Multiscale Metrologies for Process Optimization of Carbon Nanotube Polymer Composites

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ABSTRACT

Carbon nanotube (CNT) polymer nanocomposites are attractive multifunctional materials with a growing range of commercial applications. With the increasing demand for these materials, it is imperative to develop and validate methods for on-line quality control and process monitoring during production. In this work, a novel combination of characterization techniques is utilized, that facilitates the non-invasive assessment of CNT dispersion in epoxy produced by the scalable process of calendering. First, the structural parameters of these nanocomposites are evaluated across multiple length scales (10^{-10} m to 10^{-3} m) using scanning gallium-ion microscopy, transmission electron microscopy and small-angle neutron scattering. Then, a non-contact resonant microwave cavity perturbation (RCP) technique is employed to accurately measure the AC electrical conductivity of the nanocomposites. Quantitative correlations between the conductivity and structural parameters find the RCP measurements to be sensitive to CNT mass fraction, spatial organization and, therefore, the processing parameters. These results, and the non-contact nature and speed of RCP measurements identify this technique as being ideally suited for quality control of CNT nanocomposites in a nanomanufacturing environment. When validated by the multiscale characterization suite, RCP may be broadly applicable in the production of hybrid functional materials, such as graphene, gold nanorod, and carbon black nanocomposites.

1. INTRODUCTION:

Carbon nanotubes (CNTs) have generated remarkable technological interest since their emergence in the 1990s, owing to their exceptional mechanical and physical properties.[1,2] In the new millennium, these high aspect ratio nanostructures are making the transition from

laboratory curiosity to commercial material due to the development of synthetic techniques that are industrially scalable. Early synthesis techniques, such as arc discharge[3,4] and laser ablation,[5] were batch processes with relatively low yields of CNTs. However, the emergence of chemical vapor deposition[6] (CVD) has enabled continuous, high-volume, high-rate production of nanotubes.[2] High-performance polymer nanocomposites (PNCs), which use CNTs as structural reinforcements and conductive fillers, are one of a handful of CNT-based technological applications that have reached commercial scale production.[2,7–10] CNT PNCs have found applications as light-weight, corrosion resistant, readily-processable materials for mechanical reinforcement,[11,12] electro-magnetic interference shielding,[13] structural health monitoring,[14,15] and flame retardancy[16]. Most of these applications require that the CNTs be individually and homogeneously dispersed in the polymer matrix, to maximize polymer-nanotube interfacial area and/or to form electrically percolating networks at lower CNT loadings.[7,11,17–19]

Agglomeration in CNT-based composites is a significant problem due to the combination of van der Waals interactions and the high surface area of the CNTs.[20] In addition, commercially-available bulk CVD-grown nanotubes often have highly entangled structures.[2,11,21] These structures, resembling tumbleweeds, require extensive processing to break them down and untangle and uniformly distribute CNTs into the polymer matrix.[21] In light of this fact, several candidate methods for tailoring CNT dispersion have been investigated: ultrasonication,[22,23] high-speed mixing,[24] surfactant-assisted dispersion,[25] melt compounding[26] and calendaring.[27,28] However, many of these processing methods are not scalable to high-volume, high-throughput production processes.[28]

Even when processing techniques can be scaled to an industrial level, a major obstacle to the widespread use of CNT composites is the lack of high-throughput measurement methods for metrology and continuous process optimization through *microstructural evaluation*. The need for such a measurement technique is highlighted in the 2010 WTEC Panel Report on Nanotechnology Research Directions for Societal Needs in 2020, “The next decade will see many of the early nanoscale science discoveries transition to manufacturing. The need for process metrology, quality control measurements, and associated standards is acute.”[29] Such a technique should ideally probe the sample in a non-contact, non-destructive fashion and must measure a bulk property that is sensitive to the constituent properties as well as the reinforcement spatial dispersion and volume fraction. Prior to applying these techniques at the pilot or production scale, a quantitative understanding of the effects of nanocomposite morphology on the composite properties must be developed. These processing-structure-property relations are required in order to indirectly evaluate the microstructural and loading information from the measured bulk property. To support this, a suite of techniques probing the microstructure at various length scales is required, since industrially-produced CNT composites characteristically possess a hierarchical structure.[30]

In this research, we utilize a combination of imaging and scattering techniques for evaluating the multiscale structure of CNT-epoxy nanocomposites with varying CNT concentrations and dispersion states manufactured using an industrially-relevant calendering process (three-roll mill).[28,31] Various dispersion morphologies are achieved by varying the size of the smallest gap in the three-roll mill. We use novel scanning gallium-ion microscopy (SGIM) to characterize the CNT spatial arrangement at large length scales ($\approx 100\ \mu\text{m}$) with resolutions down to 100 nm. We then employ a combination of transmission electron microscopy (TEM) and reciprocal-space

small-angle and ultra-small-angle neutron scattering (SANS and USANS, respectively) to examine morphological features in the 0.1 nm to 10 μm range. This microstructural information is analyzed to obtain metrics to quantitatively evaluate the differences in CNT spatial arrangement at relevant measurement length scales.

While microscopy and scattering techniques provide a quantitative description of the nanocomposite morphology these techniques can be time consuming and can require extensive specimen preparation. There is a critical need to develop techniques capable of real-time monitoring of nanocomposite structure during the manufacturing process. Previous studies demonstrate that the electrical conductivity (alternating current (AC) and direct current (DC)) of CNT composites are strongly dependent on the spatial dispersion and mass fraction of CNTs, displaying order-of-magnitude variation as a function of CNT dispersion and concentration.[7,17,32,33] Resonant cavity perturbation (RCP) is a well-established, non-contact and non-destructive technique used to characterize the effective dielectric properties of materials at microwave frequencies.[34] We have recently demonstrated advances to this technique, which have increased its accuracy by approximately an order of magnitude for the measured properties.[35] Further, we have applied RCP to measure the effective dielectric properties of CNT materials in roll-to-roll manufacturing.[36] The sensitivity of the electrical conductivity to CNT dispersion and loading, and the ability of RCP to measure these properties accurately and in a non-contact fashion, make this technique well-suited for quality control of industrial CNT-polymer composites.

In this work we use a multi-walled carbon nanotube / epoxy nanocomposite as a model system to establish a quantitative link between the as-produced morphology, quantified using dispersion metrics obtained from established imaging and scattering characterization methods, and the

effective-medium bulk electrical properties measured using RCP. By establishing this fundamental processing-structure-property relationship we can understand the sensitivity of the RCP measurements to variation in the state of dispersion. The methodology established through combining these characterization techniques with RCP measurements may be used to both optimize processing conditions as well as to provide the necessary process control feedback data to ensure desired dispersion in an industrial setting using non-contact measurements. We believe that this methodology is broadly applicable to the quality control and process optimization of many other industrially-produced, functional, nanocomposite materials reinforced with conductive materials such as graphene, nanographite flakes, carbon black, and metallic nanowires.

2. EXPERIMENTAL

2.1. Materials

The model nanocomposite system used for this study consists of commercially-available, CVD-grown, multi-walled carbon nanotubes (MWCNT) (CM 95; Hanwa Nanotech, Korea[37]) and a low-viscosity epoxy resin system frequently used in the manufacture of composite materials. The epoxy resin system consists of a bisphenol-F epichlorohydrin epoxy monomer (EPON 862; Hexion, USA[37]) cured with an aromatic diamine curing agent (EPIKURE Curing Agent W; Hexion, USA[37]). The as-received carbon nanotubes have a highly-entangled morphology and are typically agglomerated as particles ranging from 20 μm to 200 μm in diameter (**Figure 1a**). Due to the complex structure of the agglomerates, it is difficult to accurately measure the initial individual nanotube lengths ($\approx 10 \mu\text{m}$). The average CNT diameter is found to be (14.3 ± 2.5) nm from TEM imaging (**Figure 1d**) (Unless noted otherwise, uncertainties are quoted as ± 1 standard deviation derived from multiple measurements).

2.2.Nanocomposite Processing

To produce nanocomposites with varying states of filler spatial organization for characterization, we used a calendering technique that has been identified as a scalable method for CNT dispersion. This method involves passing a mixture of CNTs and matrix through horizontal, parallel cylinders, each rotating in opposite directions at different angular velocities.[27,28,31] When passing through the small gap between the velocity-mismatched cylinders, the CNT-epoxy mixture is homogenized by a uniform shear force (**Figure 1b**). The mixture forms a thin film over the adjacent cylinders and is collected using a scraper blade.

In order to produce nanocomposites with varying concentrations and morphologies, samples were prepared with different mass fractions of carbon nanotubes as well as different gap settings between the cylinders of the three-roll-mill. A series of nanocomposites were prepared with different concentrations of CNTs by mass (0.10 %, 0.25 %, 0.50 %, 0.75 %, 1.00 %). Control specimens of unreinforced epoxy were also produced for electrical characterization. The epoxy monomer and bulk carbon nanotubes were weighed out based on the selected final mass fraction and mixed together by manual mixing. For each nanotube concentration, three processing routes were investigated by varying the gap between the rotating cylinders. Following the processing methodology established previously,[28] the mixture was passed through the three-roll-mill at progressively smaller gap settings. The mixture was first passed through the mill for five passes at a gap setting of 120 μm followed by 10 passes at a gap setting of 30 μm and 20 passes at a gap setting of 5 μm . At each gap setting, a portion of the mixture was set-aside to manufacture nanocomposites with varying degrees of dispersion. To produce the nanocomposites, curing agent was added to the mixtures at a concentration of 26.4:100 parts of curing agent to epoxy monomer. The curing agent was mixed into the epoxy/nanotube dispersion using a planetary

centrifugal mixer at $209 \text{ rad}\cdot\text{s}^{-1}$ (2000 rpm) for 150 s to ensure complete homogenization of the mixture and to assist with partial degassing. The dispersions were further degassed in a vacuum oven heated to 60°C . After degassing the nanotube/epoxy dispersions were poured into a clean aluminum mold and cured in a convection oven at 130°C for 6 h. Intuitively, one would expect the dispersion to monotonically improve with decreasing gap dimensions due to the increased specific mechanical energy (or shear force) associated with homogenization process.[31]

Figure 1. Clockwise (a) SEM image of as-received CNT powder showing large agglomerates of entangled CNTs (b) Schematic of the calendaring setup indicating direction of rotation of rollers, roller gap, material feed and collection areas. (c) Representative TEM image of the final nanocomposite structure that was used to measure CNT diameters. (d) Histogram of CNT diameters measured from TEM images.

2.3. Microstructural Characterization

2.3.1. Scanning Ion Beam Microscopy: Scanning gallium ion beam microscopy (SGIM) images of the CNT nanocomposites were obtained from polished ≈ 0.5 mm thick samples using a dual-beam focused ion beam (FIB)/ scanning electron microscope (SEM) setup. The samples were scanned using a focused Ga⁺ beam, at a voltage of 30 kV, a current of 18 pA, a spot size of 2.5 nm, and pixel size of 194 nm, and imaged using a highly-sensitive, high-performance Ion Conversion and Electron (ICE) secondary electron (SE) detector (Magnification = 250 $\times$, corresponding to a field of view of 597 $\mu\text{m} \times 402 \mu\text{m}$), in order to characterize the CNT distribution in the polymer matrix at large length scales.

2.3.2. Transmission Electron Microscopy: To observe the nanoscale CNT dispersion and local distribution (nanometer to micrometer scale), nanocomposite samples were sectioned into ≈ 100 nm thick slices using an ultramicrotome equipped with a diamond knife. The slices were then transferred onto a copper-mesh grid and imaged in a transmission electron microscope (TEM) at 300 kV in bright-field mode. A 40 μm objective aperture and a zero-loss energy filter were inserted to enhance image contrast.

2.3.3. Small and ultra-small angle neutron scattering (SANS and USANS): SANS experiments were performed on the NG7 and NGB 30 m SANS instruments at the NIST Center for Neutron Research (NCNR). Measurements were performed in the standard SANS scattering configuration with a q-range of 10^{-2} nm^{-1} to 5.5 nm^{-1} , which is roughly equivalent to a real-space length-scale interval of 1 nm to 630 nm. The USANS measurements were conducted on the cold source BT5 beamline at the NCNR. The USANS configuration allows access to a complementary real-space window that extends up to $\approx 10 \mu\text{m}$. For scattering measurements, the samples were shaped into 0.5 mm thick by 1.3 cm diameter circular pellets that were mounted

onto cadmium masks with a 1.11 cm aperture. Empty beam measurements were performed on an identical cadmium mask and used for data normalization. The data reduction was done using the Igor NCNR data reduction protocols that properly account for background subtraction, detector sensitivity and empty beam corrections, yielding absolute scattering intensity patterns (**details in supplementary material, Figure S1**).[38] The fitting of SANS and USANS data was performed using the SasView data fitting software,[39] which properly accounts for experimental data resolution during the fitting process.

2.4. Conductivity Measurements:

The RCP technique, developed by Orloff *et al.*[35] was used to measure the effective AC conductivity of the nanocomposites. The bulk composites were cut and polished into 10 mm $\times$ 3 mm $\times$ 0.5 mm samples, which were then incrementally inserted into the microwave cavity. The insertion of the sample into the cavity causes a shift in the resonance frequency and damping ratio of the cavity. By fitting these shifts versus the effective volume fraction of the sample in the cavity, the effective AC conductivity can be calculated.[35] Since we did not observe any appreciable frequency dependence (over the operating range of 7 GHz to 12 GHz) in the dielectric properties in our RCP setup, we attribute all of the microwave loss to the specimen electrical conductivity instead of dielectric relaxation. Based on this assumption we evaluated the properties of the nanocomposites in a narrow frequency range fixed around 7 GHz, which can be considered representative for the frequency range of our RCP setup between 7 GHz to 12 GHz. We performed RCP measurements for three individual samples for each nanocomposite composition and dispersion state. Further details of the measurement method are described in Orloff *et al.*[35]

3. RESULTS AND DISCUSSION:

3.1. Microstructure

3.1.1. Bulk-Scale Dispersion

When dispersed in a polymer matrix CNTs typically form hierarchical morphologies that can range from mesh-like assemblies called flocs to agglomerates of flocs that can eventually assemble into matrix-spanning networks.[30] Therefore, in these systems, two aspects of spatial dispersion are usually considered: (a) The entanglement of CNTs at the nanoscale (intra-floc structure) and (b) the micro- (local) and macroscopic (global) *distribution* of flocs.[17] This necessitates a hierarchical characterization and quantification of the CNT morphology for a proper assessment of the effect of processing on the spatial dispersion of CNTs and effect of spatial dispersion on the property of interest. **Figure 2** shows SGIM and TEM micrographs of the hierarchical dispersion of nanotubes in nanocomposites processed at a gap setting of 120 μm with a nanotube concentration of 1.00 % by mass. **Figure 2a** is a low magnification SGIM image showing the overall morphology which includes large aggregates (**Figure 2b**), diffuse agglomerates (**Figure 2c**) of carbon nanotube flocs and the intra-floc structure (**Figure 2d**).

Previous studies have extensively used transmission *optical* microscopy to quantitatively study the role of processing on the breakdown of the CNT starting material. While this technique enables the imaging of millimeter scale samples, its resolution is limited by the diffraction limit ($\approx 0.5 \mu\text{m}$) and is only useful in viewing large, micrometer-scale aggregates of CNTs.[17,40–42] Scanning electron microscopy, which facilitates imaging with large fields of view at high resolution, lacks the contrast to reliably resolve CNT networks embedded in polymers, precluding robust binarization and quantitative characterization.[31,43,44] On the other hand,

TEM images reveal CNT arrangements at the scale of individual flocs and meshed CNTs but are generally at too high of a magnification to visualize the bulk structure.[12,45,46]

Figure 2. (a) Scanning gallium-ion microscopy image showing the large-scale organization of CNT networks. (b) TEM image demonstrating the internal structure of aggregates (inverted intensities). (c) TEM image showing the local distribution of CNTs in diffuse agglomerates (inverted intensities). (d) Higher magnification TEM images showing the internal structure of CNT flocs (inverted intensities).

Here we use scanning gallium-ion microscopy (SGIM) for the imaging of the dispersion of CNT networks across the bulk sample. In this method, the incident gallium ions inject the insulating

epoxy matrix with a net positive charge, which prevents the release of secondary electrons (SEs), making these regions appear dark when using an SE detector. Since the MWCNT phase is conducting, the Ga^+ ions that are incident to the CNT rich regions have a low-resistivity path to ground, allowing for the neutralization of the accumulated charge. Therefore, the MWCNTs emit SEs more readily and appear bright in the SE detector. This mechanism results in high-contrast images showing the cross-sectional large-scale dispersion of CNTs (information is sampled from the first 40 nm of the incident surface). These images are amenable to binarization and microstructural quantification. This mode, which allows high resolution (≈ 100 nm) imaging of large fields of view ($\approx 500 \mu\text{m} \times 500 \mu\text{m}$), is readily available in standard dual-beam FIB/SEM instruments but, to our knowledge, has not been demonstrated on CNT composites, primarily due to concerns regarding the active ion milling of the sample surface during imaging. However, milling effects were found to be negligible at these magnifications as illustrated by the set of serial scans (see **Figure S3** in supplementary material).

The clarity of SGIM imaging allows us to firstly conduct a visual assessment of dispersion. **Figure 3** shows representative SGIM images of the samples investigated in this study. First, the addition of CNTs reduces the area fraction of the dark epoxy-rich regions at all gap settings. As expected, the $120 \mu\text{m}$ (largest gap size) composites exhibit the least distributed and disentangled morphologies, with large CNT-rich domains (aggregates or tumbleweeds) and non-uniformly distributed diffuse agglomerates of CNT flocs (**Figure 3**, left column). At the lowest nanotube concentration (mass fraction) these flocs are isolated from one another. Increasing the CNT concentration, above 0.50 %, shows the formation of diffuse CNT networks around the dense CNT-rich domains. The CNT-rich tumbleweeds are not observed in the $30 \mu\text{m}$ (**Figure 3**, middle column) and $5 \mu\text{m}$ (smallest gap size, **Figure 3**, right column) samples. This observation

suggests that the reduction in gap size does indeed lead to the systematic breakdown of the starting material into diffuse floccular agglomerates, which is in qualitative agreement with previous studies.[27] At concentrations up to 0.50 %, the CNT distribution in the 5 μm and 30 μm samples is qualitatively similar based on visual inspection. At higher loadings, the CNTs in the 30 μm samples become uniformly distributed over the entire sample bulk. In contrast, the 5 μm samples display a meso-structure with a non-uniform distribution of floccular networks. Since a decrease in the gap size has been shown to monotonically improve dispersion, the heterogeneity of the 5 μm dispersion is unexpected. There are several likely factors behind this observation, including thermally-activated re-aggregation during processing[24,40] or the flow-induced assembly observed in CNT suspensions sheared between gaps of size comparable to, or shorter than the CNT length[47,48]. An accurate assessment of the relative contributions of these factors is beyond the scope of this work. In order to evaluate these differences more objectively, it is essential to acquire a quantitative measure of the bulk-scale dispersion from the SGIM micrographs.

While several methods have been proposed in the literature to quantify such heterogeneous media, most of these techniques are specific to the system analyzed and lack generality.[32,49–52] The diffuse agglomerates that result from calendering are unlike the spherical CNT aggregates obtained from sonication or melt mixing. Therefore, traditional physical metrics such as intercluster distance and cluster size do not fully describe the state of dispersion.[51] Numerical *qualitative* descriptors such as relative dispersion index and chi square are primarily suited for comparing nanocomposites at a specific concentration.[32,52] We seek to use a more broadly applicable quantification method that accounts for loading conditions and dispersion quality. Khare and Burris[53] have proposed a free space length parameter (L_f), which is a

measure of the size of unfilled polymeric domains in nanocomposites. In short, a Monte-Carlo technique is used to place a statistically large number of squares of prescribed size at random locations on the surface. The number of particles within each box is counted. The size of this box is progressively reduced. The square size that corresponds to a mode of zero in the distribution of number of particles is chosen as the L_f . Poor and uniform distributions yield large and small L_f values, respectively. The choice of the initial box size and number of boxes is critical to the precision of this characterization technique and these parameters are varied to identify optimal values for L_f measurements (Figure S5).

Figure 3. Representative SGIM images demonstrating the effect of mass fraction and gap size over the various samples studied here. The horizontal and vertical field widths in these images are 597 μm and 402 μm , respectively.

The images obtained from SGIM are binarized using Otsu's thresholding method (**Figure S4**) and L_f measurements are made as prescribed.[53] The SGIM images are then smoothed (Gaussian Smooth, 1 pixel) inverted, binarized and the free space length method is applied to measure the floc-size (aggregate-length in 120 μm , L_a). We note that L_a is not the average aggregate size but the size of the square that corresponds to a mode of zero in the distribution of matrix intersections. In the presence of large CNT-rich domains, these values are expected to be insensitive to the smaller flocs.[53] This process is repeated over 5-6 images for each composite type to obtain statistically relevant measurements over a total area of 1.4 mm^2 . We note that, while this cumulative field of view is comparable to optical imaging techniques, the resolution is akin to scanning electron microscopy. The measured values are shown in **Figure 4** and **Table S2**.

From **Figure 4a**, we show that the 120 μm composites have the largest L_f at all loadings, which differ significantly from the L_f values of the other samples beyond a mass fraction of 0.50 %. This observation confirms the visual assessment that these samples have the least uniform dispersion of nanotubes. The standard deviation in L_f for 120 μm composites is also large, suggesting a heterogeneous bulk dispersion. The L_f values in the 120 μm samples decrease sharply with the addition of CNTs up to 0.50 %, beyond which the decrease is more gradual, suggesting that additional CNTs are primarily incorporated into preexisting aggregates. This hypothesis is confirmed by the observed increase in L_a values with CNT loading (**Figure 4b**). Much like free-space length, L_a values of the 120 μm samples are the largest and are comparable to the large L_f values, indicating a poor breakdown of the starting material. In the 5 μm

composites the L_f values are lower than in the 120 μm samples, have smaller standard deviations and decrease more sharply with loading. The 30 μm composites have L_f values statistically similar to the 5 μm samples up to 0.50 %. At higher loadings, however, the calculated L_f values are considerably lower in the 30 μm composites. This observation suggests that the 30 μm composites possess the best overall CNT distribution. L_a values of the 5 μm and 30 μm composites are both smaller than the highly aggregated 120 μm system (visually evident in the TEM micrographs in **Figure 6**) and the measured free space lengths are an order of magnitude lower indicating improved breakdown and distribution of nanotubes with smaller gap settings. The aggregate lengths in the 5 μm and 30 μm composites are similar up to 0.50 %. At higher loadings the L_a values of the 5 μm samples increase with the addition of CNTs. On the other hand, the 30 μm samples show negligible change in aggregate length, which explains the significant drop in L_f . At this gap size, the addition of CNTs appears to fill the matrix with more flocs.

Figure 4. Plots of (a) Free Space Length (L_f) and (b) Aggregate Size (L_a), *versus* the mass fraction of carbon nanotubes. The uncertainties indicated by the vertical bars on each point represent the standard deviation in values measured from 6 images per composite type.

3.2.2. Local Arrangement:

In order to investigate differences in the local dispersion (entanglement and micron-scale distribution) of nanotubes, the 0.50 %, 0.75 % and 1.00 % mass fraction samples – loadings with pronounced dispersion differences based on the SGIM characterization, were imaged using transmission electron microscopy (TEM) (**Figures 5 and 6**).

Figure 5. Representative TEM images of the various samples studied here demonstrating the effect of loading and gap size on the local arrangement of carbon nanotubes. All scale bars

represent 1 μm . Note that we study only the samples at the loadings where global dispersions appear or begin to appear different.

TEM images of the 120 μm samples show large CNT-rich domains surrounded by a sparse distribution of CNT-flocs and large matrix-rich regions. The internal structure of the domains is comprised of densely packed tumbleweeds held together by loosely entangled CNTs (**Figures 6a and 6b**). That said, we are mainly interested in the local structure of the diffuse agglomerates of flocs since they are the primary pathways for conduction in these composites. The TEM images (**Figure 5**) seem to qualitatively confirm the local structure implied by the bulk-scale SGIM images, but since the differences are visually slight, we investigate the local morphologies further through quantitative analysis of the TEM images

Figure 6. Representative TEM images of 1.00 % 120 μm samples showing (a) the interface between the CNT-rich domains and the matrix. A sparse distribution of loose flocs and large matrix-rich regions are observed. (b) The internal structure of CNT-rich domains showing micrometer sized tumbleweeds held together by loose CNT networks.

The TEM images were analyzed using the method presented by Luo and Koo.[54] First, the images were processed and binarized to isolate the CNT networks from the background matrix (**Figure S5**). The binary images were then skeletonized using the Skeletonize3D plugin on

ImageJ to convert the CNTs to line objects (**Figure S6**).^[55] The skeletonized images were overlaid with 20 1-pixel thick horizontal lines (**Figure S7**) and analyzed using the AnalyzeSkeleton plugin in ImageJ.^[55,56] The Euclidean lengths of the branches were size thresholded to exclude erroneous distances smaller than the CNT diameter. From the detailed branch information, the length of the straight-line sections, which correspond to the free-path spacing between nanotubes, were measured. This was repeated for 20 vertical lines. The mean and standard deviations of the free-path spacing was calculated for five images per composite type (**Table S3**). The dimensionless dispersion parameter, $D_{0.1}$, defined as the probability of the free-path distance distribution in the range of 0.9 to 1.1 times the mean, was calculated with the lognormal distribution formulated by Luo and Koo,^[54] using the measured mean and standard deviation values. A narrower distribution of free-path spacing around the mean – a smaller standard deviation and therefore a larger $D_{0.1}$ – indicates a more uniform distribution of CNTs at this scale ($\approx 4 \mu\text{m} \times 4 \mu\text{m}$). From the plot in **Figure 7** we observe the $D_{0.1}$ of the 30 μm nanocomposites to be higher, since the standard deviations in free path spacing distributions are consistently larger in the 5 μm and 120 μm samples (**Table S3**). This observation suggests that the CNTs are slightly better distributed locally in the 30 μm nanocomposites.

Figure 7. Plot of dispersion parameter $D_{0.1}$, measured from TEM images *versus* the mass fraction of carbon nanotubes. The uncertainties represent the standard deviation measured from 5 images per composite type.

SANS and USANS measurements provide a complementary picture of the dispersion ranging from nanoscopic to microscopic length scales. Due to the complexity of the system and the hierarchical structures involved, a precise model of the composite system is quite challenging. Instead, we follow a simple approach based on the changes in the q -dependence of the intensity in different q -ranges, which is commonly used in analyzing scattering signals from nanorod dispersions[57] and hierarchical particle networks.[58] In a hierarchical picture consistent with the TEM and SGIM characterization, the scattering patterns over the medium and high q -range (small length scales) should provide average bulk characterization of the CNT structure (e.g. diameter, persistence length) whereas the low- q patterns are associated with larger structural features such as the mesh size and aggregate compactness.[59] We should point out that the low- q scattering intensity, $I(q)$, from networks usually exhibits a q^{-n} behavior ($2 < n < 3$) depending on the compactness of the network, where increasing values of n (also referred to as the fractal dimension, d_f) indicate tighter network structures.[30] On the other hand, scattering from rigid

nanorods is characterized by a q^{-1} scattering behavior over a q -range that reflects length scales between the radius and the length of the nanorod. However, in the present systems, the nanotubes appear to be quite flexible and entangled in the TEM images, so a q^{-1} dependence of the intensity is not expected, especially with high incoherent background intensity, as is the case here. Instead, we adopt a flexible cylinder formalism to model the data in the higher q -range ($q > 3 \times 10^{-2} \text{ nm}^{-1}$), which yields estimates of the average nanotube diameter and the persistence length of the nanotubes.[38] In this range, the SANS 1D patterns from samples with the same CNT loading are identical regardless of the gap size used in sample processing (**Figure 8**), which indicates that the persistence length of the CNTs stays the same regardless of the processing conditions. The average CNT diameter measured by SANS ($(15 \pm 2) \text{ nm}$) is in excellent agreement with the TEM measurements shown in **Figure 1c**.

Figure 8. CNT structure of nanocomposites studied by USANS and SANS. (a) Plot of scattered intensity $I(q)$ for 0.50 % by mass CNT composites with the high, medium and low- q regions indicated. Arrows indicate the breaks in slope associated with transitions in morphological features occurring at various length scales. (b) and (c) are plots of scattered intensity $I(q)$ for 0.75 % and 1.00 % by mass CNT composites, respectively.

The persistence length ((22 ± 5) nm) found from the fits also reflects the highly wavy nature of the CNTs, as clearly seen in **Figure 5**. The onset of deviation from the flexible cylinder model at lower- q (larger length) determines the mesh size, ξ , which is indicative of the density of percolated CNTs within the diffuse agglomerates.[30] On average, the mesh size, $\xi = \pi/q_{\text{mesh}}$, is

not observed to decrease with increased concentration, with $\xi \approx (97.0, 99.0, 105.4)$ nm for CNT mass fractions of (0.50 %, 0.75 %, 1.00 %) respectively. However, differences in mesh size are observable with different gap sizes. At higher loadings (> 0.50 %), the samples prepared with the 30 μm gap show the smallest mesh size, indicating a more uniform distribution of CNTs in these samples (**Figure 9a, Table S1**). The larger mesh size observed in the other two set of samples is likely due to the larger distance between flocs i.e. a poorer distribution.

The packing density of the flocs in the agglomerates is captured by the mass fractal dimension, d_f , inferred from the USANS low q (length scale $> \xi$) slope of the log-log plot of $I(q)$ vs. q . The 120 μm gap samples demonstrate the highest d_f values at all loadings (**Figure 8b and Table S1**), which is expected given the large CNT-rich domains and tightly packed agglomerates in these samples. The most remarkable differences in the USANS scattering signals from samples prepared with different gap sizes are obtained at nanotube concentrations (> 0.50 %). At these loadings, the 30 μm gap samples demonstrate the lowest d_f values, indicating that the flocs here are more loosely packed and therefore better distributed. It is also worth noting that the absence of an obvious turnover or plateau in the USANS data indicates that the agglomerate size is larger than the maximum length scale accessed in the USANS measurements; i.e. $L_a > \pi/q_{min}$.^[59] This is calculated to be $\approx (3, 5, 10)$ μm for the (0.50 %, 0.75 %, 1.00 %) samples, respectively, and is in rough agreement with the SGIM estimates of the aggregate size (Figure 4b). Our observations of the mesh size, the fractal dimension (d_f) and the dispersion parameter ($D_{0.1}$) suggest that the gap setting does not affect the density of the flocs, but tailors the packing of flocs in the larger length scale agglomerates. Further, these observations serve to validate the hypothesis arising out of the global scale SGIM imaging. The agreement between the local ($d_f, D_{0.1}$) and large scale (L_f) morphological parameters is shown in Figure S8 in the supplementary material.

Figure 9. Plots of (a) mesh size (ξ) and (b) mass fractal dimension (d_f), as measured by SANS and USANS *versus* the mass fraction of carbon nanotubes. The uncertainties represent errors arising from the fitting process that accounts for the error in the data and fit quality.

3.2. Measuring Dielectric Properties by Resonant Cavity Perturbation:

The RCP method has the potential to be employed for quality control and process optimization in CNT-polymer nanocomposites. This microwave characterization technique enables us to measure the effective AC conductivity (and effective dielectric constant, **see supplementary material Figure S10**) of the MWCNT-epoxy nanocomposites, by treating the entire sample as a single, uniform material, i.e., using an effective medium approximation. This is unlike DC techniques, which primarily measure the conductivity along the path of least resistance and can be misleading when used to infer the microstructure from bulk data. Additionally, DC measurements can be confounded by contact resistance variability.

We find that the addition of CNTs to the matrix epoxy leads to enhancements in the AC conductivity irrespective of the gap size employed during processing (**Figure 10a**). Quantitatively, in going from a 0.10 % loading to a 1.00 % loading of conductive CNTs to the

epoxy matrix, there is a nearly 2 orders of magnitude increase in the AC conductivity.[31,60,61] With improved dispersion, the fraction of nanotubes participating in conduction is expected to increase as compared to aggregated systems which are dominated by non-participating, isolated CNT-rich domains.[17,24,31–33] Comparing the samples obtained from different gap sizes, the conductivities do not show any significant differences until a mass fraction of 0.50 % is reached. This is because at loadings < 0.50 % the CNTs are primarily in isolated pockets, due to which minor variations in dispersion resulting from the different gap sizes do not contribute significantly. At higher loadings, the 120 μm gap composites are found to be the least conductive. The large, isolated, CNT-rich tumbleweeds in the 120 μm sample, participate minimally in electron transport and additionally lower the statistical fraction of diffuse CNTs agglomerates available for conduction. The conductivity of the composites processed at a gap setting of 30 μm increases remarkably in going from a mass fraction of 0.5 % to 0.75 %, but plateaus with further CNT addition. Nevertheless, at 0.75 % and 1.00 %, the 30 μm composites have the highest conductivity. The conductivity of the 5 μm gap samples increases steadily with increased loading beyond 0.50 %, but remains lower than that of the 30 μm composites. This is consistent with the TEM and USANS results that show the composites processed at a gap setting of 30 μm show the highest degree of dispersion, and is consistent with the hypothesis that a higher degree of dispersion is correlated with increased conductivity. [31,60,61]

Figure 10. (a) Plot of AC conductivity, as measured by RCP *versus* the mass fraction of carbon nanotubes. (b) Plot of log conductivity *versus* volume fraction^{-1/3} of the various composites studied here, showing deviations from linearity at higher loadings. The uncertainties represent the standard deviation in values measured from 3 samples per composite type.

We see further evidence of the above-mentioned correlation in the plot in **Figure 10b**, which shows the relationship between the natural logarithm of AC conductivity and volume fraction (calculated from the mass fraction assuming a CNT density of 1.3 g cm⁻³). Previous studies have demonstrated that conductivity dominated by tunneling between CNTs embedded in an insulating medium follows

$$\log(\sigma) \propto -v^{-1/3} \quad (1)$$

where σ is the conductivity and v is the volume fraction. The 5 μm samples are observed to follow the linear relationship in Equation 1 at all loadings suggesting that the primary mode of conduction in these samples is tunneling in the entire weight fraction range studied here. The other samples display this linear trend only until 0.50 %. In the case of the 30 μm samples $\log(\sigma)$ assumes a steeper slope at higher loadings (lower $v^{-1/3}$) which is ascribed to an increase

in the number of CNT contacts, through improved dispersion (**Figure 3**), which facilitates the direct transport of electrons between CNTs, as opposed to the higher-resistivity tunneling pathways. The 120 μm $\log(\sigma)$ plot exhibits a linear trend but with a lowered slope beyond 0.50 %, indicating that these samples have a higher percolation threshold due to the lowering of the effective CNT aspect ratio by agglomeration.[17,31] We note that since the various morphologies are realized without any chemical modification, all property differences observed are due to processing-induced variations in dispersion.

The data in **Figure 10** shows that the AC technique is sensitive to mass fraction-induced changes in the electrical properties of the nanocomposite that were otherwise only measurable by contact-based DC techniques. The RCP results are also in qualitative agreement with previously studied dependencies of AC conductivity on CNT spatial dispersion. Without any prior knowledge of the microstructure, from the RCP results one would still be led to believe that the 30 μm and 120 μm samples had the best and worst dispersion, respectively. This is quite surprising since RCP measurements are made at microwave frequencies,[35] and microwave wavelengths (millimeters) are orders of magnitude larger than the length scales of typical microstructural variations (nanometer to micrometer). To understand this correlation between dispersion and RCP measurements better, it is essential to investigate the sensitivity of RCP to dispersion, loading and processing parameters (gap size).

3.3. Structure Property Relationships:

While the disparities in the local structure are quantifiable and affect, cumulatively (indirectly), the continuum-scale organization, they are not substantial enough to dictate the differences observed in the microwave data. It can be inferred from the quantification of the local structure that the bulk organization of the matrix-spanning networks primarily dictates the observed

electrical properties. In light of this observation, we plot the AC conductivity versus the free space length, which is dependent on of the global dispersion state as well as the loading (**Figure 11**). From these plots we observe a good correlation ($R^2 \approx 0.80$) of the conductivity with L_f , (fit by a linear function $y=ax+b$, where, x is the FSL, $a = (-0.033 \pm 0.012)$ and $b = (2.14 \pm 0.50)$, where uncertainties are determined from error propagation based on a 95% confidence interval) thereby demonstrating the sensitivity of the measurements to the continuum scale dispersion state. Additionally, these results indicate that the RCP measurements are indeed responsive to the processing parameters employed and may be used to optimize or actively monitor composite properties during manufacturing.

Figure 11. Plot of AC conductivity as measured by RCP *versus* the free space lengths measured from SGIM images. The uncertainties in the AC conductivity represent the standard deviation in values measured from 3 samples per composite type. The uncertainties in L_f represent the standard deviation in values measured from 6 images per composite type.

However, the dependence of RCP measurements on the processing parameters is fairly complex.

This is because the AC conductivity is a mass fraction-dependent function of the dispersion state,

which is in turn a complex function of gap size and loading. We illustrate this in the 3D plot in **Figure 12**. At 0.25 % loading, the L_f values are statistically similar for all gap sizes and the AC conductivity shows minor variations accordingly. The same holds true for the 0.50 % samples, but the conductivities are found to increase due to the additional 0.25 % mass fraction loading of CNTs. At 0.75 % L_f values are marginally smaller and vary with the gap size (**Figure 12**). However, the AC conductivity shows a strong dependence on L_f , which in turn manifests as a strong dependence on the gap size at these weight fractions. At 1.00 %, mass fraction loading the dispersions are markedly different for each gap size, which we see as larger changes in L_f (in comparison to the 0.75 % composites). However, at this loading, the dielectric properties have a lowered sensitivity to L_f and the dispersion state, consequently seen as a lowered sensitivity to the gap size. While the 5 μm and 120 μm gap size composites show proportional enhancements, the conductivity and the permittivity of the 30 μm gap size composites saturate due to percolation (attributable to the excellent dispersion state).

Bearing in mind these complications, in order for RCP to be effective in an industrial setting, it is imperative to perform an extensive set of experiments in a systematic fashion, as is done here, prior to high-volume (or large-scale or bulk) manufacturing. This is required for the development of quantitative processing-(structure)-property relations. In the case of composites manufactured for non-dielectric applications such as structural reinforcement or flame retardancy, the property of interest may respond to the dispersion state, loading and therefore the processing parameters in a different manner.[61] In these scenarios, it is also essential to develop relationships linking processing and structure to the property of interest and correlating that with the RCP response. The sensitivity of the RCP response around the desired value of the property of interest will determine the limitations of RCP-based metrology for a specific application. Once the

relationships have been established and optimal processing parameters have been identified, RCP may be used in real-time quality control, on a sample-to-sample basis or rolling stocks of CNT composites.[36] Further, we believe, with appropriate minor modifications, these methods are extensible to other industrially-produced, functional, nanocomposite materials reinforced with conductive reinforcements such as graphene, nanographite flakes, carbon black, and metallic nanowires.[62–65]

Figure 12. 3D plot of AC conductivity (Z axis) as measured by RCP *versus* the free space lengths (X axis) measured from SGIM images and calendering gap sizes (Y axis). The red, blue

and black data points are projections of the 3D scatter data onto the ZX, ZY and XY planes, respectively.

4. CONCLUSIONS:

With the increasing demand for carbon nanotube-polymer composites, these materials are quickly transitioning into industrial-scale production. A key challenge to sustained growth in production and adoption of these materials is the ability to perform quality control in the manufacturing environment. In this paper, using epoxy-CNT nanocomposites processed by an industrially-relevant calendering method, we have demonstrated a suite of characterization techniques that facilitate this. A variety of CNT dispersion states at various mass fractions were realized by varying the size of the smallest gap in the three-roll mill. Scanning gallium-ion microscopy, TEM and small-angle neutron scattering were used to characterize the CNT morphology across 7 decades of length scale. The differences in dispersion were found to arise out of variations in the meso and macro-scale arrangement of floccular units, rather than variations within the nanoscale floc structure: this is in contrast to what is commonly suggested in the literature. After this detailed characterization, the AC conductivity was measured using RCP, which we believe to be an excellent non-contact technique for quality control and process optimization. The measured AC properties were found to be sensitive to the mass fraction of CNTs and well-correlated with the variations in dispersion state. Beyond a critical mass fraction, improved floccular distributions were observed to display improved AC conductivity. However, prior to employing RCP for live process monitoring, a detailed understanding of the role of dispersion on AC properties needs to be evaluated in order to correlate the microwave measurements to the processing data. The characterization protocols described here enable this and could likely serve as an important component to developing and parametrizing multiscale simulation models. Once the role of processing on the dispersion and the AC conductivity is

understood, RCP may be used to monitor variations from the ideal properties and to tune the process accordingly. Broadly, we believe these techniques may be applied to other hybrid materials, where the spatial arrangements of the constituents determine the ultimate functionality.[66]

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