

MIT Open Access Articles

*Epoxy functionalized multi-walled carbon
nanotubes for improved adhesives*

The MIT Faculty has made this article openly available. **Please share**
how this access benefits you. Your story matters.

Citation: Sydlik, Stefanie A., Jae-Hwang Lee, Joseph J. Walish, Edwin L. Thomas, and Timothy M. Swager. "Epoxy Functionalized Multi-Walled Carbon Nanotubes for Improved Adhesives." Carbon 59 (August 2013): 109–120.

As Published: <http://dx.doi.org/10.1016/j.carbon.2013.02.061>

Publisher: Elsevier

Persistent URL: <http://hdl.handle.net/1721.1/101275>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of use: Creative Commons Attribution-Noncommercial-NoDerivatives



Elsevier Editorial System(tm) for CARBON
Manuscript Draft

Manuscript Number:

Title: Epoxy functionalized multi-walled carbon nanotubes for improved adhesives

Article Type: Research Paper

Corresponding Author: Prof. Timothy M Swager,

Corresponding Author's Institution: MIT

First Author: Stefanie A Sydlik, PhD

Order of Authors: Stefanie A Sydlik, PhD; Jae-Hwang Lee, BS; Edwin L Thomas, PhD; Timothy M Swager

Abstract: Three different types of epoxy-functionalized multi-walled carbon nanotubes (EpCNTs) were prepared by multiple covalent functionalization methods. The EpCNTs were characterized by thermogravimetric analysis (TGA), infrared spectroscopy (FTIR), and Raman spectroscopy to confirm covalent functionalization. The effect of the different chemistries on the adhesive properties was compared to a neat commercial epoxy (Hexion formulation 4007) using functionalized and unfunctionalized multi-walled carbon nanotubes (MWCNT) at 0.5, 1, 2, 3, 5, and 10 weight %. It was found that a EpCNT at 1 weight % increased the lap shear strength, tested using the American Society for Testing and Materials standard test D1002, by 36 % over the unfilled epoxy formulation and by 27 % over a 1 weight % unmodified MWCNT control sample. SEM images revealed a fracture surface morphology change with the incorporation of EpCNT and a deflection of the crack fronts at the site of embedded CNTs, as the mechanism accounting for increased adhesive strength. Rheological studies showed non-linear viscosity and DSC cure studies showed an alteration of cure kinetics with increased CNT concentration, and these effects were more pronounced for EpCNT.

Suggested Reviewers: Karen Schulte PhD

Professor

schulte@tu-harburg.de

For his expertise in polymer composites

Karen Winey PhD

Professor, Materials Science, U. of Pennsylvania

winey@seas.upenn.edu

For her expertise in polymer/ carbon nanotube composites.

Timothy Long PhD

Professor, Chemistry, Virginia Tech

telong@vt.edu

For his expertise in carbon nanotubes and epoxies.

Valery Khabashesku PhD

Professor, Rice University

khval@rice.edu

For his work in polymer/ carbon nanotube composites. NOTE: Two of our coauthors have recently moved to Rice and there may be a conflict of interest for this reviewer.

Epoxy functionalized multi-walled carbon nanotubes for improved adhesives

Stefanie A. Sydlik,¹ Jae-Hwang Lee,² Edwin L. Thomas,² and Timothy M. Swager^{1,*}

¹Department of Chemistry and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, 77 Massachusetts Ave. Cambridge, 18-597, Massachusetts 02139 USA

²Department of Material Science and Engineering, Rice University, MS 364, Houston, TX 77251 USA

Abstract

Three different types of epoxy-functionalized multi-walled carbon nanotubes (EpCNTs) were prepared by multiple covalent functionalization methods. The EpCNTs were characterized by thermogravimetric analysis (TGA), infrared spectroscopy (FTIR), and Raman spectroscopy to confirm covalent functionalization. The effect of the different chemistries on the adhesive properties was compared to a neat commercial epoxy (Hexion formulation 4007) using functionalized and unfunctionalized multi-walled carbon nanotubes (MWCNT) at 0.5, 1, 2, 3, 5, and 10 weight %. It was found that a EpCNT at 1 weight % increased the lap shear strength, tested using the American Society for Testing and Materials standard test D1002, by 36 % over the unfilled epoxy formulation and by 27 % over a 1 weight %

* Corresponding author. Tel/Fax: 1-617-253-4423. E-mail address: tswager@mit.edu (T. M. Swager)

unmodified MWCNT control sample. SEM images revealed a fracture surface morphology change with the incorporation of EpCNT and a deflection of the crack fronts at the site of embedded CNTs, as the mechanism accounting for increased adhesive strength. Rheological studies showed non-linear viscosity and DSC cure studies showed an alteration of cure kinetics with increased CNT concentration, and these effects were more pronounced for EpCNT.

1. Introduction

Since the landmark paper by Iijima [1], the outstanding electrical, thermal, and mechanical properties of carbon nanotubes (CNTs) have intrigued researchers. Pristine carbon nanotubes are expected to have a very high electronic conductivity and an axial modulus for extended tubes of 1 TPa, which is approximately five times stronger than steel [2]. However, these figures are theoretical and experimental results fall short of these extraordinary properties. Realization of these properties in applications has been impeded by micro structure-processing challenges. Specifically, in their pristine form CNT display strong van der Waals interactions, which cause them to aggregate into entangled bundles that prevent the formation of uniform, optimal materials [3]. To circumvent these problems, numerous covalent [4-7] and non-covalent [8-10] methods have been developed to aid in CNT dispersion.

Of particular interest is the dispersion of CNTs into polymer matrices to form composites [11]. Nanocomposites, in which the reinforcing elements are pre-dispersed in the matrix, present a convenient alternative to traditional composites. In general, conventional fiber reinforced composites with glass or carbon fibers (typical diameters are > 10 microns) are prepared using a complex molding process in which a prepreg of aligned fibers is infiltrated with the matrix material, usually a thermosetting polymer. Carbon fibers in an epoxy matrix are the most common composite for high performance applications, such as aircraft, spacecraft, watercraft, construction, and many sporting goods. Composites are the material of choice for these applications because of their higher strength to weight ratio and excellent corrosion resistance, in comparison with metals. Additionally, the two-component design of composites adds the advantage of the inherent toughness contributed by the resin in combination with the strength

properties of the fiber, to provide superior composite mechanical behavior, a major advantage over relatively brittle metals [12]. In composites, tensile failure often occurs via fiber “pull-out”, where the ultimate strength of the material is limited not by the performance of either the matrix or the fiber, but slip along the interface of the two [13]. Usually, this is limited by the strength of the non-covalent van der Waals interactions between fiber and matrix. Therefore, creating covalent bonds between the matrix and the fiber could vastly improve the performance of composites.

The power of composites for the aerospace industry was initially established in military aircraft; most recent usage includes the B2-Spirit or “Stealth Bomber”, which is made nearly entirely of composites, affording novel structural designs and a low radar cross-section [14]. Most commercial airliners use less composite materials in their construction, but recently, Boeing introduced the 787 Dreamliner which is the first commercial airliner to have a fuselage composed completely from composite materials [15]. In such structures, where significant quantities of both aluminum and composite are used, a strong bond between aluminum and composite is also highly desirable.

There have been multiple investigations wherein CNTs are incorporated into epoxy matrices [5, 6, 16-19]. In these studies, CNTs (both single and multi-walled carbon nanotubes) are subjected to harsh oxidation procedures and then the resultant carboxylic acid groups at defect sites are covalently modified to incorporate pendant amines. Such composites show improved stability and dispersability in comparison with those made using unmodified CNT. Additionally, significant increases in strength, Young’s modulus, and strain to failure have been observed [20] and when combined with carbon fiber, CNTs can give a 30% increase in interlaminar shear strength over epoxy only filled with carbon fiber

[14] U. S. Airforce. B-2 Spirit Fact Sheet. <http://www.af.mil/information/factsheets/factsheet.asp?id=82> (accessed December 27, 2012)

[15] Boeing. Boeing 7-Series. Fast Facts: Boeing 787 <http://boeing.com/news/feature/sevenseries/787.html> (accessed December 27, 2012)

[20]. Increases in shear strength and debonding properties are also observed when the composites are added into an adhesive [21].

Despite the volume of research accomplished, little work has been done to study CNTs that have epoxides directly covalently bound to the tubes and most work has been performed with amine functionalized CNT that are more synthetically accessible. A recent study reported covalently attached epoxides to single walled carbon nanotubes (SWNT) by first reducing the carbon nanotubes with sodium and reacting them with a trifunctional epoxide. An incorporation of 0.2 weight % of such functionalized SWNTs successfully increased the ultimate tensile strength by 32% [22]. However this functionalization method is non-ideal for large scale reactions in that SWNT must be first reduced with highly reactive sodium naphthalide, which is moisture sensitive and very reactive. Functionalization of the CNT with an epoxide moiety has the advantage in that the epoxide resin is a larger fraction of the thermoset than the amine hardener. Typical mix ratios are 1.5- 4 parts resin to 1 part hardener by weight or volume; typically, much more epoxy will go into the resin than amine. Therefore, if the CNTs are premixed with their respective component, a much lower weight fraction of CNTs in the resin would be needed to achieve the same overall loading. This allows for easier, more homogeneous dispersion, and improved shelf life of pre-mixed components, which is desirable for commercial applications. Furthermore, comparatively little research has been done to investigate the properties of high percentages (>4 weight %) of CNT incorporation [23]. Improvements in the bulk mechanical properties have been previously investigated for epoxies as composites, however, few studies have probed their effect on adhesive properties.

In this paper, we present three new and chemically “gentle” routes to covalent attachment of epoxide functionalities to multi-walled carbon nanotubes (MWCNT) in order to both facilitate their dispersion in epoxy matrices and provide covalent bonding to the epoxy matrix. The epoxy-functionalized MWCNTs (EpCNT) are characterized by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy and are shown to be well-functionalized and easily dispersible in epoxy resin. Good dispersions are achieved in both bisphenol-A and -F based epoxy

resins with only mechanical mixing and 1 minute of bath sonication. The adhesive properties were studied with EpCNT dispersed in a matrix of Hexion formulation 4007 [24](Epon 828 resin, Heloxy 505 modifier, and Epikure 3046) at 0.5, 1, 2, 3, 5, and 10 weight percent. The dispersions of the EpCNT are remarkably stable, with a 1 weight % dispersion of **EpCNT2** stable in Epon 828 for over 1.5 years. It was found that adding 1 weight % **EpCNT2** increased the lap shear strength by 35 % over neat Hexion 4007 and 26 % over 1 weight % unfunctionalized MWCNT. All of the samples failed via a transferred interface, where failure occurs at the aluminum-epoxy interface and jumps from one side of the joint to the other. The fracture surfaces of the 1 weight % samples were studied via scanning electron microscopy (SEM). The effect of 3 weight % the EpCNT in comparison to pristine MWCNT and neat resin were studied using a cone and plate rheometer and non-linear viscosity was observed, as previously reported for CNT dispersions [16, 25]. Gel point via rheometry remained largely unaltered except for 10 weight % **EpCNT2** and **EpCNT3**. Cure kinetics were studied using dynamic DSC to compare the **EpCNT3** dispersions to unfunctionalized MWCNT and neat Hexion 4007 and a decrease in the intensity and a shift in the cure temperature was found for the higher percentages of EpCNT due to the altered kinetics of the CNTs crosslinking in to the matrix. These EpCNTs show promise as additives for stable, MWCNT-enhanced epoxy adhesives.

2. Experimental Methods

3.1 Synthesis

Three different approaches to synthesize functionalized MWCNTs were explored. In the first approach, initial functionalization was accomplished using a zwitterionic functionalization developed by our group [26, 27]. In this approach (Figure 1), 4-dimethylaminopyridine (DMAP) participates in a conjugated addition to the activated dicarboxyacetylene to generate a zwitterionic intermediate that

^[24] Momentive Specialty Chemicals. Starting Formulation 4007, Specifications Sheet. <http://www.momentive.com/Products/StartingFormulation.aspx?id=1590> (accessed December 27, 2012)

reacts with the CNT, to produce a cationic intermediate. The displaced alkoxy group and/or other added alcohols then react with the cationic complex to release DMAP. Two variations of this route have been employed. The first uses commercially available dimethyacetylenedicarboxylate (DMAD) as the activated acetylene and the released methoxy group displaces the DMAP to give **fCNT1**. The ester groups in **fCNT1** are then hydrolyzed to give a carboxylate anion, which was treated with an excess of Bisphenol-F diglycidyl ether to yield **EpCNT1**. Alternatively terminal acetylenes can be integrated into the starting dicarboxyacetylene (**DPAD**) and the functionalization provides **fCNT2**. The terminal acetylenes allow for further functionalization with organic azides. The *in situ* formation of azidomethanol provides a convenient method to avoid handling the explosive reagent, and addition followed by a rearrangement [28] gives **OH-CNT**, which is readily water dispersable. **OH-CNT** is then necessarily treated with a stronger base, lithium isopropoxide in anhydrous dichloromethane/isopropanol solvent, to generate the primary alkoxides that react with an excess of bisphenol-F diglycidyl ether to give **EpCNT2**. The solvent combination was chosen because it solubilized and stabilized both the lithium isopropoxide and the **OH-CNT**. Furthermore, the anhydrous environment eliminated the possibility of hydroxyl ion formation, which was found to interfere with the reaction when other, more classic solvents were used.

An additional functionalization method (Figure 1) is based on a 1,3-dipolar cycloaddition developed by Georgakilas *et al* [29]. In this functionalization method, the MWCNTs are first pre-treated with piranha solution to create defects and shorten the MWCNT. Sarcosine and 3,4-dihydroxybenzaldehyde react *in situ* to form the reactive ylide, which performs the 1,3-dipolar cycloaddition on to the MWCNT to give **fCNT2**. **fCNT2** is then treated to the same post functionalization modifications as **EpCNT2** to yield **EpCNT3**. Based on simple pKa considerations, the *meta*-phenol is assumed to be the dominant reactive site for reaction with the epoxide, however there are likely a mixture of regioisomers and a small amount of double alkylation product.

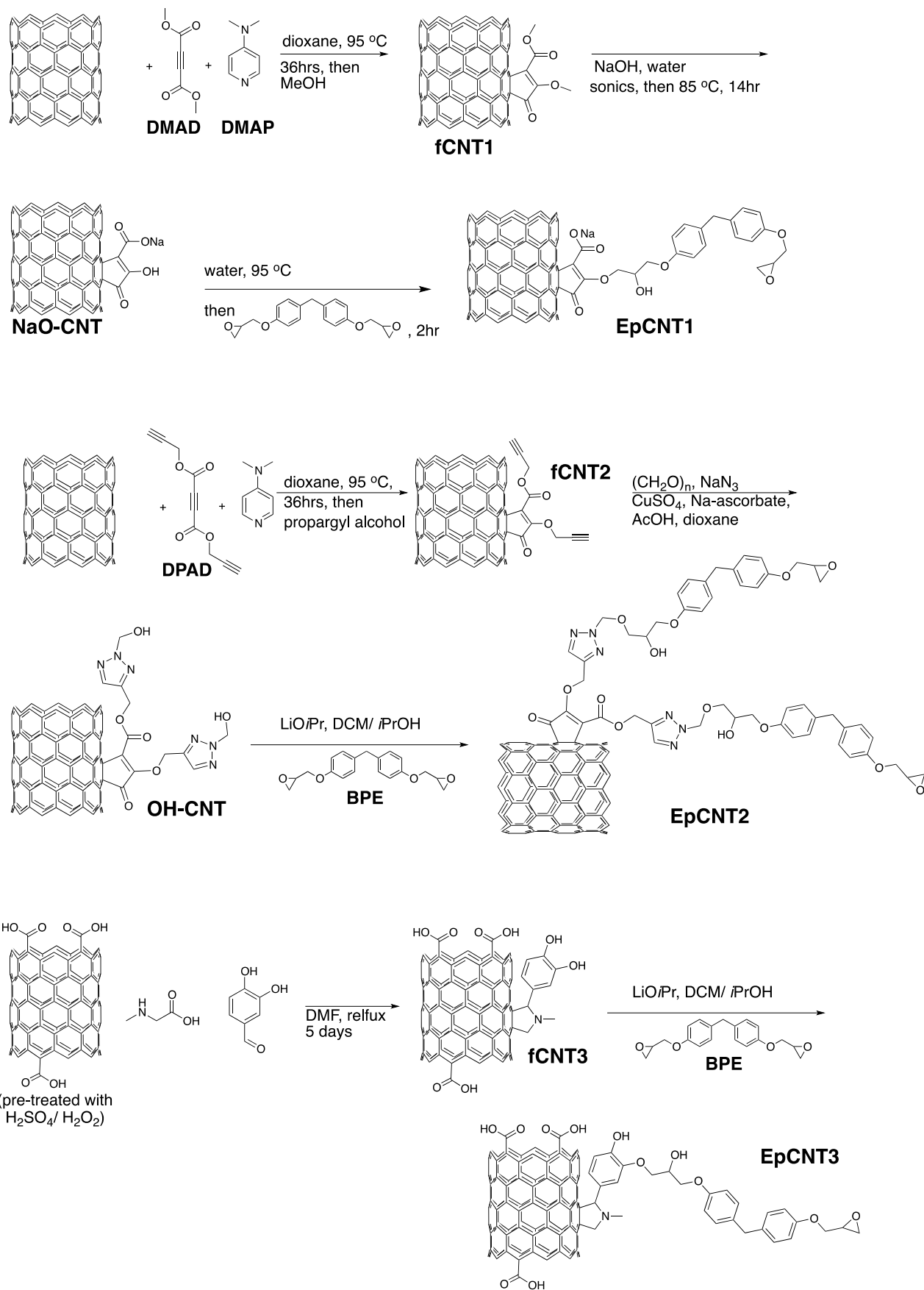


Figure 1. Synthesis of EpCNT1, EpCNT2, and EpCNT3.

3.2. Characterization Methods

Fourier transform infrared spectroscopy (FTIR) spectra were determined using a Nexus Model 470/670/870 Spectrophotometer using the Omnic software package. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q50 under nitrogen at a scan rate of 10°C/ min from 50 °C to 800 °C. Raman spectra were taken on a Horiba Lab Ram with a 785 nm laser using LabSpec 5 processing software. Dynamic cure behavior was investigated via differential scanning calorimetry (DSC) using a TA Instruments Q1000 DSC at scan rates of 10°C/ min over the range of 50 °C to 300 °C. Viscosity and gel point were measured using a TA Instruments AR2000 Rheometer. Viscosity was determined using steady shear over a shear rate of 0.2 to 2000 sec⁻¹. Gel point was measured by ramping the temperature from room temperature to 140 °C at 10 °C/ min, and then holding the temperature at 140 °C for 30 minutes using the disposable 25 mm aluminum plate geometry. A 10 Pa force was applied at 0.1 Hz during the temperature ramp and a 100 Pa force was applied at 100 Hz during the isothermal step. Gel point was recorded as the lowest temperature where G' exceeded G''. Test strips for the lap shear test were cut from aluminum sheet metal using an Omax 2626/xp JetMachining Center controlled by integrated CAD/ CAM software using garnet abrasive. Lap shear strength was measured using a Zwick/ Roell mechanical tester, model BTC-EXMACRO.001, using a 10 kN force cell. Test conditions were determined by American Society for Testing and Materials (ASTM) standard D1002. Data was analyzed using testXpert II software package. Hardness was measured by ASTM standard D2240 using a PTC Instruments Type D Durometer. Fracture surfaces were coated with gold using a Quorum Technology SC 7640 Sputter Coater. Scanning Electron Micrograph (SEM) images were acquired using a FEI Quanta 400 field emission SEM. XPS spectra were recorded on a Physical Electronics Versaprobe II X-ray Photoelectron Spectrometer equipped with a C60 cluster-ion gun.

2.3. Lap Shear Strength Measurements

ASTM D1002 determines the shear strength of adhesives for bonding metals when tested on a single-lap-joint specimen. The test is applicable for determining adhesive strength, surface preparation parameters, and adhesive environmental durability. Two metal plates are bonded together with adhesive

and cured as specified. The assembly is then cut into uniform width lap shear specimens. The test specimens are placed in the grips of a universal testing machine and pulled at 1.3 mm/min (0.05 in/min) until rupture occurs. The grips used to secure the ends of the assembly must align so that the applied force is applied through the centerline of the specimen. The type of failure can be either adhesive (the adhesive separates from one of the substrates) or cohesive (the adhesive ruptures within itself).

The recommended lap shear specimen is 25.4 mm (1") wide, with an overlap of 12.7 mm (0.5"). The recommended metal thickness is 1.62 mm (0.064") and the overall length of the bonded specimen should be 177.8 mm (7"). The specimen failure should occur in the adhesive, and not in the substrate – thus the metal thickness and the length of the overlap may be adjusted as necessary. Adhesive is applied based on manufacturer recommendations, yielding an adhesive layer usually 0.5 to 1 mm (0.02- 0.04 in) in thickness.

3. Results and Discussion

3.1 Chemical Characterization

All three of the EpCNTs were thoroughly characterized using standard methods for MWCNT characterization. TGA under nitrogen revealed an increased weight loss with each subsequent functionalization. All MWCNTs used were from the same batch to eliminate discrepancies. Unfunctionalized MWCNTs only lose 7 weight % over the temperature range of 50 to 800 °C, and in contrast purified **fCNT1**, **fCNT2**, and **fCNT3** lose 17, 22, and 10 weight %, respectively. Post functionalization modification increases the respective weight loss to 43, 38 and 37 weight % for **EpCNT1**, **EpCNT2**, and **EpCNT3** (Figure 2). In the case of **EpCNT1** and **EpCNT2**, the extent of reaction was limited so as to match the ~60 weight % MWCNT in **EpCNT3**. This allows for a fair comparison of the functionalization methods. To confirm that the MWCNT are indeed covalently bound to the epoxy matrix, a control TGA of physically mixed BPE and MWCNT was taken. The most marked difference was that the transition temperature occurred at the decomposition temperature of BPE, namely 255 °C (Figure S1), as opposed to the higher onset of weight loss (>300 °C) observed for the covalently bound groups in the functionalized CNT. Unfunctionalized MWCNT were also mixed

with BPE and subjected to the modification and purification conditions used to produce the EpCNT. After drying under vacuum, no difference from the pristine MWCNT could be observed in the TGA trace, indicating that the purification methods used were sufficient to remove non-covalently bound materials.

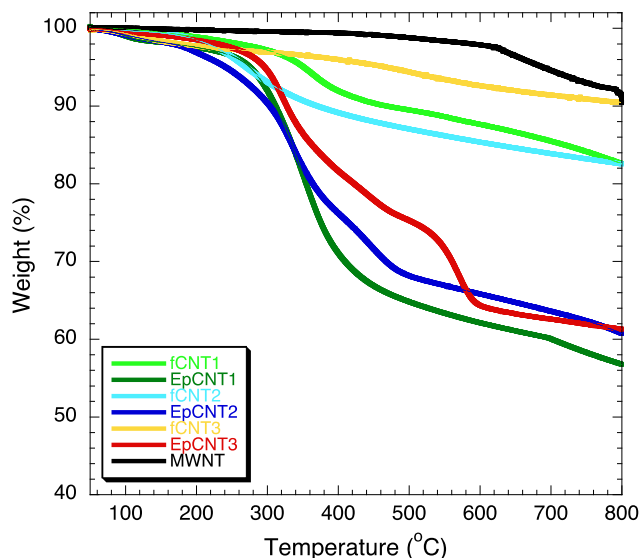


Figure 2. TGA traces of **EpCNT1-3** and precursors **fCNT1-3** ran under nitrogen. Unfunctionalized MWCNT is shown for comparison.

Subsequently, the **EpCNT** were characterized by FTIR spectroscopy. The spectra of unfunctionalized MWCNT, **fCNT1**, **EpCNT1**, and **BPE** can be found in Figure 3. **fCNT1- fCNT3** have been synthesized and published before and the spectra match those previously reported [26, 27]. Covalent functionalization was readily apparent from the spectra of the **EpCNTs** (Figure 3 and Figure S2). Initially, upon saponification of **fCNT1** to **NaO-CNT**, the carbonyl ester peak at 1730 cm^{-1} shifts to 1620 cm^{-1} , which is characteristic of the carbonyl of a carboxylate anion. In model studies on C_{60} , this saponification procedure displaced both methoxy groups, confirmed by the complete disappearance of the CH_3 umbrella mode vibration at 1290 cm^{-1} (Figure S3). In **NaO-CNT**, however, the displacement of the 3-methoxy group is incomplete, since the peak, at 1240 cm^{-1} for the CNT analogue, is still visible. Upon reaction with **BPE**, the carbonyl peak remains at 1630 cm^{-1} , rather than shifting to the ester region above 1700 cm^{-1} , as one would expect if the carboxylate anion had acted as the nucleophile in the

opening of the epoxide. Instead, we propose that the hydroxyls present at the 2-position of the ring acts as the nucleophile to open the epoxide. A broadening of the C-O vibrational peak at 1030 cm^{-1} , suggests an altered environment of the bond, consistent with covalent attachment to the MWCNT at this position. Additionally, for **EpCNT1**, peaks at 2890 and 2900 cm^{-1} , characteristic of the sp^3 hybridized C-H of the **BPE** methylene and a sharp peak at 1230 cm^{-1} , characteristic of the epoxide C-O bond, appear along with other peaks characteristic of **BPE** appear in the fingerprint region. The spectra of unfunctionalized MWCNT, **fCNT1**, **NaO-CNT**, **EpCNT1**, and **BPE** can be found in Figure 3. Similar shifts and peaks can be observed in the spectra of **EpCNT2** and **EpCNT3** (Figure S2).

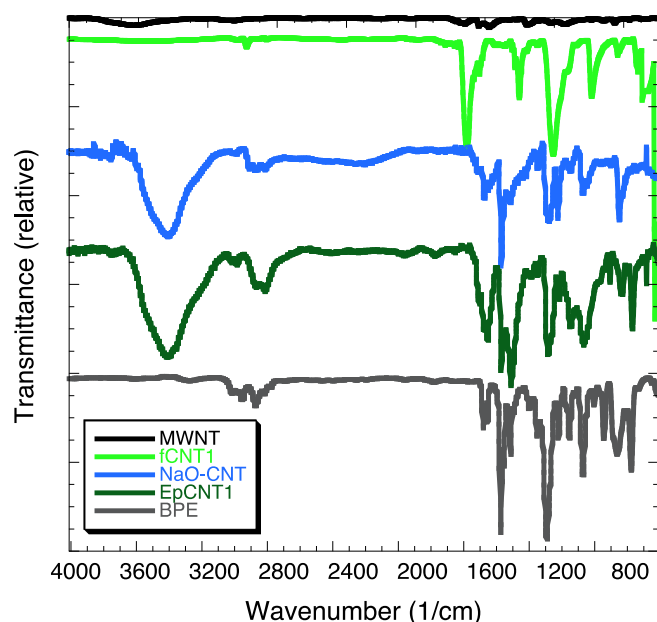


Figure 3. FTIR Spectra of **EpCNT1** and precursors **NaO-CNT** and **fCNT1**. Unfunctionalized MWCNT and **BPE** spectra are also shown for comparison. Other FTIR spectra can be found in Figure S2.

Raman spectroscopy is generally less informative for MWCNT materials than for SWNT compositions. The difference is that MWCNT typically have more inherent defects than SWNT and covalent functionalization is often tracked by an increase in defects in the carbon lattice, characterized by the Raman D band at about 1350 cm^{-1} , in comparison to the vibrations from the graphene network,

characterized by the G band at about 1600 cm^{-1} . Despite this lower sensitivity, the Raman spectra of the **fCNTs** showed the expected increases in the disorder (D) band at 1360 cm^{-1} in comparison with the graphene (G) band at 1590 cm^{-1} . The D to G ratio, which can be taken as an indication of the extent of covalent functionalization increases from 0.95 for the pristine MWCNT to 1.2, 1.1, and 1 for **fCNT1**, **fCNT2**, and **fCNT3** (Figure S4). It is interesting to note that the lowest D to G ratio is observed for **fCNT3**, which uses pre-oxidized MWCNT for the functionalization. This suggests that the efficiency of covalent functionalization achieved for **fCNT1** and **fCNT2** is higher. All spectra were taken using a 785 nm laser, as this wavelength is more sensitive to the G band and thus affords a better quality spectra [30, 31].

Further evidence of the proposed transformations was gathered from X-ray photoelectron spectroscopy (XPS). Pure MWCNT are >95% carbon with the balance being oxygen and trace metals (<1%). The XPS is perhaps the least useful for **EpCNT1**, given that only functionalities including carbon and oxygen are introduced in the novel functionalization. Despite this, the XPS gives evidence for functionalization by showing 79.1% C, 19.3% O, and 1.6% Na (Figure S6). The large elemental trace of sodium indicates that some of the carboxylate groups remain after reaction with the epoxy, which is expected as the reaction was not allowed to go to completion in order to allow for the same degree of functionalization for all of the EpCNT. **EpCNT2** contains 84.5% C, 14.7% O and 0.9% N (Figure S6). Given that the functional group itself is only 9% nitrogen, this corresponds to approximately 1 in 30 CNT carbons having an epoxy functional group attached. Finally, **EpCNT3** shows incorporation of 70.7% C, 28.7% O, and 0.6% N (Figure S7). The higher oxygen content is a relic of the pre-functionalization oxidation, while the lower nitrogen content is a reflection of the low percentage of nitrogen in the functional group (3%).

After establishing covalent functionalization, the only task that remained was establishing the ability of the functional group to covalently bond to the epoxy matrix via the crosslinking amine. For our studies, Epikure 3046, an aliphatic adidoamine, was to be used as the crosslinker. To prove the ability of the EpCNT to covalently bond to this material, 500 mg of each EpCNT and MWCNT were sonicated in

500 mL dioxane, and then allowed to react with 2 mL Epikure 3046 at 100 °C overnight. The reaction mixtures were centrifuged and washed with organic solvents and the residue was analyzed via TGA and XPS to establish covalent bonding (Figures S8 and S9). The MWCNT was compared as a control, as it is known that amines have an affinity for non-covalent interactions with CNT. Some degree of non-covalent adsorption was observed via an increase in weight loss in TGA and an incorporation of 2 nitrogen for every 98 carbon in XPS for MWCNT. Convincingly, a greater weight loss and nitrogen incorporation was seen for each of the EpCNT, so evidence for covalent bonding was established.

3.2. Material Properties

After functionalization, an improvement in the processability was apparent. EpCNT were readily dispersible in organic solvents that solvate **BPE**, including dimethyl formamide, tetrahydrofuran, and even acetone in the case of **EpCNT2**. Most importantly, the EpCNT form stable dispersions in epoxy resin. To disperse EpCNT in Bisphenol A or F-based epoxy resins, simple mixing with a stirring rod and 1 minute of sonication resulted in a good dispersion, and a 1 weight % dispersion of **EpCNT2** prepared by this method has demonstrated stability for over 1.5 years. As evident in Figure 4, unfunctionalized MWCNT (center image) settle out of a similar dispersion in only 30 minutes, which is less than the time of curing.

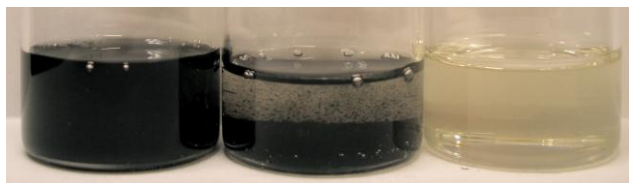


Figure 4. Photograph of uncured epoxy resin taken 30 minutes after mixing with 1 weight % **EpCNT2** (left) and 1 weight % MWCNT (center). The neat epoxy is shown (right).

3.3. Lap Shear Strength Measurements

We have investigated the lap shear strength as an indication of adhesive strength and the suitability for these composites in metal-composite hybrid applications. To perform these tests, Hexion/Momentive formulation 4007 was selected for its room temperature cure, tolerance for slight surface contamination,

and proven performance as a structural adhesive in metal-to-metal bonding. This 3-component epoxy system contains Epon 828, a Bisphenol-A/ epichlorohydrin based resin, Heloxy 505, a low viscosity polyepoxide modifier, and Epikure 3046 an aliphatic amidoamine crosslinker. The exact chemical structures are not provided by the manufacturer [24].

Following the American Society for Testing and Materials (ASTM) standard test D1002, aluminum alloy 2024 test strips were cut using an Omax 2626/xp JetMachining Center controlled by integrated CAD/ CAM software to give test strips 1.5 x 101.6 x 25.4 mm (0.064 x 4.00 x 1.00 in.) Details on ASTM standard test D1002 can be found in the Supplementary Data. Surfaces were prepared by wiping with acetone, then isopropanol, and finally acetone, as suggested by the manufacturer. Epoxy formulations were prepared at 0.5, 1, 2, 3, 5, and 10 weight % MWCNT for the total weight of the combined epoxy. For EpCNT, only the weight of the CNT, or 60 % of the total mass, was used for this percentage. For example, to prepare the 1 weight % **EpCNT1** 59 mg **EpCNT1** (or 36 mg CNT) were dispersed into 2.252 g Epon and 0.749 g Heloxy with mechanical mixing, followed by 1 minute of bath sonication. Subsequent addition of 0.723 g of Epikure brought the total mass of the mixture to 3.76 g, or exactly 0.96% CNT by weight. The final resin homogenized with mechanical mixing, followed by 1 minute of bath sonication created a mixture that was directly applied to the prepared aluminum surfaces to create the joints used for the lap shear test. The quantities of components used for other formulations can be found in Table S1. The test-strips were adhered with 0.3 mL of the epoxy mixture to give thicknesses in the range of 0.5- 1.0 mm (0.02- 0.04 in) (Table S2), with thickness variations resulting primarily from the various resin viscosities. The length of test-strip overlap in these double cantilever test specimens as specified by ASTM D1002 was 12.7 ± 1 mm (0.5 ± 0.04 in, see Figure 5).

Samples were loaded in a Zwick mechanical tester with a 10 kN load cell. Overlap of the sample ends with the clamps was 1 inch and the load was applied at an extension rate of 1.3 mm/ min (0.05 in/min). Lap shear strength was recorded as the force applied at failure divided by the adhesive area. Five test samples were measured for each concentration and the standard deviations were less than 1.5 MPa (13 % error). All of the samples failed via a transferred interface, meaning that the fracture path traveled

along the aluminum surface **a**, propagated through the adhesive, and continued along the other aluminum surface, **b**. (Figure 5)

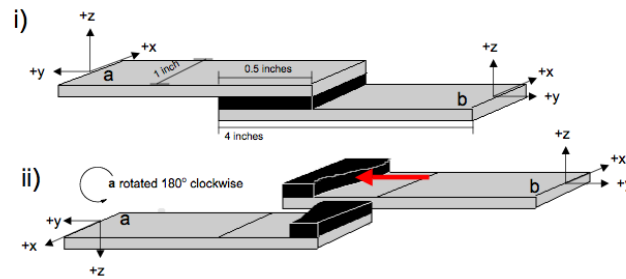


Figure 5 i) Schematic of the set-up used for the lap shear test. Force is applied in the y-direction. ii) Shows the top aluminum strip (**a**) rotated 180° counter clockwise to reveal a typical fracture pattern, with failure occurring via debonding on one surface and typically one long crack propagating through the adhesive along the z-direction. The red arrow indicates the angle from which the SEM images were taken. The actual thickness of the adhesive layer ranged from 0.5- 1.0 mm (0.02-0.04 inches) and is exaggerated in this schematic.

The most significant improvements in adhesion were seen for the lower weight percent composites. At 1 weight %, addition of functionalized or unfunctionalized MWCNTs improved the lap shear strength over the neat epoxy (14.0 MPa). The lap shear strength was increased to 15.0 MPa upon the addition of 1 weight % unfunctionalized MWCNT, and further improvements to 15.8 and 19.1 MPa were respectively observed for **EpCNT1** and **EpCNT2**, which is a 36 % increase over neat epoxy and a 27 % increase over the same amount of pristine MWCNT additive (Figure 5). The greater increase in properties seen in **EpCNT2** over **EpCNT1** can be ascribed to the greater stability of functional group used to attach the BPE. Ester linkages are likely more susceptible to rupture than the triazole or ether linkages and hence it is chemical intuitive that **EpCNT2** would display superior properties. The addition of 1 weight % **EpCNT3** only slightly increased the lap shear strength to 14.8 MPa. Since optical and SEM images showed that the uniformity of the dispersion was similar to that of **EpCNT1** and **EpCNT2**, the more modest increase in properties for this material is presumably due to the pre-functionalization oxidation, which is known to shorten and otherwise damage MWCNT and result in inferior mechanical

properties [7]. It should be noted that, thicker adhesive layers have been shown to decrease adhesive properties [32]. Thus, because the adhesive layers of the 1 weight % MWCNT, **EpCNT1**, and **EpCNT2** samples were 41%, 46%, and 38% thicker than the neat epoxy sample, as necessitated by their greater viscosity, an additional increase of up to 30% in the lap shear strength could be expected.

For comparison, we tested amine-functionalized MWCNT produced in our group by a well-known azide functionalization method [33] (Scheme S2) at 1 weight % in the same matrix using the same conditions and found a lap shear strength of 16.2 MPa, which is similar to the improvement seen for the **EpCNT**. However, disadvantages arise in the shelf life of this CNT dispersion. If these amine functionalized MWCNT are introduced to the higher volume fraction epoxide part of the resin before crosslinking is desired, the amines could react non-uniformly to give gelation at a point, which would result in decreased mechanical properties.

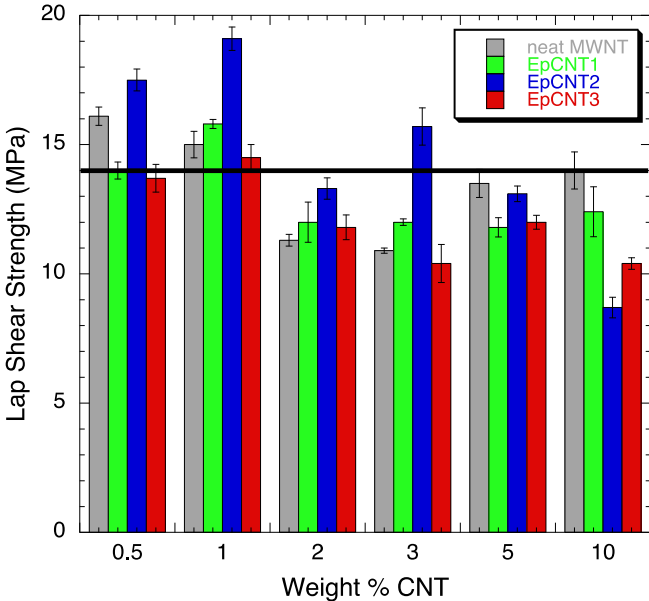


Figure 5. Lap shear strength of composites. The black line indicates the lap shear strength of the reference neat Hexion 4007 at 14.0 MPa. Five test samples were measured for each MWCNT concentration and the standard deviations were less than 1.5 MPa (<13% error, given by the vertical bars)

3.4. Sample Morphology

Since the mode of failure was primarily adhesive failure, the mechanism of strengthening by the CNTs was not obvious. However, since the crack propagated across the bulk epoxy as it transferred once from one face to the other, it was hypothesized that the CNTs deflected the crack as it propagated through the adhesive layer, giving rise to the increased strength. To ascertain the validity of this theory, the transverse fracture interfaces were studied using SEM. SEM was chosen over TEM for analysis since a larger area could be surveyed and since MWCNT are large enough that individual tubes are readily observable. In this way, we felt we could get a more true analysis of the dispersion and behavior of the CNTs in the bulk material. Since the best lap shear strength was observed for the 1 weight % composites, SEM studies were focused on the 1 % loading samples. The fracture interfaces of failed lap shear joints were sputter-coated with gold, then loaded in the SEM at an angle that allowed the crack face to be viewed.

From the SEM images, it was apparent that a different surface morphology exists along the crack if CNT are present, with the increased fracture surface roughness becoming more pronounced with covalent functionalization. The roughness of the morphology of the crack surface increases with increasing lap shear strength, suggesting less facile crack propagation, especially in **EpCNT2**. While the EpCNT appear somewhat inhomogeneous on the macroscopic scale (Figure S13), further magnification this sample reveals in addition to tangled MWCNT clusters, shapes characteristic of MWCNT reasonably homogeneously dispersed throughout the matrix, suggesting their role in the altered morphology and increased strength. Higher magnification shows the characteristic parabolic marking indicative of crack initiation by a CNT cluster located at the base of the parabola (Figure 7d). From these images, it can be ascertained that the EpCNT play an important role in the strengthening of the composites.

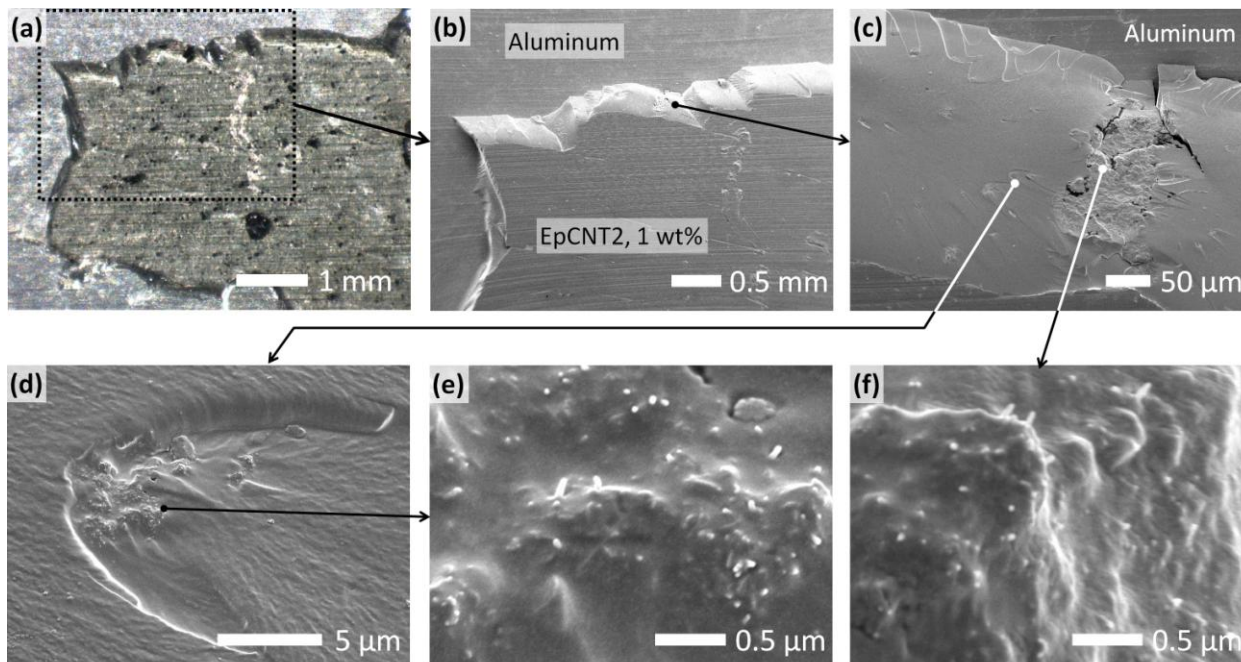


Figure 7. Typical cohesive and adhesive fracture features for **EpCNT2**. (a) Optical micrograph of the fracture of 1 wt % **EpCNT2**. (b) Low magnification SEM image of the fracture surface corresponding to the optical micrograph in (a). (c) At medium magnification, various sized clusters of CNTs are apparent on the fracture surfaces. (d) Higher magnification shows the characteristic parabolic marking indicative of crack initiation by a CNT cluster at the base of the parabola. Crack path is from left to right. (e) & (f) At still higher magnification, single CNTs are observed.

A different pattern of fracture can be observed in the samples of 3 weight % **EpCNT3** (Figure 8). Here, the shortened, oxidized CNT can be seen homogeneously dispersed in the sample (with a few large clusters). Fracture surfaces run nearly parallel to the surface of the aluminum, indicating better adhesion. Given that the lap shear strength of this 3 weight % composite is lower, this suggests that the bulk material is weaker. **EpCNT1** and unfunctionalized MWCNT show similar fracture patterns, although the poor dispersion is apparent (clusters apparent in optical images, Figure S13) and the lap shear strength was not as good. Despite the stability of the dispersions, the lap shear strength fell off beyond the addition of 1 weight % CNT in all cases. In fact, for the 10 weight % **EpCNT2**, the nature of the failure started to take on a highly ductile (“viscous”) nature. At the fracture surface of this sample, large tangled clusters became apparent (Figure S13), which gives insight towards the origin of the decreased mechanical properties.

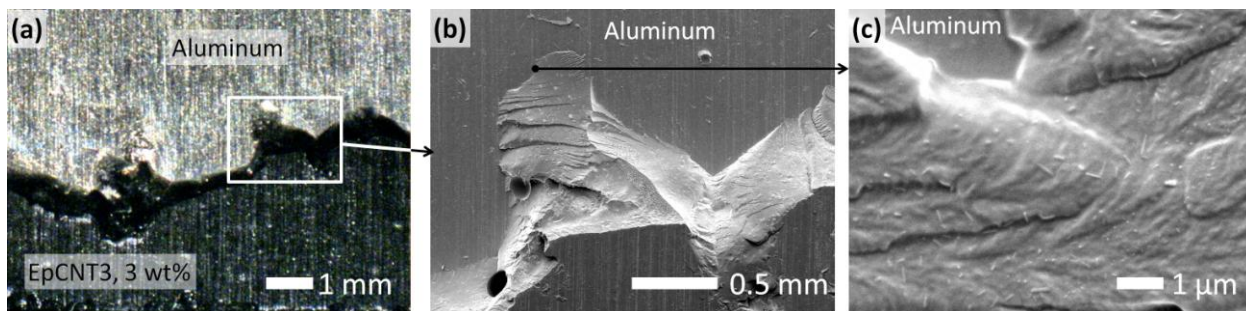


Figure 8. Typical cohesive and adhesive fracture regions in **EpCNT3**. (a) Optical micrograph of the fracture of 3 wt % **EpCNT3**. Some fracture surfaces run nearly parallel to the surface of the aluminum strip through the adhesive. For example, the boxed area, which indicates fracture inside the adhesive and stronger adhesion at the aluminum-epoxy interface. (b) Low magnification SEM image of the fracture surface corresponding to the optical micrograph in (a). (c) Well dispersed EpCNT3s are evident, with typical lengths less than a micron.

3.5. Cure Kinetics

To further elucidate the origin of the decrease in mechanical properties, we endeavored to study how the larger quantities of CNT were affecting the cure kinetics and the extent of cure. To do this, a dynamic cure study was devised using differential scanning calorimetry (DSC). In this study epoxy samples including the EpCNTs or MWCNT were thoroughly dispersed in the Epon and Heloxy similar to the materials prepared for the lap shear tests, then an appropriate amount of Epicure was added and the components thoroughly mixed. Approximately 3 mg of the resin was transferred to a hermetic aluminum DSC pan which was placed in the DSC, and immediately equilibrated at 50 °C for 5 minutes, followed by a temperature ramp of 10 °C/ min to 300 °C. A similar procedure has been previously used to study the extent of cure for neat and oxidized MWCNT in epoxy [17, 34]. For the first round of tests, the thermogram of neat epoxy was compared with 1 weight % of pristine MWCNT and each of the EpCNTs (Figure S10).

There are two exothermic peaks that result from the cure process, even for the neat Hexion 4007 epoxy. While both Heloxy 505 and Epon 828 are known to crystallize, it is not likely that one of the exotherms comes from a crystallization process; no peaks are observed when each of the three components are run individually. Furthermore, a discrete peak cannot be ascribed to the reaction of the Epon or the Heloxy with the Epikure 3046. Rather, the two-stepped cure probably originates from the variety of reactive groups in the amidoamine curing agent. The first peak at 122 °C is likely organization

and gelation and the second exothermic peak peak 227 °C is characteristic of the complete cure. Neither of the peaks is observed in a second heating cycle, once the epoxy is fully cured and no difference between the neat epoxy and the epoxy filled with CNT is observed (Figure S12).

No substantial changes were apparent between the neat epoxy and the 1 weight % composites (Tables S3 and S4). Non-systematic decreases in the intensity first exothermic peak at 122 °C, attributed to the enthalpy of gelation, were observed. The enthalpy of 176 J/g in the neat epoxy dropped to 116 J/g in the 1 weight % MWCNT, with the enthalpies of the EpCNT being intermediate values, can be observed. The peak of the exotherm remains largely unaltered. The peak at 227 °C, attributed to the enthalpy of cure, shows greater variation. The peak of the exotherm decreases in temperature to 222 °C for **EpCNT3**, and increases to 233 °C for the MWCNT. The variations in the enthalpy of cure are also scattered ($\pm 12\%$), with the lowest enthalpy cure exhibited by **EpCNT3** (99 J/g vs. 112 J/g for neat epoxy). Since the lowest temperature, lowest intensity cure peak is observed for 1 weight % **EpCNT3**, it is possible that residual carboxylic acid groups from the oxidation serve to catalyze the cure.

To more deeply probe the effect of the functionalization of the CNT on the cure, a second test set was run, including 0.5, 1, 2, 3, 5, and 10 weight % MWCNT (Figure S12) and **EpCNT2** (Figure 9). From these data sets, a trend starts to emerge. While the first exotherm remains largely unaltered, as additional **EpCNT2** is added, the cure peak shifts from 240 °C (0.5 weight %) to 204 °C (10 weight %) and decreases in intensity. The enthalpy of the cure drops to 54.1 J/g in 10 weight % EpCNT2 from 111.7 J/g in the neat hexion, suggesting an incomplete cure. This is different than the previously observed effect of catalysis by the addition of amine and acid-functionalized CNT [32]. The effect with the pristine MWCNT was less pronounced, with the peak temperature of the cure exotherm shifting to 210 °C and the enthalpy of the cure increasing modestly to 140 J/g.

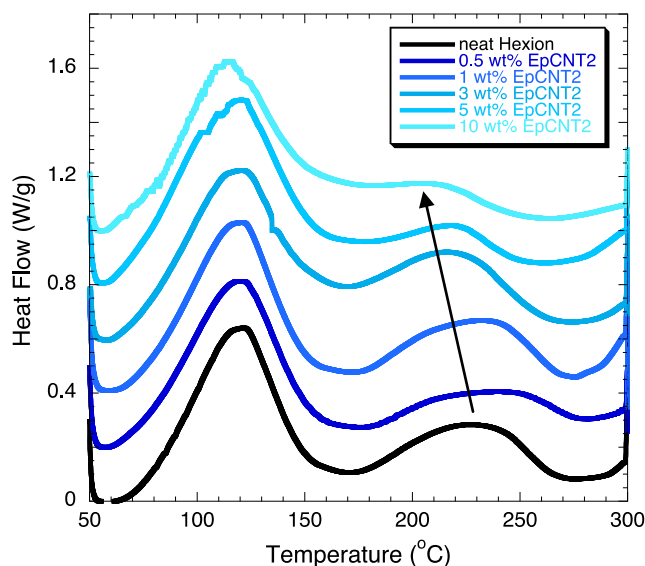


Figure 9. DSC cure traces for neat Hexion, 0.5, 1, 3, 5, and 10 weight % EpCNT2. Each series is offset by 0.2 W/g for clarity.

3.6. Rheology

We studied the rheology to determine if increased viscosity of the CNT-resin composite contributed to a decreased extent of cure and to determine the effect of the addition of CNT on the gel point of the epoxy. To determine the gel point, Hexion 4007 was prepared neat or with the appropriate weight % of MWCNT or EpCNT, in the same ratios as reported for the lap shear studies. 0.4 mL of the thoroughly mixed resin was placed on the bottom 25 mm disposable aluminum rheometer plate and the top plate was brought down to a geometry gap of 1100 μm . The oven was closed and the sample was allowed to equilibrate for 3 minutes, and then the temperature ramped at 10 $^{\circ}\text{C}/\text{min}$ to 140 $^{\circ}\text{C}$, where it was held for 30 minutes to ensure complete cure. A steady shear force of 10 Pa was applied at a frequency of 0.1 Hz over the temperature sweep test. The gel point was reported as the temperature where the storage modulus (G') was higher than the loss modulus (G''). The gel point of 133 $^{\circ}\text{C}$ found for neat Hexion rose several degrees upon the incorporation of 0.5 weight % MWCNT or EpCNT, and was found to drop with the incorporation of increasing quantities of CNT, down to 100 $^{\circ}\text{C}$ with 10 weight % incorporation of **EpCNT2**. The shear modulus and other properties of the cured composites determined by rheometry will be discussed at length in another publication.

In the preparation of the composite, it was obvious that the presence of CNT increased the viscosity; however, what role this plays in the final mechanical properties was unclear. Here, the viscosity of the epoxy component before the addition of the curing agent was tested using a cone and plate rheometer over a steady shear of 0.2 to 2000 s⁻¹. The viscosity of the neat epoxy was compared with the addition of 3 weight %, pristine MWCNT and **EpCNT1- 3**. Three weight percent was chosen as an intermediate quantity, where it was qualitatively observed that the viscosity was affected but the resin still flowed easily. Lower weight % compositions of CNTs showed less distinction in the resin viscosity amongst the different surface functionalities. A strong increase in the near-zero shear rate viscosity was observed for the pristine MWCNT, **EpCNT1**, and **EpCNT2** samples which then displayed significant shear thinning (Figure 10). **EpCNT3** behaved much differently, instead showing a much lower near-zero shear rate viscosity with nearly Newtonian behavior with increasing shear rate. This is likely due to the shorter length CNTs from the oxidation before functionalization. These results are similar to what previous researchers have observed, with higher, non-Newtonian viscosities observed for compositions with good CNT affinity for the matrix and comparatively lower viscosities observed for shortened CNTs [25] (i.e. **EpCNT3**). This non-Newtonian behavior suggests that the CNTs are well dispersed and align with the flow at higher shear rates [16].

Of the samples included in the rheological study, the observed lap shear strength was the highest for the 3 weight % **EpCNT2**. Given that the viscosity of this sample is significantly higher than neat epoxy, higher viscosity (and therefore lower diffusivity and hence reactivity) does not seem result in the decreased strength and incomplete cure in this system. No correlation between the viscosity and resultant gel point can be drawn. Assuming that after the initial mixing of the components, the large CNTs are essentially fixed in comparison with the much more mobile lower molecular weight components, gelation will occur earlier in the cure cycle since the EpCNTs act as giant network interconnectors. This also suggests that the EpCNTs are well-dispersed in the matrix, since incomplete cure would more likely result from inhomogeneous composition.

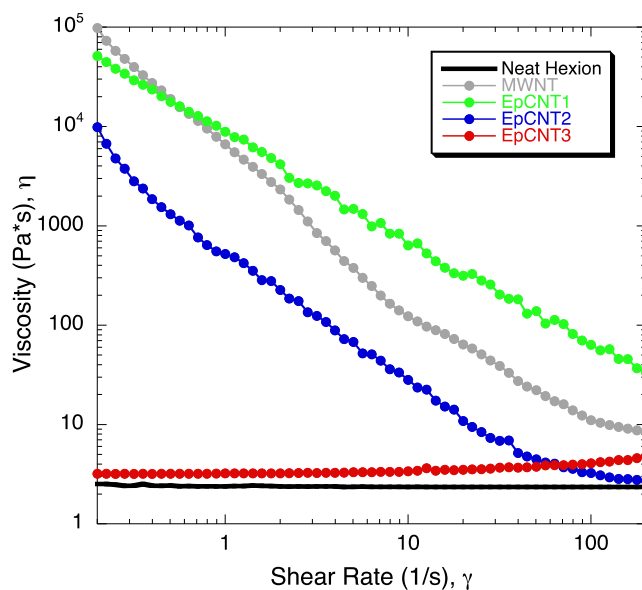


Figure 10. Dependence of the viscosity on shear rate for a neat Hexion resin, and four different 3 weight % CNT composites. The Hexion resin is Newtonian while the EpCNT composites are strongly shear thinning. Note the strong increase of the zero shear rate viscosity does not occur for the **EpCNT3** sample, which has the shortest carbon nanotubes and also behaves like a Newtonian fluid.

4. Conclusions

Three different epoxy-functionalized multi-walled carbon nanotubes (**EpCNTs**) were prepared having epoxides covalently bound to the graphene walls of the nanotubes. The **EpCNTs** were characterized by TGA, FTIR, and Raman spectroscopy to confirm thorough covalent functionalization. The effect of these different chemistries on the adhesive properties was compared to neat epoxy Hexion formulation 4007 and unfunctionalized MWCNT at 0.5, 1, 2, 3, 5, and 10 weight %. It was found that the adhesive properties could be improved by adding small amounts of the functionalized EpCNT, but the enhancement fell off at higher **EpCNT** loadings. Most notably, It was found that at 1 weight % **EpCNT3** increased the lap shear strength, by 36 % over the unfilled epoxy formulation and by 27 % over 1 weight % unmodified MWCNT. SEM images revealed a morphological change at the fracture surface with functionalization and evidence of crack deflection as the mechanism for increased joint strength. Rheological studies revealed strong shear thinning for the EpCNT containing epoxy, but little

effect of the cure temperature and properties. DSC cure studies showed an alteration of cure kinetics with increased CNT concentration, with more pronounced effects for EpCNT. Additional investigations of the shear properties of the nanocomposites used in this study are underway and will be presented in a future publication.

Acknowledgements. This work was supported by the U.S. Army through the Institute for Soldier Nanotechnologies and the National Science Foundation through a Graduate Research Fellowship. The authors would like to thank Dr. Joseph Walsh for advice and assistance with initial adhesive testing, and Jan Schnorr for synthesizing the amine-functionalized MWCNT.

Appendix A: Supporting Data

Experimental details including materials, instrumentation, and detailed synthetic procedures. Additional characterization of materials including FTIRs of fCNT1, EpCNT2, fCNT3, EpCNT3 and Raman spectra of fCNTs. XPS spectra for the EpCNTs. TGA and XPS spectra from control experiments. Additional details from lap shear tests including quantities of reagents, thickness of the adhesive layers, values of shear deformation at failure, and typical stress-strain curves. Gel points from rheology and values of enthalpies of cure and gelation. Additional DSC curves from dynamic cure study, and additional SEM images.

References

- [1] Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**; 354 (6348): 56-58.
- [2] Sinnott, S. B. and Andrews, R. Carbon nanotubes: synthesis, properties, and applications. *Crit. Rev. Solid State Mat. Sci.* **2001**; 26 (3): 145- 249.
- [3] Filleter, T.; Bernal, R.; Li, S; Espinosa, H. D. Ultrahigh strength and stiffness in cross-linked hierarchical carbon nanotube bundles *Adv. Mater.* **2011**; 23 (25): 2855- 2860.

- [4] Karousis, N.; Tagmatarchis, N. Current progress on the chemical modification of carbon nanotubes. *Chem. Rev.* **2010**; *110* (9): 5366- 5397.
- [5] Gojny, F. H.; Nastalczyk, J.; Roslaniec, Z.; Schulte, K. Surface modified carbon nanotubes in CNT/ epoxy-composites. *Chem. Phys. Lett.* **2003**; *370* (5-6): 820- 824.
- [6] Zhu, J; Kim, J.; Peng, H; Margrave, J. L.; Khabashesku, V. N.; Barrera, E. V. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. *Nano Lett.* **2003**; *3* (8): 1107- 1113.
- [7] Winey, K. I.; Moniruzzaman, M. Polymer nanocomposites containing carbon nanotubes. *Macromolecules*, **2006**; *39* (16): 5194- 5205.
- [8] Gong, X.; Liu, J.; Baskaran, S.; Voise, R. D.; Young, J. S. Surfactant-assisted processing of carbon nanotube/ polymer composites. *Chem. Mater.* **2000**; *12* (4): 1049- 1052.
- [9] Chen, J.; Liu, H. "Polymer and Method for Using the Polymer for Noncovalently functionalizing Nanotubes." U. S. Patent 6,905,667 B1, June 14, 2005.
- [10] Vaisman, L.; Wagner, H. D.; Marom, G. The role of surfactants in dispersion of carbon nanotubes. *Adv. Coll. Inter. Sci.*, **2006**; *128- 130*: 37- 46.
- [11] Coleman, J. N.; Khan, U.; Blau, W. J.; Gun'ko, Y. K. Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites. *Carbon*, **2006**, *44* (9): 1624- 1652.
- [12] *Impact Engineering of Composites*; Abrate, S.; CISM Courses and Lectures, Volume 526; Springer, New York, 2011.
- [13] Bekyarova, E.; Thostenson, E. T.; Yu, A.; Kim, H.; Gao, J.; Tang, J. et al. Multioscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites. *Langmuir*, **2007**; *23* (7): 3970- 3974.

- [16] Kim, J. A.; Seong, D. G.; Kang, T. J.; Youn, J. R. Effects of surface modification on the rheological and mechanical properties of CNT/ epoxy composites. *Carbon*, **2006**; *4* (10): 1898- 1905.
- [17] Gojny, F. H.; Schulte, K. *Comp. Sci. and Tech.* **2004**, *64*, 2303- 2308.
- [18] Choi, W. J.; Powell, R. L.; Kim, D. S. Curing behavior and properties of epoxy nanocomposites with amine functionalized multiwall carbon nanotubes. *Poly. Comp.* **2009**; *30* (40): 415-421.
- [19] Zhu, J. ; Peng, H.; Rodriguez-Macias, F.; Margrave, J. L.; Khabashesku, V. N.;Imam, A. M.; Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes *Adv. Func. Mater.* **2004**; *14* (7): 643- 648.
- [20] Gojny, F. H.; Wichmann, M. H. G.; Kopke, U.; Fielder, B.; Schulte, K. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. *Comp. Sci. Tech.* **2004**, *64*, (15): 2363- 2371.
- [21] Meguid, S. A.; Sun, Y. On the tensile and shear strength of nano-reinforced composite interfaces. *Materials & Design*, **2004**, *25* (4): 289-296.
- [22] Martinez-Rubi, Y.; Ashrafi, B.; Guan, J.; Kingston, C.; Johnston, A.; Simanrd, B. *et al* Toughening of epoxy matrices with reduced single-walled carbon nanotubes. *ACS Appl. Mater. Interfaces*, **2011**, *3* (7): 2309- 2317.
- [23] Xie, W.L.; Mai, Y.-W.; Zhou, X.-P. Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Mater. Sci. Eng. R* **2005**; *49* (4): 89-112.
- [25] Fan, Z.; Advani, S. G. Rheology of multiwall carbon nanotube suspensions. *J. Rheol.* **2007**, *51* (4): 585- 604.
- [26] Zhang, W.; Sprafke, J. K.; Ma, M.; Tsui, E. Y.; Sydlik, S. A.; Rutledge, G. C.; Swager, T. M. Modular functionalization of carbon nanotubes and fullerenes. *J. Am. Chem. Soc.*, **2009**; *131* (24): 8446- 8454.

- [27] Zhang, W.; Swager, T. M. Functionalization of single-walled carbon nanotubes and fullerenes via a dimethyl acetylenedicarboxylate-4-dimethylaminopyridine zwitterion approach. *J. Am. Chem. Soc.* **2007**; *129* (25): 7714- 7715.
- [28] Kalisiak, J.; Sharpless, K. B.; Folkin, V. V. Efficient synthesis of 2-substituted-1,2,3-triazoles. *Org. Lett.* **2008**; *10* (15): 3171- 3174.
- [29] Georgakilas, V.; Bourlinos, A.; Gournis, D.; Tsoufis, T.; Trapalis, C.; Mateo-Alonso, A.; Prato, M. *J. Multipurpose organically modified carbon nanotubes: from functionalization to nanotube composites. Am. Chem. Soc.* **2008**; *130* (27): 8733- 8740.
- [30] Dresselhaus, M. S.; Dresselhaus, G.; Saito, R.; Jorio, A. Raman spectroscopy of carbon nanotubes. *Physics Reports*, **2005**, *409* (2): 47- 99.
- [31] Costa, S.; Borowiak-Palen, E.; Kruszyńska, M; Bachmatiuk, A.; Kaleńczuk, R. Characterization of carbon nanotubes by Raman spectroscopy. *J. Mat. Sci.- Poland*; **2008**, *26* (2): 433- 441.
- [32] Tomblin, J. S.; Yang, C.; Harter, P. *Investigation of Thick Bondline Adhesive Joints*; DOT/FAA/AR-01/33; NTIS: Springfield, VA, 2001.
- [33] Gao, C.; He, H.; Zhou, L; Zheng, X.; Zhang, Y. Scalable functional group engineering of carbon nanotubes improved by one-step nitrene chemistry. *Chem. Mater.* **2009**; *21* (2): 360- 370.
- [34] Choi, W. J.; Powell, R. L.; Kim, D. S .Curing behavior and properties of epoxy nanocomposites with amine functionalized multiwall carbon nanotubes. *Poly. Comp.* **2009**; *31* (4): 415-421.

Supplementary Material

[Click here to download Supplementary Material: EpoxyMWNT_20121231_SuppData.docx](#)

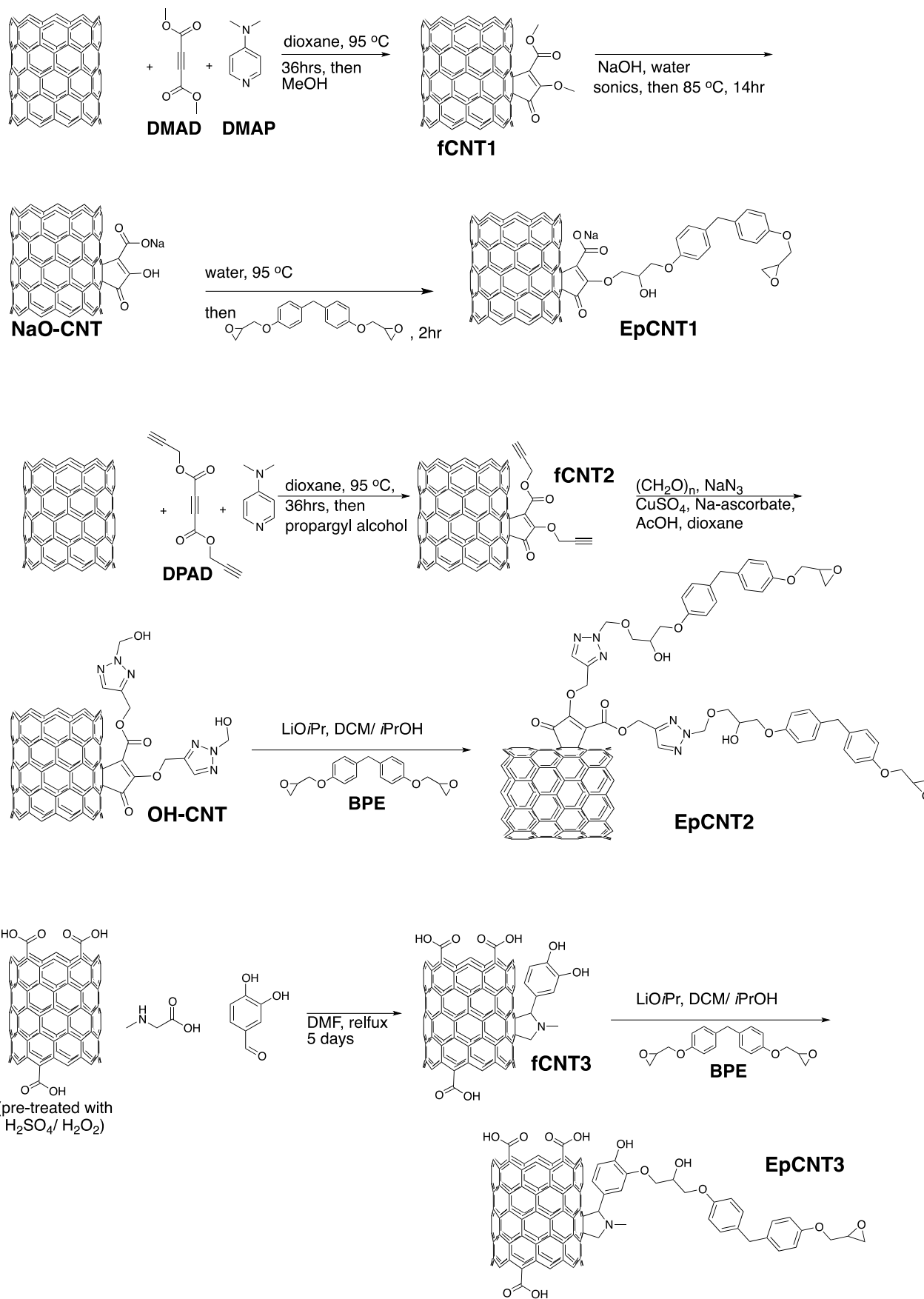
Epoxy Functionalized Multi-walled Carbon Nanotubes for Enhanced Adhesives

Stefanie A. Sydlik,¹ Jae-Hwang Lee,² Edwin L. Thomas,² and Timothy M. Swager^{1,*}

¹Department of Chemistry and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, 77 Massachusetts Ave. Cambridge, MA 02139, Massachusetts 02139 USA

²Department of Material Science and Engineering, Rice University, MS 364, Houston, TX 77251 USA

Figures.



Scheme 1. Synthesis of EpCNT1, EpCNT2, and EpCNT3.

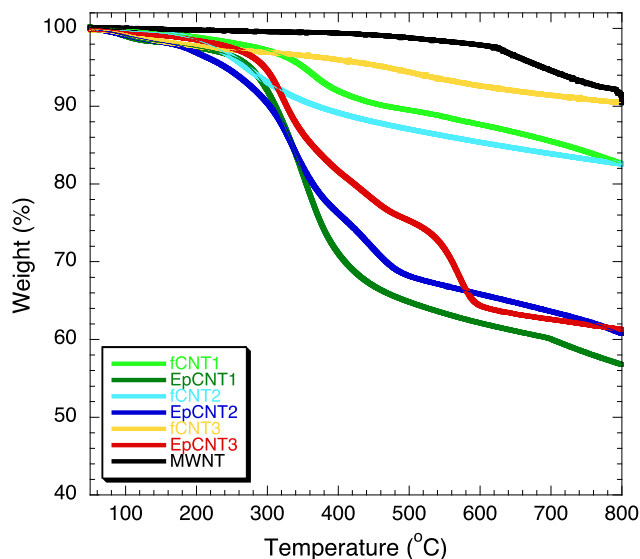


Figure 1. TGA traces of **EpCNT1-3** and precursors **fCNT1-3** ran under nitrogen. Unfunctionalized MWNT is shown for comparison.

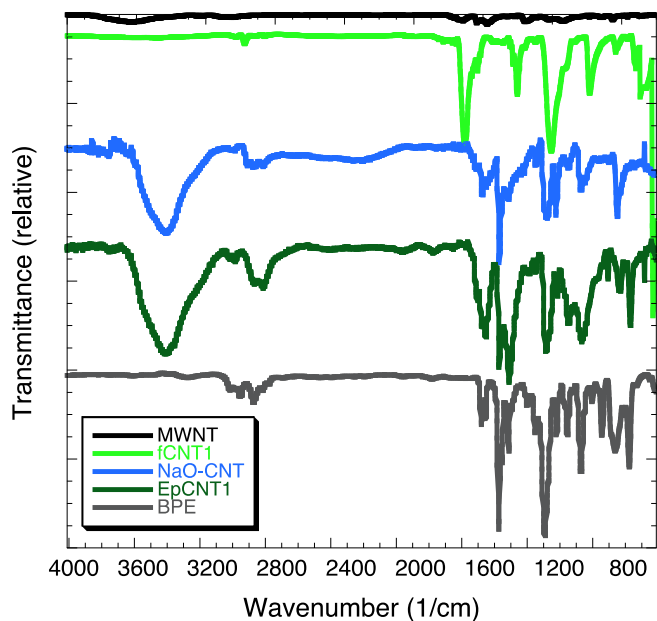


Figure 2. FTIR Spectra of **EpCNT1** and precursors **NaO-CNT** and **fCNT1**. Unfunctionalized MWNT and **BPE** spectra are also shown for comparison. Other FTIR spectra can be found in Figure S2.

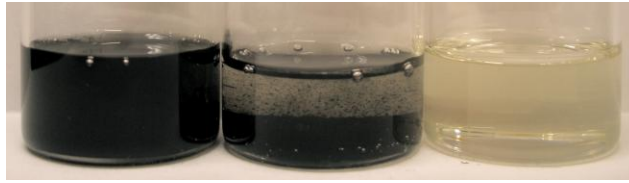


Figure 3. Photograph of uncured epoxy resin taken 30 minutes after mixing with 1 weight % **EpCNT2** (left) and 1 weight % MWNT (center). The neat epoxy is shown (right).

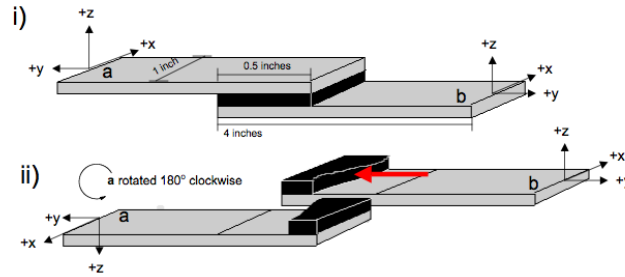


Figure 4 i) Schematic of the set-up used for the lap shear test. Force is applied in the y-direction. ii) Shows the top aluminum strip (**a**) rotated 180° counter clockwise to reveal a typical fracture pattern, with failure occurring via debonding on one surface and typically one long crack propagating through the adhesive along the z-direction. The red arrow indicates the angle from which the SEM images were taken. The actual thickness of the adhesive layer ranged from 0.5- 1.0 mm (0.02-0.04 inches) and is exaggerated in this schematic.

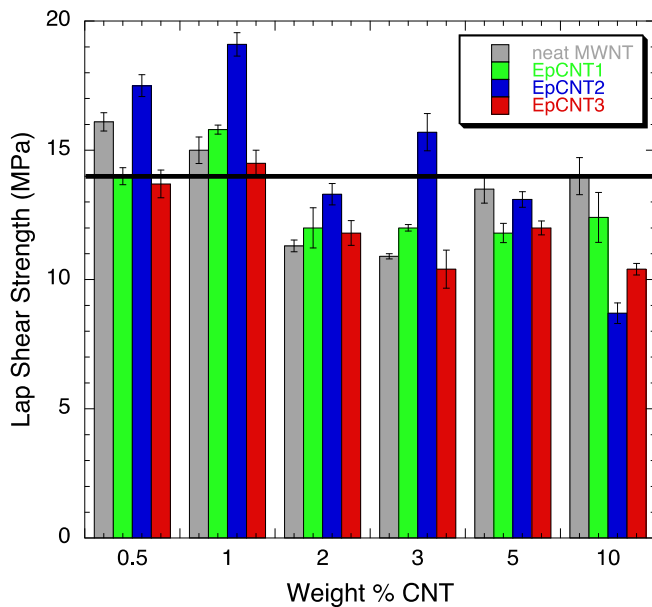


Figure 5. Lap shear strength of composites. The black line indicates the lap shear strength of the reference neat Hexion 4007 at 14.0 MPa. Five test samples were measured for each MWNT concentration and the standard deviations were less than 1.5 MPa (<13% error, given by the vertical bars)

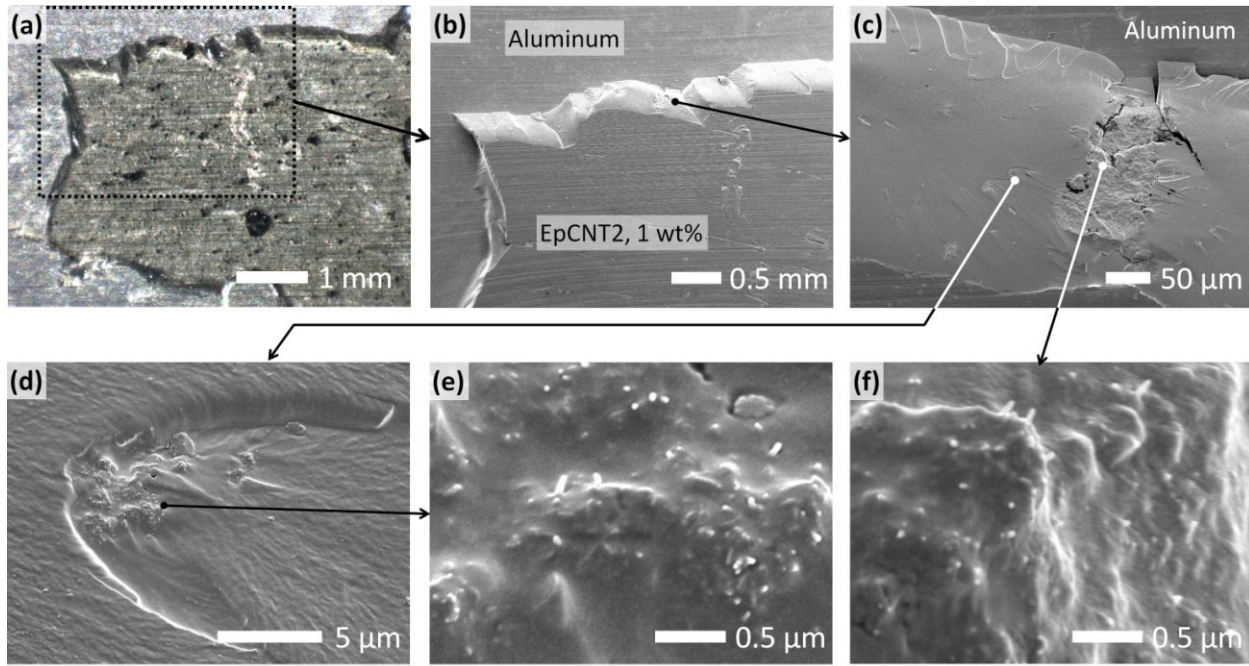


Figure 6. Typical cohesive and adhesive fracture features for **EpCNT2**. (a) Optical micrograph of the fracture of 1 wt % **EpCNT2**. (b) Low magnification SEM image of the fracture surface corresponding to the optical micrograph in (a). (c) At medium magnification, various sized clusters of CNTs are apparent on the fracture surfaces. (d) Higher magnification shows the characteristic parabolic marking indicative of crack initiation by a CNT cluster at the base of the parabola. Crack path is from left to right. (e) & (f) At still higher magnification, single CNTs are observed.

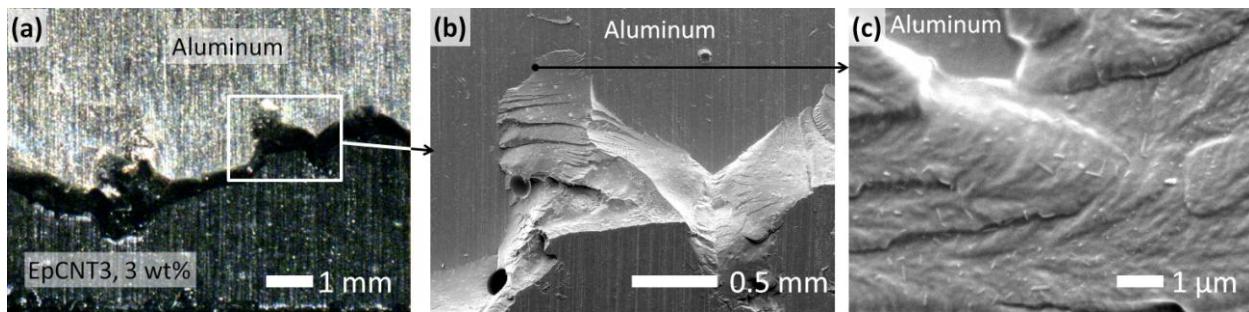


Figure 7. Typical cohesive and adhesive fracture regions in **EpCNT3**. (a) Optical micrograph of the fracture of 3 wt % **EpCNT3**. Some fracture surfaces run nearly parallel to the surface of the aluminum strip through the adhesive. For example, the boxed area, which indicates fracture inside the adhesive and

stronger adhesion at the aluminum-epoxy interface. (b) Low magnification SEM image of the fracture surface corresponding to the optical micrograph in (a). (c) Well dispersed EpCNT3s are evident, with typical lengths less than a micron.

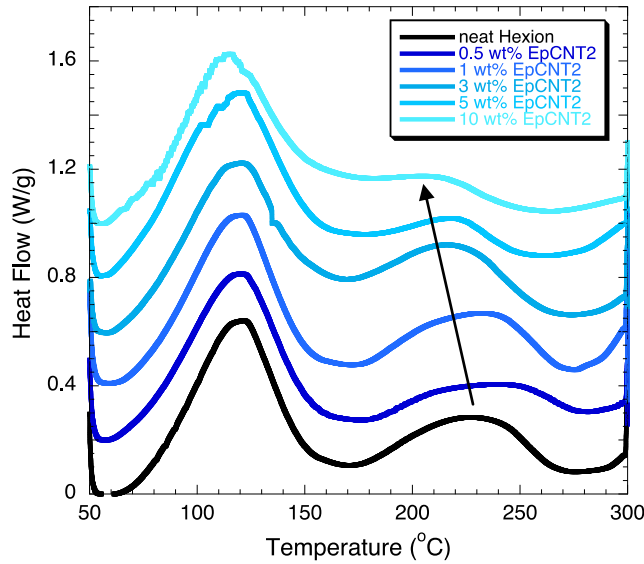


Figure 8. DSC cure traces for neat Hexion, 0.5, 1, 3, 5, and 10 weight % EpCNT2. Each series is offset by 0.2 W/g for clarity.

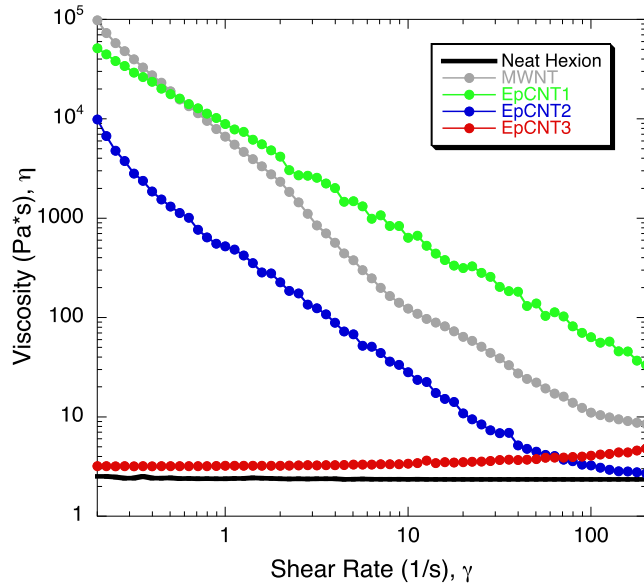
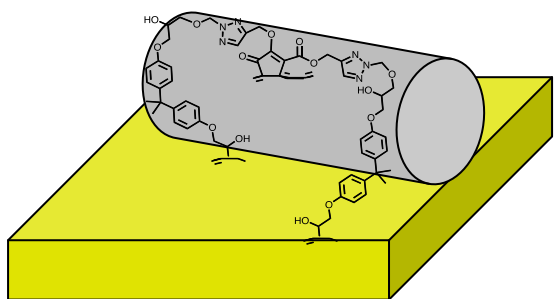


Figure 9. Dependence of the viscosity on shear rate for a neat Hexion resin, and four different 3 weight % CNT nanocomposites. The Hexion resin is Newtonian while the EpCNT nanocomposites are strongly shear thinning. Note the strong increase of the zero shear rate viscosity does not occur for the EpCNT3 sample, which has the shortest carbon nanotubes and also behaves like a Newtonian fluid.

SYNOPSIS TOC: For Table of Contents use only.



CARBON submission checklist

Please check the following points before approving the pdf file for your manuscript. Quotes are from the Guide for Authors. Please read it. Manuscripts defective in any of the following will be returned for correction and resubmission, which is a waste of everybody's time. You must be able to answer "yes" to all of the following questions. Items 11 and 14 may not be applicable.

1. Is the whole manuscript (**including References**) "double-spaced with wide margins and a font size of 12 pt." (Times or New Times Roman preferred)?

Yes

2. Have you given "Full postal addresses and affiliations ... for all co-authors."?

Yes

3. Does the manuscript include a one paragraph abstract of less than 200 words (Review articles and Research papers) or less than 100 words (Letters)? Make sure the abstract is included in the manuscript. For the manuscript of a Letter separate the abstract from the text by an extra line space or a horizontal line.

Yes

4. Is the "corresponding author identified by * and contact details (tel/fax number and e-mail address) given as a **footnote** to the first page." Do not include the postal address, which should be included in the ms heading as part of the author affiliations. Use the following format **precisely**, only the E-mail address is **required**:

*Corresponding author. Tel/Fax: +44 1692 678161. E-mail address: p.thrower@virgin.net (P.A. Thrower)

NOTE: There should be ONE corresponding author. This is not necessarily the submitting author or the most senior author. It is the person who will handle any correspondence arising from the publication.

Yes

5. Are "sections ... given Arabic numbers with subsections numbered using the decimal system?" For example:

- 2. Experimental
- 2.1 Sample preparation
- 2.1.1 Sample modification

NOTE: Acknowledgements and References sections are **not** numbered.

Yes

6. References.

- are they formatted and punctuated as shown in the Guide for Authors?
- are they each given a different number? (do **not** use 14a. b. c etc.)
- do they all include manuscript titles and page spans?
- have you given the first six author names followed by et al.?
- are they archival? "Web pages, private communications, unpublished results, etc. should be given as footnotes."

Yes

7. Are all symbols translated correctly in the pdf file?

Yes

8. Do figure and table captions appear on the same page as the item they describe?

Yes

9. Have you designated all illustrative items as Figures? "Charts, diagrams, schemes and photographs are all to be referred to as Figures".

Yes

10. Have you included the carbon in abbreviations (CNT, CNF, MWCNT etc.)?

CARBON **insists** that you do so,

NOTE: English grammar dictates that the abbreviation must refer to the **singular**. We do not use the plural noun as an adjective (fiber composites, fruit salad, nanotube dimensions, vegetable soup, etc.) We say "the production of MWCNTs", but "MWCNT production", "MWCNT properties", etc.

Yes

11. For a Letter to the Editor – is the text, including references, less than FIVE double-spaced pages? AND are there no more than five figures + tables combined?

Yes

12. Have you provided a list of names and e-mail addresses for at least three suggested **international** (at least two countries) peer reviewers? ALSO include a short rationale for the suggested reviewer choice.

Yes

13. Does your use of abbreviations conform to the following guidelines given in the Editorial in CARBON 44/5?

1. To define an abbreviation, first write the term in full followed by the abbreviation in parentheses. "X-ray diffraction (XRD) examination showed that the samples were" Do not do the reverse.
2. Never use or define an abbreviation in the manuscript title.
3. Never use abbreviations in the Abstract without defining them, and only define them if they are used later **in the Abstract**.
4. Define an abbreviation the first time it is used in the text, even though it may also have been necessary to define it in the Abstract.
5. Only define an abbreviation if you are going to use it later.

14. If this is a resubmission as a result of comments from the Editor-in-Chief, have you included replies to these comments in your cover letter?