Superior electrical and mechanical characteristics observed through the incorporation of coiled carbon nanotubes, in comparison to non-coiled forms, in polymers

S.-H. Park [a], D.-J. Yun [a], P. Theilmann [b], P.R. Bandaru [c,*]

[a] Samsung Advanced Institute of Technology (SAIT), San 14-1 Nongseo, Yougin, Gyeonggi, Republic of Korea
[b] Department of Electrical Engineering, Engineering 1, MC 0407, University of California, San Diego, La Jolla, CA, USA
[c] Materials Science Program, Department of Mechanical Engineering, Engineering 2, MC 0411, University of California, San Diego, La Jolla, CA 92093, USA

ABSTRACT

It is shown that the addition of coiled carbon nanotubes (CCNTs), to polymer matrices confers a *two-fold* increase of the relative electrical permittivity, in addition to an improvement in the mechanical characteristics. A *four-fold* augmentation of the elastic modulus and a *two-fold* improvement in the ultimate tensile strength (compared to the polymer) at ~2 vol% filler fractions was also obtained. Such attributes are shown to be superior to those obtained through the use of linear (both single-walled and multi-walled) CNTs.

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1. Introduction

Nonlinear morphologies of carbon nanotubes (CNTs) promise varied functionalities following the paradigm of *"function follows form"* [1]. We show that polymer composites using coiled CNT (CCNT) fillers exhibit superior mechanical and electrical characteristics, compared to when linear CNTs are used as fillers. The CCNTs were rationally synthesized [2] through the addition of In/Sn based precursors to conventional thermal chemical vapor deposition (CVD) of CNTs — Fig. 1(a). The formation of the CCNTs was explained as due to a combination of (1) specific metal catalyst (*e.g.*, In/Sn) — nanotube interactions, as well as (2) entropy driven interactions. More specifically, as In and Sn have large wetting angles of ~160° with respect to the graphitic surface [3] (note that commonly used metal catalysts for the growth of linear CNTs such as Fe, Co, and Ni have wetting angles of <75°), it was hypothesized that the former promote coiling of the CNTs, so as to avoid contact and reduce the surface free energy. Alternatively, a greater overlap between alternate segments, obtained through coiling of the nanotube, could increase the entropy of the ambient. It was then estimated that the non-wetting behavior of In/Sn could provide a large enough driving force of the order of ~50 $k_B T$/nm (where k_B is the Boltzmann constant ~1.38 × 10^{-23} J/K and T is the temperature) which could overcome the bending energy of ~8 $k_B T$/nm (the calculations were done for a 10 μm long CNT of 25 nm diameter). The entropy driven interaction energy was estimated to be of the order of ~1 $k_B T$/nm, which may be sufficient to bend shorter CNTs/initiate the bending.

2. Experimental procedures

The CCNT fillers were uniformly dispersed into a Reactive Ethylene Terpolymer (RET: Elvaloy 4170) polymer matrix — Fig. 1(b). Linear CNT (both single and multi-walled)/RET composites were also synthesized for property comparison. The uniformity of the dispersion was gauged by considering micrographs at different length scales, *i.e.*, 1 μm, 5 μm, 10 μm, 50 μm, 200 μm, etc., and counting the average number of CNTs/unit area. We also considered the contrast ratio (=Standard deviation/mean) through image processing software and determined the uniformity of dispersion. We have previously reported the detailed experimental procedures for the dispersion of the CNTs into the polymer [4]. In brief, the CCNTs were dispersed in toluene with sonication for 20 min. Concomitantly, the RET polymer was added to toluene solvent with heating, to ~60 °C for 2 h, and subsequent stirring. The CCNT dispersion was then added to the RET solution and the mixture

* Corresponding author.
 E-mail address: pbandaru@ucsd.edu (P.R. Bandaru).
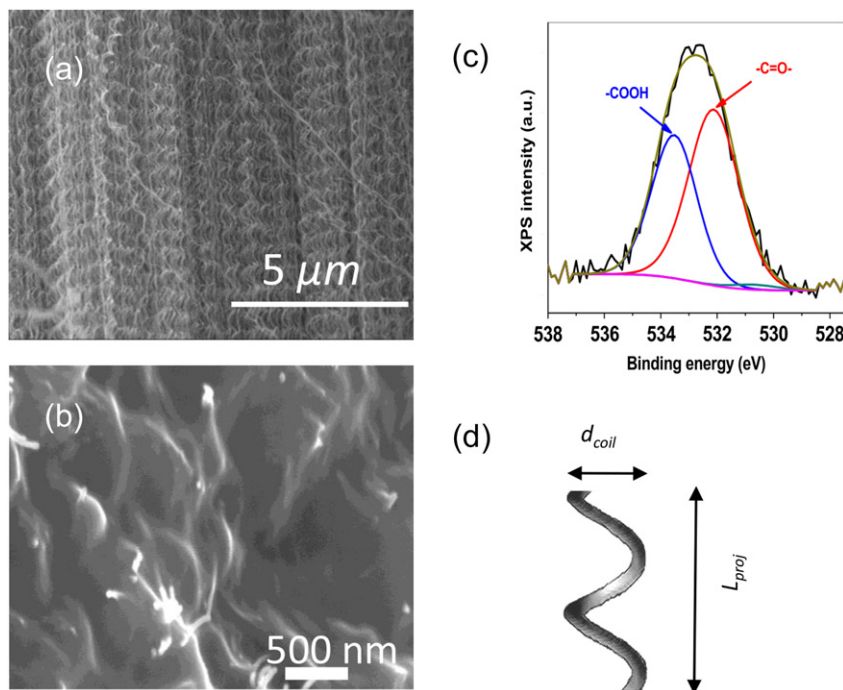
Fig. 1. Scanning electron microscope (SEM) micrographs of synthesized (a) coiled carbon nanotubes (CCNTs) on a Si substrate, and (b) uniformly dispersed into a RET polymer matrix, (c) XPS O1s spectra of CCNTs indicating the presence of intrinsic −COOH and the −C=O groups, (d) The definition of the average projected length (L_{proj}) and the coil diameter (d_{coil}) of CCNTs, constituted of individual CNTs of average diameter: d_{CNT}.

sonicated again for ∼50 min. To remove excess solvent, the mixture was stirred, at 60 °C for 3 h, and poured into glass dishes, and evacuated in vacuum (1 mTorr) for 12 h. Subsequently, a hot press was used to press the composites into desired thickness.

The chemical reactions between the −COOH functional groups on the CNTs with the epoxy groups on the RET, and the formation of ester linkages (evidenced through Fourier Transform Infrared Spectroscopy: FTIR) have been shown to result in stable interfacial bonding. X-ray photoelectron spectroscopy (XPS) of the O1s peak spectra also seem to indicate substantial presence of the −COOH and the −C=O groups on the CCNTs − see Fig. 1(c), as was also observed [4] through FTIR. In this paper, we discuss CCNTs as indicated in Fig. 1 dispersed in the 0−2.5 volume% range. While the average projected length (L_{proj}) and the coil diameter (d_{coil}) was ∼15 μm and ∼0.5 μm, respectively − see Fig. 1(d), the fully extended length (L_{ext}) was recorded to be ∼50 μm and the constituent individual CNT diameter (d_{CNT}) was ∼20 nm. The coiled nanotube parameters: L_{proj}, d_{coil}, L_{ext}, and d_{CNT} were measured independently, using scanning electron microscopy (SEM) and atomic force microscopy (AFM) based imaging, through subjecting them to similar procedures as were used for the composite fabrication. This involved, for instance, (i) scraping off the synthesized coiled nanotubes from the substrate, (ii) rinsing the CNTs in a mixture of sulfuric and nitric acids (in a 3:1 ratio) for removing impurities, (iii) further rinsing with deionized water, and (iv) then drying at 60 °C for 10 h. Both −COOH functionalized and unfunctionalized/pristine single-walled CNTs (SWCNTs) with a length to diameter aspect ratio, in the range of 500−1300, were also considered as fillers in RET to compare their performance with that of the CCNTs.
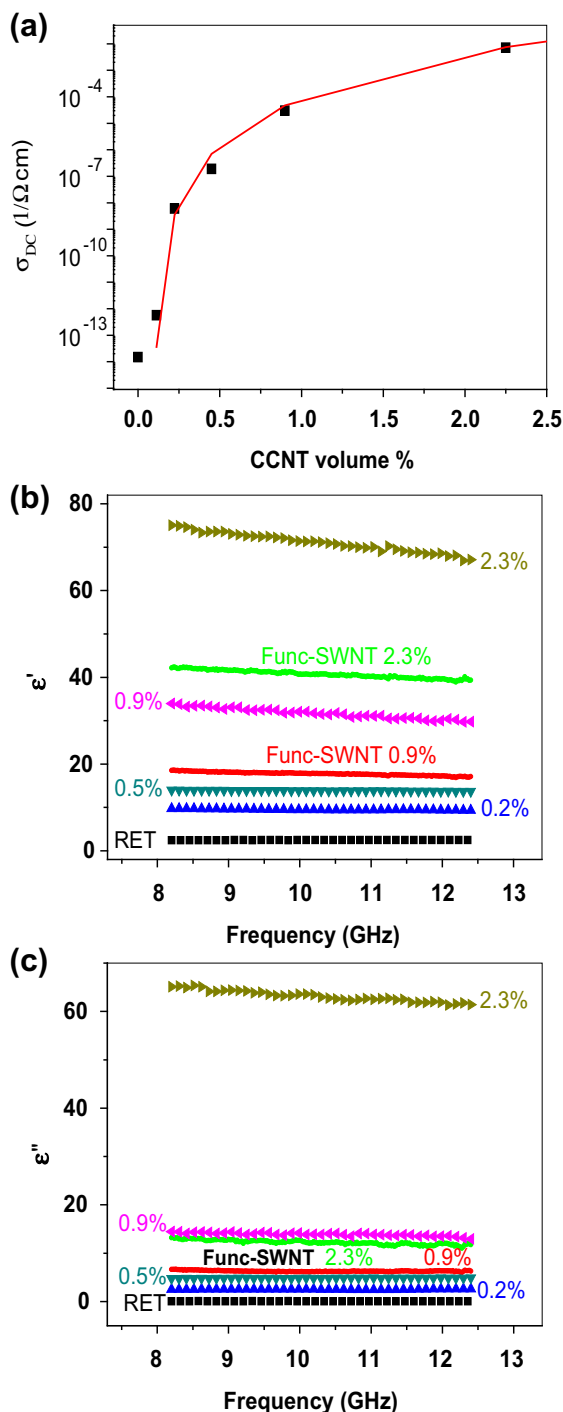
Subsequently, the DC electrical conductivity (σ_{DC}) was measured on the composite samples through four-point electrical measurements. The S-parameters (S_{ij}) [5] were measured in the microwave frequency ($f = \omega/2\pi$) range (8.2−12.4 GHz: X-band) using a two-port vector network analyzer (Agilent 5242A PNA-X). The X-band is used

for both civil and military communications with applications as diverse as weather monitoring, vehicular detection and air traffic control and defense tracking. The determination of S_{11} and S_{21} enables the calculation of the complex permittivity ($\varepsilon = \varepsilon' + j\,\varepsilon''$) and permeability ($\mu = \mu' + j\,\mu''$), where $j = \sqrt{-1}$, along with the reflection and transmission coefficients [4,6]. The mechanical properties of the composites, in the form of 25 mm × 9 mm × 0.7 mm test samples, were monitored 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 mm/min. Isothermal testing conditions were ensured to prevent thermal effects. At least five specimens were tested to obtain averaged values. 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.

3. Results and discussion

3.1. Electrical conductivity percolation and dielectric permittivity increase

A percolation-like behavior in the variation of the σ with CCNT volume fraction − Fig. 2(a), was observed and fit to an expression of the form: $\sigma \sim \sigma_0 (p - p_c)^\beta$, where p_c is the percolation threshold volume fraction (p) and β a critical exponent. σ_0 is a constant for a particular filler−polymer combination. The obtained values of p_c (∼0.1%) and β (∼4.2), are appropriate for a thick film resistor-like configuration with elongated fibers [7]. In our study, we mainly compare the properties of the coiled CNTs with those of the single walled CNTs, as we found that the use of multi-walled CNTs was not useful for significant enhancement of the electrical properties. The DC conductivity (σ_{DC}) measurements were used to note that the σ_{DC} was similar at ∼10^{-3} Ω^{-1} m^{-1} for the polymer composites constituted from CCNTs and single walled CNTs, for appropriate comparison.

Fig. 2. (a) The DC electrical conductivity (σ_{DC}) of the CCNT constituted polymer composites was observed and fit to a percolation-like behavior. The X-band frequency variation of the (b) real (ε') and (c) imaginary (ε'') permittivity of CCNT constituted composites (numbers indicate % volume fractions), compared to single walled CNTs (SWCNTs).

matrix serves as the capacitor dielectric and contributes to the AC conductance. The increased number of parallel resistors and capacitors in the CCNTs due to the coiled structure, compared to linear CNTs, decreases the overall resistance and capacitive impedance ($X_c \sim 1/2\pi f C$) of the composite due to the availability of several alternative electrical conduction paths. Consequently, the observed differences do seem to be intrinsic and unique to the coiled structure, *e.g.,* the capacitive coupling between alternate windings of the CCNT, which is absent in a single walled CNT.
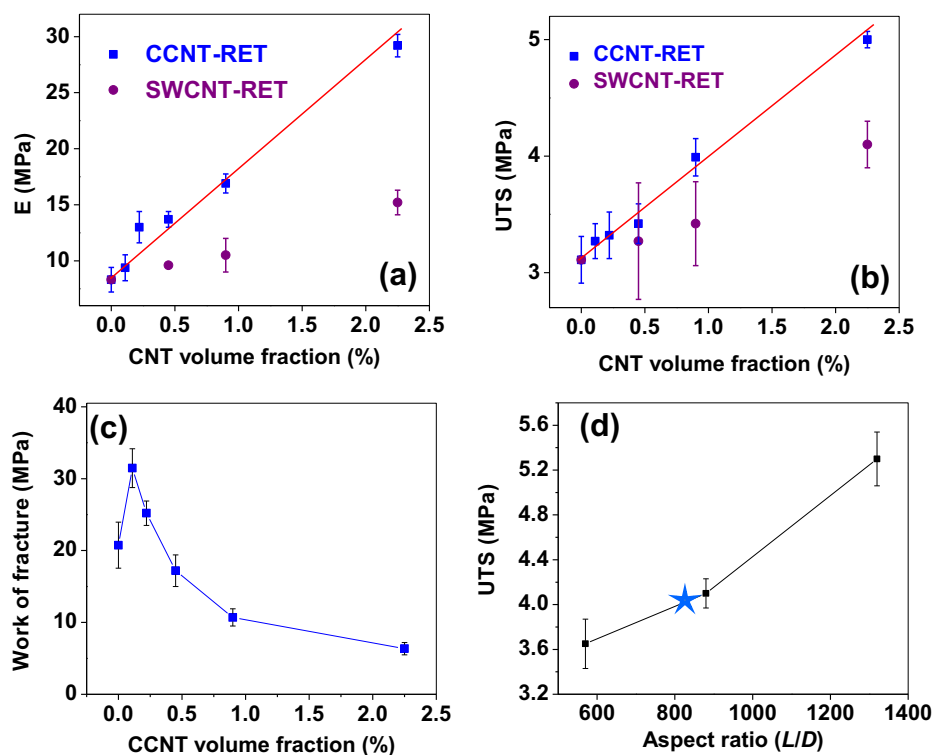
A monotonic variation of the ε' and ε'' with increasing CCNT content was seen − Fig. 2(b) and (c), and could be ascribed to increased capacitive coupling between alternate windings and concomitantly the $\sigma_{AC} (= \omega \varepsilon_0 \varepsilon'')$. Also shown in the graphs, for comparison, is the behavior of functionalized single walled (SWCNTs) at two particular volume fractions (*i.e.,* 0.9 vol% and 2.3 vol%), where the superiority of CCNTs, with increased ε is evident. The ε increase could be related to the CCNT structure, where pentagons on the outer/convex side of the coil and heptagonal structures on the inner/concave side are invoked to accommodate for the curvature − Fig. 1(d). The change in the interactions of the π−orbitals in the non-hexagonal structures could then result in a charge transfer from the concave to the convex side, inducing local dipole moments [9]. The orbital rehybridization along with the multi-shell characteristics of multi-walled CNTs have also been implicated in curvature induced interfacial electric fields [10]. Additionally, the smaller projected length aspect ratio (*i.e.,* L_{proj}/d_{coil} for the CCNT, $\sim$30) in contrast with that of an SWCNT (typically $\sim$1000), would also imply a larger depolarization electric field. We have previously shown that such characteristics translate to a larger electromagnetic interference (EMI) shielding efficiency for the CCNT based composites. We also found that the use of multi-walled CNTs/non-functionalized SWCNTs was not useful for enhancing the electrical properties yielding ε' and ε'' close to those of RET.

3.2. Improved mechanical properties through the use of coiled nanotubes

The mechanical properties (see Fig. 3), examined through the stress−strain curves of the composites with varying loading of CCNT fillers, indicated a monotonic increase with increasing CCNT volume fraction in the (a) elastic modulus (E) − defined from the slope of the stress−strain curves, (b) the ultimate tensile strength (UTS) − defined from the maximum of the stress−strain curves, and (c) toughness/work of fracture − defined through the total area under the stress−strain curve. In the range of tested CCNT volume fractions, *i.e.,* 0 to ~2.5 vol%, we observe a close to a *four-fold* increase in the E, and a *two-fold* increase in the UTS. These values are all *superior* (by about a factor of two) to those obtained through the use of the pristine SWCNT/polymer composite.

It was initially hypothesized that the larger aspect ratio of the CCNTs (*i.e.,* through the L_{ext}/d_{CNT} ratio of $\sim$2500) compared to single walled CNTs ($\sim$900) would lead to a greater amount of stress transfer for a given strain yielding mechanical property improvement. However, from the experiments with the CCNT/RET composites it was unclear as to whether the L_{proj}/d_{coil} ratio ($\sim$30) or the L_{ext}/d_{CNT} ($\sim$2500) needs to be considered to understand the influence of geometry on the mechanical characteristics. For instance, the UTS of a composite ($\sim$4 MPa) constituted of $\sim$1% CCNTs, *e.g.,* from Fig. 3(d), could be seen to be equivalent to that of a functionalized SWCNT dispersed composite with an aspect ratio $\sim$900, which is close to the L_{proj}/d_{CNT} ratio ($\sim$750).

The observed increase in the mechanical properties, due to the reinforcement of the polymer matrix [11–13], such as the E and the UTS is larger than previously reported in literature (*e.g.,* see Tables I-IV in Ref. [12]) and is also larger than that obtained through the use

While σ_{DC} would be similar, the AC conductivity, σ_{AC} (computed through $\sigma_{AC} = \omega \varepsilon_0 \varepsilon''$ [8], where $\omega = 2\pi f$ and $\varepsilon_0 = 8.854 \cdot 10^{-12}$ C^2/Nm^2) may not be the same. As was seen, the CCNT based materials have a higher σ_{AC} compared to the linear CNT based composites, even though the σ_{DC} was similar. We could explain, qualitatively, the enhanced σ_{AC} on a simple model based on the formation of parallel resistors and capacitors in the composite. In this model, the CNTs contribute to the electrical resistance while the polymer

Fig. 3. A comparison of the (a) elastic modulus (*E*) (b) the ultimate tensile strength (UTS) toughness/work of fracture, and the (c) work of fracture, property values of the CCNT/RET and the pristine/unfunctionalized SWCNT/RET polymer composites. (d) The UTS of a CCNT/RET composite (~4 MPa) constituted of ~1% CCNTs (indicated by the ★) is comparable to that obtained through the use of functionalized SWCNT fillers, in the polymers, with an aspect ratio of ~800.

of single walled CNTs indicating that the coiled structure may be crucial. We hypothesize that plausible reasons for the improvement could incorporate (1) a lower degree of agglomeration promoted through reduced coil–coil interactions, (2) a greater extent of interaction with the polymer matrix due to localized charges and dipoles, (3) use of optimized processing conditions such as a mild acid based sonication treatment for functionalization [14], (4) a short and strong covalent linkage between the functionalized CNT and the epoxy polymer [15], and (5) the choice of RET polymer (which does not seem to have been employed, hitherto, in the fabrication of CNT/polymer composites) which may contribute to a lowered viscosity of the mixture prior to curing, in addition to strength.

It was also interesting to note that the volume fraction at which the maximum was observed, *i.e.*, ~0.1 vol%, as well as the magnitude of the work of fracture was similar to that observed for −COOH functionalized SWCNT based composites [14]. We had initially hypothesized that the larger L_{proj} of the CCNTs (with a higher *E*) would improve composite toughness, whereby the crack opening and propagation would be hindered due to the nanotubes bridging the faces of the crack in the polymer matrix [16]. However, the similar values are actually encouraging in that the increased strength of the CCNT/RET composites does not seem to diminish the toughness, as typically observed [16]. The curvature of the CCNTs may also induce a partial relaxation of the polymer matrix on either side of the crack [11]. It would nevertheless be desirable to understand and demonstrate higher work of fracture values, with simultaneous toughening and strengthening, through the use of CCNTs.

4. Summary

We suggest the use of alternative, nonlinear nanostructured morphologies for electrical permittivity as well as structural

property improvement of polymers. Many significant parameters related to the geometry of the CCNTs, *e.g.,* the extended and the projected length, as well as the coil and the individual nanotube diameter, can be used to tailor and influence electrical and mechanical characteristics with promising avenues of investigation.

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