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

S. Park, P.R. Bandaru

Department of Mechanical & Aerospace Engineering,
University of California, San Diego

Introduction

Polymer composites containing conducting fillers have been extensively investigated for multi-functional applications incorporating structural reinforcement[1], electromagnetic interference (EMI) shielding[2], and high charge storage capacitors[3]. 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. However, there is a limit to the impregnation of polymers with such traditional filler material due to possible embrittlement beyond a certain loading. 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 coupled with a large interfacial area > 1300 m^2/g. 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.

In this paper, we suggest a possible method to enhance the mechanical properties of polymer composites incorporating homogeneously dispersed CNT and enhanced nanotube-polymer interface bonding, facilitated through mutual localized chemical reactions between functional groups on the single-walled and multi-walled CNTs (SWCNTs and MWCNTs) with other groups on the polymer. We then show that ultimate tensile strength (*UTS*) and elastic modulus (*E*) of such functionalized CNT/polymer composites, at identical CNT filling fractions, are superior to those using unfunctionalized CNTs. Additionally, we show that simultaneous toughening and strengthening could be achieved when the average length of the uniformly dispersed CNTs was adequate to bridge incipient cracks. We propose models to explain the observed mechanical characteristics.

Experimental

We chose, a polymer matrix composed of reactive ethylene terpolymer (RET: Elvaloy 4170) constituted of (1) polyethylene, (2) a polar methyl-methacrylate group, and (3) epoxide functional groups – Figure 1 (a). While (1) and (2) contribute to mechanical 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 and is amenable for effective anchoring of the constituent ring bonds with functional groups(*e.g.*, -OH, -COOH, -NH$_2$ etc.) on the CNTs. As the functional groups are associated with defects on the CNTs[4] and are randomly

dispersed, isotropic bonding of the nanotubes with the polymer matrix was implied and yields uniform CNT dispersion. The treated SWCNTs and MWCNTs were first dispersed/solution blended along with the RET, in toluene with sonication. A hot press was then used to prepare the composites into desired thickness. It was determined that, subsequent to sonication, the average length of the SWCNTs is reduced to ~ 4.3 μm with a bundle diameter ~4.8 nm, resulting in an aspect ratio of ~ 880. Concomitantly, the MWCNTs have a reduced average length of 5.6 μm with a diameter ~190 nm, yielding an aspect ratio of ~ 30. The mechanical properties of CNT/RET composites, were then measured at room temperature and fracture surfaces probed through scanning electron microscopy (SEM).

Results and Discussion

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[5] resulted in a more uniform dispersion of the CNTs in the polymer over a wide range of nanotube volume fractions, *i.e.,* 0.2 vol % - 4.5 vol%. The covalent bonding between COOH-functionalized SWNTs and the RET also contributes to enhanced shear strength of the interface [5].
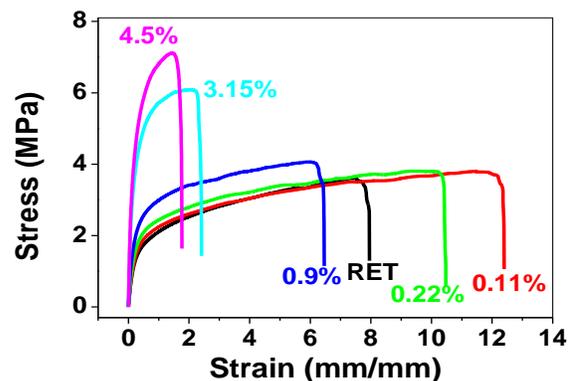

Fig. 1 Stress-strain curves of functionalized SWCNT/RET composites with varying SWCNT vol %,

The examination of the stress-strain curves of the composites with varying loading of SWCNTs, as depicted in Fig. 1, seems to indicate transitions in the mechanical behavior at filling fraction of ~ 0.9 vol % and ~ 0.11 vol %, as reflected through an increase in the *E* and reduction in the toughness, respectively. The beneficial effects of functionalizing the SWCNTs through a uniform and linear increase of the *UTS* is evident, *e.g.,* at ~ 4.5 vol%, the *UTS* was more than doubled over the untreated RET polymer and substantially higher than compared to unfunctionalized SWCNTs' dispersion. 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 (~5). The variation of the *E* with SWCNT volume fraction - Figure 2 - 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 (~ 880) compared to MWCNTs (~ 30) would lead to a greater amount of stress transfer for a given strain.
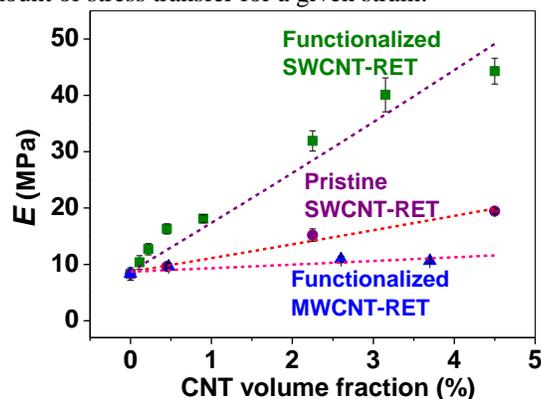

Fig. 2 Elastic modulus, *E*, of functionalized SWCNTs and MWCNT– RET composites and pristine SWCNT/RET composites with varying CNT vol %. The data were fit (*dotted lines*) through a modified Halpin-Tsai equation

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[6], through introducing a measure of reinforcement (*i.e.,* the CNT) geometry as expressed through, $c = 2\left[\dfrac{L_{NT}}{r_{NT}}\right] \times p$, where L_{NT} and r_{NT} were the CNT length and radius, and *p* is related to the degree of CNT aggregation. Note that *p* could be used as a rough measure of the reduction of load transfer and could also account for curvature. A best fit of the *E* to the CNT volume fraction indicated that *p* ~ 18 for functionalized SWCNT based composites whereas *p* ~ 67 for unfunctionalized SWCNT impregnated polymer composites. Consequently, an approximately *four-fold* increase in agglomeration may be indicated in the latter. On the other hand, a fit for MWCNT based composites was obtained with *p* ~ 10.

As was seen through the stress-strain curves in Fig. 1, a maximum in the toughness occurs at ~ 0.11 vol% for the functionalized SWCNT/RET composites. 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 μm) bridging by the CNTs decelerating polymer failure. A subsequent decrease in the toughness, beyond 0.11 vol %, would then arise due to the CNTs forming a percolating network and dominating the properties of the composite. Indeed, we have seen in experiments probing the electrical conductivity of the studied composites that electrical percolation is achieved at ~ 0.11 vol % [5] and it is tempting to speculate a close correspondence to the value of the toughness maximum. Consequently, with E_{CNT}

(~ 700 GPa) >> E_m (~ 8.3 MPa), the toughness is reduced. A simple model of such a transition is shown in Fig. 3.
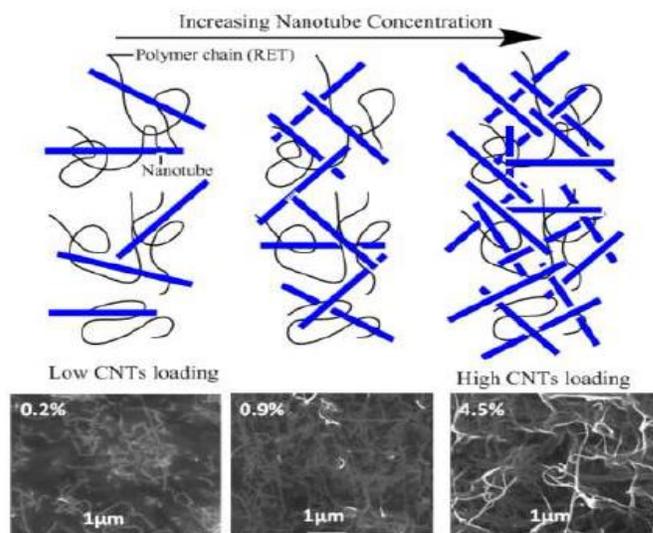

Fig.3 A schematic to explain the mechanical characteristics of the CNT/polymer composites with increased CNT filler loading. At small loading, the CNTs contribute to an increased toughness of the polymer matrix, while with increased loading the higher elastic modulus of the CNTs causes decreased toughness ultimately leading to embrittlement.

Conclusions

We propose that localized chemical reactions, enabling the interaction of the functional groups on the SWCNTs with the polymer matrix, helps in homogenous dispersion of CNT fillers. Consequently, the interfacial bonding and load transfer is enhanced enabling an increase in the *E* and *UTS*. A larger aspect ratio seems imperative in enhancing the strength. A toughness maximum is indicated at low CNT volume fractions, and is facilitated through incipient crack bridging by CNTs. However, toughness is diminished at increased CNT loading due to mechanical percolation effects.

References

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