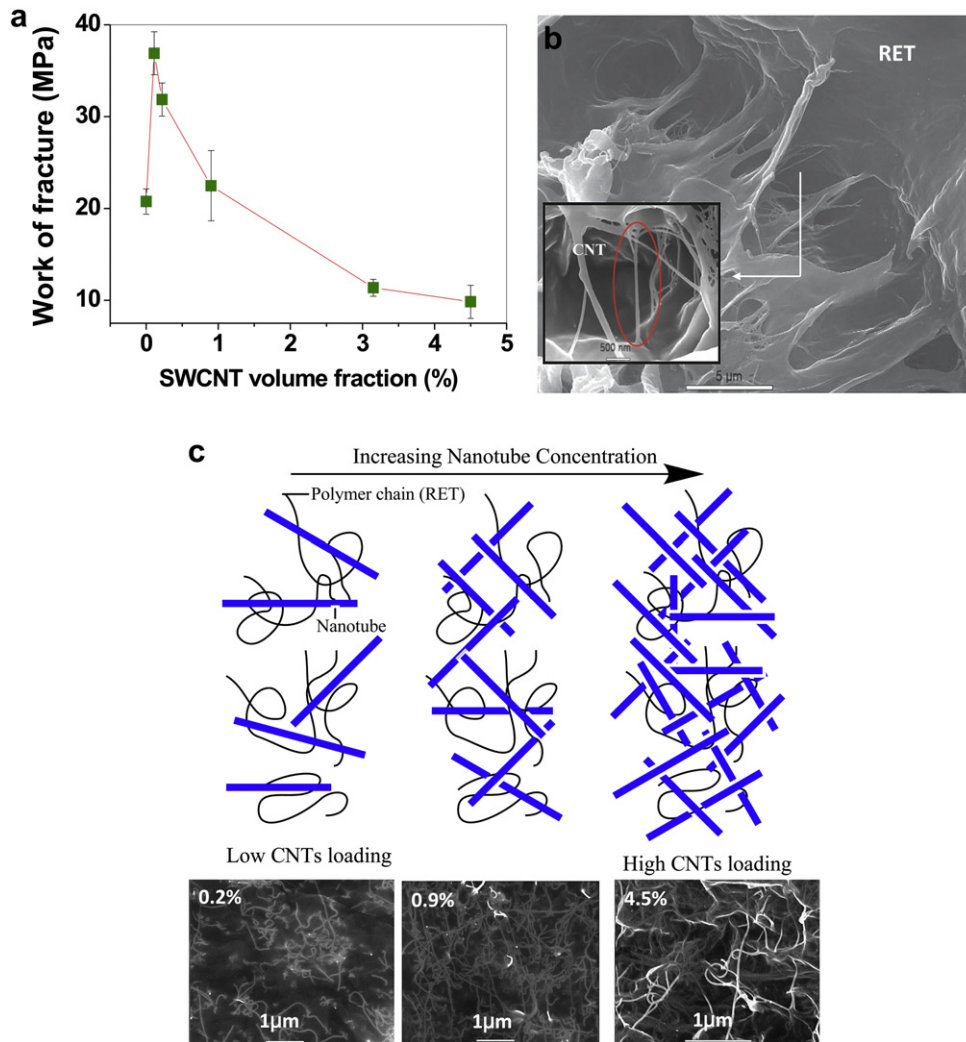
#### 3.2. Characterization and modeling of the mechanical properties of functionalized SWCNT/RET composites

The examination of the stress–strain curves of the composites with varying loading of SWCNTs, as depicted in Fig. 2(a), seems to indicate transitions in the mechanical behavior at filling fraction of  $\sim 0.9$  vol% and  $\sim 0.11$  vol%, as reflected through an increase in

the  $E$  and reduction in the toughness, respectively. The variation of the UTS, marked as the peak stress, as a function of the SWCNT volume fraction is shown next in Fig. 2(b) for both – COOH functionalized and unfunctionalized SWCNT/polymer composites. The beneficial effects of functionalizing the SWCNTs through a uniform and linear increase of the UTS is evident, *e.g.*, at  $\sim 4.5$  vol%, the UTS was more than doubled over the untreated RET polymer and was also substantially higher when compared to the case of unfunctionalized SWCNTs' dispersion. While the reason for the UTS maxima in the latter case was not well understood, inhomogeneous SWCNT dispersion Fig. 1(d) – could possibly be implicated. From comparison with literature, it was also seen that the UTS enhancement is much higher than could be accomplished at an equivalent volume fraction of platelet clay/talc fillers with a smaller aspect ratio ( $\sim 5$ ), and which may be weakly bonded to the RET [29].

The variation of the  $E$  with SWCNT volume fraction – Fig. 2(c) – again compares the effect of functionalization and contrasts with the use of MWCNTs as fillers. While functionalization implies a net strengthening of the polymer matrix, the larger aspect ratio of the SWCNTs ( $\sim 880$ ) compared to MWCNTs ( $\sim 30$ ) would lead to a greater amount of stress transfer for a given strain.

To predict the  $E$  of the composites, we considered their mechanical properties to be akin to those of a semi-crystalline polymer with CNTs as a constituent reinforcement phase. Such a system could be modeled through the Halpin–Tsai system of equations, taken from the original references [9,30] and as often presented in CNT-polymer composite literature [16,20,31], where it was assumed that the  $E$  was insensitive to the matrix and the CNT Poisson ratio. We present a slightly modified form of the Halpin–Tsai



**Fig. 3.** (a) The determined work of fracture of functionalized SWCNT–RET composites with varying CNT vol%, (b) SEM micrographs of functionalized SWCNT–RET composites subsequent to tensile testing, where the nanotubes seem to be bridging incipient cracks. The inset indicates a magnified view, as indicated by the arrow (c) A schematic to explain the mechanical characteristics of the CNT–polymer composites with increased CNT filler loading. At small loading, the CNTs contribute to an increased work of fracture of the polymer matrix, while with increased loading the higher elastic modulus of the CNTs causes decreased toughness ultimately leading to embrittlement.

equation below, to take into account the agglomeration effects, the influence of which has not been much quantitatively discussed in literature.

In this case, the CNTs with intrinsic elastic modulus,  $E_{NT}$  ( $\sim 700$  GPa) for 5 nm bundle of SWNTs [32] and at a volume fraction- $v_f$ , are modeled as serving to enhance the effective elastic modulus of the polymer matrix ( $E_m$ ) through:

$$E = \frac{1 + c\eta v_f}{1 - \eta v_f} E_m \quad \text{where } \eta = \frac{\left(\frac{E_{NT}}{E_m}\right) - 1}{\left(\frac{E_{NT}}{E_m}\right) + c} \quad (1)$$

The parameter  $c$  could be a measure of reinforcement (*i.e.*, the CNT) geometry and was expressed through,  $c = 2\left(\frac{L_{NT}}{r_{NT}}\right) \times p$ , where  $L_{NT}$  and  $r_{NT}$  were the CNT length and radius, and  $p$  is related to the degree of CNT aggregation. We have introduced  $p$  as a semi-empirical parameter, related to the extent of CNT bunching/agglomeration, as schematically depicted in the inset to Fig. 2(c). Note that  $p$  could be used as a rough measure of the reduction of load transfer and could also account for curvature [13,16,17] that is often observed in CNT/polymer composite processing, *e.g.*, as was seen in Fig. 1(c).

A best fit of the  $E$  to the CNT volume fraction, as shown in Fig. 2 (c), indicated that  $p \sim 18$  for functionalized SWCNT based composites whereas  $p \sim 67$  for unfunctionalized SWCNT impregnated polymer composites. Consequently, an approximately *four-fold* increase in the degree of agglomeration may be indicated in the latter, *c.f.*, Fig. 1(b) and (d). On the other hand, a fit for MWCNT based composites was obtained with  $p \sim 10$ , which implies that agglomeration effects were further reduced in these materials. The smaller MWCNT aspect ratio ( $\sim 30$ ) was probably responsible for the diminished  $p$ , while elevated bundling in the SWCNTs could be traced to greater mutual van der Waals forces. Due to the increased agglomeration it would be difficult to compare, at the present time, slightly differing SWCNT aspect ratios. We have also seen [33,34] that the percolation threshold varies exponentially with the aspect ratio which implies that for discernible mechanical property differences, large aspect ratio changes would be needed. We have then shown [35] that variability in the CNT aspect ratio/lengths, results in a percolation threshold, whose probability distribution function could be determined to be of the Weibull type. Consequently, the variation in the mechanical properties could also follow the Weibull distribution, as was also indicated previously for the mechanical properties of nanofibers [36].

As remarked earlier, and as was seen through the stress–strain curves in Fig. 2(a), a maximum in the work of fracture (defined as the area under the stress–strain curves) occurs at  $\sim 0.11$  vol% for the functionalized SWCNT/RET composites – Fig. 3(a). A plausible physical mechanism for the initial increase was motivated through the observed incipient crack (corresponding to the observed nanotube bundle length of  $<4.3 \mu\text{m}$ , see Section 2.1) bridging by the CNTs [37,38] – Fig. 3(b), decelerating polymer failure [39]. We have also noted a close correlation and similar shape between the work of fracture and the elongation at break – as the graphs look quite similar, we choose to include only the former. Generally, the addition of nanoscale fillers, such as CNTs, to polymers (e.g., RET [22,23,29], PVA [18], etc.) often increases the composite strength but may be accompanied by a reduced toughness/elongation at break. However, simultaneous toughening and strengthening could be achieved through uniform dispersion of large aspect ratio CNT fillers and through modification of the nanotube/polymer interface [40]. In our study, at low CNT filler loading, we invoke the crack bridging mechanism [41] for toughness enhancement. Generally, whether crack bridging occurs depends on the ratio of the nanotube length ( $L$ ) to the crack size ( $d$ ). It was seen that for large cracks, i.e., when  $d \gg L$ , CNTs were not found in the space between the crack faces. For small/incipient cracks, when  $L \gg d$ , we saw that the CNTs were often laid across the crack in the polymer, as shown in Fig. 3(b), possibly preventing further separation of the faces constituting the crack. The CNTs are not pulled out completely, presumably due to their strong adhesion to the polymer matrix, facilitated through our proposed covalent bonding functionalization scheme. As can also be seen through a careful examination of the inset to Fig. 3(b), there are also a few CNTs that are not completely stretched but seem to be curved, possibly due to a partial relaxation of the polymer matrix on either side of the crack. We then surmise as was done earlier [39], that the crack opening and propagation is hindered due to the CNTs laid across/bridging the two faces of the crack constituted in the polymer matrix. A toughening of the polymer composite may then result – as was seen through Fig. 3(a)–due to the CNTs bridging the crack as additional energy absorption/work to fracture is necessitated through the relative motion of the CNTs and the adjacent polymer matrix. The bridging CNTs are then hypothesized to toughen the polymer, as the closure strength could be a few times larger than that of the RET polymer, and the limiting separation would scale with the product of the size of the CNT filler and the ultimate strain that could be experienced by the CNTs.

Typically, as the crack length increases and more CNTs bridge the crack, higher driving forces would be necessary to maintain the growth. Crack bridging then represents a failure of linear elastic fracture mechanics (LEFM) and further analysis of this phenomena would hinge on the determination of the parameter [41],  $(\delta_o E)/\sigma_o$ , where the limiting separation ( $\delta_o$ ), composite modulus ( $E$ ), and the bridging strength ( $\sigma_o$ ) all need to be determined but which is outside the scope of the present work.

It is also to be noted that an opposing effect could be at play, e.g., at high CNT loading, covalent bonding between CNTs and polymer chain could restrict the flexibility of RET matrix, implying a toughness maximum at an intermediate loading, as was observed in our study – Fig. 3(a). Enhanced stress concentration at the ends of the nanotubes could also serve as crack initiator sites, e.g., due to notch-like effects, and enhance embrittlement. At large CNT loadings, the number of such sites would be increased and serve as an additional contributor to the decreased work of fracture.

The observed morphology and bridging geometry could then be due to the location of the functional groups, which are preferentially situated at the ends due to ambient enhanced defect density [42]. An increasing stress ultimately results in the separation of the

SWCNTs from the matrix [43]. A subsequent decrease in the work of fracture, beyond 0.11 vol%, would then arise due to the CNTs forming a percolating network and dominating the properties of the composite. With  $E_{\text{CNT}} (\sim 700 \text{ GPa}) \gg E_m (\sim 8.3 \text{ MPa})$ , the work of fracture could be reduced with increased CNT filler loading. A simple model of such a transition is shown in Fig. 3(c). At high CNT loading, while the  $E$  and  $UTS$  are enhanced the flexibility of the polymer could seemingly be diminished. It would be pertinent to consider whether the maximum in the work of fracture could be changed, i.e., whether an increase/decrease would occur through a decrease/increase in the aspect ratio and/or through modifying the CNT-polymer interface [40,44].

Indeed, we have seen in experiments probing the electrical conductivity of the studied composites that electrical percolation was achieved at  $\sim 0.11$  vol% [28] and it is tempting to speculate a close correspondence to the value of the maximum in the work of fracture. It is to be noted that SEM micrographs are two-dimensional representations of percolating networks in three dimensions. As depicted in the bottom of Fig. 3(c), micrographs have been listed for 0.2 vol%, 0.9 vol%, and 4.5 vol%, all above the theoretically and experimentally determined (through electrical conductivity measurements) percolation threshold ( $\phi_c$ ) of  $\sim 0.11$  vol%. Below the  $\phi_c$  the micrographs consist of randomly placed CNTs and are not illustrative.

The  $\phi_c$  was analytically determined through the following formula, for a given  $L$  and diameter,  $D$ , of the nanotube, and where  $V_{\text{ex}}$  is defined as the excluded volume [45]: the space circumscribed around the CNT by the center of another CNT, whereby both CNTs contact each other but do not overlap, and related to the connectivity of  $N_c$  CNTs.

$$\phi_c(L) = \frac{V_{\text{ex}} N_c}{\frac{4\pi}{3} D^3 + 2\pi D^2 L + \frac{\pi}{2} D L^2} \left( \frac{\pi D^3}{6} + \frac{\pi D^2 L}{4} \right) \quad (2)$$

From the measurement of the  $L$  and  $D$ , of the dispersed CNTs in the RET matrix, we have then seen that the  $\phi_c$  was  $\sim 0.1$  vol%. Such an analysis was then confirmed through electrical measurements, reported elsewhere [28,33] where again the  $\phi_c$  was  $\sim 0.1$  vol%. Further studies to probe the percolation thresholds for electrical and mechanical properties are in progress to confirm the above hypotheses.

### 3.3. Comparison of the effects of functionalization with mechanical property enhancement

At the very outset, we have found that the improvement in the elastic modulus and the ultimate tensile strength are larger than reported in literature, and underlies the worthy effects of the adopted methodology for enhanced structural characteristics. We mainly compare with epoxy-based polymers, due to their similarity with the RET material – Table 1 indicates a sampling of the presently used functionalization schemes and compares it to the current study. A more detailed discussion follows.

Generally, both non-covalent and covalent reaction methods could be used for functionalizing and later dispersing CNTs in polymer matrices. The former technique employs van der Waals interactions of the functional molecules with the CNT surface, while the latter utilizes chemical reaction between the functional groups and reactive sites on the CNTs– fostered through breakage of the C–C bonds in the CNTs, and may be considered to be more beneficial. In a study [46] comparing the efficacy of covalent vs. non-covalent functionalization of CNTs, using polyethylene imine (PEI) as the functionalizing agent, it was found that while both techniques could induce uniform dispersion in epoxy polymers due to surfactant-like action, the former could be more relevant for

**Table 1**  
Comparison with a few previously used functionalization schemes for the synthesis of epoxy polymer-CNT composites, employing various functional groups (Func. group). While in a majority of cases, the elastic modulus ( $E$ ) is enhanced, other structural characteristics are adversely affected.

Epoxy:Func group; CNT type	Mechanical property changes	Reference
Epon862:–COOH: 0.5 wt% SWNT	Enhanced $E$ shear, and flexural strength Lower toughness	Bekyarova et al. [49]
Epon862:PAMAM-0 dendrimer: 1 wt% SWNT	Enhanced $E$ , tensile strength, Enhanced toughness	Sun et al. [20]
Epon862:Amine-alkyl carboxy: 1–4 wt% SWNT	Enhanced $E$ , and tensile strength Toughness reduced	Zhu et al. [64]
Epon828:Pollyacryloyl: 1 wt% MWNTs	$E$ reduced, Toughness unaffected	Zou et al. [60]
Epon862:Maleic anyhydride: 0.1–1 wt% MWNT	Enhanced $E$ , and tensile strength Toughness reduced	Tseng et al. [50]
Epon828: Epoxide monomer: 0.5–3 wt% MWNT	Enhanced $E$ , and flexural strength	Chen et al. [54]
RET: –COOH: 0.1–4 wt% SWNTs; 0.2–4 wt% MWNTs	Enhanced $E$ , and tensile strength initial toughness increase	Present study

mechanical property enhancement due to intimate adhesion between the CNT and the polymer.

As mentioned earlier, the epoxide group in the RET has high reactivity [21] and is amenable for effective anchoring of the constituent ring bonds with the –COOH groups on the CNTs. It is also feasible that the methacrylate groups may be conformally coated onto the nanotubes further enhancing the load transfer [47]. Our adapted method of intimate bonding of the CNT functional group with that of an epoxide group has been previously shown to strengthen the CNT-polymer interface and increase the intrinsic toughness of the polymer composite, as manifested through an increase in the composite glass transition temperature ( $T_g$ ) [48]. For instance, the superior structural characteristics of epoxy resins [49] were considered in the preparation of Epon862 (diglycidyl ether of bisphenol A)- CNT composites [49], where an ~ 50% enhancement in the shear and flexural strength was observed on 0.5 wt% SWCNT loading. However, the stiffness diminished with CNT loading beyond 0.2 wt%. In another study, epoxy/SWCNT composites were prepared by oxidation and functionalization of SWCNT surfaces using poly-amidoamine generation-0 (PAMAM-0) dendrimer [20], where the amine groups on the dendrimer could interact with the –COOH groups on the CNT as well as with the polymer. However, with 1 wt% SWCNT incorporation, the elastic modulus and the UTS was enhanced by ~ 15% and 30% respectively, less than that observed in our study. The use of maleic anhydride, combined with amine groups, resulted in an enhancement of the tensile strength of about ~50% with 1 wt% MWCNTs, while the toughness/elongation at break diminished at increased loading fractions [50].

An interesting variant used the functionalization of the CNT with the same monomer/functional groups on the CNT as those of the matrix polymer, and could arguably provide a high degree of solubility [51] of the CNTs with the polymer. Previously, both polystyrene (PS)/CNT [52] and poly-vinyl alcohol (PVA)/CNT [53] composites had been synthesized in this manner. Such a principle was also used for other epoxy-based polymer composites, where a two step functionalization process, *i.e.*, (1) employing the grafting of epoxy groups on acid-functionalized CNTs, as well as (2) the use of an initiator for the epoxy matrix homo-polymerization resulted in enhanced CNT dispersion [54] through the formation of  $\beta$ -hydroxyester bonds. However, the modulus was unaffected while a flexural strength increase was noted. The complexity of the linkage, *c.f.*, a simple ester group in our study, could explain the insensitivity to enhancement of certain structural characteristics. It is also feasible to have alternate chemical groups, besides –COOH, on the CNTs [55], as hydrogen bonding among the constituent acid groups could lead to compact stacking of the CNTs and cause bundling. Consequently, amino-group functionalization was attempted (as in Table 1) and manifested a modest increase in the impact and flexural strength [56,57] in addition to accelerating the curing kinetics [58].

It would also be important to note that mild-acid treatments could be less harmful of the intrinsic CNT properties, as the electrical conductivity of epoxy-composites could be severely diminished

when stronger oxidizing agents are used [59]. In one study [60], such treatment was advocated to minimize oxidative damage where polyacryloyl groups were used as bridging agents between the CNTs and the epoxy polymer, in a similar manner to the ester groups. Consequently, significant improvement in the tensile strength by ~45% and the elastic modulus by ~90% was determined at low loading (~0.1 wt%) of MWCNTs. Yet another example, where the impact strength was doubled, was provided through the grafting of triethylenetetramine (TETA) on acid-functionalized CNTs which serve for CNT-epoxy polymer linkages [61,62]. However, a more modest increase in the tensile strength, of <20%, was obtained [63] through the use of butyl-amine linkages between fluorinated CNTs and epoxy polymers, which may indicate that the size of the linkages would also be important. Attesting to the importance of the sidewall linkage size, another study [64] incorporated alkyl carboxyl groups on the SWNTs along with acyl peroxide groups to link the CNTs to the polymer, where the modulus was seen to be enhanced by ~ 50% while the UTS was increased by only 15%. It was evident, from our previous work [28,33], that our functionalization procedure did not harm the electrical properties [65], while enhancing the structural characteristics, as the electrical conductivity percolation threshold was close to the theoretically expected value.

In summary, our functionalization methodology was specific to the RET and serves for (a) tethering the polymer to the CNT, (b) uniform dispersion, as well as for (c) strengthening the CNT-polymer matrix interface. The significant enhancement in the modulus, tensile strength, and toughness observed could be construed as a result of the use of several variables that incorporate the currently known optimal conditions, *i.e.*, (i) use of a mild-acid based sonication treatment to functionalize the SWCNTs, (ii) a short and strong covalent linkage between the functionalized CNT and the epoxy polymer, and (iii) the choice of RET polymer (which to our knowledge has never been employed in the fabrication of CNT-polymer composites) incorporating the use of MMA and polyethylene groups, which may contribute to a lowered viscosity of the mixture prior to curing, in addition to increasing the strength.

#### 4. Conclusions

We have proposed that the use of localized chemical reactions, enabling the interaction of the functional groups on the SWCNTs with the polymer matrix, helps in the homogenous dispersion of the nanotube fillers. Such a method can be used specifically for polymer with epoxide ring structure, such as diglycidyl ethers [49], and the principle more generally. Consequently, the interfacial bonding and load transfer could be enhanced enabling an increase in the  $E$  and UTS compared to when unfunctionalized SWCNTs are used for filler material. It was also observed that a larger aspect ratio was imperative in enhancing the strength through comparison with functionalized MWCNT reinforced composites. A maximum in the work of fracture was indicated at low nanotube volume fractions, which could be facilitated through incipient crack bridging by the CNTs. This implies that the toughness of the

composite could be diminished at increased CNT loading due to mechanical percolation effects. Future work would focus on further understanding such issues *vis-a-vis* CNT volume fraction. It should also be possible to introduce defects at various locations, other than the ends, to further improve the work of fracture [26].

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