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Multiscale 3D dispersion characterization of carbon nanotubefilled polymer composites using microscopic imaging and data mining

Hessam Yazdani¹, Benjamin E. Smith² and Kianoosh Hatami³

¹School of Civil Engineering and Environmental Science, The University of Oklahoma, 202 W Boyd St, Room 329, Norman, OK 73019, USA

²Samuel Roberts Noble Microscopy Laboratory, The University of Oklahoma, 770 Van Vleet Oval, 214 NML, Norman, OK 73019, USA

³School of Civil Engineering and Environmental Science, The University of Oklahoma, 202 W Boyd St, Room 450B, Norman, OK 73019, USA

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Introduction

Dispersing a sufficient quantity of fillers such as carbon nanotubes (CNTs), carbon blacks (CBs) and metal nanopowders within a polymer matrix results in a composite that typically offers improved properties compared to the host polymer in pristine form. The extent of this improvement, however, depends not only on the concentration of the filler but also on the quality of its dispersion. The term dispersion generally refers to the nearly-uniform distribution of individual fillers in a matrix. However, this definition needs to be adjusted for CNTs that possess an inherent thermodynamic drive to create physical entanglement with neighboring tubules, which form aggregated morphologies, called bundles. Each bundle contains hundreds of tightly-packed CNTs, which are bound to each other by van der Waals attraction energies of approximately 500 eV/ μ m per CNT-CNT contact (Thess et al. 1996; Girifalco et al. 2000). This entanglement tendency is especially strong due to the generally high aspect ratio and flexibility of CNTs (Lourie et al. 1998). Therefore, a dispersion state described as "uniform" or "good" for CNT individuals in the bundle scale might be a misleading or inaccurate description for their dispersion state in micro- or macroscale systems, where CNTs are typically found in the form of bundles and agglomerates. In this regard, distinction is made between nanoscopic dispersion, which refers to the disentanglement of CNT bundles/agglomerates, and micro- and macroscopic dispersion, which refers to the distribution of individual CNTs and more likely their bundles or agglomerates throughout the composites (Li et al. 2007).

Overview of microscopy techniques to assess dispersion quality

There have been various recent advances in the synthesis of stable and homogeneous dispersion of CNTs in polymers (e.g. Ma et al. 2010). Since CNT agglomerates within a composite generally serve as zones of stress concentration, the quality of their dispersion could be linked to the magnitude of adverse effects observed in the mechanical properties (especially the strength) of the resulting composites (Hilding et al. 2003; Liu and Wagner 2005). However, there are currently limited imaging techniques to help quantify the dispersion state of CNTs on different length scales. Nevertheless, nanoscopic and microscopic visualization techniques could help to gain a deeper and more direct insight into the quality of filler dispersion in polymer composites.

Different imaging techniques such as atomic force microscopy (AFM), scanning probe microscopy (SPM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and bright-field microscopy (BF) have been used to visualize inclusions from micrometer-sized agglomerates to nanoscale, suspended CNTs (Islam et al. 2003). However, these techniques have different advantages and drawbacks as described below.

The AFM, SPM and SEM techniques are primarily suitable for observations near the surface of a composite sample or a cross-section that contains the CNT network (Li and Bauhofer 2014). Many studies have involved the use of a particular SEM mode known as charge-contrast imaging in order to examine the morphology of the filler network in conductive nanocomposites (Campbell et al. 1983; Croitoru et al. 2005; Loos et al. 2005; Kovacs et al. 2007; Lillehei et al. 2009; Zhao et al. 2015). Compared to the conventional SEM, the charge-contrast imaging mode enables a deeper penetration of highly-energetic electrons into the sample, yielding more information about the structure of its 3D filler network. However, this subsurface information is localized (e.g. on the scale of a few nanotubes at a time) and limited to shallow depths (a few hundred nm), and therefore, cannot reliably represent the quality of CNT dispersion in the entire sample. Also, the compositional similarity between polymers (carbon as the constituent element) and CNTs (carbon

as the only element) reduces the contrast between the CNT and the polymer matrix, particularly at relatively high CNT concentrations (Li et al. 2011; Li and Bauhofer 2014). Furthermore, insulating materials (e.g. PVC in the study described here) when subjected to sufficiently high-voltage electrons accumulate electrical charge. As a result, it would be difficult to produce a threshold contrast at high voltages and therefore, the conductive filler cannot be readily distinguished from the imagery background noise and the insulating matrix.

Other techniques such as TEM and BF lack positional information (e.g. interferometry and percolation), or require destructive sectioning of the material (Loos et al. 2005). To circumvent these shortcomings, laser diffractometry has been used as an alternative (and effective) technique to characterize dispersion. However, this method does not provide information on positional distributions. Particle-sizing methods, such as laser diffractometry are based on the assumption that the filler particles are primarily spherical in shape (e.g. Ma et al. 2000). Therefore, these methods have been shown to be inaccurate in determining the size of extremely non-spherical particles such as CNTs in suspension form before they are embedded in a polymer matrix (Ivakhnenko and Eremin 2006).

Optical microscopy has also been used to visualize individual CNTs (Huang et al. 2008; Zhang et al. 2013; Novak et al. 2014). However, observation of CNTs in these studies has been limited to those deposited on a substrate. It was only until recently that the current authors reported a successful visualization of CNTs that were deeply embedded in a composite using laser scanning confocal microscopy (LSCM – Smith et al. 2015). The technique used by the authors, which is briefly described in Section in this chapter, is unprecedented with respect to its capability to provide a substantial amount of subsurface information on a composite sample. However, the limit of the voxel resolution of LSCM images (1 μm^3) does not allow the precise measurement of small CNT bundles.

The above discussion indicates that none of the conventional imaging techniques available to date is capable of characterizing filler dispersion in all instances and for all desired length scales. Therefore, a combination of different imaging techniques, each operating on a particular length scale, should be used for the multiscale visualization and dispersion assessment of fillers in composites.

Influence of filler dispersion on the properties of polymer nanocomposites

The electrical properties are particularly important in polymer composites, which when accompanied by other desirable characteristics (e.g. flexibility, affordability and resistance to corrosion), make the composites technologically and economically attractive in a wide range of applications. Example applications of conductive polymer composites include electromagnetic interference (EMI) shielding (i.e. the ability to block electromagnetic radiation, particularly in the radio frequency régime – Luo and Chung 1999; Geetha et al. 2009), structural self-sensing (the ability of a structural material to sense its own condition – Yazdani et al. 2014, 2015a), drug delivery systems, biomedical implants and tissue engineering (Kaur et al. 2015).

The conductivity of polymer composites stems from the formation of a continuous, interconnecting network of a conducting agent in a host polymer. The minimum concentration of the agent required to form such a network is termed the percolation threshold, beyond which an abrupt insulator-to-(quasi)conductor transition in the conductivity behavior of the composite is observed (Yazdani et al. 2014). A continuous, interconnecting network does not imply that all conducting particles are necessarily in physical contact with one another. Rather, due to quantum tunneling, electrons can "hop" between the particles within a few tens of nanometers (Kilbride et al. 2002;

Kymakis and Amaratunga 2006). The percolation threshold of nanocomposites is influenced by several factors such as the filler type and its physical properties (e.g. chirality of nanotubes – Bai and Allaoui 2003; Bryning et al. 2005), the polarity of the polymer (Zhang et al. 2007), and the processing method and conditions (Barrau et al. 2003; Du et al. 2003, 2005). Interested readers are referred to a detailed review by Bauhofer and Kovacs (2009) for the percolation threshold and electrical conductivity of CNT-filled polymer composites.

As previously stated, CNTs have a tendency to self-assemble into bundles. Bundling can reduce the percolation threshold, as higher-percolation-threshold fillers can have significantly better dispersion than lower-percolation-threshold fillers (Grady 2011). However, bundling does not necessarily lead to improved mechanical properties. Bundles and large aggregates can also function as stress concentration zones within a composite, and consequently reduce the strength of the material (Song and Youn 2005; Blond et al. 2006).

Achieving a desired level of CNT bundling in a blend requires an optimum input of shear energy to overcome the intra- and inter-bundle van der Waals forces. The term optimum refers to the shear energy that is primarily used to disentangle bundles to a certain pre-defined level. Effort exceeding this level will break up the CNT particles and aggregates, reducing their size distribution. It should be noted that a truly random distribution and orientation of CNTs is not generally anticipated because stronger van der Waals interactions between aligned CNTs result in their further alignment and a lower thermodynamic free energy level in the CNT network. Therefore, the orientation of CNTs is rather skewed toward aligned (as opposed to randomly dispersed) CNTs (Grujicic et al. 2004).

From the above discussion, it can be concluded that identification of efficient dispersion techniques and characterization of their corresponding dispersion quality are essential (albeit challenging) steps in the design of CNT-polymer composites. In this chapter, we discuss a novel and practical technique for the multiscale 3D characterization of the dispersion and distribution of inclusions (i.e. fillers) and their aggregates in autofluorescent materials using a combination of LSCM, SEM and TEM. Dispersion characteristics of specimens prepared using different mixing methods are quantitated and correlated with the electrical conductivity of the corresponding specimens. Details of sample preparation, conductivity and mechanical tests, and the imaging technique used in a recent study to evaluate the quality of CNT dispersion in the composite samples are described in the following sections. This method can also be expanded to non-autofluorescent materials by integrating a trace amount of fluorescent dye into the host polymer.

Experimental program

Materials

Polyvinyl chloride (PVC) plastisol in liquid form (denoted here as PL) with a density of $\rho_p = 1.37$ g/cm³ was used as the polymer matrix for the composites investigated in the authors' recent study. Multi-walled carbon nanotubes (MWCNT), with the properties given in Table 6.1, were used as the filler. The density of the MWCNT filler was assumed to be the same as that for pure graphite (i.e. $\rho_f = 2.045$ g/cm³). An auxiliary plasticizer (bis(2-ethylhexyl) phthalate; denoted here as PR) with a density of $\rho_p = 0.985$ g/cm³ was used to lower the melt viscosity of the composite.

Properties of the MWCNT used in the authors' recent study (as measured, or as provided by the supplier)

Outerdiameter (nm)	Length (µm)	Aspect ratio	Carbon purity (%)	D/G ratio from Raman ⁽¹⁾	BET area ⁽²⁾ (m ² /g)	surface	Density $ ho_{ m f}(m g/cm^3)$
7.8	74	95	> 98	1.52	250		2.045

² a measure for the purity and defects of a CNT. It is inversely proportional to the quality of a CNT.

⁽²⁾ Nitrogen Adsorption Surface Area measured using the BET Theory (Brunauer et al. 1938 – ASTM D-6556; micropores included).

Specimen fabrication

Specimens were made in three stages. First, the MWCNTs were dispersed into the plasticizer using a mixing method (described later) to form a blend termed here as pigment. The resulting pigment was then manually blended with plastisol for 5 minutes to make a visually-homogenous composite in liquid form. Finally, the composite was compression-molded to form specimens for conductivity and imaging experiments.

Following ASTM D5225, a series of viscosity tests was carried out on mixtures with different mixing ratios of the composite's ingredients (i.e. PL, PR and MWCNT) in order to obtain a PR/MWCNT ratio that would result in a pigment blend with a viscosity in the range of 3 - 10 Pa•s. Prior experience had indicated that this range of viscosity would result in a processable blend, yet with a minimum concentration of plasticizer that would not compromise the mechanical properties of the final composite (Hatami et al. 2014). MWCNT concentration was kept constant at 0.5 wt.% in all tests while a range of PR/MWCNT ratios was tested to obtain a desirable viscosity for the blend. A PR/MWCNT ratio of 24 was found to result in a composite with the target viscosity.

Mixing techniques

As previously stated, dispersion of filler particles in a host polymer is a central step in the production of conductive polymer composites with a desired level of accuracy and consistency in their electrical and mechanical performance. Chemical methods (covalent treatment) and physical methods (non-covalent treatment) are the approaches generally used to disperse CNTs in polymer matrices (Ma et al. 2010). Chemical methods use surface functionalization or surfactants (third component) to improve the wetting or adhesion characteristics of the CNTs, thus reducing their tendency to agglomerate. In contrast, physical methods utilize mechanical energy to separate CNT agglomerates and bundles. Both physical and chemical methods can alter the aspect ratio and statistical distribution of the nanotubes, changing the properties of their host composite. Specimens in the recent study described here were prepared using four different physical mixing methods, as described in the following sections.

Bath sonication (BS)

BS methods use ultrasonic energy to disperse particles in a blend (Yamamoto et al. 2008). In BS, an ultrasonic vibration propagated through water is transmitted across the walls of the blend container, uniformly affecting the entire blend. In the authors' recent study, first 2.4 g of MWCNT

was manually mixed with 57.6 g of the auxiliary plasticizer (PR/MWCNT = 24) in a beaker to make 60 g of visually-uniform pigment blend. The blend was then sonicated in an ultrasonication bath. The sonicator power was set at 70 W for 60, 120 and 240 minutes in order to investigate the influence of combinations of sonication power and duration on dispersion characteristics.

Probe sonication (PS)

A probe sonicator (also known as sonic dismembrator) fractures and disperses solids primarily through a sequence of bubble nucleations and collapses. High-voltage pulses of energy generated by an ultrasonic electronic generator are transformed to mechanical vibrations which are then transmitted to a probe. Rapid oscillation of the probe's tip in turn produces a conical field of high energy where the formation, growth and implosion of bubbles, collectively referred to as acoustic cavitation, take place. The significant amount of energy released in the cavitation zone due to the implosion of bubbles results in the fragmentation and dispersion of particles in a blend. Compared to a bath sonicator, a probe sonicator has a more identifiable cavitation zone and produces localized heat and energy, posing a major problem to ultrasonic agitation, especially for temperature-sensitive samples. Hence, it is recommended that the probe be operated in pulse mode in order to reduce the heat gain in the sample by repeatedly allowing it to resettle after each burst.

In the study described here, 60 grams of the manually-mixed pigment blend was poured into a 100ml beaker. Subsequently, the pigment was sonicated at 55 W for 30, 60 and 90 minutes at 50% pulse mode (i.e. total durations of 60, 120 and 180 minutes) to produce the final pigment blend.

Batch mixing (BM)

BM (also known as batch high shear mixing) is commonly used in process industries for solid-liquid dispersion, dissolving, and grinding as well as liquid-liquid homogenization, dispersion and emulsification. In the study described here, a batch mixer comprising of a bowl-shaped, closed chamber with a maximum volume of 300 ml and two up-mounted, corkscrew-patterned, eccentric fins was used to disperse the MWCNT into the plasticizer. In a batch mixer, the disentanglement of CNT bundles and fragmentation of CNT individuals concurrently take place due to the flow with high velocity gradients and turbulence formed in the small gap (here ~10 mm) between the surrounding, stationary chamber and the rotary fins. The controllable heat applied through the oil circulating through the body of the chamber decreases the viscosity of the blend. In the study described here, 60 grams of the manually-mixed pigment blend was poured into the chamber. Then, the mixer was run at a rotational speed of 150 rpm and two different temperatures of 65 and 100 °C for 10 and 20 minutes.

Mechanical stirring (MS)

A mechanical stirrer was used to mix 60 g of the pigment blend at room temperature. The mechanical stirrer had a propeller with three pitched blades inclined at 26.5° from horizontal and a 5-cm-diameter swept area. Three different rotational speeds of 750, 1500 and 3000 rpm were used for 3 minutes. The stirring duration of 3 minutes was selected as CNT agglomeration was observed in the blends mixed for more than 3 minutes, regardless of the rotational speed employed.

Molding of samples

Once the mixing of the coating was complete, the blended material was compression-molded at 1 MPa and 180 °C for 15 minutes to fabricate approximately 0.8-mm-thick specimens for the conductivity and tensile tests, and microscopy experiments.

Dispersion assessment

As mentioned earlier, bundling could impact the mechanical and electrical properties of CNT-filled composites. Therefore, these properties could be used as indirect indicators together with nanoscopic and microscopic visualization techniques to gain a more complete insight into the quality of inclusion dispersion in polymer composites. Further details on the conductivity measurements, mechanical tests and visualization techniques used are provided in the following sections.

Conductivity measurements

Information germane to the specimens that were prepared for conductivity tests is given in Table 6.2. For each formulation listed in the table, three nominally-identical specimens were tested to improve the reliability of the test results. The specimen thickness, which was required for the calculation of resistivity, was measured with a precision of 0.01 mm at the central point and three points 120° apart on the specimen periphery, and the mean value was reported as the thickness. A direct current (DC) high-resistance meter (Agilent Model 4339B), operating based on the two-point probe method (Schroder 2006), was used to measure the volume conductivity of the specimens in accordance with ASTM D4496. When working with the device, one would need to find a proper contact load that is adequately large to provide a robust contact between the electrodes and a specimen, and yet small enough to prevent damage to the specimen. In the study described here, a contact force of 50 N was found suitable for the conductivity tests. All measurements were carried out using an electrification time of 60 s in order to establish a steady-state current in the specimens, as recommended in the instrument's manual. The electric potential difference on the specimens was kept below 10 V to protect them from overheating.

It is worth noting that the two-point probe method was preferred over the four-point probe method because none of the recommended types of electrodes in the four-point probe method in the ASTM D4496–13 standard was found practical for the composites tested in the study described here. According to this standard, either a conductive connection or a large contact force between the electrodes and the specimen is required in the four-point probe method. For the composites studied, it was practically impossible to apply the contact force required (which is a function of the specimens' width) to the specimens without damaging them or (at a minimum) changing their thickness significantly. Nevertheless, the prospects of the four-point method were explored. Silver epoxy adhesive was used to affix four short copper wires (electrodes) to the specimens. However, the epoxy was not able to establish a strong and reliable connection between the specimens and the electrodes, leading to significant variance in the data. In addition, resistivity values of the composites were found to be typically > $10^4 \Omega$.m, which are within the operating range of the two-point probe method. Therefore, the two-point probe method was deemed more suitable and reliable for this study.

Information on the specimens that were used in electrical conductivity tests in the study described here. Notes: three specimens were used for all conductivity tests listed in the table. Three replicates were visualized using LSCM with a subset of them tested in SEM and TEM. Only a subset of cases was also subjected to mechanical testing as indicated

Mix ID ⁽¹⁾	Mixing method	Values for methods	No. of specimens			
		Power (W)	Rotational speed (rpm)	Temperature (°C)	Total duration (min)	for mechanical properties
Manual	Manual	-	-	-	5	3
BS/70/60	BS	70	-	-	60	-
BS/70/120	BS	70	-	-	120	-
BS/70/240	BS	70	-	-	240	-
BM/150/65/20	BM	-	150	65	20	4
BM/150/100/10	BM	-	150	100	10	-
BM/150/100/20	BM	-	150	100	20	4
MS/750/3	MS	-	750	-	3	-
MS/1500/3	MS	-	1 500	-	3	-
MS/3000/3	MS	-	3 000	-	3	-
PS/55/60	PS	55	-	-	60 ⁽²⁾	-
PS/55/120	PS	55	-	-	120 ⁽²⁾	4
PS/55/180	PS	55	-	-	180 ⁽²⁾	-

⁽¹⁾CNT concentration was zero for the Manual case (i.e. 75% PL + 25% PR); 0.5 wt% for all other test cases. ⁽²⁾ Duration corresponding to the 50% pulse mode (i.e. net duration is half the value shown)

Mechanical properties

Tensile strength tests were carried out in accordance with ASTM D1708 to determine the relationships between the dispersion state and the strength, strain at failure, tensile modulus and Poisson's ratio of the composites. Information on the specimens that were prepared for conductivity and mechanical property tests is summarized in Table 6.2. For the mechanical property tests, for each formulation listed in the table, four nominally-identical, dog-bone-shaped specimens were punched out from the conductivity samples using a die expulsion press. The specimens were tested at a strain rate of 2 %/min using a tensile testing machine.

Microscopic characterization

SEM, TEM and LSCM were used to visualize CNT particles and bundles in the specimens at different length scales. Further details on the microscopy techniques used in the study described here are given in the following sections.

Scanning electron microscopy (SEM)

SEM images were taken using a Zeiss Neon 40 EsB microscope in the charge-contrast imaging mode (Kovacs et al. 2007; Lillehei et al. 2009) to examine the dispersion quality of the CNTs in the coating

specimens. For selected combinations of composite formulation and mixing method, the crosssectional surfaces of cryofractured specimens were observed under the microscope. The specimens were bonded to the SEM stubs using a conductive silver paint. No metal coating was necessary since the CNTs charged by a high-accelerating voltage were visible due to emitting-enriched secondary electrons. Different combinations of voltages and incident angles were tried for the incident electron beam in order to maximize the signal-to-noise ratio and the contrast in the charging patterns of the specimens. Eventually, a 10-kV electron beam at an incident angle normal to the specimen thickness was used to scan the cross-sectional surface of the specimens.

Transmission electron microscopy (TEM)

TEM forms images from the interaction of a beam of electrons passing through an ultra-thin specimen, making it possible to visualize very high-resolution images to a scale of 0.2 nm. Compared to SEM, TEM tomography creates a 3D reconstruction of a specimen from a series of tilted 2-D images at 5–10-nm resolution. However, the 3D image is not manifest, as the limitations of TEM only make it possible for the specimen to be tilted \pm 60/70°. In addition, the preparation of specimens is laborious and requires thin-sectioning in a technical and tedious procedure (Wilson and Bacic 2012).

A TEM was used in the study described here in order to determine the volume occupied by CNTs in CNT bundles. Samples were cryosectioned at 150 K with a section thickness of 100–110 nm. The sections were then mounted on 600-mesh hexagonal grids and imaged in bright field on a JEOL 2000FX TEM at an accelerating voltage of 200 kV.

Laser scanning confocal microscopy (LSCM)

LSCM is a light microscopy technique which can create 3D reconstructions of a sample, with up to 300 nm resolution in all directions. Conventional microscopes require samples to be capable of transmitting light, and bundles not to obscure one another. LSCM circumvents this limitation by utilizing light in the reflected light path, while also blocking any out-of-focus light, creating an image as thin as 300 nm axially, referred to as an optical section. A 3D reconstruction of a volume within an intact specimen is generated by collecting a series of optical sections along the optical axis (Z-axis).

In the study described here, test specimens were imaged using a Leica SP8 laser scanning confocal microscope in order to compare the MWCNT dispersion in samples that had been prepared using different mixing methods. Specifically, the distribution of bundle volumes was measured *in situ* to image PVC autofluorescence in a sample volume of 246 μ m × 246 μ m × 105 μ m. The PVC was found to autofluoresce with UV excitation, so the samples were imaged using a 405-nm diode laser, and the emission intensity was measured between 446 nm and 554 nm. High-resolution 3D images of the CNT bundles were acquired by means of a 63× 1.4 NA oil immersion objective. Oil immersion was chosen primarily due to the similarity of its refractive index, 1.52, to that measured for PVC (Masadome et al. 2002), helping to reduce optical aberrations that would otherwise compromise the resolution. Since CNTs are highly absorbent in the optical range (Nakanishi et al. 2013), the imaging resulted in a negative image of the CNT bundles (Figure 6.1a). The images were then deconvolved using an adaptive point-spread function over 10 iterations (AutoQuant X v3.0.3 64-bit) in order to better delineate the boundaries of the bundles in the high-resolution 3D images (Figure 6.1b). An isosurface was then rendered around the resulting dark bundles (Figure 6.1c), delineating the bundles from the surrounding PVC (Imaris ×64 v8.0.1) and allowing for a quantitative 3D

analysis of dispersion. The same microscope setup and isosurface threshold was used for every image to ensure that the samples were cross-comparable.



FIGURE 6.1

LSCM 3D imaging of CNT bundles in BS/70/120. (a) Orthogonal sections from a 3D image of PVC autofluorescence in a CNT composite sample. The white lines show where the corresponding orthogonal sections are located in each image. (b) Image (a) post-deconvolution. (c) Orthogonal views of the entire 3D image with an isosurface rendering around each bundle. Note: Scale bars = $50 \,\mu\text{m}$

The volume and position of each bundle within an image was quantified by measuring the volume and centroid of each isosurface within an image (Imaris ×64 v8.0.1). The distribution of bulk carbon within each image was measured by binarizing an image series, such that a voxel containing carbon had an intensity of 1 while PVC had an intensity of 0 (Image J v1.49m). The percentage amount of the total volume of a 3D bin occupied by CNTs was calculated as:

% total volume =
$$\frac{\text{\# of voxles containing CNTs}}{\text{total \# of voxles}}$$
 (1)

Statistical analysis and plotting was performed using R (R \times 64 v3.1.2). Interested readers are referred to a study by Smith et al. (2015) for further details on the 3D imaging of composite materials using LSCM.

Dispersion assessment results

Quantitative analysis of the dispersion associated with each mixing method listed in Table 6.2 and the corresponding electrical conductivities are discussed in the following sections.

Dispersion and electrical conductivity

Measured electrical conductivities of the specimens listed in Table 6.2 are plotted in a descending order in Figure 6.2. The magnitude and repeatability of the conductivity results together with the analysis of the data corresponding to the 3D imaging of samples using LSCM were collectively used

to quantitate the quality of CNT dispersion that was obtained using each mixing method. Also, SEM images shown in Figure 6.3 are used for the qualitative assessment of CNTs dispersion.



FIGURE 6.2

Volume conductivity of composite specimens filled with 0.5 wt.% MWCNT and produced using different mixing techniques. Note: three specimens were tested for each mixing case shown



FIGURE 6.3

SEM images for (a) pure PL, (b) PS/55/60, (c) PS/55/120, (d) PS/55/180, (e) BS/70/120, and (f) BM/150/100/20 (after Yazdani et al. 2015)

The few bright spots observed in the pure specimen (Figure 6.3a) are attributed to the presence of impurities and contaminants in the plastisol matrix and they lack the needle-shaped appearance of CNTs. In addition, due to the fibrous structure of CNTs, cryofracturing the specimens splits the CNTs crossing the fracture line leaving protrusions on the fractured surfaces. These protrusions generate large quantities of secondary electrons causing them to appear brighter in SEM images (e.g. Figure 6.3b).

It can be seen from Figure 6.2 that PS/55/120 specimens exhibit significantly-higher conductivity with lower scatter as compared to other specimens. Comparison of the conductivities of the PS/55/120, PS/55/60 and PS/55/180 specimens and their corresponding SEM images in Figure 6.3bd indicates that sonication power applied over 120 minutes is practically optimal to disperse the MWCNT bundles and construct a three-dimensional, interconnected conductive network (Figure 6.3c). Longer durations deliver excessive energy that breaks the CNT network into isolated CNT bundles (Figure 6.3d). This is consistent with the findings of Lu et al. (1996) who observed a significant increase in the intensity of the D-band in the Raman spectroscopy of CNT-filled composites subjected to prolonged ultrasonication. This increase is due to the disordered sp³ carbon in CNTs and indicates the generation of defects on their surface that convert CNTs into amorphous carbon nanofibers and deteriorates both the electrical and mechanical properties of their host composites (Mukhopadhyay et al. 2002). Different degrees of brightness observed in Figure 6.3c indicate the positions of the CNTs in the specimen: the depth of a CNT's location in the specimen is inversely proportional to its brightness in the image. However, no information was accessible from the regions located deeper than approximately 50 nm even by increasing the acceleration voltage, as also observed by Loos et al. (2005) and Kovacs et al. (2007).

The results of the BS method shown in Figure 6.2 indicate that no combinations of the sonication power and duration were adequate to overcome the intermolecular interactions between the bundled CNTs in the pigment (e.g. Figure 6.3e). Recall from Section 1.1 that the energy of van der Waals attraction is on the order of 500 eV/ μ m per CNT-CNT contact. Even though the BS and PS methods transmitted comparable energies to the pigment, the more-defined cavitation zone and localized energy in the PS method (together with the locally-generated heat) appeared to be more effective in disentangling the CNT bundles.

The results corresponding to the BM and MS methods in Figure 6.2 indicate that they were not able to produce specimens with high conductivity at low filler concentrations. The poor quality of the filler dispersion resulting from these methods can be seen in a representative SEM image shown in Figure 6.3f. This poor dispersion quality could be attributed to CNT fragmentation during the mixing process that dominates the disentanglement of CNT bundles and results in split and partially-disentangled bundles. Comparison of the results of the two mixtures BM/150/100/10 and BM/150/100/20 indicates that the mean electrical conductivity was not affected by the mixing duration. In addition, comparison of the results for BM/150/65/20 and BM/150/100/20 shows a slight increase in the mean conductivity of the composite as a result of increasing temperature from 65 °C to 100 °C during the mixing process. Among all the mixing methods and combination of influential factors examined, the BM/150/100/10 combination was found to yield the highest degree of consistency (i.e. lowest variance) in the conductivity results, possibly due to the heat-induced improvement in the homogeneity of the pigment.

Distribution of bundle volumes

In order to assess the quality of MWCNT dispersion in the samples beyond the 50 nm limit of the SEM analysis, LSCM was used to image MWCNT bundles up to 100 μ m below the sample surface.

Assuming a completely-stochastic shearing of MWCNT bundles during mixing, a log-normal distribution was hypothesized for MWCNT bundle volumes. This hypothesis was based on a study by Kolmogoroff (1969) who developed a mathematical algorithm to determine the probability of gradual fragmentation of particles in an unlimited refinement process. According to Kolmogoroff's algorithm, the rate at which the particles break down decreases as they become smaller and their particle size distribution approaches a log-normal distribution.

The distribution of bundle volumes was represented in a histogram (see Figure 6.4a for a representative specimen), and the null hypothesis of a log-normal distribution was tested using a probability plot, where the distribution of the measured volumes was plotted against a projected log-normal distribution of the same mean and standard deviation (Figure 6.4b). As can be observed for the representative specimen, the majority of the volumes fall along the reference normal distribution except for those on the extreme ends. The deviation of the lower end from the expected distribution occurs at the limit of the voxel resolution of the LSCM images (1 μ m³), suggesting that while the aggregates smaller than 1 μ m³ are detectable, their volume cannot be precisely measured. On the other hand, the deviation of the upper end from the expected distribution could be due to the sampling bias arisen from centering the largest aggregates in the microscope's field of view in order to avoid having them cropped out, which might have otherwise resulted in an underestimation of their abundance. The null hypothesis that all specimens had a log-normal distribution was also tested using several methods including those introduced by Anderson and Darling (1952), Shapiro and Wilk (1965), Jarque and Bera (1980), Doornik and Hansen (2008) and Kolmogorov and Smirnov (Kolmogorov 1933; Smirnov 1933). These normality tests, which are supplementary to the visual assessment of normality, compare the actual frequency distribution of a sample (the actual values) with a theoretical normal distribution (the expected values) that possesses the same mean and standard deviation. All these tests accepted the null hypothesis for the distribution of bundle volumes in the study described here. However, for brevity, only the Shapiro-Wilk test results are reported in Table 6.3.



FIGURE 6.4

(a) Histogram of the distribution of the MWCNT bundle volumes in the BS/70/120 specimens, with the superimposed curve showing the corresponding log-normal distribution. (b) Corresponding probability plot showing the distribution of bundle volumes relative to a log-normal distribution

Mean and standard deviations of MWCNT volume log-normal distributions in different filled specimens. Note: The values indicate the Shapiro-Wilk test results and the mean values of three independent experiments

Mix ID	Mean (µm³)	volume	Standard deviation (μm^3)
PS/55/60	2.32		0.25
PS/55/120	2.43		0.21
PS/55/180	2.77		0.26
BS/70/60	3.04		0.08
BS/70/120	3.02		0.32
BS/70/240	2.84		-
BM/150/65/20	3.12		0.13
BM/150/100/10	3.19		0.12
BM/150/100/20	3.18		0.13
MS/750/3	2.70		0.17
MS/1500/3	3.24		-
MS/3000/3	1.89		0.20

In addition to the quantitative analysis above, the 3D distribution of CNT bundles in a representative sample was characterized in order to visualize the position, size and appearance of bundles in a single image. To this end, the isosurface rendering of CNT bundles from a 3D confocal image series shown in Figure 6.1c was overlaid by the corresponding color coded Z-position of each bundle (Figure 6.5).



FIGURE 6.5

3D distribution of CNT bundles in BS/70/120 specimens from LSCM images. (a) Isosurface rendering of CNT bundles from a 3D confocal image series. (b) The corresponding color coded Z-position of each bundle in image (a). (c) An overlay of images (a) and (b) showing the three-dimensional position of each bundle within the image stack. Scale bar in each image = $50 \,\mu\text{m}$

As previously stated, a predetermined amount of mixed pigment was blended with PVC plastisol to produce the final CNT-filled composite samples. Since the distribution of CNT bundles within the constituent pigment is not expected to be completely uniform, the CNT concentration in the resulting composite samples in their liquid form (and in the corresponding cured specimens) does not necessarily match that of their parent pigment. Therefore, information on the CNT density in

individual bundles together with the bundle volume from LSCM could be used to estimate the density of CNTs in a cured composite specimen.

The CNT density in individual bundles can be obtained using TEM. The CNTs within a bundle in a representative sample visualized using LSCM (Figure 6.6a) is shown in Figure 6.6b. The white sections in the bundles shown in Figure 6.6a are CNTs whilst the dark spots represent the polymer within the bundles. Figure 6.6b shows a TEM micrograph of a single bundle showing the density and arrangement of loosely-entangled CNTs impregnated with PVC.



FIGURE 6.6

CNT density in individual bundles in a PS/55/60 specimen. (a) A single confocal optical section of CNT bundles (white) showing PVC (black) impregnation within each bundle. (b) A TEM micrograph of a single bundle showing loosely-packed CNTs impregnated with PVC. A high-pass spatial frequency filter was applied to image (b) in order to increase the contrast of the CNTs

Comparison of mixing methods

Differences in the quality of CNT dispersion as obtained through the mixing methods described here were quantified in order to determine which method(s) would result in comparable dispersion of the MWCNT bundles in the specimens. As discussed previously, stochastic shearing of CNT bundles should theoretically yield a log-normal distribution of bundle volumes (Kolmogoroff 1969 – See Section 3.2). Accordingly, the similarity in the degree of bundle shearing for a given methodology can be quantified as the Pearson product-moment correlation coefficient (PPMCC) (Pearson 1895). To measure the Pearson coefficient, the bundle volume measurements for each dispersion method were first binned logarithmically to get the normal percent frequency distribution of bundle volumes for each method. The percent frequency distributions were then compared against one another by calculating the corresponding PPMCC (ρ) values, which were then plotted as a correlation heat map (Figure 6.7).

The correlation matrix was used as a similarity matrix, or a distance matrix using the complement of the correlation coefficient $(1-\rho)$ to cluster methods with similar dispersion properties together. Specifically, the unweighted pair group method with arithmetic mean was used to generate a hierarchical dendrogram of the similarity between bundle volume distributions for different dispersion methods examined in the study described here (Figure 6.7). In the example shown in



Figure 6.7, there are two main groups of methods which are clustered primarily by the technique applied rather than their duration, suggesting that the method used to shear the CNT bundles has a greater influence on their size than the power or duration used in each method.

FIGURE 6.7

Hierarchical clustering of CNT dispersion methods in filled PVC composites based on the CNT aggregate volume distributions

In addition to evaluating the dispersion quality of CNT particles in polymer composites as a function of the mixing method, the correlation between the dispersion quality and the composite sample conductivity (or resistivity) was examined. The Spearman correlation coefficient was used to determine the correlation between an array of quantitative metrics of CNT aggregate volumes and sample resistivity. This was done to determine which characteristics of the CNT dispersion were most predictive of the conductivity of the composite samples. It was understood that the areas of the sample that were imaged in each technical replicate might not have been the best representatives of those which had the greatest contribution in the sample conductivity. Therefore, to remove any potential sampling effects, the CNT aggregate volume distributions within each technical replicate were iteratively shuffled and reassigned to the corresponding conductivity measurements followed by measuring the distribution of the resulting Spearman correlations (Figure 6.8). A technical replicate in the above discussion refers to the same sample which was analyzed multiple times.

The volume of the larger aggregates within a sample had an increasingly-negative correlation with sample resistivity, suggesting that as the largest aggregates within a sample increased in volume, so did the sample conductivity. Interestingly, contrary to previously-published studies (e.g. Rui et al. 2014), no significant correlation was observed between the conductivity of the polymer composite and the percent sample volume filled by the CNT aggregates.



FIGURE 6.8

Correlation between quantitative metrics of CNT dispersion and resistivity. Note: the dashed lines represent correlations that are statistically significant (p < 0.05)

Dispersion and mechanical properties

The relationship between dispersion quality and mechanical properties was examined by testing selected specimens chosen according to the conductivity data shown in Figure 6.2. Specimens exhibiting the highest electrical conductivity (i.e. PS/55/120) were compared against the BM/150/65/20 specimen as a representative of low-conductivity specimens. The specimen showing an abnormally-high conductivity among those prepared using the BM/150/100/20 combination was also tested as a representative for mediocre dispersion. In addition, specimens made of the pristine (i.e. no CNT) host matrix comprising of 75% PL and 25% PR were tested to obtain a baseline value for mechanical properties.

According to Table 6.4, the mean values of tensile strength, elastic modulus and failure strain of the pristine specimens are 7.4 MPa, 1.14 MPa and 450%, respectively, which change in entirely different ways upon dispersing 0.5 wt.% MWCNT into the matrix. The tensile strength of the filled specimens with respect to dispersion quality follows a reverse trend as compared to their electrical conductivity. Well-dispersed MWCNT fillers in a PVC matrix slightly enhance its tensile strength but result in a higher percolation threshold. In contrast, for the concentration examined, a less-uniform dispersion of CNTs reduces the tensile strength of the pristine matrix. Reduction in tensile strength in the latter case can be attributed to the formation of stress concentration zones at the polymer-CNT interface around the CNT bundles promoting the failure of the composite (Song and Youn 2005; Blond et al. 2006).

Mix ID	Tensile strength (MPa)	Failure strain (%)	Elastic modulus (MPa)
Manual	7.43	448.70	1.14
PS/55/120	6.64	152.94	9.04
BM/150/100/20	6.96	162.06	7.94
BM/150/65/20	6.53	155.78	8.45

Influence of dispersion technique on the mechanical properties of PVC-MWCNT composites

The influence of MWCNT on the composite's failure strain was found to be more significant. According to Table 6.4, adding MWCNT to the pristine matrix significantly reduced the failure strain regardless of the dispersion quality. However, less-uniformly-dispersed specimens experienced a larger reduction in their failure strain. These observations could be due the fact that the bundles present in poorly-dispersed (less-uniformly-dispersed) specimens facilitate the formation of stress concentration zones and the initiation of nanocracks at the polymer-CNT interface promoting failure in the composite (Song and Youn 2005; Fathi et al. 2012). The crack initiation is primarily due to the weak interfacial bonding between the polymer matrix and the outermost layer of the MWCNTs which impedes a full stress transfer between the two solid phases at the nano-/microscale (Schadler et al. 1998; Allaoui et al. 2002; Kearns and Shambaugh 2002). The dispersion quality and the CNT/polymer adhesion can be improved by chemical functionalization of CNTs and covalent attachment of polymer chains (Shanmugharaj et al. 2007; Koval'chuk et al. 2008). Apart from debonding at the CNT/polymer interface, the weak van der Waals forces holding the individual graphene shells constituting MWCNTs are not sufficient to prevent so-called telescopic fracture, where MWCNTs are pulled out from the matrix due to the tensile stresses at the tip of the cracks (Yu et al. 2000; Liu et al. 2004; Song and Youn 2005). A detailed description of the possible fracture mechanisms of CNTs in a polymer matrix can be found in a study by Gojny et al. (2005).

The elastic modulus values of the specimens are given in Table 6.4. It can be seen that dispersing 0.5 wt.% MWCNT within the PVC matrix significantly increases its tensile modulus irrespective of the difference in the dispersion quality of the specimens. However, the specimens exhibiting higher conductivity (i.e. PS/55/120) possess larger elastic modulus values. This observation can be explained by the fact that the bundles in these specimens act as large particles as if a higher filler concentration were present. These bundles confine the polymer chains in their interspace, and consequently, the composite behaves as if it were mostly made from CNTs and had a lower polymer concentration (Song and Youn 2005).

The elastic modulus of polymer composites reinforced with uniformly-dispersed fillers as a function of the properties of the constituent elements is commonly predicted using the Halpin-Tsai model (Halpin and Kardos 1976). The model, which was originally proposed for composites filled with aligned and short fibers, was extended by Thostenson and Chou (2003) for nanotube reinforced composites. The modified model was adopted in the study described here to approximate the elastic modulus of MWCNT/PVC composites. Since the model assumes a perfect dispersion of the filler in the matrix, the difference between the elastic modulus values predicted by theory and those obtained in laboratory experiments could be used as a measure of dispersion quality in the composite. The modified model predicts the value of the composite modulus, E_c , as (Gojny et al. 2004; Koratkar 2013):

$$\frac{E_{\rm c}}{E_{\rm m}} = \frac{3}{8} \left(\frac{1 + \zeta \eta_{\rm L} \varphi}{1 - \eta_{\rm L} \varphi} \right) + \frac{5}{8} \left(\frac{1 + 2\eta_{\rm T} \varphi}{1 - \eta_{\rm T} \varphi} \right)$$
⁽²⁾

where E_m is the elastic modulus of the pristine matrix (1.14 MPa), $\zeta = 2l/d$, with *l* and *d* representing the length (74 nm) and the mean outer diameter (7.8 nm) of the filler (MWCNT), φ is the filler volume fraction which can be converted from its weight counterpart using (Mamunya et al. 2008):

$$\varphi = w_{\rm f} \rho_{\rm m} / (w_{\rm f} \rho_{\rm m} + w_{\rm m} \rho_{\rm f}) \tag{3}$$

where $w_{\rm f}$ is the weight concentration of the filler (0.5 wt.%) and $w_{\rm m}$ is the weight concentration of the matrix (calculated as the summation of the weight concentrations of plastisol, $w_{\rm PL}$ = 12 wt.%, and plasticizer, $w_{\rm PR}$ = 87.5 wt.%), $\rho_{\rm f}$ is the density of the filler (2.045 g/cm³) and $\rho_{\rm m}$ is the density of the matrix calculated as the weighted mean of the densities of plastisol, $\rho_{\rm PL}$ = 1.37 g/cm³, and plasticizer, $\rho_{\rm PR}$ = 0.985 g/cm³, as:

$$\rho_{\rm m} = (\rho_{\rm PL} w_{\rm PL} + \rho_{\rm PR} w_{\rm PR}) / (w_{\rm PL} + w_{\rm PR}) \tag{4}$$

Substitution of the above values into Equations3and 4 yields φ = 0.32 vol.%. In addition, in Equation (2):

$$\eta_{\rm L} = \frac{E_{\rm f} / E_{\rm m} - 9}{E_{\rm f} / E_{\rm m} + \zeta} \tag{5}$$

$$\eta_{\rm T} = \frac{E_{\rm f} / E_{\rm m} - 3}{E_{\rm f} / E_{\rm m} + 29} \tag{6}$$

where E_t is the elastic modulus of MWCNTs (1 TPa – Gojny et al. 2004) and $\vartheta = d/4s$, where *s* is the shell separation (3.4 Å – Yazdani and Hatami 2015). Substituting these values into Equation 2 yields $E_c = 5.4$ MPa, which is well within the range of experimentally-obtained values shown in Table 6.4. Results shown in Figures 6.2 and 6.4–6.7 indicate that comparative differences between the theoretical prediction of the elastic modulus and the measured values for composites that were made using different blending methods, together with the microscopic imaging data and measured electrical conductivity values of the corresponding specimens can be used to correlate the quality of filler dispersion in a composite with its properties.

Conclusions

A methodology was presented in this chapter to quantitatively evaluate the three-dimensional dispersion of carbon nanotubes (CNTs) within a composite material *in situ* and on different length scales. Different imaging techniques were used to assess the quality of filler dispersion including laser scanning confocal microscopy (LSCM), scanning electron microscopy (SEM) and transmission

electron microscopy (TEM). MWCNT-filled PVC composites were prepared using four different mixing methods which included probe sonication (PS), bath sonication (BS), batch mixing (BM) and mechanical stirring (MS). Differences in the dispersions obtained using different mixing methods were quantitated using the Pearson product-moment correlation coefficient (PPMCC). The specimen properties including electrical conductivity, tensile strength, ultimate strain and elastic modulus were correlated to the corresponding dispersion characteristics. The composite samples that were produced through an optimum combination of power and duration in the probe sonication (PS) method exhibited the lowest percolation threshold and adequate electrical conductivity and statistical consistency. It was also observed that better quality samples exhibited higher ultimate strengths and failure strains, whereas poorly-dispersed specimens had greater elastic modulus values. These observations were found to be consistent with those predicted by the Halpin-Tsai model.

The visualization technique discussed in this manuscript can be used in subsurface imaging of filled composites to considerable depths without compromising the spatial resolution. Since the tools used in this technique, especially laser scanning confocal microscopy, are widespread across a wide array of scientific disciplines, this imaging technique could be readily adopted in a variety of nanocomposite research studies, especially on composites that are filled with particles of higher dimension (e.g. graphene).

References

- 1. Allaoui, A., Bai, S., Cheng, H. M., and Bai, J. B. (2002). "Mechanical and electrical properties of a MWNT/epoxy composite." *Composites Science and Technology*, 62(15), 1993–1998.
- Anderson, T. W., and Darling, D. A. (1952). "Asymptotic Theory of Certain 'Goodness of Fit' Criteria Based on Stochastic Processes." *The Annals of Mathematical Statistics*, 23(2), 193– 212.
- 3. Bai, J. B., and Allaoui, A. (2003). "Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of nanocomposites—experimental investigation." *Composites Part A: Applied Science and Manufacturing*, 34(8), 689–694.
- 4. Barrau, S., Demont, P., Perez, E., Peigney, A., Laurent, C., and Lacabanne, C. (2003). "Effect of Palmitic Acid on the Electrical Conductivity of Carbon Nanotubes-Epoxy Resin Composites." *Macromolecules*, 36, 9678–9680.
- 5. Bauhofer, W., and Kovacs, J. Z. (2009). "A review and analysis of electrical percolation in carbon nanotube polymer composites." *Composites Science and Technology*, 69(10), 1486–1498.
- Blond, D., Barron, V., Ruether, M., Ryan, K. P., Nicolosi, V., Blau, W. J., and Coleman, J. N. (2006). "Enhancement of Modulus, Strength, and Toughness in Poly(methyl methacrylate)-Based Composites by the Incorporation of Poly(methyl methacrylate)-Functionalized Nanotubes." Advanced Functional Materials, 16(12), 1608–1614.
- 7. Brunauer, S., Emmett, P. H., and Teller, E. (1938). "Adsorption of Gases in Multimolecular Layers." *Journal of the American Chemical Society*, 60(2), 309–319.
- 8. Bryning, M. B., Milkie, D. E., Islam, M. F., Kikkawa, J. M., and Yodh, A. G. (2005). "Thermal conductivity and interfacial resistance in single-wall carbon nanotube epoxy composites." *Applied Physics Letters*, 87(16), 161909.

- Campbell, E. R., Reisner, J. H., and Chung, K. T. (1983). "Charging phenomenon in conductor-insulator composites as displayed by the scanning electron microscope." *Journal of Applied Physics*, 54(2), 1133–1134.
- 10. Croitoru, M. D., Bertsche, G., Kern, D. P., Burkhardt, C., Bauerdick, S., Şahakalkan, S., and Roth, S. (2005). "Visualization and in situ contacting of carbon nanotubes in a scanning electron microscope." *Journal of Vacuum Science & Technology B*, 23(6), 2789–2792.
- 11. Doornik, J. A., and Hansen, H. (2008). "An Omnibus Test for Univariate and Multivariate Normality"." Oxford Bulletin of Economics and Statistics, 70, 927–939.
- 12. Du, F., Fischer, J. E., and Winey, K. I. (2003). "Coagulation method for preparing singlewalled carbon nanotube/poly(methyl methacrylate) composites and their modulus, electrical conductivity, and thermal stability." *Journal of Polymer Science Part B: Polymer Physics*, 41(24), 3333–3338.
- 13. Du, F., Fischer, J. E., and Winey, K. I. (2005). "Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites." *Physical Review B*, 72(12), 121404.
- 14. Fathi, A., Hatami, K., and Grady, B. P. (2012). "Effect of carbon black structure on lowstrain conductivity of polypropylene and low-density polyethylene composites." *Polymer Engineering & Science*, 52(3), 549–556.
- 15. Geetha, S., Satheesh Kumar, K. K., Rao, C. R. K., Vijayan, M., and Trivedi, D. C. (2009). "EMI shielding: Methods and materials—A review." *Journal of Applied Polymer Science*, 112(4), 2073–2086.
- 16. Girifalco, L. A., Hodak, M., and Lee, R. S. (2000). "Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential." *Physical Review B*, 62(19), 13104–13110.
- Gojny, F. H., Wichmann, M. H. G., Fiedler, B., and Schulte, K. (2005). "Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – A comparative study." *Composites Science and Technology*, 20th Anniversary Special Issue, 65(15–16), 2300–2313.
- Gojny, F. H., Wichmann, M. H. G., Köpke, U., Fiedler, B., and Schulte, K. (2004). "Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content." *Composites Science and Technology*, Developments in carbon nanotube and nanofibre reinforced polymers, 64(15), 2363–2371.
- 19. Grady, B. P. (2011). *Carbon Nanotube-Polymer Composites: Manufacture, Properties, and Applications*. John Wiley & Sons, Hoboken, NJ.
- Grujicic, M., Cao, G., and Roy, W. N. (2004). "A computational analysis of the percolation threshold and the electrical conductivity of carbon nanotubes filled polymeric materials." *Journal of Materials Science*, 39(14), 4441–4449.
- 21. Halpin Affdl, J. C., and Kardos, J. L. (1976). "The Halpin-Tsai equations: A review." *Polymer Engineering & Science*, 16(5), 344–352.
- 22. Hatami, K., Hassanikhah, A., Yazdani, H., and Grady, B. (2014). "Tensoresistive PVC Coating for Sensor-Enabled Geogrids." *Journal of Nanomechanics and Micromechanics*, 4(4), A4013016.
- 23. Hilding, J., Grulke, E. A., George Zhang, Z., and Lockwood, F. (2003). "Dispersion of Carbon Nanotubes in Liquids." *Journal of Dispersion Science and Technology*, 24(1), 1–41.
- 24. Huang, S., Qian, Y., Chen, J., Cai, Q., Wan, L., Wang, S., and Hu, W. (2008). "Identification of the Structures of Superlong Oriented Single-Walled Carbon Nanotube Arrays by Electrodeposition of Metal and Raman Spectroscopy." *Journal of the American Chemical Society*, 130(36), 11860–11861.

- Islam, M. F., Rojas, E., Bergey, D. M., Johnson, A. T., and Yodh, A. G. (2003). "High Weight Fraction Surfactant Solubilization of Single-Wall Carbon Nanotubes in Water." *Nano Letters*, 3(2), 269–273.
- 26. Ivakhnenko, V., and Eremin, Y. (2006). "Light scattering by needle-type and disk-type particles." *Journal of Quantitative Spectroscopy and Radiative Transfer*, VIII Conference on Electromagnetic and Light Scattering by Nonspherical Particles, 100(1–3), 165–172.
- 27. Jarque, C. M., and Bera, A. K. (1980). "Efficient tests for normality, homoscedasticity and serial independence of regression residuals." *Economics Letters*, 6(3), 255–259.
- Kaur, G., Adhikari, R., Cass, P., Bown, M., and Gunatillake, P. (2015). "Electrically conductive polymers and composites for biomedical applications." *RSC Adv.*, 5(47), 37553– 37567.
- 29. Kearns, J. C., and Shambaugh, R. L. (2002). "Polypropylene fibers reinforced with carbon nanotubes." *Journal of Applied Polymer Science*, 86(8), 2079–2084.
- Kilbride, B. E., Coleman, J. N., Fraysse, J., Fournet, P., Cadek, M., Drury, A., Hutzler, S., Roth, S., and Blau, W. J. (2002). "Experimental observation of scaling laws for alternating current and direct current conductivity in polymer-carbon nanotube composite thin films." *Journal of Applied Physics*, 92(7), 4024–4030.
- 31. Kolmogoroff, A. N. (1969). *The logarithmically normal law of distribution of dimensions of particles when broken into small parts*. NASA Publication.
- 32. Kolmogorov, A. N. (1933). "Sulla determinazione empirica di una legge di distribuzione." *Giornale dell' Istituto Italiano degli Attuari*, 4, 83–91.
- 33. Koratkar, N. (2013). *Graphene in Composite Materials: Synthesis, Characterization and Applications*. DEStech Publications, Inc, Lancaster, PA.
- Kovacs, J. Z., Andresen, K., Pauls, J. R., Garcia, C. P., Schossig, M., Schulte, K., and Bauhofer, W. (2007). "Analyzing the quality of carbon nanotube dispersions in polymers using scanning electron microscopy." *Carbon*, 45(6), 1279–1288.
- Koval'chuk, A. A., Shevchenko, V. G., Shchegolikhin, A. N., Nedorezova, P. M., Klyamkina, A. N., and Aladyshev, A. M. (2008). "Effect of Carbon Nanotube Functionalization on the Structural and Mechanical Properties of Polypropylene/MWCNT Composites." *Macromolecules*, 41(20), 7536–7542.
- 36. Kymakis, E., and Amaratunga, G. A. J. (2006). "Electrical properties of single-wall carbon nanotube-polymer composite films." *Journal of Applied Physics*, 99(8), 084302.
- Li, J., Ma, P. C., Chow, W. S., To, C. K., Tang, B. Z., and Kim, J.-K. (2007). "Correlations between Percolation Threshold, Dispersion State, and Aspect Ratio of Carbon Nanotubes." *Advanced Functional Materials*, 17(16), 3207–3215.
- 38. Lillehei, P. T., Kim, J.-W., Gibbons, L. J., and Park, C. (2009). "A quantitative assessment of carbon nanotube dispersion in polymer matrices." *Nanotechnology*, 20(32), 325708.
- 39. Liu, L., and Wagner, H. D. (2005). "Rubbery and glassy epoxy resins reinforced with carbon nanotubes." *Composites Science and Technology*, 65(11–12), 1861–1868.
- 40. Liu, T., Phang, I. Y., Shen, L., Chow, S. Y., and Zhang, W.-D. (2004). "Morphology and Mechanical Properties of Multiwalled Carbon Nanotubes Reinforced Nylon-6 Composites." *Macromolecules*, 37(19), 7214–7222.
- 41. Li, W., and Bauhofer, W. (2014). "Visualization of CNTs in Polymer Composites." *Polymer Nanotube Nanocomposites*, V. Mittal, ed., John Wiley & Sons, Inc., 405–428.
- 42. Li, W., Buschhorn, S. T., Schulte, K., and Bauhofer, W. (2011). "The imaging mechanism, imaging depth, and parameters influencing the visibility of carbon nanotubes in a polymer matrix using an SEM." *Carbon*, 49(6), 1955–1964.

- Loos, J., Alexeev, A., Grossiord, N., Koning, C. E., and Regev, O. (2005). "Visualization of single-wall carbon nanotube (SWNT) networks in conductive polystyrene nanocomposites by charge contrast imaging." *Ultramicroscopy*, 104(2), 160–167.
- 44. Lourie, O., Cox, D. M., and Wagner, H. D. (1998). "Buckling and Collapse of Embedded Carbon Nanotubes." *Physical Review Letters*, 81(8), 1638–1641.
- 45. Lu, K. L., Lago, R. M., Chen, Y. K., Green, M. L. H., Harris, P. J. F., and Tsang, S. C. (1996). "Mechanical damage of carbon nanotubes by ultrasound." *Carbon*, 34(6), 814–816.
- 46. Luo, X., and Chung, D. D. L. (1999). "Electromagnetic interference shielding using continuous carbon-fiber carbon-matrix and polymer-matrix composites." *Composites Part B: Engineering*, 30(3), 227–231.
- 47. Mamunya, Y., Boudenne, A., Lebovka, N., Ibos, L., Candau, Y., and Lisunova, M. (2008). "Electrical and thermophysical behaviour of PVC-MWCNT nanocomposites." *Composites Science and Technology*, 68(9), 1981–1988.
- Ma, P.-C., Siddiqui, N. A., Marom, G., and Kim, J.-K. (2010). "Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review." *Composites Part A: Applied Science and Manufacturing*, 41(10), 1345–1367.
- 49. Masadome, T., Asano, Y., Imato, T., Ohkubo, S., Tobita, T., Tabei, H., Iwasaki, Y., Niwa, O., and Fushinuki, Y. (2002). "Preparation of refractive index matching polymer film alternative to oil for use in a portable surface-plasmon resonance phenomenon-based chemical sensor method." *Analytical and Bioanalytical Chemistry*, 373(4-5), 222–226.
- 50. Ma, Z., Merkus, H. G., de Smet, J. G. A. E., Heffels, C., and Scarlett, B. (2000). "New developments in particle characterization by laser diffraction: size and shape." *Powder Technology*, 111(1–2), 66–78.
- 51. Mukhopadhyay, K., Dwivedi, C. D., and Mathur, G. N. (2002). "Conversion of carbon nanotubes to carbon nanofibers by sonication." *Carbon*, 40(8), 1373–1376.
- 52. Nakanishi, R., Kitaura, R., Warner, J. H., Yamamoto, Y., Arai, S., Miyata, Y., and Shinohara, H. (2013). "Thin single-wall BN-nanotubes formed inside carbon nanotubes." *Scientific Reports*, 3.
- Novak, M. A., Surwade, S., Prokop, J., Bolotin, K., Hone, J., Brus, L., Nuckolls, C., and Liu, H. (2014). "Visualizing Individual Carbon Nanotubes with Optical Microscopy." *Journal of the American Chemical Society*, 136(24), 8536–8539.
- 54. Pearson, K. (1895). "Note on Regression and Inheritance in the Case of Two Parents." *Proceedings of the Royal Society of London*, 58(347-352), 240–242.
- 55. Rui, Y., Guo, J., Harwell, J., Nakanishi, T., Kotera, S., and Grady, B. P. (2014). "Electrical, mechanical, and crystallization properties of ethylene-tetrafluoroethylene copolymer/multiwalled carbon nanotube composites." *Journal of Applied Polymer Science*, 131(22), n/a–n/a.
- 56. Schadler, L. S., Giannaris, S. C., and Ajayan, P. M. (1998). "Load transfer in carbon nanotube epoxy composites." *Applied Physics Letters*, 73(26), 3842–3844.
- 57. Schroder, D. K. (2006). *Semiconductor Material and Device Characterization*. John Wiley & Sons, Hoboken, New Jersey.
- Shanmugharaj, A. M., Bae, J. H., Lee, K. Y., Noh, W. H., Lee, S. H., and Ryu, S. H. (2007). "Physical and chemical characteristics of multiwalled carbon nanotubes functionalized with aminosilane and its influence on the properties of natural rubber composites." *Composites Science and Technology*, 67(9), 1813–1822.
- 59. Shapiro, S. S., and Wilk, M. B. (1965). "An analysis of variance test for normality (complete samples)." *Biometrika*, 52(3-4), 591–611.

- 60. Smirnov, N. V. (1933). "Estimate of deviation between empirical distribution functions in two independent samples." *Bulletin Moscow University*, 2, 3–16.
- 61. Smith, B., Yazdani, H., and Hatami, K. (2015). "Three-dimensional imaging and quantitative analysis of dispersion and mechanical failure in filled nanocomposites." *Composites Part A: Applied Science and Manufacturing*, 79, 23–29.
- 62. Song, Y. S., and Youn, J. R. (2005). "Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites." *Carbon*, 43(7), 1378–1385.
- Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y. H., Kim, S. G., Rinzler, A. G., Colbert, D. T., Scuseria, G. E., Tománek, D., Fischer, J. E., and Smalley, R. E. (1996). "Crystalline Ropes of Metallic Carbon Nanotubes." *Science*, 273(5274), 483–487.
- 64. Thostenson, E. T., and Chou, T.-W. (2003). "On the elastic properties of carbon nanotubebased composites: modelling and characterization." *Journal of Physics D: Applied Physics*, 36(5), 573.
- 65. Wilson, S. M., and Bacic, A. (2012). "Preparation of plant cells for transmission electron microscopy to optimize immunogold labeling of carbohydrate and protein epitopes." *Nature Protocols*, 7(9), 1716–1727.
- Yamamoto, T., Miyauchi, Y., Motoyanagi, J., Fukushima, T., Aida, T., Kato, M., and Maruyama, S. (2008). "Improved Bath Sonication Method for Dispersion of Individual Single-Walled Carbon Nanotubes Using New Triphenylene-Based Surfactant." *Japanese Journal of Applied Physics*, 47(4), 2000–2004.
- 67. Yazdani, H., and Hatami, K. (2015). "Failure criterion for graphene in biaxial loading—a molecular dynamics study." *Modelling and Simulation in Materials Science and Engineering*, 23(6), 065004.
- 68. Yazdani, H., Hatami, K., and Grady, B. P. (2015a). "Sensor-enabled geogrids for performance monitoring of reinforced soil structures." *ASTM Journal of Testing and Evaluation*, 10.1520/JTE20140501.
- 69. Yazdani, H., Hatami, K., Khosravi, E., Harper, K., and Grady, B. P. (2014). "Strain-sensitive conductivity of carbon black-filled PVC composites subjected to cyclic loading." *Carbon*, 79, 393–405.
- 70. Yazdani, H., Smith, B., and Hatami, K. (2015b). "Multi-walled carbon nanotube-filled polyvinyl chloride composites: influence of processing method on dispersion quality, electrical conductivity and mechanical properties." *Composites Part A: Applied Science and Manufacturing*, Under Review.
- 71. Yu, M.-F., Lourie, O., Dyer, M. J., Moloni, K., Kelly, T. F., and Ruoff, R. S. (2000). "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load." *Science*, 287(5453), 637–640.
- 72. Zhang, R., Baxendale, M., and Peijs, T. (2007). "Universal resistivity–strain dependence of carbon nanotube/polymer composites." *Physical Review B*, 76(19), 195433.
- 73. Zhang, R., Zhang, Y., Zhang, Q., Xie, H., Wang, H., Nie, J., Wen, Q., and Wei, F. (2013). "Optical visualization of individual ultralong carbon nanotubes by chemical vapour deposition of titanium dioxide nanoparticles." *Nature Communications*, 4, 1727.
- 74. Zhao, M., Ming, B., Kim, J.-W., Gibbons, L. J., Gu, X., Nguyen, T., Park, C., Lillehei, P. T., Villarrubia, J. S., Vladár, A. E., and Liddle, J. A. (2015). "New insights into subsurface imaging of carbon nanotubes in polymer composites via scanning electron microscopy." *Nanotechnology*, 26(8), 085703.