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**Preparation of Nanoscale Multi-walled
Carbon Nanotube Dispersions in a
Polyetheramine Epoxy for Eco-
Toxicological Assessment**

Version 1.0

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Chelsea S. Davis
Jeremiah W. Woodcock
Jeffrey W. Gilman
*Materials Science and Engineering Division
Material Measurement Laboratory*

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Penny Pritzker, Secretary

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Willie E. May, Under Secretary of Commerce for Standards and Technology and Director

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Foreword

This special publication is one in a series stemming from the National Nanotechnology Initiative (NNI) Nano-Environmental Health and Safety (Nano-EH&S) Research Strategy. The NNI has identified Nanomaterial Measurement Infrastructure as one of the essential areas of research needed to develop an effective risk assessment and management plan regarding various aspects of nanotechnology in consumer products pertaining to human health, exposure and the environment. The National Institute of Standards and Technology (NIST) was identified as a lead agency in the development of measurement strategies for the detection and characterization of nanomaterials within commercial products. Carbon nanotubes in commercial products, the focus for this special publication series, were one of the nanomaterials identified in the Nano-EH&S research strategy.

The current guideline presents a strategy for preparing nanocomposites comprised of multi-walled carbon nanotubes (MWCNT) embedded in an epoxy matrix. Sample preparation and techniques allowing for good dispersion of the MWCNT in a polyetheramine thermoset resin are presented. Updates to this protocol may be released in the future. Visit <http://nist.gov/mml/np-measurement-protocols.cfm> to check for revisions of this protocol, or new protocols in the series. We also encourage users to report citations to published work in which this protocol has been applied.

1 Introduction

Carbon nanotubes (CNT) are a widely studied nanomaterial due to their unique electrical, thermal, and mechanical properties which can be transferred to commercially-relevant products.¹⁻⁴ As a result, several industries have made significant efforts to incorporate CNT into a variety of commercial products, largely consisting of nanocomposite materials for personal protective apparel and sporting equipment applications.⁵⁻⁷ Detection of CNT within commercial products, however, can be quite challenging due to the large amount of processing variables including CNT concentration, composition of the matrix material, and the identity of other additives that are typically deemed proprietary by the manufacturer. Researchers at the National Institute of Standards and Technology (NIST) have worked to characterize technologically relevant, representative multi-walled carbon nanotube (MWCNT)/epoxy composites comparable to those used industrially in an effort to develop characterization strategies which may be applied to CNT-containing commercial products in future Nano-Environmental Health and Safety (Nano-EH&S) studies. Since the vast majority of commercially available CNT products contain multi-walled carbon nanotubes, this document focuses on the fabrication of MWCNT-based materials. The procedure described here is representative of methods that can be employed to disperse and form nanocomposite structures but is not definitive and should be considered as a starting point for developing processing conditions suited to one's individual CNT composite manufacturing needs.

2 Principles and scope

The primary goals of this NIST Special Publication Series are to outline methods and procedures that should be employed for the preparation of typical CNT-containing nanocomposites and characterization of CNT content and subsequent CNT release from these nanocomposite materials. Before detailed measurement and analysis of MWCNT composite systems can be accomplished, an industrially relevant sample preparation process must be developed to allow reproducible production of well-dispersed MWCNT composites. The purpose of this special publication is to identify methods and techniques appropriate for the preparation of such MWCNT composite samples. Characterization of samples prepared according to the procedures outlined here can be found in other NIST Special Publications. The techniques employed herein are commonly utilized in industry and the technical details such as instrument power, velocity, processing time, etc. must be adjusted depending on the materials and desired properties.

3 Terminology

Carbon Nanotube
Composite
Crosslinking
Curing
Dispersion
Epoxy
Filler
Matrix
Multi-Walled CNT
Nanocomposite
Sonic Probe
Speed Mixer

4 Materials and equipment

4.1 Starting materials/samples

As stated in Section 3, our primary goal was to create well-dispersed CNT composites from industrially relevant starting materials. For this reason, we selected commercially available CNTs, epoxide monomers and commonly employed polyetheramine crosslinkers. Testing the abrasion and release properties of the composite samples prepared here yields a measurement representative of industrially produced materials.

4.1.1 Filler/Nanoreinforcement

Multi-walled carbon nanotubes (MWCNT, Arkema Graphistrength® C100 (R&D) Batch 110314, Lot 005, King of Prussia, PA, nanoparticle) – The MWCNT used in this procedure contained approximately 12 mass% metal catalysts and were used as received. Arkema is one of the major producers of MWCNT on an industrial scale so these particular MWCNT are representative of commercially available CNT composites.

4.1.2 Monomer

Diglycidyl ether bisphenol A (DGEBA, Sigma D.E.R.TM 332 Epoxy Resin, Sigma Life Science, St. Louis, MO, monomer) – DGEBA is a commonly used monomer in crosslinked epoxy systems^{8,9} and a commercial-grade material was chosen instead of a lab quality monomer in keeping with the goal of using “real world” materials.

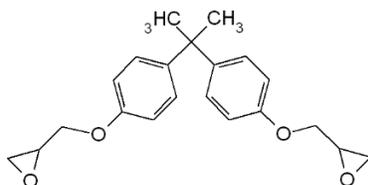


Figure 1: Chemical structure of DGEBA

4.1.3 Hardener/Curing Agent

Polyetheramine (Huntsman JEFFAMINE D-230 and D-2000, The Woodlands, TX, curing agent) – These two polyetheramines contain two amine end groups (both ends treated as two reaction sites each) and repeat units of oxypropylenediamine. The numbers 230 and 2000 refer to the approximate relative molecular masses of each Jeffamine, respectively. A small amount (10 mass%, details in Section 6.1.1 and Section 7) of D-2000 was added to the formulation to serve as a compatibilizer. D-2000 has a higher affinity for CNT than D-230 and was found to be an effective dispersing agent.

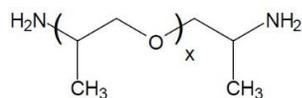


Figure 2: Chemical structure of polyetheramine where $x \approx 2.5$ for D-230 and $x \approx 33$ for D-2000.

4.2 Sample preparation equipment

In an effort to develop well-dispersed samples, several proven CNT dispersal and mixing techniques were applied. Thostensen et al. have reviewed the various processing methods that have been studied for MWCNT with polymers.^{10,11} To minimize contamination of the samples from the mixing equipment, a specialized mixer which was comprised of a rotating drum spinning counter to a sealed sample container was employed. The result was a mixture that did not have any visible clumps or aggregates. Upon closer examination, the sample morphology was found to consist of some individually dispersed tubes as well as CNT-rich domains with a rough domain size of approximately 1 μm to 2 μm (see Figure 6).

4.2.1 Probe Sonication

This technique employs a piezo-driven probe actuated at high frequencies (Cole Palmer, Ultrasonic Processor GE 50, 20 kHz, 750 W). The probe has a diameter of 6.4 mm and moves vertically (extending and contracting) within the liquid sample (see Figure 3). Upon each contraction of the probe, tiny cavities are formed in the CNT/liquid epoxy mixture, which serve to separate large aggregates and further disperse the CNT within the epoxy matrix. This technique is commonly used in the incorporation of CNT into liquid samples.^{9,12-15} An important drawback or concern associated with the sonic probe technique is the extremely high energy imparted to the sample locally (directly at the probe tip). This high energy can result in high temperatures that could potentially damage the sample and melt a plastic mixing vessel (such as the polypropylene cups used in the SpeedMixer, Section 5.2.2). To mediate the high temperatures, the mixing vessel is placed in an ice bath and cycles of 5 min sonication followed by 5 min rest are applied to allow the sample to cool between sonication steps. Another more technical concern is the known phenomenon of CNT damage and scission that can occur from sonication.^{16,17} Limiting the amount of total sonication time and thus the overall energy imparted to the sample can help mediate CNT damage caused by this method.¹⁸



Figure 3: Representative image of probe sonicator.¹⁹

4.2.2 High Shear Mixing

This technique employs a specialized mixer (shown in Figure 4) that has a rotating drum spinning counter to a sealed sample container (FlackTek, Inc., SpeedMixer DAC 150 SP, Landrum, SC). By combining two concentric but oppositely spinning directions in the same device, very high shear can be imparted to small amounts of liquid. The SpeedMixer utilizes disposable polypropylene mixing containers with screw cap lids that comprise a completely closed, contamination-free system during mixing. The level of shear imparted to each sample is controlled by solution viscosity, outer drum rotational velocity and cup diameter. The SpeedMixer is employed here to fully incorporate all sample components and further enhance CNT dispersion within each sample.^{14,20–22}



Figure 4: High shear mixer: whole device (left) and closeup view of cup holder and mixing chamber (right).²³

4.2.3 Elevated Temperature Curing

A vacuum oven (Fisher Scientific Isotemp Model 281A) allows temperature control in a reduced pressure environment. This device was employed to remove excess air that was incorporated into the sample during sonication and mixing. Due to the large amount of surface area of CNT, a relatively high volume of air can be trapped through surface energetics. During curing, this gas can be released and form undesirable air bubbles which result in permanent spherical voids within the fully cured samples. We determined that a degassing step prior to pouring and curing appeared to significantly decrease the formation of bubbles.

4.2.4 Molding

To impart and maintain a consistent sample geometry, molds of crosslinked silicone (Mold Star Fast 30) were used to form square CNT/epoxy specimens. Silicone molds measuring 18 mm x 18 mm x 0.1 mm were prepared. The product used to form the molds is a fast curing, two-part silicone kit, which solidifies in 30 min at room temperature ($T \approx 20$ °C). The molds themselves were approximately 90 mm x 90 mm x 10 mm thick and had negative cavities for nine CNT composite samples each.

4.3 Sample Imaging

4.3.1 Preparation for imaging

To determine the microstructure of the CNT/epoxy samples discussed here, thin slices of material were carefully prepared. A microtome (Leica Ultracut UC-7) equipped with a diamond knife (Diatome Histo 45°) was used to section 500 μm x 500 μm x 0.1 μm films. The films floated directly from the blade onto the surface of a water bath located behind the knife. Sections were then picked up from the water bath with a loop tool (Perfect Loop, Ted Pella) and transferred onto a freshly cleaved highly oriented pyrolytic graphene substrate (HOPG, Ted Pella) to ensure a conductive pathway to ground for scanning lithium ion microscopy. Additional films were transferred onto copper grids for transmission electron microscopy.

4.3.2 Scanning Lithium Ion Microscopy

Images of the highest and lowest CNT concentration samples (1.00 mass% and 0.01 mass%, fabricated as described in Section 7 below) were obtained using a scanning lithium ion microscope developed at NIST.²⁴ The technique uses variations in conductivity for contrast, which allows CNT to be distinguished from the surrounding epoxy matrix material. For additional details on the lithium ion microscope, the reader is referred to Twedt et al.²⁴

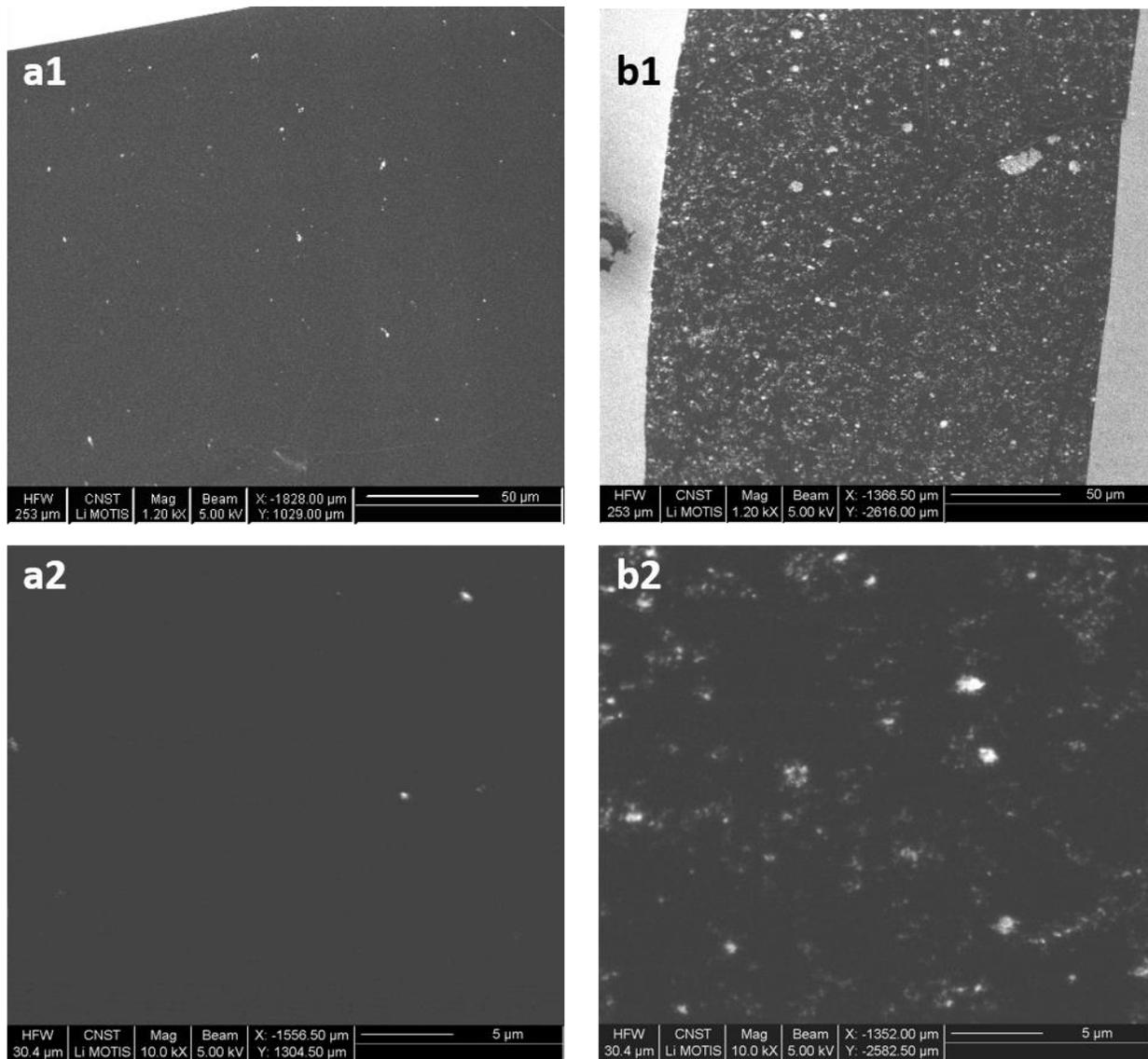


Figure 5: Scanning lithium ion micrographs of CNT composite samples at CNT concentrations of 0.01 mass% (a1-a2) and 1.00 mass% (b1-b2). White regions are CNT-rich domains while the dark regions are the epoxy.

4.3.3 Transmission Electron Microscopy

Images of the highest and lowest CNT concentration samples (1.00 mass% and 0.01 mass%, fabricated as described in Section 7 below) were also obtained using a transmission electron microscope (TEM, FEI Titan 80-300). The technique is commonly utilized to observe nanoscale morphological details of nanocomposite materials. For additional details on TEM of dispersed CNT systems, the reader is referred to several articles and reviews for a more comprehensive treatment of this technique.²⁵⁻²⁸

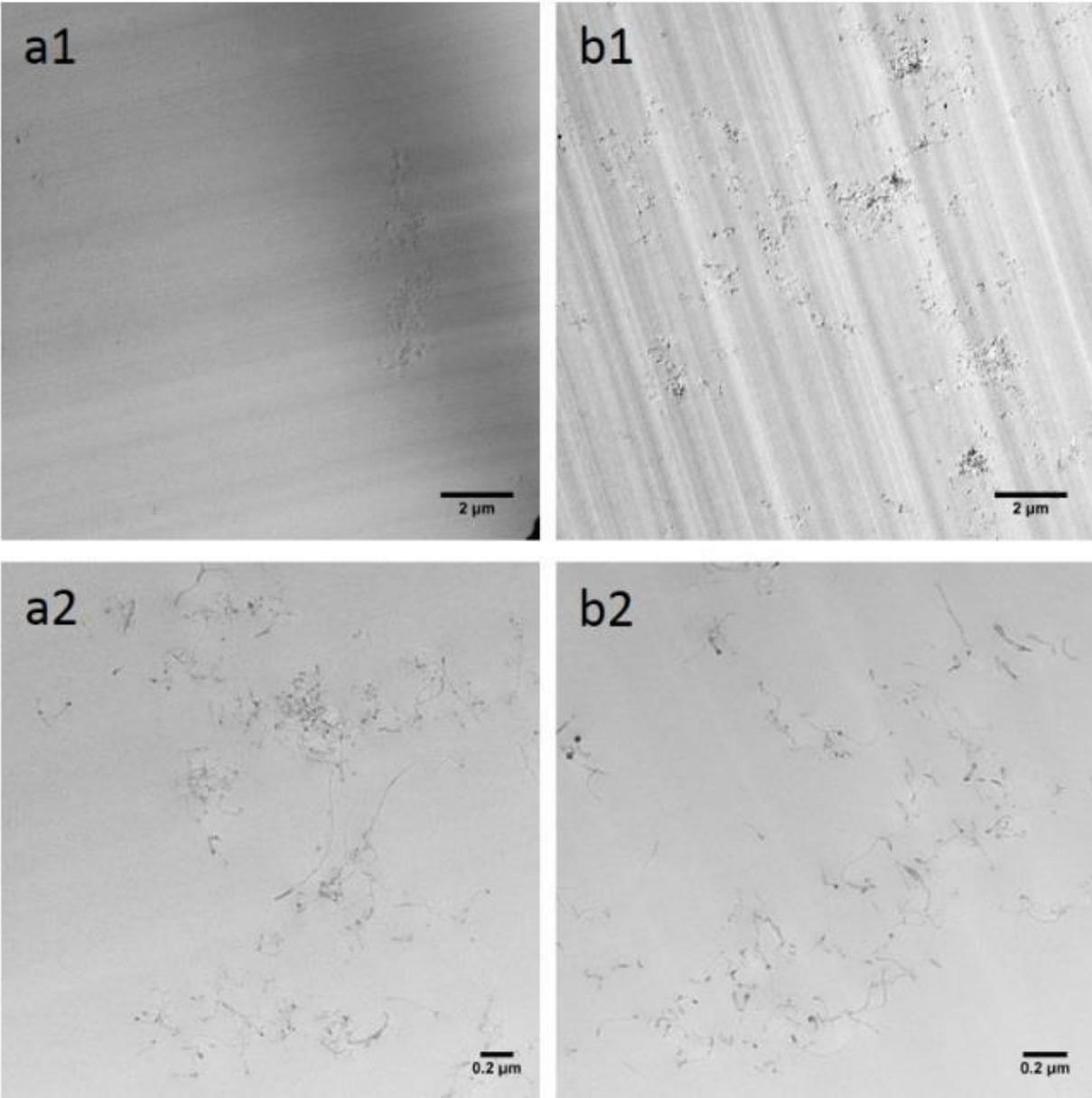


Figure 6: Transmission electron micrographs of MWCNT composite samples of 0.05 mass% (a1-a2) and 1.00 mass% (b1-b2) CNT concentrations. Dark lines or particles are MWCNTs while the light regions are the epoxy. The striations visible in the low magnification images are attributed to imperfections on the diamond knife blade used for sample preparation.

5 Challenges, considerations, solutions and/or opportunities for preparation of well-dispersed MWCNT composites

5.1 Sample dispersion challenges: Solutions, considerations and opportunities

5.1.1 Achieving good dispersion of CNT in liquid epoxy matrix

CNT are not naturally very miscible in polyetheramine. Therefore, care must be taken in materials selection and processing to ensure that a good dispersion and a stable suspension of CNT nanoparticles is achieved. To this end, a small amount of a co-curing agent (JA D-2000) was incorporated into the suspension. The D-2000 has a higher affinity for CNT and increased the stability of the suspension. Also, a mixture of the curing agent and CNT was prepared and thoroughly sonicated with the probe sonicator prior to addition of the DGEBA monomer. When CNT mixtures were prepared in one-step (CNT/DGEBA/JA) or alternatively by adding MWCNT to the DGEBA first (CNT/DGEBA, then JA), the dispersion and stability of the suspension was visibly poorer. The use of a two-step mixing process (first with a sonic probe and then with the high shear mixer) with serial additions (CNT/JA, then DGEBA) was found to be an effective method for achieving well-dispersed CNT/epoxy samples.

5.1.2 Reducing the CNT length and/or introducing surface defects to the CNT

The use of probe sonication is known to damage CNT by both decreasing their length through mechanical fracture and introducing surface defects as a result of the high energy applied to the CNT near the probe tip.¹⁶⁻¹⁸ Depending on the final application of the CNT nanocomposite being prepared, consideration of the amount of damage acceptable might preclude the use of probe sonication. A bath sonicator may be a suitable, lower energy substitute to probe sonication but might prove less effective in dislodging large aggregates of CNT, particularly in larger volume samples.

5.2 Sample defects introduced during curing: Solutions, considerations and opportunities

5.2.1 Sample planarity

Through the CNT dispersion methods discussed above, well-dispersed, highly viscous suspensions were produced. This high viscosity made pouring and curing nanocomposite samples in molds extremely difficult. Some of the suspensions (particularly those loaded at 1 mass% CNT) had the consistency of a thixotropic material such as ketchup, which led to wavy, uneven sample surfaces. For most of the tests and protocols discussed in this NIST Special Publication 1200 series, the planarity of each sample is paramount. A potential solution for this difficult to spread mixture is the use of a Myer or draw-down bar rather than poured mold samples.

Although the low concentration samples (<0.3 mass% CNT) had a lower viscosity, sample planarity was still difficult to achieve due to surface tension effects. The use of a silicone mold allowed for easy release of the samples after curing but introduced the unforeseen complication of dewetting of the uncured CNT/epoxy mixture. To overcome dewetting of the material from the edges of each mold, the cavities in the silicone were overfilled and surface tension prevented the liquid from overflowing the mold. The resulting samples, once cured, had a curved surface profile.

Through grinding and milling after curing, the samples could be machined to be planar but the native nanocomposite-air surface was lost through this process.

5.2.2 Air bubbles/excess gas in mixture

In any molding process where a liquid is cast and then cured into a solid, there is a concern that bubbles will form and be trapped in the solid sample. In CNT/epoxy systems, the large amount of free volume surrounding the dry nanoparticles prior to addition into the liquid epoxy and the gas incorporated by the mixing process itself exacerbate this concern. The most obvious and straightforward solution to avoid the formation of macroscopic bubbles upon curing is to thoroughly degas the final mixture prior to casting into the mold. This is achieved by placing the mixture in an open or loosely covered container in a vacuum chamber or oven. Additionally, when pouring, care should be taken to avoid the introduction of bubbles.

Other processes and techniques commonly utilized to avoid bubble formation during curing are to degas the silicone mold prior to casting the liquid epoxy mixture or, alternatively, to place the filled mold under pressure during curing.

5.2.3 Reaggregation and settling of CNT during curing

After so much care is taken to achieve an effective dispersion of CNT within the liquid epoxy mixture, reaggregation may be an undesirable but often unavoidable phenomenon. Empirical experimentation with curing times and temperatures is often the best approach to determine the conditions, which allow the highest degree of dispersion to be maintained. Epoxy formulations that rapidly cure will reach a high viscosity and prevent reaggregation of the CNT. However, if the epoxy cures too quickly, the working time is greatly reduced and degassing and casting into molds might become difficult.

Settling of the CNT by Brownian motion, thermal fluctuations and/or gravity is another common problem observed in CNT/epoxy nanocomposites. In thick samples, a CNT concentration gradient through the sample thickness can lead to high variability in the local electrical, mechanical and nanoparticle release properties of each sample. Also, an unfilled epoxy “skin” layer tends to form on the upper surface due to settling.²⁹ This skin layer complicates any surface characterization measurements and must be either removed (mechanically, thermally, or otherwise) or accounted for in subsequent measurements.

6 Example of experimental protocol

To prepare a nanocomposite comprised of multi-walled carbon nanotubes (MWCNT) and polyetheramine epoxy at various loadings, the following procedure was implemented. First, a stock dispersion of MWCNT (1 mass% MWCNT) in a curing agent mixture containing two polyetheramines (Huntsman Jeffamines D-230 and D-2000) was prepared. To enhance epoxy toughness, a mixture of 10 mass% D-2000 (2.042 g, 1.02 mmol) with 90 mass% D-230 (18.075 g, 78.60 mmol) was placed in a flat bottom, cylindrical polypropylene jar with a tight-fitting screw cap lid (max capacity 100 g or 500 mL, diameter 7 cm).

The MWCNT (Graphistrength C100 (R&D), Batch 110314, Lot 005) used here were obtained as a black powder from Arkema (King of Prussia, PA). The MWCNT were used as received and had

a nominal catalyst content of ≤ 12 mass% (aluminum oxide ≤ 7 mass% and iron oxide ≤ 5 mass%). The powdered material was stored in an opaque polypropylene container at room temperature until used.

MWCNT were added to the Jeffamine mixture (0.7346 g) to achieve a 1 mass% concentration in the final epoxy formulation. The Jeffamine/MWCNT mixture was placed in a SpeedMixer jar and mixed in the SpeedMixer at 365 rad/s for 5 min to achieve an initial coarse dispersion of the MWCNT in the polyetheramine mixture. The cup containing the mixture was then placed in an ice bath and the dispersion was further mixed with a sonic probe (Ultrasonic Processor GE-50, Cole-Palmer) for six cycles of 5 min sonication, 5 min rest to prevent overheating (30 min total sonication). The sonicator was fitted with a flat tip, 6.4 mm diameter probe and had a maximum power output of 750 W at an operating frequency of 20 kHz.

Bisphenol A diglycidyl ether (DGEBA, D.E.R.TM 332, Sigma Life Science, St. Louis, MO) was then added to the sonicated dispersion in the jar (5.504 g, 16.20 mmol) to attain a fully crosslinked epoxy network upon completion of curing. The lid was screwed tightly onto the jar and the sealed container was placed in a mixing system (FlackTek, Inc. SpeedMixerTM DAC 150 SP, Landrum, SC) at 365 rad/s for 20 min. Following mixing, the cap was removed and the dispersion was degassed in a vacuum oven (Fisher Scientific Isotemp Model 281A) at 80 °C for 10 min.

The degassed MWCNT/epoxy dispersion was poured slowly into a silicone mold with care being taken to ensure that no gas bubbles were introduced and that the mold was placed on a level surface. The epoxy was allowed to cure in the mold for 48 h at 80 °C.

7 Abbreviations

CNT	Carbon nanotube
D	Diameter
DGEBA	Diglycidyl ether of bisphenol A
JA	Jeffamine
L	Length
MWCNT	Multi-walled carbon nanotube
mass%	Mass percent
TEM	Transmission electron microscope/microscopy

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