MULTIFUNCTIONAL NANOTUBE POLYMER NANOCOMPOSITES FOR AEROSPACE APPLICATIONS: ADHESION BETWEEN SWCNT AND POLYMER MATRIX

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Introduction

Multifunctional structural materials can enable a novel design space for advanced aerospace structures. A promising route to multifunctionality is the use of nanotubes possessing the desired combination of properties to enhance the characteristics of structural polymers. Recent nanotube-polymer nanocomposite studies have revealed that these materials have the potential to provide structural integrity as well as sensing and/or actuation capabilities. Judicious selection or modification of the polymer matrix to promote donor acceptor and/or dispersion interactions can improve adhesion at the interface between the nanotubes and the polymer matrix significantly. The effect of nanotube incorporation on the modulus and toughness of the polymer matrix will be presented. Very small loadings of single wall nanotubes in a polyimide matrix yield an effective sensor material that responds to strain, stress, pressure, and temperature. These materials also exhibit significant actuation in response to applied electric fields. The objective of this work is to demonstrate that physical properties of multifunctional material systems can be tailored for specific applications by controlling nanotube treatment (different types of nanotubes), concentration, and degree of alignment.

Experimental

A dilute SWCNT (purified HiPco, CNI) suspension, typically around 0.05 wt%, in N,N-dimethylacetamide (DMAc), was prepared by homogenizing for 10 min (750 rpm with a 6 mm diameter rotor homogenizer) and sonicating for 1 h at 40 kHz. The sonicated SWCNT suspension was used as a solvent for the poly(amic acid) synthesis with 2,6-bis(3-aminophenoxy)benzonitrile ((β-CN)APB) diamine and 4,4-oxydiphthalic anhydride (ODPA). The entire reaction was carried out with stirring in a nitrogen purged flask immersed in a 40 kHz ultrasonic bath until the solution viscosity increased and stabilized. Sonication was stopped, but stirring continued for several hours to form a SWNT-poly(amic acid) solution. Cast solutions were cured thermally to form thin SWCNT-Polyimide films. High resolution electron, scanning probe (SPM), and optical microscopy were used to examine the level of SWCNT dispersion in the polymer. Raman and Infrared spectroscopy and SPM were employed to study interactions between SWCNT and various functional groups. A modified Rheovibron, thermally stimulated current spectroscopy, an Angstrom resolver, and an Instron microtester equipped with a suite of electrometers were used to measure the electromechanical properties of the nanocomposites.

Strategies for Effective SWCNT Dispersion

Translation of the superior properties of nano inclusions on a macroscopic scale to a nanocomposite is optimized by effective incorporation of these nanoinclusions into a polymer matrix composite. In general, there are two major approaches to achieving stable dispersions of SWCNT in a solvent or a polymer solution. The first one is a kinetically assisted approach and the second one is a thermodynamically assisted approach.

1. Kinetic approach

The kinetic approach utilizes physical forces such as high shear (mechanical stirring, homogenization), sonication (cavitational force), melt mixing (extrusion, pultrusion, injection molding, capillary rheometry, fiber spinning), or *in-situ* polymerization (hydrodynamic force). Sonication is often used to disperse SWCNTs in a solvent before and after mixing with a polymer. The sonication (cavitation) force and time should be optimized to achieve good dispersion depending on the nature of the initial SWCNT materials. While low frequency (around 20kHz), high power horn-type sonicators are effective in breaking up closely-packed agglomerated SWCNTs, high frequency (40–60kHz), low power bath-type sonicators are beneficial for dispersing fluffy, loosely-packed SWCNTs without damaging the sp^2 surface. Highly concentrated solution spinning (gel spinning or dry-jet spinning) can also induce high shear to disperse SWCNT effectively at an elevated temperature [1]. Combining two or more of these techniques can maximize the efficacy of this kinetic approach. For example, *in-situ* polymerization under simultaneous

sonication and high shear can yield excellent dispersion of SWCNTs in the polymer solution compared to simple mixing with a stirrer [2].

2. Thermodynamic approach

The thermodynamic approach may be divided into two categories. One is chemical functionalization via covalent bonding and the other is compatibilization via non-covalent bonding. The former includes acid etching with strong acids (HNO_3, H_2SO_4, HCl, HF) and chemical functionalization of the tube surface using fluorination [3], vigorous reflux with amines for the acid etched tubes [4], or electrochemistry [5]. Chemical functionalization attaches specific functional groups on the SWCNT surface that can strongly interact with a host polymer matrix, provided the extent of the functionalization reaction can be controlled. Unfortunately, no synthetic method for controlling the functionalization reaction has been reported yet and most reactions tend to occur at reactive defect sites which are randomly distributed in number and location. Moreover, even a low degree of covalent bonding on the nanotube surface can significantly disrupt the extended π orbital system, which is mainly responsible for the suite of excellent properties of carbon nanotubes. For example, several reports indicate that chemical functionalization with covalent bonding can decrease the conductivity of nanotubes significantly [6–8]. Alternative thermodynamic routes involve enhancing polymer/SWCNT interactions via amphiphilic surfactants, hydrophobic interaction with nanotubes, physical wrapping with conjugated polymers which exhibit enhanced dispersion interactions by adopting a π-stacked geometry [9], donor-acceptor interactions via charge transfer [10], Zwitterion complex formation [11], and non-specific interactions using DNA or peptide sequences [12]. While the use of amphiphilic surfactants or similar types of small molecules has been the most popular technique, the incorporated surfactants are often difficult to remove and residual surfactants often degrade other physical properties. Donor-acceptor interactions have been utilized with a number of small molecules or atoms to dope carbon nanotubes owing to the amphoteric nature of carbon nanotubes (i.e. the nanotube can either accept or donate electrons depending on the character of the interacting molecules). If a strong electron-withdrawing functional group (e.g. nitrile) approaches a nanotube, the tube behaves like an electron donor. Conversely, if a strong donating functional group (e.g. amine) approaches a nanotube, the tube behaves like an electron-acceptor. Therefore, if one can judiciously select or design a polymer with appropriate functional groups (electron-withdrawing or donating), the van der Waals interaction between the tube and the matrix polymer can be augmented with donor-acceptor interactions, enabling the production of well dispersed CNT polymer solutions or composites [10]. The dispersion interaction is enhanced when the monomers of the matrix polymer include an aromatic moiety, e.g., phenyl rings or derivatives thereof. The dispersion force of the dispersion interaction can be further augmented and controlled by introducing electron donors or electron acceptors in the aromatic moiety of the polymer [14].

Results and Discussion

Figure 1 shows a high voltage (15kV) high resolution scanning electron micrograph (HRSEM) of a good dispersion of SWCNT in a polyimide matrix that takes advantage of donor-acceptor and dispersion interactions to achieve dispersion.

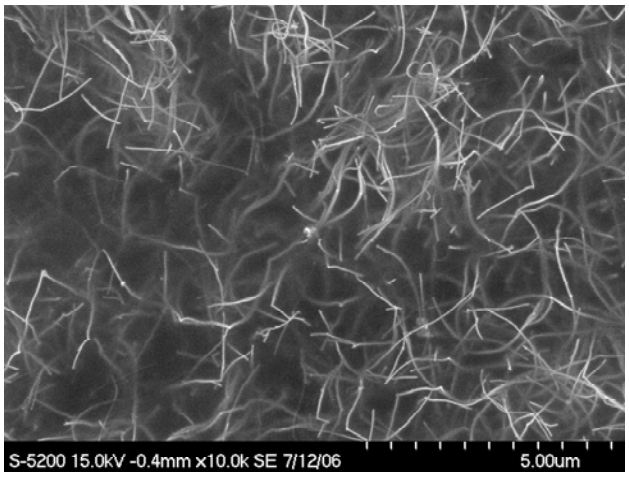

Figure 1. HRSEM of 0.5wt%SWCNT/polyimide nanocomposite.

The interaction between alkyl and aryl functional groups and SWCNT surfaces was studied both experimentally (using functionalized AFM tips) and computationally as shown in Figure 2. A summary of the results is shown in Table 1 [14]. These results indicate that aryl (aromatic) functional groups tend to have higher adhesion forces (interfacial interaction) with the SWCNT surface than alkyl groups, due largely to their enhanced dispersion interactions. Strong electron donors (e.g. amine) and acceptors (e.g. nitrile) exhibited enhanced interactions with the amphoteric SWCNT surfaces, likely a result of the emergence of donor-acceptor interactions. The qualitative trend from the preliminary results of the computational study was consistent with the experimental data.

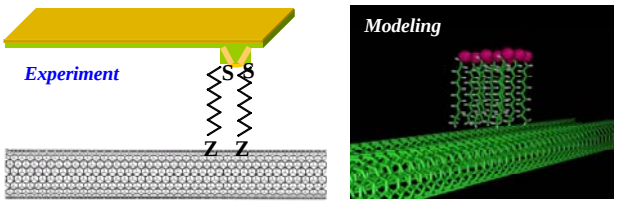

Figure 2. Schematics of experimental and computational adhesion studies of functionalized AFM tips with SWCNT surfaces.

Quantification of the visualized nanotube dispersion in the spatial domain was attempted based on the results of radial power spectral density measurements obtained from the high voltage HRSEM images. The resulting measurements provide information concerning bundle diameter, segment length, spacing between bundles, and fractal dimension. [15]. The dispersion images and the quantified information support the dispersion strategies described above.

Electrical and dielectric properties of the nanocomposites show that a percolated SWCNT network can form even at SWCNT loadings below 0.05 wt% if good dispersion is achieved. The resultant SWCNT/polyimide composites exhibited excellent sensing and actuation capabilities compared t0 state-of-the-art electroactive materials [16].

Table 1. Summary of the adhesion study between various functional groups and SWCNT surfaces. [14]

Alkyl-thiol Endgroup	Experiment Force/Molecule (pN)	Modeling (pN)
–OH	9.6 ± 2	
–perfluoro	8.7 ± 3	
–SH	9.2 ± 3	
$–CH=CH_2$	8.1 ± 2	
$–CH_3$	7.6 ± 2	1.92
–COOH	12.2 ± 3	
$–NH_2$	23.4 ± 4	2.98
Aryl-thiol Endgroup		
4-methylbenzene	18.9 ± 5.7	
4-nitrobenzene	21.8 ± 5.3	
4-aminebenzene	22.6 ± 4.7	
4-bromobenzene	26.9 ± 3.6	
4-hydroxybenzene	32.0 ± 8.4	
4-fluorobenzene	39.5 ± 8.8	
4-methoxybenzene	41.5 ± 10.9	
H-benzene	46.8 ± 11.8	
4-Nitrilebenzene	56.9 ±15.5	

Summary

Two major approaches (kinetic and thermodynamic) to achieving uniform dispersion of SWCNTs in a polymer matrix were introduced. Well-dispersed SWCNT/polyimide nanocomposites were obtained by employing *in-situ* polymerization under simultaneous shear and sonication and by leveraging donor-acceptor and dispersion interactions. The resultant nanocomposites exhibited excellent electroactive properties as well as outstanding mechanical reinforcement.

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