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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

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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.

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_BT/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_BT/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_BT/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).

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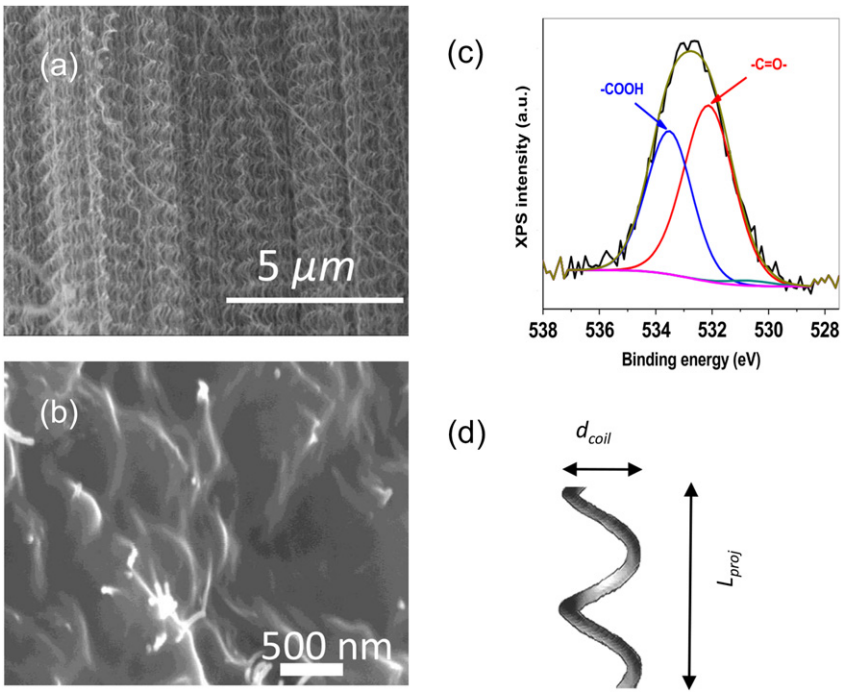

Fig. 1. Scanning electron microscope (SEM) micrographs of synthesized (a) coiled carbon nanotubes (CCNTs) on a Si substrate, and (b) uniformly dispersed into a RET polymer matrix, (c) XPS O1s spectra of CCNTs indicating the presence of intrinsic −COOH and the −C═O groups, (d) The definition of the average 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.