

Nanocomposite Dispersion: Quantifying the Structure-Function Relationship

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## ABSTRACT

The dispersion quality of nanoinclusions within a matrix material is often overlooked when relating the effect of nanoscale structures on functional performance and processing/property relationships for nanocomposite materials. This is due in part to the difficulty in visualizing the nanoinclusion and ambiguity in the description of dispersion. Understanding the relationships between the composition of the nanofiller, matrix chemistry, processing procedures and resulting dispersion is a necessary step to tailor the physical properties. A method is presented that incorporates high-contrast imaging, an emerging scanning electron microscopy technique to visualize conductive nanofillers deep within insulating materials, with various image processing procedures to allow for the quantification and validation of dispersion parameters. This method makes it possible to quantify the dispersion of various single wall carbon nanotube (SWCNT)-polymer composites as a function of processing conditions, composition of SWCNT and polymer matrix chemistry. Furthermore, the methodology is utilized to show that SWCNT dispersion exhibits fractal-like behavior thus allowing for simplified quantitative dispersion analysis. The dispersion analysis methodology will be corroborated through comparison to results from small angle neutron scattering dispersion analysis. Additionally, the material property improvement of SWCNT nanocomposites are linked to the dispersion state of the nanostructure allowing for correlation between dispersion techniques, quantified dispersion of SWCNT at the microscopic scale and the material properties measured at the macroscopic scale.

*To my wife*

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## LIST OF ABBREVIATIONS

one, two and three dimensional (1D, 2D and 3D)

single wall carbon nanotube (SWCNT)

weight percent or percent by weight (wt%)

scanning electron microscope (SEM)

transmission electron microscope (TEM)

scanning probe microscope (SPM)

optical microscope (OM)

high-resolution scanning electron microscope (HR-SEM)

laser ablated single walled carbon nanotubes (LA-SWCNTs)

high pressure carbon monoxide (HiPCO) SWCNT

polymer 1 (LaRC CP-2™)

polymer 2 ( $\beta$ -CN)APB/ODPA

polymethylmethacrylate polymer (PMMA)

polystyrene polymer (PS)

polymethylmethacrylate/polystyrene copolymer(PMMA/PS)

dimethylformamide (DMF)

National Institute of Standards and Technology (NIST),

radial power spectral density (RPSD),

polar power spectral density (PPSD)

and full width at half maximum (FWHM)

Hurt parameter (H)

fractional Brownian motion (fBm)

fractal dimension (Df)

scaling parameter (B)

power spectral density (PSD)

transfer function (FT)

discrete Fourier transform (DFT)

fast Fourier transform (FFT)

probability (PG)

total probability (PTG)

coefficient of determination ( $R^2$ )

through the lens detector (TTL)

modulation transfer function (MTF)

small angle neutron scattering (SANS)

small angle x-ray scattering (SAXS)

differential scanning calorimetry (DSC)

glass transition temperature ( $T_g$ )

## ATTRIBUTION

Study One was published in the Institute of Physics – Journal of Nanotechnology entitled “*A quantitative assessment of carbon nanotube dispersion in polymer matrices*” with coauthors Peter T. Lillehei<sup>1</sup>, Jae-Woo Kim<sup>2</sup> and Cheol Park<sup>2,3</sup>. The manuscript is available online at [stacks.iop.org/Nano/20/325708](http://stacks.iop.org/Nano/20/325708)

The supplemental section, Supplemental A, was published online by the Institute of Physics – Journal of Nanotechnology as a supplemental section to the manuscript and is available online at [stacks.iop.org/Nano/20/325708](http://stacks.iop.org/Nano/20/325708)

Supplemental B is provided here to expand upon the published version. The published manuscript reflects research which began when I participated in the Langley Aerospace Research Summer Scholars (LARSS) program before coming to Virginia Tech and continued as the focus of my doctoral studies. I came to Virginia Tech through the National Institute of Aerospace (NIA, Hampton, VA) Graduate Research Assistantship program and completed my Ph.D. by attending courses via virtual classrooms that link the NIA with classrooms at a handful of Universities including Virginia Tech. I performed all research within the Advanced Materials and Processing Branch of the NASA Langley Research Center (NASA LaRC, Hampton, VA) via a cooperative agreement with the NIA. Dr. Lillehei was my official NASA mentor throughout this research. Dr. Kim and Dr. Lillehei were my co-mentors during the LARSS program. Dr. Park was an unofficial NIA mentor during my time at NASA LaRC. The material in Study One is the result of mentors guiding me and contributing to a research project that was assigned to me as a LARSS participant and willfully continued during the Virginia Tech/NASA/NIA Graduate Research Assistantship program.

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The general high-resolution scanning electron microscope procedure provided in Appendix A was modified from the original version written by Peter T. Lillehei to account for operational changes since 2007.

## 1.0 CHAPTER ONE: INTRODUCTION

### *1. The Nanoscale*

History has defined scientific thinking and growth in terms of material categories, such as the Stone age, Bronze age and Iron age. Perhaps scientific thinking can also be associated with the physical size of materials, in terms of a deviation from the scale in which the human mind is most conversant. Thus, leaps in scientific thinking can be attributed to such considerations as the stars and heavenly bodies themselves, or questioning what composed physical materials and the natural world itself. Scientific thought always begs validation through experimentation, which is the definition of scientific growth. As the physical size of the materials in question deviated from a familiar scale, new tools such as the telescope and microscope become necessary for experimentation and provide another dimension to describe scientific progress in terms of scale. As new tools allow for the observation at smaller and smaller scales, new materials and methods are developed to manipulate matter at smaller scales. Leaps in scientific growth may be measured by the tools developed to investigate, understand and manipulate materials at a given scale. With regard to the very small, scientific progress today can be defined as existing in the Nanoscale age.



A—POTS HAVING SPOUTS. B—POTS WITHOUT SPOUTS. C—LIDS.

**Figure 1.** “Using Sulphur” from 'De Re Metallica' by Georg Bauer, better known as Agricola Giclee (1494-1566). The brick making “laboratory” documented in the beginning of the early modern period of history shows fundamental similarities with nanoscale laboratories of today.

## 2. Nanomaterials

Nanomaterials are typically two to three orders of magnitude smaller than the width of a single human hair and may possess truly extraordinary physical properties not attainable outside the realm of the nanoscale. An inherent obstacle to the natural advance of the scientific process is

to create new tools and devices that utilize the extraordinary properties of the astonishingly tiny nanosized materials.

Fabricating nanocomposites, by combining nanomaterials within a hosting material, is a potential method to produce macroscopic material systems which benefit from the nanosized constituents. However, methodical distribution of enormous amounts of the nanosized constituents proves to be an intrinsic obstacle complicated by attractive forces between the nanomaterials themselves. Many nanofiller dispersion techniques have been widely utilized. The next step of scientific progress in the field of nanocomposites is the validation of dispersion techniques by quantitatively describing the state of nanomaterial dispersion as well as performing experiments to investigate the relationship between the state of dispersion at the nanoscale and measured physical properties at the macroscale.

### *3. Nanocomposite dispersion*

It is known that the dispersion of the nanofiller within hosting material manipulates the resulting physical properties of the nanocomposite. Traditionally, nanocomposite dispersion methods are categorized in terms of the processing technique. A recent review categorized the five general dispersion methods as dispersion-reaction, dissolution-dispersion-precipitation, dispersion –dispersion-precipitation, melt mixing, and non-fluid mixing [1]. These techniques when utilized to fabricate single wall carbon nanotube (SWCNT) based nanocomposites have been thoroughly documented [2-5]. Without elaborating on the details of these methods, for the purposes of this research, a simplified description of the dispersion methods are characterized from the point of view of the nanotubes. The non-mutually exclusive methods of dispersion include kinetic, thermodynamic and modification procedures. Kinetic methods are composed of various means of physical mixing. The thermodynamic approach concerns pairing the nanofiller and hosting material in order to reduce the enthalpy and entropic penalties of mixing. Modification approaches consist of altering the structure of the nanotube or adding dispersive agents to enhance the interaction between the nanofiller and hosting material, and thus improve the resulting dispersion. This is admittedly a simplistic view to categorize dispersion techniques but allows for the description and analysis of specific dispersion states as an effect of the simplified dispersive approach.

Nanocomposite formation based upon thermodynamic approaches and/or modification approaches generally require some degree of kinetic based mixing. Kinetic based mixing methods to disperse nanotubes within the low viscosity monomers include shear mixing and sonication [6-11]. The approaches of adding dispersion agents and functionalization may result in the presence of unwanted dispersion agents in the final composite and damage to the structure of the nanotubes, respectively. This may result in diminished material properties when compared to nanocomposites which obtain equivalent dispersion without modification-based methods [12-38]. However, kinetic based mixing methods may also degrade the nanotubes through mechanical deformation as a result of the shear mixing or sonication and lead to shorter or damaged nanotubes. Alternatively, thermodynamic based approaches do not risk damaging the extraordinary structure of the SWCNT, which is the foundation of the equally extraordinary material properties, which in turn is the original motivation for creating the nanocomposites.

#### *4. The structure of SWCNT*

The structure of conductive carbon nanotubes is phenomenal. Carbon atoms typically bond with four other atoms to fill the outer valence band of electrons to obtain entropic stability. However, in a conductive carbon nanotube, defined by the armchair pattern of bonding, and individual carbon graphene sheets, which are essentially unrolled carbon nanotubes, carbon atoms only bond with three other carbon atoms. This process can be explained by orbital hybridization, where the first two atomic orbitals combine to form a single orbital seeking a total of 8 electrons. The result of this type of bonding, called  $sp^2$  bonding in reference to the s and p orbital hybridization, in league with the shape generates the unique properties of the carbon nanotube. This type of unique bonding is present in aromatic compounds, such as benzene. However, carbon nanotubes and graphene sheets are composed solely of this type of bonding.

The strength of the  $sp^2$  bond gives rise to the remarkable mechanical properties. Ballistic thermal conduction also originates as a result of the  $sp^2$  bonding allowing for bond stability at high temperature. The enhanced thermal conduction can be conceptualized as vibrational energy being transmitted along rigid  $sp^2$  bonds. Perhaps the modification in electronic conduction due to the  $sp^2$  bonding is the most interesting. The conductive carbon nanotubes and graphene sheets can be analyzed as 2D planar objects, and as such are 2D conductors quantified by the quantum Hall effect rather than the traditional Hall effect applicable to 3D conductors. Conductive carbon

nanotubes and graphene sheets are the only known materials that exhibit the quantum Hall effect close to room temperature, as other 2D conductors reveal this effect only at very low temperatures near 0 Kelvin. This can also be explained as a result of sp<sup>2</sup> bonding. The sp<sup>2</sup> bonding between carbon atoms effectively delocalize electrons which are not tied to specific atoms, such as with other conducting materials. The electron cloud can be considered to encompass the entire structure that is formed by sp<sup>2</sup> bonding. Thus, in a conductive carbon nanotube or graphene sheet, without any structural bonding defects, the conduction of electrons can be considered a property of the structure of the material rather than a property of the electrons tied to specific atoms within a material. This complete delocalization of electrons as a result of the sp<sup>2</sup> bonding within the geometrically unique conductive carbon nanotubes and graphene sheets yield conduction that surpasses that of silver, nature's best conducting metal.

##### *5. The importance of thorough dispersion*

One motivation to research and fabricate nanocomposites results from the potential of constructing macro-sized materials that benefit from the phenomenal properties of the nanofiller. The properties of individual SWCNT and the influence upon the resulting material properties of the nanocomposite can be found in numerous review articles [2-5]. However, these articles do not assess dispersion states of SWCNT within the formed nanocomposite materials beyond presenting microscopy images to highlight the difference between “well dispersed” and extremely “poor dispersed” specimens. The aim of the proposed research is to provide dispersion characterization methods to quantitatively assess and compare the quality of the so-called “well dispersed” nanocomposites, where the term well dispersed is applied to specimens with homogeneous SWCNT dispersion throughout the nanocomposite.

One of the thin film nanocomposites presented in this dissertation includes the combination of SWCNT with poly(methyl methacrylate) (PMMA), commonly called Plexiglas™. This material system provides an opportunity to investigate the motivation for thorough SWCNT dispersion. Dielectric absorption in polymer film is a phenomenon where an electrically charged material may not completely discharge, but retain some percentage of the original voltage. If PMMA is first heavily saturated with electrons then allowed to electrostatically discharge, the absorbed electrons, localized to specific atoms, will leave their respective locations and travel to electrical ground with such force that the PMMA is fractured

down to the molecular level [39]. This phenomenon gives to the Lichtenberg figure within PMMA shown below.



**Figure 2.** *Lichtenberg figure. Courtesy of Robert G. Bryant, NASA Langley Research Center.*

Lynchburg figures resemble the mechanism of a lightning bolt traveling from an electrically charged cloud. Notice how the fractal structure of the electrical pathways exists in both the original and magnified images. One motivation for developing SWNCT polymer composites is the development of structural electrostatic discharge shielding materials. Thus the importance of dispersing a conductive nanomaterial within an insulating matrix down to the microscopic (molecular, local or nano) level becomes necessary to avoid dielectric breakdown and realize the benefits of nanocomposites in structural applications. Creating nanocomposites for other functional purposes will also benefit from the ability to control and measure dispersion down to the microscopic level. Furthermore, a method to quantitatively measure and evaluate dispersion characteristics at the microscopic level will provide insight into the relationship between specific attributes of dispersion at the nanoscale and the resulting physical properties measured at the macroscale.

#### *6. Dispersion Considerations*

Complete realization of the potential of SWCNT polymer composites requires dispersion that is not only thorough and homogenous, but also stable over the service life of the composite. Maximizing the benefits of the nanofiller is realized by achieving homogeneous dispersion at the local (microscale) and global (macroscale) levels with methods that do not damage the sp<sup>2</sup> structure of the SWCNT. This goal is particularly important for materials in aerospace applications and extreme environments, where thermal and mechanical cycles can result in the re-aggregation of kinetically dispersed carbon nanotubes. To maximize this stability without sacrificing the sp<sup>2</sup> SWCNT structure, the nanofiller and polymer can be selected to enhance the thermodynamic dispersive ability. The general approach is shown through the Gibbs free energy of mixing equation below and is the definition of the thermodynamic dispersion method [40].

$$\downarrow \Delta G = \downarrow \Delta H - \uparrow \Delta S \cdot T \quad (1)$$

Requiring the change in the Gibbs free energy of mixing to be negative or near zero will produce a stable dispersed state but also may efficiently disentangle and disperse the SWCNT. In order to create a stable composite system the Gibbs free energy of the final state must be less than the free energy of the initial state. This is accomplished by attempting to reduce the change in the Gibbs free energy of mixing,  $\Delta G$ , by decreasing the change in the enthalpy of mixing,  $\Delta H$ ,

and increasing the change in the entropy of mixing,  $\Delta S$ . For example, reducing the enthalpy of mixing is accomplished by selecting a hosting polymer (or copolymer) with either strong donor-acceptor interactions or an aromatic ring system, such as benzene, that will strongly interact with nanotubes [41-45]. Selecting polymer traits to increase the entropy of mixing can be accomplished by utilizing a polymer chain that has a similar diameter, helical shape and flexibility to the given type of nanotube [46].

### *7. Measuring Dispersion*

The ability to select or even design polymers and copolymers that exhibit favorable enthalpic and entropic traits to progressively improve nano-filler dispersion and thermodynamic stability begs for validation and interpretation. Currently, no method exists to quickly and affordably assess dispersion at the nanoscale. Such a method could also be utilized to determine the effectiveness of the kinetic and modification dispersive methods.

The lack of adequate dispersion characterization and the need for the definition of terms to distinguish dispersion states has been noted in the two most recent review articles (2010) on the subject of carbon nanotube dispersion [1,47]. These articles detail the difficulties and limitations associated with the current techniques available to measure and describe carbon nanotube dispersion. Such articles are rare, as the majority of review articles do not cover techniques to assess dispersion, use a single technique with known limitations or evaluate dispersion in a solvent before the nanocomposite is fabricated. Often, articles covering carbon nanotube composites assume the dispersion state of the carbon nanotubes and analyze the relationship between carbon nanotube network structure and experimental results without respect to the actual dispersion at the local level.

### *8. Measuring Dispersion at the Nanoscale*

Dispersion at the microscopic level will encourage the adaptation of future nanocomposites. Furthermore, dispersion techniques that do not alter the  $sp^2$  bonding structure are strategically advantageous. However, the relationship between the dispersion methods, formed dispersion and physical properties of SWCNT-polymer nanocomposites have not been adequately studied because an acceptable dispersion quantification method capable of describing specific local attributes of dispersion over relatively large areas, such as average bundle size, did

not exist before the development of the techniques presented in this dissertation [1, 43]. Understanding this relationship will permit the manipulation of dispersion and, consequently, tailoring the physical properties of nanocomposite materials.

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## 2.0 CHAPTER TWO: STUDY ONE

The following study was published in the Institute of Physics – Journal of Nanotechnology as “*A quantitative assessment of carbon nanotube dispersion in polymer matrices*”, and is available from [stacks.iop.org/Nano/20/325708](https://stacks.iop.org/Nano/20/325708)

# A quantitative assessment of carbon nanotube dispersion in polymer matrices

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## Abstract

Quantifying the nature and extent of the dispersion of nanomaterials in polymer matrices is the important first step in understanding the relationship between the nanoscale structure and the bulk scale functional performance of nanocomposites. We present here a methodology for using scanning electron microscope images of nanocomposites taken under high accelerating voltages to quantify four parameters that relate to the dispersion of the nanomaterial. This image analysis methodology is general and applicable to images from other microscopes as well. The analysis performed here was done on representative local areas of six samples to determine the effects of processing conditions, matrix chemistry, and carbon nanotube composition on the level of dispersion. Future work will involve expanding this analysis to rapidly cover larger areas and reducing the data in a manner that is similar to the approach of small angle scattering studies.

 Supplementary data are available from [stacks.iop.org/Nano/20/325708](http://stacks.iop.org/Nano/20/325708)

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The development of advanced aerospace vehicles relies heavily on the use of structural, multifunctional materials. As such, structural composites are being considered for many of these new aerospace platforms. These composite materials perform excellently in structural applications, but often need additional fillers or special coatings to enhance their mechanical, electrical, and thermal properties. Single walled carbon nanotubes (SWCNT) have been examined as an ideal filler to increase the mechanical properties of the resins used in composites and to enable tailorability of the electrical and thermal properties of these structures [1–7]. Several recent reviews describe in more detail the performance of a wide variety of carbon nanotube composite systems [8–11].

New polymer matrices suitable for aerospace applications were designed and synthesized to have a very strong interfacial adhesion to the carbon nanotube backbone and then a

systematic study was undertaken to assess their performance. The comparison of these different systems was hampered however by a fundamental lack of characterization tools to quantitatively assign a level of dispersion. The focus of this paper is to highlight the methodology that has been implemented to quantify the dispersion through image analysis.

Visualization of the nanomaterial in the host matrix that is suitable for assessing the dispersion can be accomplished using a scanning electron microscope (SEM) [12–16], transmission electron microscope (TEM) [17, 18], scanning probe microscope (SPM) [19–22], or optical microscope (OM) [23]. Quantification of the level of dispersion of a nanomaterial has typically been done using size exclusion chromatography [24], small angle neutron scattering (SANS) [25–27] or by using image analysis techniques on optical microscope images [23]. This paper reports a general method to use image analysis techniques on SEM images to collect data that is similar

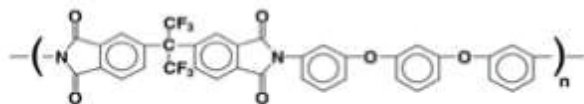


Figure 1. Structure of CP-2 (polymer 1).

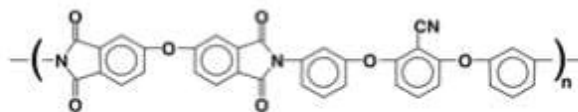


Figure 2. Structure of (β-CN)APB/ODPA (polymer 2).

in structure to SANS data, and to use that data to extract information that is useful for the quantification of nanotube dispersions in polymer matrices.

## 2. Experimental details

### 2.1. Materials

Adequately characterizing the dispersion of a nano-inclusion within a host material requires reference materials with distinctive degrees of dispersion. Six such nanocomposites were fabricated to systematically vary the level of dispersion. The processing method and materials were progressively altered to improve the level of dispersion.

Sample 1 was a solution cast thin film fabricated by a direct mixing of 1.0 vol% laser ablated single walled carbon nanotubes (LA-SWCNTs) (Tubes@Rice, Houston, TX) into a colorless polyimide made from the monomers 4,4'-(hexafluoroisopropylidene)diphthalic anhydride and 1,3-bis-(3-aminophenoxy)benzene (figure 1, LaRC CP-2™, polymer 1) [28, 29]. Sample 2, also comprised of 1.0 vol% LA-SWCNT in polymer 1, was made using an *in situ* polymerization protocol where the nanomaterial and the monomers are mixed together in solution prior to initiating polymerization [5]. Sample 3, 1.0 vol% LA-SWCNT in polymer 1, was fabricated by the *in situ* polymerization protocol but with added sonication [6]. Sample 4 was fabricated like sample 3 but with 0.5 vol% nanotube concentration. Sample 5 was fabricated like sample 4, except the matrix was changed to the polyimide made from the monomers 2,6-bis(3-aminophenoxy)benzonitrile and 4,4 oxidiphthalic anhydride (figure 2, (β-CN)APB/ODPA, polymer 2) [30], which has a better interaction with carbon nanotubes [31]. Sample 6 is identical to sample 5 except the composition of the nanotubes was changed to 0.5 vol% HiPCO-SWCNT (High Pressure CO, Carbon Nanotechnologies, Inc., Houston, TX).

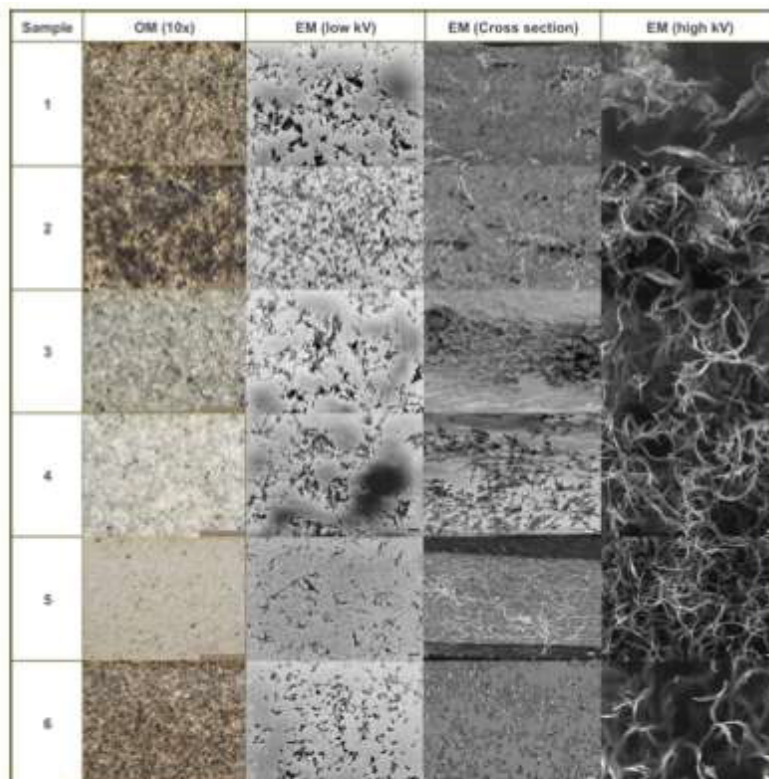
### 2.2. Visualization techniques

Several optical, electron and probe microscopy tools were utilized in order to establish their effectiveness at visualizing carbon nanotubes in polymer matrices [32]. First, large-scale optical tools can very effectively visualize micron scale agglomerates. These assessments were carried out using various optical microscopes to qualitatively evaluate macro-scale dispersion. The first column in figure 3 shows six samples evaluated using optical microscopy. Samples 1 and 2 show visible aggregation while samples 3–6 show no visible aggregation and are labeled as optically dispersed. In figure 3 electron microscopy (EM) surface and cross-section images at low accelerating voltages ( $\leq 1$  kV) are shown in

columns 2 and 3, respectively. Sample 1 clearly shows a poor dispersion quality. Sample 2 shows an improved dispersion over the direct mixing technique. Samples 2, 3, 4 and 6 had a dispersion quality that cannot be distinguished from each other using these images. Sample 5 shows an improved dispersion over the other samples containing LA-SWCNT and contains no visible aggregates, very small bundles and no resin rich areas. Electron microscopy surface images at high accelerating voltages ( $\geq 15$  kV) are shown in column 4. This procedure provides sufficient detail to quantitatively assess the dispersion. Accurate details about the bundle diameter, bundle (or segment) length, and spacing between bundles is evident. Sample 1 shows poor dispersion quality, large bundle sizes, twisted and looped tubes due to the direct mixing procedure. Samples 2–6 show longer, straighter tubes and smaller bundle sizes than Sample 1 due to the *in situ* polymerization procedure, but now there is enough detail to quantify the effects of sonication, SWCNT concentration, polymer chemistry and SWCNT composition.

From figure 3 it is evident that conventional optical microscopy (OM) tools are insufficient to investigate the level of dispersion. Samples 1, 2, and 6 show incomplete dispersion with some coagulated nanotubes while samples 3–5 appear well dispersed and nearly identical under OM. For some applications this simple assessment is sufficient, but it does not afford many details about the microstructure. What was needed was a tool that could assess dispersion at a level beyond that provided by optical tools and provide detailed information sufficient to quantify the dispersion.

Under low kV imaging conditions EM tools were able to detect nanotubes in, and the influence of nanotubes on, the surrounding polymer matrix. In these images visualizing the presence of SWCNTs at or near the surface is enabled through the use of an electric field (or charge) contrast. Although this is an artifact imaging technique [33], it can still be used to effectively determine the distribution of nanotubes at or near the surface [16]. It was necessary to measure the distribution both at the surface and through the cross-section to get an accurate distribution of nanotubes through the bulk. One problem with this technique was that the electric field contrast is sensitive to many factors including the voltage and current of the primary electron beam as well as the scanning speed. The sensitivity between the electrical conductivity of the sample and the imaging conditions is evident from the different types of contrast seen in the cross-section images. In samples 3 and 4 the nanotubes are dark, whereas in samples 1, 2, and 6 the nanotubes show contrast inversion i.e. they appear both dark and bright. The most troubling problem was that the contrast was also due to the accumulated charge history. Thus, images taken in succession would have an apparent increase in the area



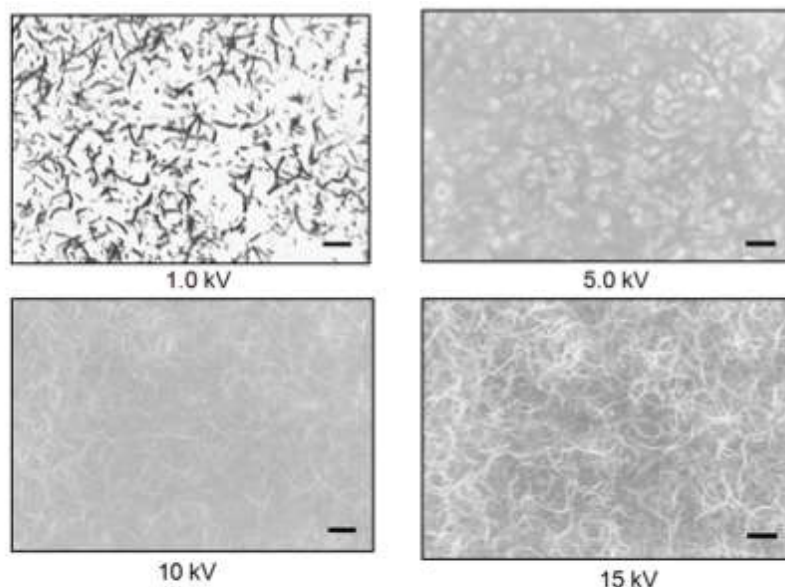
**Figure 3.** Column 1: OM images assessing the dispersion quality of SWCNT in polymer composites. Scale bar in column 1 is 200  $\mu\text{m}$ . Columns 2 and 3: EM surface and cross-section images at low accelerating voltages ( $\leq 1$  kV). Scale bars in columns 2 and 3 are 4  $\mu\text{m}$  and 1  $\mu\text{m}$ , respectively. Column 4: high accelerating voltage ( $\geq 15$  kV) EM images. Scale bar in column 4 is 500 nm. Note: EM images for samples 1–3, 5 and 6 in columns 2 and 3 are reproduced with permission from reference [32].

occupied by the nanotubes. To use this electric field artifact to quantify the dispersion of nanotubes would require great care to ensure that stable and repeatable imaging conditions were maintained.

A method to visualize nanotubes in the polymer matrices that was independent of the charge history and that sampled an adequate volume to enable a quantification of the three-dimensional distribution of the carbon nanotubes was required. If the sampling volume was sufficient, then the need for imaging cross-sections could be eliminated. Using protocols for imaging conductive fillers in insulating matrices at high acceleration voltages [12–16] the non-conductive polymer essentially becomes transparent up to a depth that is specific to both the sample and imaging conditions. This ‘poly-transparent’ (high kV) imaging protocol allows for an accurate measure of nanotube distribution near the surface. By using the poly-transparent technique it was possible to visualize the difference in dispersion level for all six samples as shown in column 4 of figure 3. Furthermore, as shown in figure 4, the improved visualization is realized when comparing the low kV and high kV images of the same area. Notice how the darkest and thickest nanotubes in the low kV images correspond to the brightest nanotubes in the high kV images.

The accelerating voltage necessary to generate these low and high kV images is specific to the sample and instrument.

When imaging conductive fillers in insulating matrices, low kV images are generally obtained between 0.5 and 1.5 kV. Typically, imaging above 1 kV produces increased charging in the insulating material. At approximately 5 kV a crossover point is reached where both low kV and high kV information is shown simultaneously, although not as clearly in either the low or high kV images. This crossover voltage point can be thought of as the point at which the polymer matrix can no longer sustain a stable generation of secondary electrons from the primary beam, but rather allows the primary beam to penetrate straight through the polymer. This is analogous to the polymer reaching a breakdown voltage whereupon the material becomes electrically conductive. The crossover voltage for sample 5 is approximately 5 kV and is shown in figure 4. Subsequently, images taken at or above 15 kV result in exclusively high kV imaging. Similar to low kV imaging, high kV imaging produces the clearest images at voltages specific to the sample which can range from 15 to 30 kV for samples 1–6. Therefore, when comparing either low kV or high kV images, it is most important to capture images of samples with similar image properties, such as imaging depth, charging, and contrast, rather than capturing images at identical voltages. The voltage necessary for high kV images and the imaging depth seem to be related to the dispersion of the samples. For example, the poorly dispersed sample 1 required a high kV



**Figure 4.** Voltage dependent EM images of sample 5 captured using electric field imaging and poly-transparent imaging of the same area. Scale bar in all images are 2  $\mu\text{m}$ .

voltage of 30 kV and produced the lowest imaging depth while the well-dispersed sample 5 required 15 kV and produced the largest imaging depth.

### 2.3. Imaging depth

The penetration depth of the primary electron beam can be on the order of several microns for the samples and imaging conditions investigated. However, due to the low energy nature of the secondary electrons that are generated from the primary beam, the escape depth of secondary electrons is typically confined within 50 nm of the surface [34]. Here, we provide details regarding the imaging depth of conductive nanofillers in insulating matrices that were observed for these samples. The imaging depth differs from penetration depth in that the penetration depth is the depth the electron beam infiltrates the sample and the imaging depth is the depth that information can be retrieved via the detectors and captured in the images.

With the secondary electron detectors used<sup>5</sup>, the presence of nanotubes much beyond 50 nm in depth should not be detected due to their low escape depth. Our studies indicate that we are seeing much deeper into the sample, with an imaging depth up to 1000 nm for some samples, see supplemental information (available at [stacks.iop.org/Nano/20/325708](http://stacks.iop.org/Nano/20/325708)). Although, determining an unambiguous depth is impossible due to the relationship of the imaging depth to material properties, machine capabilities, and imaging conditions. Regardless, we have developed a general method to calculate a minimum depth for individual material samples. The minimum imaging depth ( $d$ ) can be

determined by capturing high kV images at different tilt angles ( $\theta$ ) and calculating the projected distances ( $x$ ) between a surface feature and a nanotube deep within the sample.

$$d = \frac{x_1 \cos \theta - x_2}{\sin \theta}$$

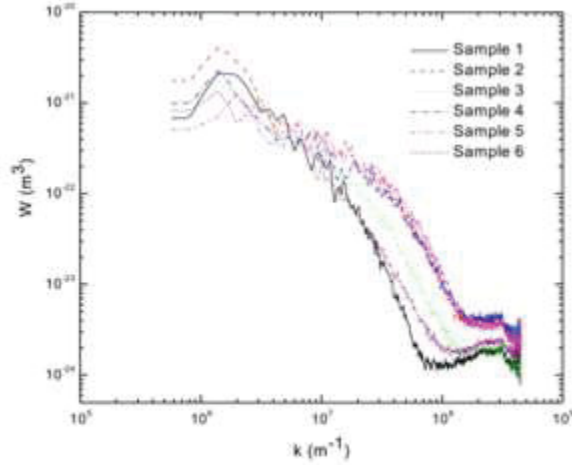
where  $x_1$  is the projected distance between the surface feature and the subsurface nanotube at  $\theta = 0$  and  $x_2$  is the projected distance at  $\theta > 0$ . We verified this method using a NIST certified grid with a step height of  $105.3 \pm 2.4$  nm under equivalent imaging conditions and the results were within the standard deviation. Using these methods, most samples had a minimum imaging depth of at least 700 nm. Based on the immense imaging depth, the sampling volume should be sufficient to begin quantifying the dispersion for these samples.

### 2.4. Image analysis techniques

The quantification of nanotube dispersion was accomplished in the spatial domain through analysis of the high kV images. Analyzing the radial power spectral density (RPSD), fractal dimension, and Minkowski functionals provide parameters that allow for fundamental quantification of the dispersion. The RPSD is an imaging analysis tool that describes the frequency of spatial features in an image regardless of direction or orientation. Taking the average of the polar power spectral density (PPSD) in two dimensions and summing over all polar angles produces the RPSD [36–39]. This technique provides detailed information regarding the dominant features present in an image that can be understood in terms of length, thickness, spacing, and regularity.

The fractal dimension associated with images provides information essentially concerning the degree of order or

<sup>5</sup> The scanning electron microscope used to collect all of the EM images was a Hitachi S-5200 equipped with a through the lens (TTL) detector. A description of TTL detectors can be found in [35].



**Figure 5.** Radial power spectral density from high kV images of samples 1 through 6. The peak positions correspond to the average feature size and the FWHM corresponds to the standard deviation of those feature sizes.

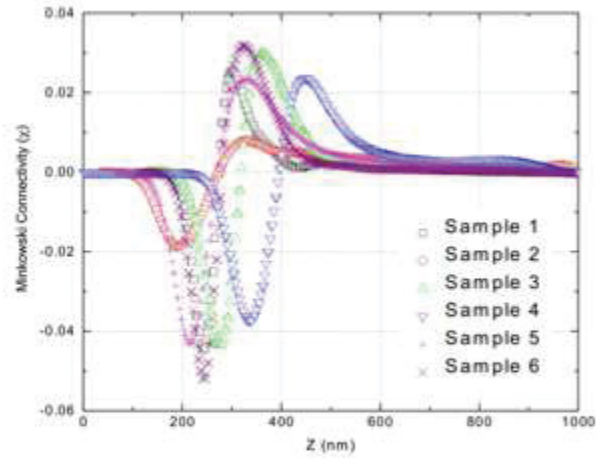
randomness present in images by effectively ranking the degree of complexity between the second and third Euclidean dimension. The amount of randomness, or ordering, of the samples must be determined to proficiently describe the dispersion. A method of calculating the fractal parameter that was invariant to the scale of the image was required to most effectively describe the degree of randomness in the images [36, 40–42]. The calculation of the fractal parameter based on the partitioning function [43] was able to effectively describe the randomness in all the images regardless of the scale.

Minkowski functionals represent a method to describe the amount of connectivity by analyzing the relationship of connected pixels and unconnected pixels present in an image. Minkowski functionals are very effective at describing complex morphologies observed in images [44–47]. The Minkowski functional connectivity ( $\chi$ ) is defined as the number of connected pixels minus the number of holes divided by the total number of pixels [44–47]. Using this measurement we were able to determine the local structure associated with each high kV image. Positive values of  $\chi$  correspond to cylindrical structures<sup>6</sup> while negative values correspond to connected structures with holes. The point where  $\chi = 0$  is the length scale ( $z$ ) at which the image becomes periodic.

### 3. Results and discussion

Figure 5 shows the results of RPSD measurements obtained from the high kV images (column 4) in figure 3. The RPSD measurements provide feature information from the high kV images concerning the bundle diameter, segment length, and spacing between the bundles.

<sup>6</sup> Positive values of the  $\chi$  parameter can also indicate spherical structures. In our case we can limit our analysis to consider only cylindrical structures due to the nature of the nanofiller geometry.



**Figure 6.** Minkowski connectivity ( $\chi$ ) for the carbon nanotube reinforced polymer nanocomposites (samples 1–6).

**Table 1.** Dispersion summary of samples 1 through 6.

| Sample | Bundle diameter (nm) | Segment length (nm) | Bundle spacing (nm) | Fractal dimension |
|--------|----------------------|---------------------|---------------------|-------------------|
| 1      | 181 ± 32             | 746 ± 120           | 722 ± 204           | 2.67              |
| 2      | 83 ± 15              | 719 ± 207           | 184 ± 21            | 2.73              |
| 3      | 63 ± 6               | 821 ± 180           | 152 ± 24            | 2.76              |
| 4      | 67 ± 11              | 932 ± 183           | 269 ± 113           | 2.77              |
| 5      | 44 ± 14              | 715 ± 128           | 228 ± 59            | 2.78              |
| 6      | 122 ± 27             | 767 ± 221           | 332 ± 57            | 2.72              |

Each of the peaks of figure 5 corresponds to dominant features in the high kV images. The most dominant characteristics associated with each image are associated with the tallest peaks and can be evaluated by inverting the  $x$ -axis value at each major peak. Each peak was fit to a Gaussian amplitude function and their average and full width at half maximum (FWHM) were recorded. Careful analysis was required to determine if the origin of the peaks was due to the diameter, length, or spacing between tubes. Table 1 summarizes the information obtained from the six samples after assigning the peaks in the RPSD to the corresponding features. In the case of multiple peaks corresponding to a particular feature, the positions of the peaks were averaged and their FWHM, which was also the standard deviation, were propagated to determine an overall standard deviation.

Table 1 also summarizes the results of the fractal dimension calculated using the partitioning method. It can be seen from the data that the degree of randomness increases from samples 1 through 5 and then decreases for sample 6. This can be seen in the high kV image of sample 6 showing well ordered ‘ribbons’ of nanotubes.

The Minkowski functional connectivity, shown in figure 6, serves as another tool to evaluate and quantify the local structure as well as to verify the RPSD results. Together, these tools prove useful for 3D computational modeling of multifunctional nanocomposites and the prediction of the dispersion characteristics.

Due to the inherently small scale necessary to produce high kV images, only localized information is produced. In order to account for the dispersion throughout the bulk of the material, observing low kV images at magnifications similar to columns 2 and 3 of figure 3 is necessary to determine if the particular location is representative of the general overall level of dispersion. Capturing high kV images from multiple locations to ensure the overall dispersion is represented and averaging the results are recommended. Additionally, to ensure the analyzed area is representative of the entire sample, the fractal dimension associated with high kV images taken at various locations and magnifications should be similar, provided the magnification is high enough to discern individual nanofillers. If the fractal dimension is not comparable for high kV images captured at different locations and magnifications then the dispersion should be assumed to be inhomogeneous. Only after the dispersion is deemed homogeneous should the RSPD, fractal dimension, and Minkowski connectivity be utilized to describe and understand the overall dispersion of a nanofiller.

The high kV images represent a two-dimensional projection of a three-dimensional volume and therefore the resulting values for the segment length, bundle spacing, fractal dimension, and Minkowski connectivity are not literal. However, this method can be successfully utilized to establish a standardizing procedure to rate and quantify the quality of dispersion against a benchmark level of dispersion for the type of composite material. Theoretically, regarding nanotubes, maximizing the segment length and the fractal dimension while minimizing the bundle diameter and spacing will provide the best dispersion. Optimizing dispersion of composites with different nanofillers can be understood in terms of shape features specific to the nanofiller.

Using all of this information we could finally quantitatively assess the level of dispersions in these samples. This lets us determine the effect that parameters such as mixing conditions, sonication, polymer chemistry, and even SWCNT composition can have on the prevalent dispersion of the samples. Comparing sample 1 to sample 2 shows that the *in situ* polymerization protocol reduces the average bundle diameter and spacing. The bundle spacing is also more uniform as can be seen in the reduction in the standard deviation of the bundle spacing and an increase in the fractal dimension. Comparing samples 2 and 3 shows that the addition of sonication to the *in situ* polymerization protocol further reduces the average bundle diameter while increasing the average length of the segments. The bundle spacing and fractal dimension also improve slightly. The mild sonication (<40 kHz) that samples 3–6 experienced was sufficient to debundle the agglomerated nanotubes with no observed damage or breakage of the tubes.

Comparing samples 3 and 4 shows that reducing the concentration of SWCNT does not appreciably affect the bundle diameter and slightly improves the segment length. The observed bundle spacing is commensurate with a reduction in concentration by a factor of 2. From the Minkowski functional in figure 5 we observe that sample 4 had a minimum at the largest value of  $z$ . This indicated that sample 4 had the largest interconnected structure. Sample 4 also had a maximum at the

largest value of  $z$  indicating the longest cylindrical structures, also validating the RPSD results.

Comparing samples 4 and 5 allowed a means to observe the effect of changing the matrix chemistry. Polymer 2 was predicted to have a stronger interaction with the SWCNTs when compared to polymer 1 and this was confirmed as a reduction in the average bundle diameter and bundle spacing. However, the segment length also decreased indicating the SWCNTs are bending more in polymer 2 compared to polymer 1. This unexpected experimental result could be due to a more effective debundling of the SWCNT by polymer 2 during the *in situ* polymerization process, but this will require further study to fully understand.

Lastly, comparing samples 5 and 6 showed the result of changing the composition of SWCNT from LA-SWCNT to HiPCO-SWCNT. The HiPCO-SWCNT formed very well-dispersed ropes, which can be seen as a larger bundle diameter and a larger spacing between the bundles. The lengths of the bundles, however, were relatively unchanged. The ordering of the ribbons also reduced the fractal dimension from 2.78 to 2.72.

## 4. Summary

Using the protocol of high kV imaging and three-dimensional image analysis we have shown that nanocomposites can be sampled on a sufficiently large volume to differentiate the extent of dispersion. This dispersion is expressed as a dominant bundle size, persistence length, and spacing between the bundles along with the fractal dimension to determine the degree of ordering. From this data we can quantitatively discern the effect that parameters such as mixing conditions, sonication, polymer chemistry, and SWCNT composition and type have on the overall quality of dispersion of a conducting nano-inclusion within an insulating host matrix. Additionally, the quantification of bundle diameter, length, and spacing are very valuable data for nano-structural mechanical, electrical, and thermal analyses as well as 3D computational modeling of practical nanocomposites.

## Acknowledgments

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## 5. Supplemental Information

### 5.1 Supplemental A

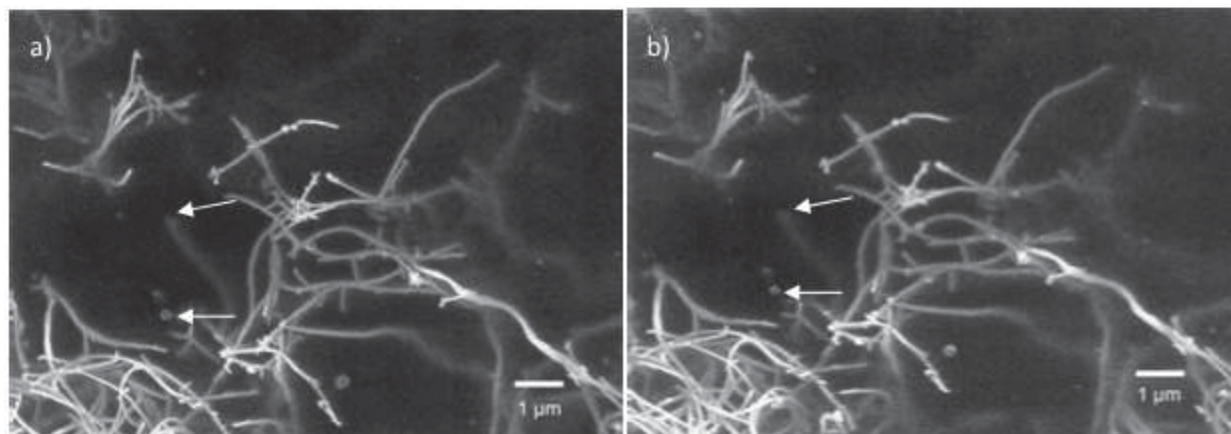
The following supplemental section, supplemental section A, was published online with Study 1, “*A quantitative assessment of carbon nanotube dispersion in polymer matrices*”, and is available from [stacks.iop.org/Nano/20/325708](https://stacks.iop.org/Nano/20/325708)

Poly-transparent or high kV imaging allows for imaging of conductive nano-fillers within insulating matrices to depths previously unattainable. Under high kV imaging conditions the maximum depth that nano-fillers can be distinguished from the surrounding matrix, referred to as imaging depth, is specific to the sample properties, imaging conditions, and scanning electron microscope (SEM) capabilities. Confirming the imaging depth distinctive to high kV images assists in providing new insights regarding how the level of dispersion impacts the material properties.

A procedure to ascertain the imaging depth for a given sample has been demonstrated to be reliable and repeatable. The geometric relations utilized have been verified with a grid of known step height that has been certified by NIST. The basic procedure for determining imaging depth begins with capturing a series of images at different angles over the same area. A reference image should be captured with zero tilt under imaging settings that depict surface features while still visualizing poly-transparent phenomena. This is necessary to determine which specific nano-fillers are located at the surface. This again is specific to the sample and imaging conditions. An alternative method is to capture and overlay low kV and high kV images of the same area. The remaining images should be captured at known angles under pure poly-transparent conditions. Any two pure poly-transparent images at known angles can then be employed to determine the distance between a nano-filler located on the surface of the composite with another located deep within the sample. The deepest discernible nano-filler present in both tilted high kV images should be selected. Measuring the apparent distance from the two-dimensional high kV images in association with the known tilt angle ( $\theta$ ) yields the imaging depth ( $d$ ) by engaging the following equation:

$$d = \frac{x_1 \cos \theta - x_2}{\sin \theta}$$

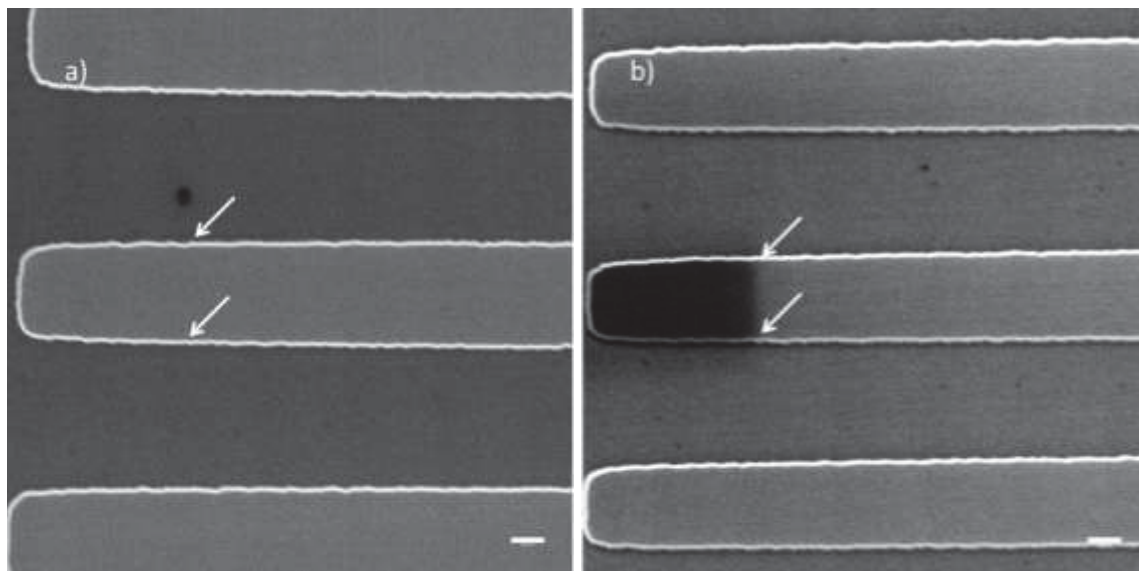
Where  $x_1$  is the projected distance between the surface feature and the subsurface nanotube at  $\theta = 0$  and  $x_2$  is the projected distance at  $\theta > 0$ . Figure 1 shows two SEM images of sample 2 at  $\theta = 0^\circ$  and  $\theta = 20^\circ$ . Separate arrows label the lower edge of a surface feature and a point on the end of a nanotube. From these images  $x_1 = 2060$  nm and  $x_2 = 1664$  nm. Using this information the point on the nanotube is determined to be 794 nm below the surface. This type of an analysis can be repeated for multiple points in the image to determine a minimum imaging depth.



**Figure S1.** SEM images taken at a)  $\theta = 0^\circ$  and b)  $\theta = 20^\circ$  for sample 2. The arrows point to a surface feature and a point on a deeply embedded nanotube.

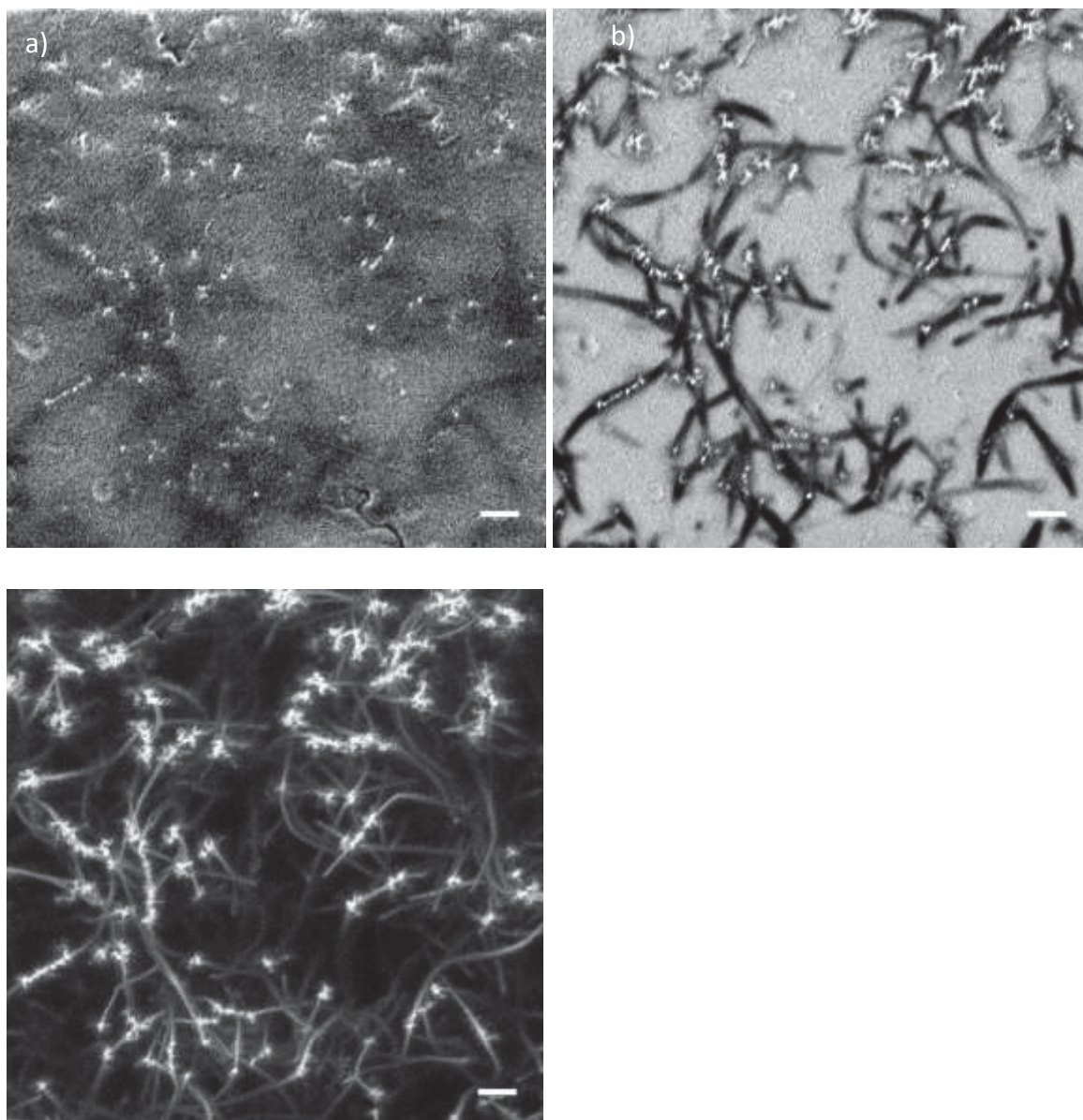
## 5.2 Supplemental B

The geometric relations utilized in Study One and Supplemental A have been verified with a grid of known step height that has been certified by NIST. A NIST-certified grid with a step height of  $105.3 \pm 2.4$  nm (figure 1 below) was utilized to validate the imaging depth procedure under equivalent imaging conditions and the results were within the standard deviation.



**Figure S1.** HR-SEM image of the NIST certified grid used to validate the imaging depth procedure at a)  $\theta = 0^\circ$  and b)  $\theta = 20^\circ$ . The arrows point to the upper edge and the bottom corner of a channel of the grid. The scale bars are 500 nm.

The contrast inversion seen within the cross section images is also seen in the images of low and high kV SWCNT dispersion (figures 3 and 4). Figure 2 below shows sample 5 after silver particles were preferentially deposited at the locations where the SWCNT network provided the best electrical grounding sites on the surface of the specimen. The surface features (captured under the same imaging conditions as low kV imaging but with a faster scan), low kV and high kV images were all captured over the same position. Notice how the conductive silver particles do not show the same contrast inversion as the subsurface SWCNT.



**Figure S2.** The a) surface feature (1.0 kV), b) low kV (1.0 kV) and c) high kV (15 kV) images of the same area over sample 5 after silver particles were preferentially deposited along near surface SWCNT. The scale bars in the images are 500 nm.

### 3.0 CHAPTER THREE: STUDY TWO

#### *“Carbon Nanotube Dispersion within Polymer Nanocomposites: Systematic Quantification of Dispersion using Fractal Geometry”*

##### *Abstract*

The dispersion quality of nanoinclusions within the hosting material is often overlooked when relating the effect of nanoscale structures on both the functional performance and processing/property relationships of nanocomposites. This is due in part to the difficulty in visualizing the nanoinclusion within a formed composite and ambiguity in the description of dispersion without an understanding of the dispersion in terms of relationships between the composition of the nanofiller, matrix chemistry and processing methods. Describing dispersion and understanding these relationships are necessary steps towards tailoring the physical properties of nanocomposite materials. The dispersion analysis method presented in Study One allows for quantification and validation of dispersion parameters thorough the visualization of conductive nanofillers deep within insulating polymer matrices. This method makes it possible to quantitatively evaluate the dispersion of certain nanocomposites, such as single wall carbon nanotube (SWCNT)-polymer composites, in such specified terms as nanotube/bundle diameter, persistence length and spacing/separation distance. However, the previous study is primarily concerned with analyzing dominant lengths present in the material. Here we expand the quantitative dispersion evaluation technique in order to describe dispersion quality in a different manner that is potentially representative of the overall dispersion throughout the material. This is accomplished by analyzing SWCNT dispersion with fractal geometry. The use of fractal geometry will provide a parameter proportional to the fractal dimension to describe how the nanomaterial is dispersed locally within images captured through high-contrast (poly-transparent, high kV or voltage-contrast) imaging via high resolution scanning electron microscopy. High-contrast imaging allows for the 3D visualization of a conductive network within an insulating polymer. Analyzing the dispersion of SWCNT within the hosting polymer through analyzing the fractal nature of SWCNT dispersion provides a measure of the structure of dispersion over specified dimensions. An approximate value for the fractal dimension of the 2D projection of

SWCNT dispersion can be determined directly from the high-contrast images. Here, a standardized procedure is developed to repeatedly measure and interpret the images of dispersion.

### *1. Introduction*

Building upon the previous investigation presented in Study One, an expanded and improved dispersion analysis methodology is presented. This study provides a systematic method for the quantitative evaluation of single wall carbon nanotube (SWCNT) dispersion within polymer matrices of thin film nanocomposites. In an effort to build the framework in which to investigate the relationship between dispersion and physical properties, this study will provide a dispersion quantification methodology based upon fractal geometry for self-affine and scale-invariant systems. Self-affinity can be conceptualized as an object composed of pieces scaled by different amounts. Scale-invariance of an object is observed when features observed at different magnifications are related through a constant scaling parameter. The dispersion will be quantified in terms of this scaling parameter, and related fractal dimension, over specified spatial dimensions and will be shown to meet the requirements for a self-affine and scale-invariant system. It is proposed to use radial power spectral density (RPSD) analysis on high-contrast high-resolution scanning electron microscope (HR-SEM) images to directly determine the approximate scaling parameter and linked fractal dimension.

It is proposed that HR-SEM high-contrast images of SWCNT dispersion represent “objects” that meet both requirements for the application of fractal geometry; that the object has a fractal dimension greater than its Euclidian dimension and that the object exhibits self-similarity or self-affinity (self-affinity in this case) [1]. Euclidian space is defined as 1D, 2D or 3D space commonly defined using a Cartesian coordinate system. Interestingly, the three physical mechanisms which naturally give rise to fractals [2]:

- i. when a Laplacian field, such as diffusion, causes forced instability
- ii. through Brownian motion
- iii. when descriptive parameters follow a power law distribution

can each be attributed to the dispersion formation process. Foremost, the SWCNT are diffused throughout the hosting component of the nanocomposite. At the microscopic (molecular, local or

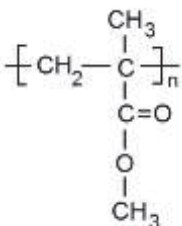
nano) level, it is Brownian motion that is most likely responsible for dispersing nanotubes. It will be shown here that a scaling parameter that describes the shape of the SWCNT network can be determined from a power law distribution obtained after analyzing HR-SEM images of dispersion.

## 2. Materials and methods

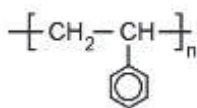
### 2.1 Materials

#### 2.1.1 PMMA and PMMA/PS nanocomposites

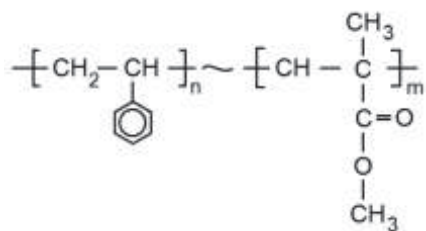
The sample set consists of thin film nanocomposites created with varying amounts of nanotubes with a polymer and its copolymer, which is hypothesized to result in improved dispersion through the addition of an aromatic moiety in the form of a phenyl ring. Polymethylmethacrylate (PMMA), polystyrene (PS) and the copolymer of both (PMMA/PS), shown below in figures 1, 2 and 3, respectively, were combined with varying amounts of single-walled carbon nanotubes in hopes of creating nanocomposites with enhanced properties. The two matrices were chosen due to their different hypothesized interaction with SWCNT and the resulting dispersion.



**Figure 1.** Structure of polymethylmethacrylate (PMMA).



**Figure 2.** Structure of polystyrene (PS) showing the aromatic moiety.



**Figure 3.** Structure of PMMA/PS copolymer.

Several thin film nanocomposite samples were fabricated along with the corresponding neat polymers. These samples are summarized in table 1 below.

**Table 1.** PMMA and PMMA/PS nanocomposite thin films compositions.

| Sample      | Polymer composition | Percent SWCNT (weight %) |
|-------------|---------------------|--------------------------|
| PMMA 0      | 100 % PMMA          | 0                        |
| PMMA 1      | 100 % PMMA          | 1.0                      |
| PMMA 5      | 100 % PMMA          | 5.0                      |
| PMMA/PS 0   | 70 % PMMA - 30% PS  | 0                        |
| PMMA/PS 0.1 | 70 % PMMA - 30% PS  | 0.1                      |
| PMMA/PS 0.5 | 70 % PMMA - 30% PS  | 0.5                      |
| PMMA/PS 1   | 70 % PMMA - 30% PS  | 1.0                      |

The PMMA and PMMA/PS batches were purchased from Polyscience Inc. and purified high pressure carbon monoxide (HiPCO) SWCNT (diameter ~0.7 – 1.3 nm) were purchased from Carbon Nanotechnologies, Inc., Houston, Texas. PMMA or PMMA/PS were directly dissolved in a dilute (0.075 wt%) SWCNT- dimethylformamide (DMF) solution within a round bottom flask equipped with a mechanical shear stirring rod and nitrogen gas flowing in and out thorough calcium sulfate drying tubes. The SWCNT-DMF solution was not pre-sonicated before

addition to the flask but rather mechanically stirred for 5 minutes before directly mixing the PMMA or PMMA/PS and mechanically stirred for an additional 5 minutes before sonication. The flask was submerged in a water bath and subjected to ultrasonic sonication (40 kHz) during the first four hours of mixing. Additional stirring under nitrogen gas occurred until the presence of moisture was absent within the flask, approximately 24 hours. The solid content of the SWCNT-polymer solution was 15% in DMF. The mixture was then cast onto glass plates and dried in a dry nitrogen-flowing chamber for 48 hours. Finally, the mixture was cured under vacuum for 5 hours at 60 °C to remove the DMF and acquire self-supporting films.

### *2.1.2 Motivation for PMMA and PS nanocomposite study*

The homopolymer PMMA and copolymer PMMA/PS were chosen for this material study to investigate the potential of selecting a matrix with traits to encourage SWCNT dispersion. PMMA was chosen due to its optical clarity and the hypothesized molecular attraction between the carboxyl group ( $O = C - C$ ) of PMMA and both the open ends of the SWCNT and defect locations along the surface of the SWCNT [3, 4]. The copolymer with PS was chosen due the enhanced dispersibility of SWCNT instigated by the intermolecular attraction between the 6 member  $sp^2$  bonded ring on the SWCNT surface and the aromatic moiety in the form of a benzene ring side chain [4]. A benzene ring also contains a 6 membered  $sp^2$  bonded carbon ring which is attracted to the 6 membered  $sp^2$  bonding carbon rings along the SWCNT surface. The 70/30 PMMA/PS concentration was chosen due to the unique ability to disperse SWCNT. The more prevalent PMMA will attract the ends of the SWCNT and the less prevalent PS attracts the surface of the SWCNT. Thus the ends of SWCNT will preferentially be seated in the more prevalent PMMA and be drawn to seek PS in relatively more localized regions within the copolymer.

## *2.2 Methods*

### *2.2.1 Imaging and measuring SWCNT dispersion*

The previous chapter, published in the Institute of Physics Journal of Nanotechnology in August 2009, described the development of microscopy techniques for dispersion analysis of high-contrast HR-SEM images. High-contrast imaging is the SEM imaging technique that allows for imaging of the nanofiller deep within the hosting material as long as the nano-filler is

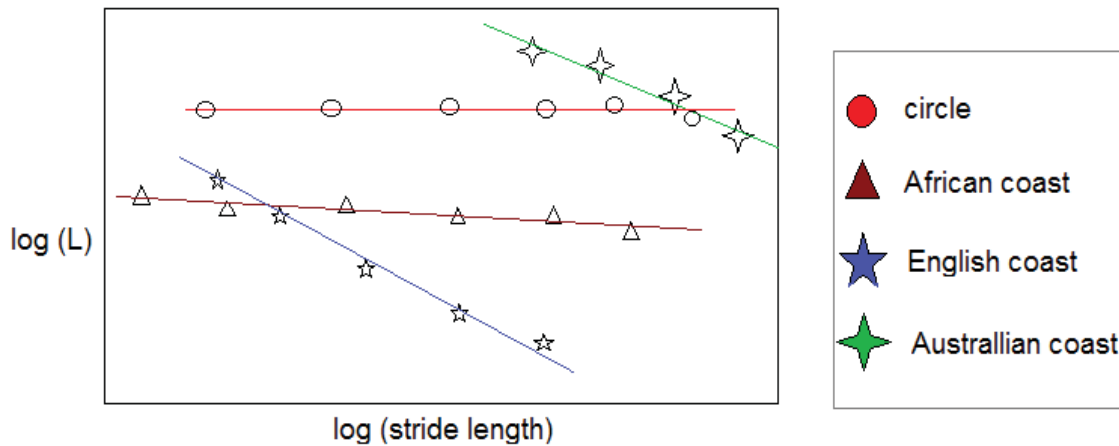
conductive, the matrix is insulative and a sufficient electrical percolation threshold has been reached. The depth of visualization of the nanofiller with the hosting material is dependent upon the individual sample and SEM capabilities but is generally around 1  $\mu\text{m}$  for samples that have adequately realized an electrical percolation network and are imaged in a HR-SEM [5]. Study One was cited multiple times in a recent article on high-contrast imaging method and the potential imaging depth [6]. In the case of imaging with a Hitachi S-5200 with a through the lens secondary electron detector, the imaging depth is only predicted to be 50 nm from theoretical secondary electron generation. However, the high-contrast technique detailed in the previous study allows for visualization of the nanofiller at a depth 20 times deeper. Visualization to this depth provides an adequate depiction of local dispersion (sampling volume) and, for the first time, the ability to quantitatively characterize dominant lengths can be utilized to characterize the dispersion. An additional image analysis technique, using Minkowski functionals can be called upon to verify the quantified parameters. However, the previous dispersion analysis method is dependent upon selecting dominant lengths to analyze and correlating the dominant lengths to features present in the HR-SEM images.

In February 2011, the author of one of the most recent review papers on nanotube dispersion entitled “Recent developments concerning the dispersion of carbon nanotubes in polymers “ contacted the authors of Study One for permission to use image number 4 in an upcoming book concerning carbon nanotube polymer composites. Additionally, based upon the author’s comment in the review article ”At this time, there is no way to make this [dispersion quantification measure in terms of characteristic parameters, such as average bundle size] measurement in bulk polymers and, aside from laborious transmission electron microscopy (TEM) procedures, it will be very difficult in the foreseeable future to be able to make such measurements”, the future publication may recognize the previous dispersion analysis method as the only available method to assess dispersion in terms of quantifiable parameters [7].

#### *2.2.1.1 Fractal geometry*

Fractal geometry is a branch of mathematics that is used to describe irregular shapes found in the natural world [1]. Here, it is proposed to use fractal geometry to help quantify SWCNT dispersion within the hosting polymer by analyzing high-contrast HR-SEM images of thin film nanocomposites. In the previous study, the RPSD was used to measure dominant

attributes of SWCNT dispersion. Measuring the “shape” of a network of SWCNT requires a different analysis method. A measurement of shape for an object often requires a measurement of the objects perimeter. However, consider the following dilemma that Richardson faced in 1961 when attempting to measure the shape of coastlines [8]. The measured length of a coast was dependent upon the length of measurement stick used to measure the coast. Thus the perimeter of an island cannot be explicitly measured and is dependent upon the scale of the map and the size of the measurement device. Richardson compared the measurements of the perimeter of coastlines as a function of the measurement unit. For example, comparing the perimeter measured using a kilometer measurement scale to an inch based measurement system, Richardson noticed a region of constant slope when the perimeter versus measurement unit length was logarithmically plotted, as shown in figure 4. Strikingly, the measured slope varied from coastline to coastline measured. Therefore, the perimeter of California’s coast, or more descriptively called roughness, could be distinguished from the roughness of Virginia’s coast based upon the slope the so-called Richardson plots. A larger slope corresponds with highly irregular coastlines while Euclidean boundaries, such as straight lines, produce Richardson plots of zero slope.



**Figure 4.** Representation of the Richardson plot for coastline length ( $L$ ) measured with a varying stride length for the African coast, the English coast, the Australian coast and a circle (inspired by the original data of L.F. Richardson [8]).

Richardson's work was one of the earliest observations of fractal behavior. Regardless of the map scale or measurement unit, a parameter directly proportional to the slope of the Richardson plot can be used to describe the shape of a class of objects in which traditional descriptions of shape do not apply. The work of Richardson motivated B.B. Mandelbrot to coin the term fractal in 1975 to describe objects and shapes that exhibit such scale-invariant behavior. A fractal shape is defined by its distinction from the traditional Euclidean shapes characterized in terms of a distinguishing size or scale. Therefore, a Euclidean shape can be defined in terms of a characteristic feature, such as the perimeter of a circle, where a fractal shape, such as a coastline, must be defined in terms of a scale-invariant characteristic, such as the slope of the Richardson plot.

A fractal is a geometric shape that exhibits self-similarity over a wide length range, meaning that a similar structure is observed at different magnifications. Regardless of the appropriateness of the definition for a fractal, it is obvious to any observer of nature that traditional Euclidean shapes are not often useful in describing the shape of a natural object, such as a mountain range and the structure of organization found in nature such as the growth of tree limbs. Fortunately, since the inception of fractal geometry, fractals and scale-invariant systems have been extensively used to describe and model many natural and man-made phenomena, ranging from music, fracture surfaces, diffusion limited aggregation and coastlines [1].

A fractal can be conceptualized as its difference from 1D and 2D Euclidean objects. A 1D straight line between two points can be described by the distance between those points. The dimension of an object can be defined in terms of its scaling property. For example a straight line can be divided into  $N$  equal parts and thus is scaled by the scaling ratio,  $r$ :

$$r = N^{-(1/1)} = N^{-1} \quad (1)$$

Similarly, the shape of a filled 2D square can be described in terms of the side length. A 2D square can be divided into  $N$  equal parts scaled by:

$$r = N^{-1/2} \quad (2)$$

A 3D cube can be divided into  $N$  equal parts scaled by:

$$r = N^{-1/3} \quad (3)$$

Following the same procedure, an object exhibiting scale-invariant properties can be divided into  $N$  equal parts of itself is scaled by:

$$r = N^{-1/D_f} \quad (4)$$

where  $D_f$  is the fractal dimension of the object such that:

$$r * N^{-1/D_f} = 1 \quad (5)$$

In this case, the scaling parameter is the fractal dimension.

Furthermore, a line between two points can be drawn with a repeated pattern that never crosses itself. Imagine that such a line can be drawn with such precision that as the magnification along any seemingly straight section of the line is increased the same repeated pattern is observed at finer and finer scales, such as the coastline length studies by Richardson. The dimension of such a line is greater than the dimension of a 1D straight line but less than that of a filled 2D square and may therefore be characterized by the deviation from these Euclidian definitions of shape. The dimension of such a “curve”, or coastline, therefore ranges between the 1st and 2nd Euclidean dimensions and is measured as:

$$D_f = E + (1 - H) \quad (6)$$

$$E < D_f < E + 1 \quad (7)$$

where  $E$  is the Euclidian dimension and  $H$  is a scaling parameter, called the Hurst parameter, which characterizes the degree of fractal nature regardless of the dimension and ranges from  $0 < H < 1$ . A low value of  $H$  corresponds to a very wiggly line or rough surface. A value of  $H$  closer to 1 describes a less fractal object and thus conceptually  $H$  is inversely proportional to  $D_f$ .

The fractal dimension is a term for a measure that describes how completely a fractal fills space over a given length range and is often used a measure of the texture or roughness of a fractal object. As fractal curves approach a fractal dimension of 2 the curves loose a linear appearance and increasingly fill planar space, eventually resembling a filled 2D shape. A similar argument holds when describing fractal behavior between the 2nd and 3rd Euclidian dimensions

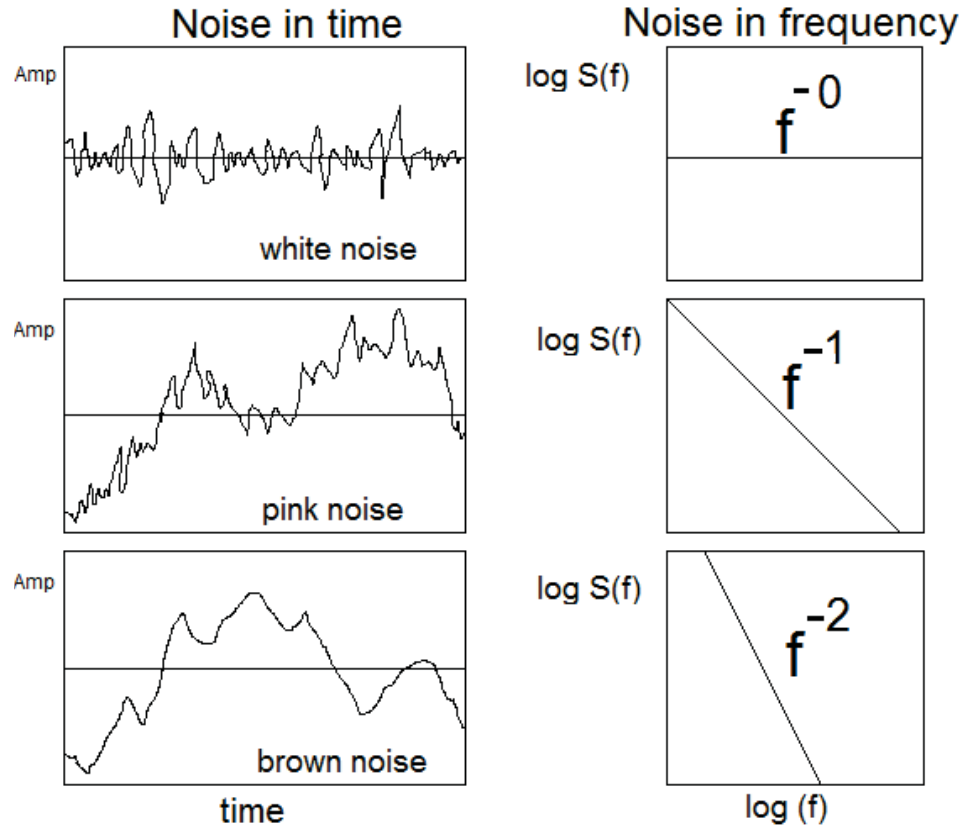
and is useful when describing such natural phenomenon as clouds, snowflakes and landscapes.

Multiple definitions and methods to determine the fractal dimension for a system (object, function or process) exist and fall into two general classes. The first type includes the previously mentioned  $Df$ , also known as the Hausdorff dimension, and is defined by the division of shapes as a function of scale. The partitioning method of the Study One falls under this category [9]. The second concerns the characterization of the random character of a fractal. These methods include the semivariogram and power spectrum methods, both which are based upon the fractal character of brown noise [10].

#### *2.2.1.2 The power spectrum and noise*

The power spectrum, in general terms, is a measure of how often (called the power or intensity) a specific variable (such as length or time) occurs as a measure of the variable itself. In the case of the Richardson plot, the specific variable was the length of the measurement stick and the power was the measured perimeter. A logarithmic plot of the intensity of length features verses the length of the features themselves will provide an approximate measure proportional to the fractal dimension of the system along any region of constant slope. In this case the system is said to exhibit fractal or scale-invariant behavior over the range of constant slope. The same methodology holds true for analysis of changes in time rather than space.

The concept of characterizing noise in the time domain provides an analogy for the dispersion analysis process in the special domain. The term noise is used to describe random changes of some attribute of a system with time. One can analyze a function with random fluctuations in time, such as noise, in the time domain or transform the signal into the temporal frequency domain. Similarly, one could analyze a random spatial system, such as a fracture surface, in the spatial domain or the spatial frequency domain. Figure 5 shows a representation of white, pink and brown noise in the time domain on the left and the logarithmic frequency domain on the right. The  $y$ -axis of the frequency domain plot is termed spectral density. The power spectrum is the plot of the spectral density, or power spectral density (PSD), as a measure of how often specific frequencies are present in the analyzed noise signal. In the time domain, these frequencies represent the deviation from the  $x$ -axis, or more specifically, the amplitude of the signal at any given point in time.



**Figure 5.** Representations of a) white, pink and brown noises and b) the power spectrum for each (inspired from [11]).

White noise is the most random type of noise and is completely uncoordinated from point to point. Analogous to characterizing coastlines, the noise can be described in terms of the slope of the logarithmic power spectrum. For the case of white noise, all frequencies are equally represented and thus the power spectrum is flat and the scaling ratio ( $r$ ) varies as:

$$r_{white} \sim f^0 \quad (8)$$

where  $f$  is the frequency in figure 5. White noise was termed “white” because of the resemblance to the white light’s equal distribution of PSD over the visible range of the electromagnetic spectrum. Pink noise, also known as  $1/f$  noise, is characterized by a power spectrum where the

PSD is inversely proportional to the frequency. Thus, for the case of pink noise the power spectrum varies as:

$$r_{pink} \sim f^{-1} \quad (9)$$

Brown noise, also known as Brownian noise and more descriptively appropriate as red noise, can be generated by reproducing Brownian motion in the spatial domain, also called a random walk. Brownian motion is technically the integral of white noise and, like pink noise, is characterized by more low frequency than high frequency deviations. A random walk is a mathematical method to describe a random trajectory, such as the fluctuations of the stock market, the foraging of an animal or the motion of a particle moving in a liquid. Consider the case of a particle moving thorough a liquid, as it will be an analogy called upon to describe the dispersion of SWCNT as the motion of nanotubes within the solvent or polymer during the fabrication of SWCNT-nanocomposites. The motion of the particle is due to the random collisions with the surrounding liquid molecules. The power spectrum can be thought of as a measurement of the length of travel between collisions. As the distance between collisions increases, the probability of the particle colliding with a liquid molecule also increases, thus giving rise to the slope of the power spectrum and the Brownian characterization of weighted low frequency deviations. Such a type of seemingly random, yet coordinated, motion is very well understood in mathematics and varies as:

$$r_{brown} \sim f^{-2} \quad (10)$$

Pink noise can be used as an analogy to describe and measure a fractal object. Interestingly, pink noise with a  $1/f$  scaling represents the most common form of “structure” in nature, and is found in the luminosity of stars, the flow of the river Nile and the sand flow of an hour glass [12]. The origin of this  $1/f$  scaling in nature remains mysterious but has been recently examined as a possible tool to describe systems in terms of equally mysterious unifying or critical features [13]. In fact, the self-organized criticality model was developed to understand fractals and  $1/f$  noise [14]. The physics and origin of white and brown noise are well understood and are presented here as 1D noise and 2D noise. Pink noise, like fractals which fall in between Euclidian dimensions, fall in between the two well defined categories of white and brown noise.

Furthermore, the specific “shade of noise” between white and brown can be further described in terms of:

$$r_{shade} \sim f^{-J} \quad (13)$$

where  $J$ , like the Hurst parameter  $H$ , is a scaling parameter but with the range,  $0 < J < 2$ .

Similar to the Richardson plots, here the scaling parameter of the system is determined by the slope of constant region on the logarithmic power spectrum, as shown in figure 5. The logarithmic region of constant slope describes scale-invariant behavior in the system. As with the Richardson plots, the shade of noise, or dimension of noise, can be directly determined from a power spectrum of the form:

$$S(k) \sim f^{-B} \quad (14)$$

where the constant  $B$  represents the scaling parameter describing the dimension of the system. Therefore, the relationship between the variable (such as spatial or temporal frequency) and the occurrence of the variable (the power or intensity) follow a power law relationship. In fact a power law is a mathematical relation that describes scale-invariance for a given system. A useful equation to describe power law follows:

$$F(x) = r x^B \quad (15)$$

where  $r$  is a scaling constant and  $B$  is the scaling parameter (positive or negative). Thus scaling by a constant proportionately scales the function itself, which is the definition of scale-invariance:

$$F(ax) = r(ax)^B = c F(x) = z x^B \quad (16)$$

Thus rescaling by moving position or scale (magnification) changes the constant of proportionality,  $z$ , yet retains the overall structure of the original function including the scaling parameter,  $B$ . When plotted on a logarithmic scale, the power law argument takes the form:

$$\log(F(x)) = B \log(x) + \log(r) \quad (17)$$

with logarithmic slope  $B$ . Thus regardless of the position or scale of a self-affine function, the scaling parameter  $B$  can be approximated.

#### *2.2.1.3 The scale-invariant mystery of measuring nature*

The underlying method to investigate the power spectrum and describe some very mysterious phenomena has historically been accomplished utilizing what is known as Zipf's law. Zipf's law is basically the analysis of the slope of a power spectrum when such a region of constant slope exists on a logarithmic scale and can be fit with by a power law. Zipf's law takes the general form:

$$F(x) = r x^{-B} \quad (18)$$

where  $r$  is a constant and  $B$  is the scaling parameter. The equation for Zipf's law is equivalent to equation 15 describing a general power law with a negative exponent.

Benford's law also shows similarities to the more general concept Zipf's law [15]. Benford's law was been used to describe many forms of natural numerical behavior from stock market data to census results to material properties [17, 18]. Through use of Benford's law, it has been shown that spatial power spectrums of natural images generally scale as:

$$S(k) = A k^{-(2-n)} \quad (19)$$

where  $k$  is the magnitude of the spatial frequency and  $A$  is a constant dependent upon the overall image contrast [20]. Most natural images scale with  $n=0.19$  in the spatial domain over multiple decades of spatial frequency, revealing limited scale-invariant behavior [20, 21]. This scaling is attributed to the occlusion that occurs when a 3D volume is captured in a 2D image and that the occurrence of lengths features associated with arrangement in natural environments simply follow a power law relation [20]. Each of these laws utilizes a logarithmic plot to determine the scale-invariant nature of the system of interest.

#### *2.2.1.4 The power law and dispersion*

A system follows a power law if the frequency of an occurrence varies as a power of some measure of the occurrence, and the scaling parameter is directly proportional to the slope of

the logarithmic power spectrum. A measure of the fractal dimension of the SWCNT dispersion will effectively describe the nature of the dispersion in terms of, essentially, the degree of randomness, or how crumpled and crinkled the images of the dispersion appear. Proving that nanocomposites dispersion has some degree of fractal nature by measuring a scale-invariant parameter representative of the fractal dimension over a sufficiently large length range and volume will allow for the estimation of the dispersion quality throughout the overall nanocomposites, and thus eliminate the need for labor-intensive dispersion imaging and evaluation. There have been many studies concerning the fractal behavior of various systems including some which have shown that surfaces of most materials have a fractal surface at the microscopic scale [22, 23]. Previous work has shown the usefulness of analyzing a power spectrum to gather information on the system being analyzed. Small angle studies have also been used to characterize the fractal dimension SWCNT dispersion in suspensions [24-26], within formed epoxy and ceramic based nanocomposites [27, 28] as well as analyze the characteristic size of colloidal dispersed silica particles [29].

#### *2.2.1.5 Mathematically modeling a fractal system*

One method to model a fractal-like system is the fractal Brownian motion model, fBm, which is an extension of the more general random walk model. Interestingly, it was Einstein in 1905 that first predicted that Brownian motion, or the seemingly random motion observed when particles are immersed in liquid, is due to the random hyperactive nature of molecules observed at the local scale [30]. Einstein's model of Brownian motion validated his molecular theory of liquids, confirmed Avogadro's number and predicted the size of the theoretical molecules [30]. In fact, through Einstein, the Brownian motion model led to the general acceptance of the existence of molecules and atoms [31]. One of Einstein's accomplishments in developing his model of Brownian motion was to realize that the motion of the particles could be observed and measured in terms of their mean-square displacements instead of the more difficult measurements, such as velocity.

Specifically, it is the variance of fBm with time or space that produces the slope of the power spectrum. Performing the logarithmic function on a plot such as a power spectrum and measuring differences (such as lengths) effectively converts the data from a measure of absolute difference into a relative difference (akin to a percentage). Therefore, the scaling parameter of

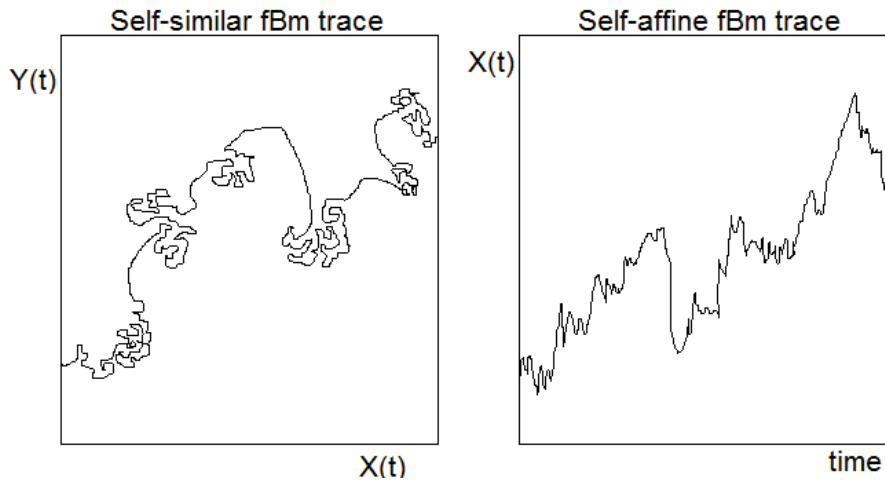
the fBm can be determined regardless of the scale of measurement, such as with the Richardson plots. The fBm can be approximated thorough the use of various algorithms in order to determine the scaling parameter. The scaling behavior of fBm is quantified by the same scaling parameter  $H$  as in equation 6. Consider the trace of pink noise in figure 5 not as noise but as a trace of fBm motion or the ridgeline of white, pink and brown mountain ranges. The scaling parameter  $H$  defines the relationship between the change in the amplitude,  $A$ , over a change in space,  $x$ , and is scaled by:

$$\Delta A \sim \Delta x^H \quad (20)$$

This type of scaling defines fBm and the general concept of self-affinity. Self-affinity differs from the self-similarity described through the coastline analogy in that self-similar shapes are statistically repeated as the scale (or magnification) of the system is altered. Alternatively, when a variable in a self-affine fBm system, such as length, is scaled by a scaling ratio,  $r$ , to become  $rx$ , the fBm function,  $A(x)$ , does not also scale with  $r$  (as is the case in self-similar systems) but rather with the following scaling ratio,  $r_0$ :

$$r_0 \sim r^{-H} \quad (21)$$

where  $H$  is again the Hurst scaling parameter defined in equation 6. A simple comparison of self-similar and self-affine functions is shown below in figure 6.



**Figure 6.** Representation of self-similar versus self-affine behavior (inspired from [11]).

### 2.2.1.6 Modeling fractals as generalized fractional Brownian motion by the power spectrum method

Of the various methods to model fractal behavior, the most adequate model for the random fractals found in nature is the fBm model [32-34]. The fractal dimension of a function that varies with time can be evaluated in terms of temporal components (in time,  $t$ ) or the temporal frequencies ( $t^{-1}$ ). Similarly, the fractal dimension of an object can be analyzed in terms of spatial components (in space,  $k$ ) or the spatial frequencies ( $k^{-1}$ ). In terms of the HR-SEM images of dispersion, the spatial components are the grid of pixels that compose the image and the frequency components compose the Fourier power spectrum. A Fourier transform function transforms an original function (or HR-SEM image) described in spatial or temporal components into/from a function described in terms of the spatial or temporal frequency components. From the fBm model, the power spectrum method, also called the Fourier filtering method, was developed in 1991 to estimate the fractal dimension based upon the slope of the power spectrum of brown noise. Knowing the slope of the logarithmic power spectrum of brown (or Brownian) noise allows for the relation of the slope of the logarithmic power spectrum to the known Hurst parameter for brown noise ( $H = 1/2$ ). By analyzing Brownian motion in multiple dimensions, the relationship between the Hurst parameter,  $H$ , and the logarithmic power spectrum slope,  $B$ , has been shown to be related by [32, 33]:

$$B = 2H + E \quad (22)$$

where  $E$  is the dimension of analysis. The relation above can be used in conjunction with equation 6 to approximate the fractal dimension for systems with Hurst parameter ranging from  $0 < H < 1$ :

$$D = E + 1 - H = E + 1 - \left[ \frac{(B-E)}{2} \right] \quad (23)$$

Therefore, in general, a function of one variable,  $f(x)$  with a power spectral density,  $S(k)$ , proportional to:

$$S(k) \sim k^{-B} \quad (24)$$

represents fBm with a logarithmic spectral density slope defined by:

$$B = 2H + 1 \quad (25)$$

where a function of one variable,  $S(k)$ , and  $0 < H < 1$  with  $E < D < E + 1$  yields spectral density slopes from  $1 < B < 3$ . A spectral density slope of 2 corresponds to brown noise, a slope of 1 corresponds to pink noise and a slope of 0 corresponds to the white noise. A spectral density slope of 3 would correspond to the situation when  $H = 1$  and the subsequent Euclidian dimension can describe the system. Therefore, the fractal dimension can be gleaned from the spectral densities of random functions in time or space and characterized by the deviation from the spectral density of the characteristic Brownian function with  $H = \frac{1}{2}$  and  $B = 2$ , pink noise observed when each octave is equally represented in the spectrum and white noise when the system is not fractal.

### 2.2.7 Fourier analysis

Spectral densities,  $S(k)$ , can be utilized to characterize random functions in space or time [35, 36]. The PSD has been used to determine dominant feature sizes for ion-sputtered surfaces and used as a measure of detection of interstitial lung disease in radiographic images [37, 38] and was utilized to determine the dominant feature sizes of SWCNT dispersions in Study One [5]. The slope of the logarithmically plotted PSD has been used to characterize the nature of a system and is generalized as Zipf's law. Examples in the literature have been used to provide a measure of the fractal nature include radiographic and X-ray computed tomography images of bone, images of landscapes, optical microscope images of premalignant lesions, cytologic images of cell nuclei, SEM images of particle surfaces, cluttering statistics in cosmology plus the small angle scattering studies previously mentioned [39-46].

Algorithms such as the discrete Fourier transform (DFT) can be used to approximate the PSD. As previously stated, the evaluation of self-affine SWCNT networks is based upon a 2D fBm model based upon the work of Mandelbrot and later expanded by J.C. Russ [1, 2]. The HR-SEM high-contrast images capture this 3D network as a 2D projection and can be interpreted as a 2D self-affine surface. Therefore, in Cartesian coordinates, the 2D self-affine surface can be analyzed as a series of horizontal slices,  $f(x)$ , through the (2+1) dimensional self-affine surface. The HR-SEM image is composed of a given amount,  $Y$ , of vertically stacked horizontal slices dependent upon the pixel density of the image. Each slice is effectively a profile of the self-

affine surface at a given position (row) from the bottom to the top of the surface (0 to  $Y$ ).

Therefore the DFT, as represented in the spatial domain, can be stated as:

$$F(k, Y) = \int_0^Y f(x) \cdot e^{ikx} dx \quad (26)$$

where the surface is evaluated from 0 to  $Y$  and  $k$  is the spatial frequency component corresponding to the spatial length component,  $x$ . A useful property of DFT is the fact that it is a linear transform operator. It has been proven that a linear transform of fBm produces another fBm function yet preserves the original fractal dimension [47]. Therefore, the fractal dimension can be determined in either the original domain of the signal (space or time) or the frequency domain representation of the signal. Another very useful aspect of the chosen 2D fBm model, and self-affinity in general, is that the 1D slices experience the same Hurst scaling parameter as the 2D surface. This relationship can be conceptualized by the ridgeline analogy of mountains in that mountain terrain and the projected ridgeline of any “slice” of the terrain are characterized with the same Hurst scaling parameter. Considering the surface as self-affine constrains the description of the slice to:

$$f(x) = f(rx) \cdot r^{-H} \quad (27)$$

where  $r$  is a scaling parameter. Combining with the previous equation yields:

$$F(k, Y) = \int_0^Y f(rx) \cdot e^{ikx} \cdot r^{-H} dx \quad (28)$$

and substituting for  $q = rx$  gives

$$F(k, Y) = r^{-(H-1)} \int_0^{rx} f(q) \cdot e^{\left(\frac{ikq}{r}\right)} dq \quad (29)$$

Examining the relationship between equations 27 and 29 yields:

$$F(k, Y) = r^{-(H-1)} \cdot F\left(\frac{k}{r}, rx\right) \quad (30)$$

The spectral density, also called the power spectrum or power spectrum density (PSD) function,  $S(k)$ , is defined by the relation:

$$S(k) = \frac{1}{k} |F(k, Y)|^2 \quad (31)$$

Inputting equation 30 into 31 yields:

$$S(k) = S\left(\frac{k}{r}\right) \cdot r^{-(2H+1)} \quad (32)$$

which takes the form of equation 24:

$$S(k) \sim k^{-B} \quad (33)$$

where  $B = 2H + 1$  and  $H$  is the Hurst scaling parameter as described in equation 6. Thus the slope of the 1D power spectrum can be used to approximate the fractal dimension. Equation 23 will be modified to take in to account how the PSD is determined:

$$D = E + 1 - \left\lceil \frac{(B-E_0)}{2} \right\rceil \quad (34)$$

where  $E_0$  is the dimension of the PSD function. The dimension of the PSD is determined by the amount of variables. Thus, analyzing a self-affine surface as a series of 1D slices produces a 1D PSD. In this case,  $E_0 = 1$  and the following relationship can be used to determine the fractal dimension:

$$D = 2 + 1 - \left\lceil \frac{(B-1)}{2} \right\rceil = \frac{(7-B)}{2} \quad (35)$$

The transfer function, FT, is represented in terms of magnitude and phase where magnitude is representative of the quantity associated with the component and the phase represents the location of the component. The PSD is defined as the squared magnitude of the DFT, as shown above in equation 31. Therefore, the PSD retains information regarding the quantity associated with the frequency component (length) while removing the association of the location (position), allowing for the analysis of 2D spatial information in a 1D plot. The ability to separate the association with position will allow for direct determination of dominant frequency/length components. In fact, this method was applied in Study One to determine the dominant lengths from the HR-SEM images of SWCNT dispersion.

The PSD is defined both as the squared magnitude of the DFT (equation 31) or the FT of the autocorrelation function. The autocorrelation function in 2D Cartesian coordinates is evaluated in as:

$$ACF(m, n) = \iint_{-\infty}^{\infty} a_1 a_2 \cdot P(a_1 a_2, m, n) da_1 da_2 \quad (36)$$

where  $a_1$  and  $a_2$  represent the measured values at locations  $(x_1, y_1)$  and  $(x_2, y_2)$ ,  $m = (x_1 - x_2)$ ,  $n = (y_1 - y_2)$ , and  $P(a_1, a_2, m, n)$  is the 2D probability density function. The probability density function of a random variable measures the potential of the random variable residing at a given location. The 1D autocorrelation function of a horizontal slice of a 2D fBm system with Gaussian distribution is:

$$ACF_x(m) = c^2 \cdot e^{-\left(\frac{m}{L}\right)^2} \quad (37)$$

where  $c$  is the root mean square deviation of the measured value locations  $(x_1, y_1)$  and  $(x_2, y_2)$  and  $L$  is the autocorrelation length. The root mean square deviation is expressed in units of length and therefore the 1D autocorrelation function with Gaussian distribution has units of length squared. The assumption of Gaussian distribution is relevant because fBm is defined as a Gaussian process.

The 2D PSD of a process, stated in terms of the Fourier transform of the autocorrelation function, is the frequency domain representation of the process:

$$S(k_x, k_y) = \iint_{-\infty}^{\infty} \frac{ACF(m, n)}{4\pi} \cdot e^{-i(m \cdot k_x + n \cdot k_y)} dm dn \quad (38)$$

The 1D PSD of a horizontal slice of a 2D fBm system is evaluated as:

$$S(k_x) = \int_{-\infty}^{\infty} S(k_x, k_y) dk_y \quad (39)$$

As previously mentioned, the PSD can be approximated with an algorithm, such as the DFT (equation 31). The DFT can be efficiently computed utilizing a fast Fourier transform (FFT) algorithm. In this case the FFT yields:

$$S(k_x) = \frac{2\pi}{hNM} \sum_{l=0}^N |V_l(k_x)|^2 \quad (40)$$

where  $h$  is the pixel width,  $M$  and  $N$  represent the horizontal and vertical pixel number in the image and  $V_l(k_x)$  is the Fourier coefficient of slice  $l$ :

$$V_l(k_x) = \frac{h}{2\pi} \sum_{j=0}^N a_{jl} \cdot e^{-ijhk_x} \quad (41)$$

Assuming the 2D fBm surface has Gaussian distribution yields:

$$S(k_x) = \frac{c^2 L}{2\sqrt{\pi}} \cdot e^{-\left(\frac{k_x L}{2}\right)^2} \quad (42)$$

where units in terms of length cubed.

The radial PSD (RPSD), utilized in Study One, is the generation and integration of the 1D PSD function in terms of radial slices as opposed to horizontal or vertical slices. The 1D RPSD can also be calculated along radial slices of a 2D fBm surface as:

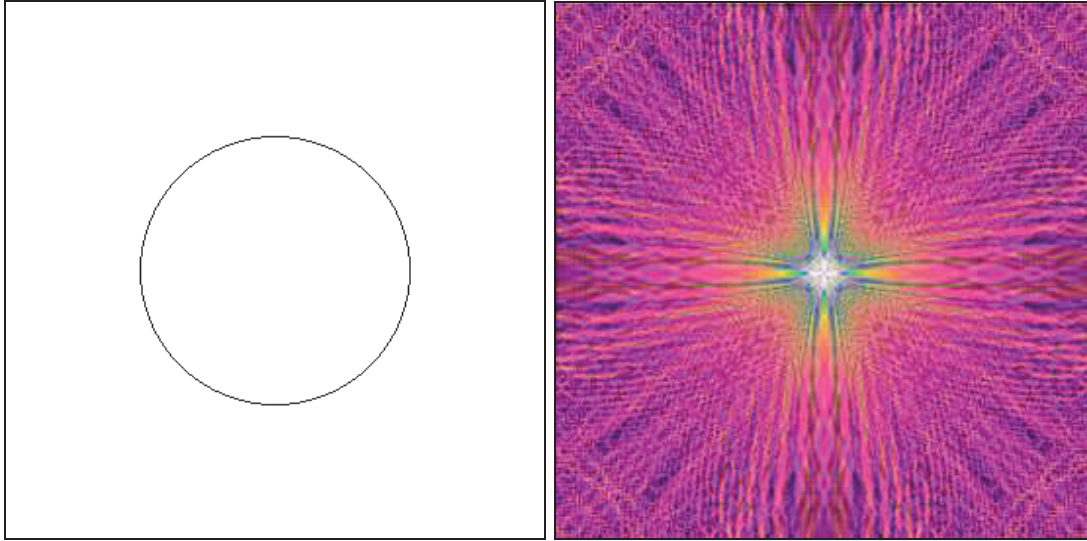
$$S_r(k) = \int_0^{2\pi} k \cdot S(k \cos \theta, k \sin \theta) d\theta \quad (43)$$

and with Gaussian distribution yields:

$$S_r(k) = \frac{c^2 L^2}{2} k \cdot e^{-\left(\frac{kL}{2}\right)^2} \quad (44)$$

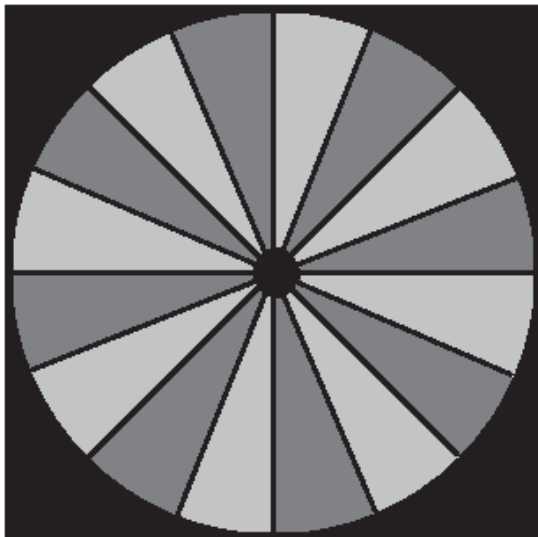
which also has units of length cubed and contains the same information as the 1D Cartesian PSD. Gwyddion, a free open source software for scanning probe microscopy image analysis, is perfectly suited to determine the 1D PSD and RPSD in the specified manner [48]. Gwyddion was developed by the initiative of Czech Metrology Institute and is supported by a worldwide group of volunteers. It has been utilized for image analysis in various instances included the investigation of the fractal dimension of silica glass [49], to characterize cellulose nanocrystals [50], quantification of nanoscale surface features [51], grain size distribution [52], and to characterize the geometry of stretched collagen fibrils [53].

Plotting the RPSD is a process that can be conceptualized by examining the 2D PSD of image shown below in figure 7. The 360 x 360 pixel image consists of a circle drawn with a 3 pixel wide line.



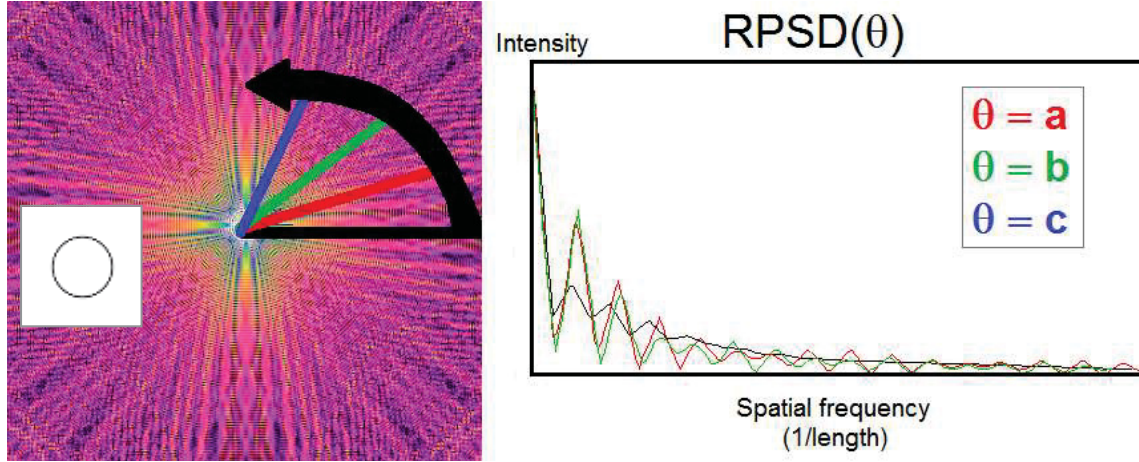
**Figure 7.** The a) 360x360 image of a circle and b) the corresponding 2D PSD.

Each radial line composing the 2D PSD can be thought of as the 1D radial slice composing the image. Each slice of the image is represented in the 2D PSD as a wedge or slice of pie in the figure below.



**Figure 8.** Representation of the PSD in terms of radial PSD slices.

A 360 pixel by 360 pixel image will require 360 slices to fully map the surface. In this case figure 8 would be composed of 360 radial slices of 1 degree. The 1D PSD for each radial slice of the image conceptually represents a radial line in the 2D PSD as shown below in figure 9. All 1D PSD radial slices are averaged to plot the RPSD.



**Figure 9.** The RPSD is generated from integrating the PSD of all radial slices to produce the average spatial frequency profile of the image. The 2D PSD of the circle (a) can be used to conceptualize building the RPSD (b).

Each slice of the image is converted into a numerical sequence (equation 27), a process referred to as sampling. Generating the RPSD is a method of sampling the original image and therefore is subject to the Nyquist sampling theorem. The Nyquist sampling theorem states that a function is completely determined when the sampling rate is at least twice the highest waveform frequency. The Nyquist frequency ( $N_f$ ) is the highest frequency needed to fully reconstruct the original signal:

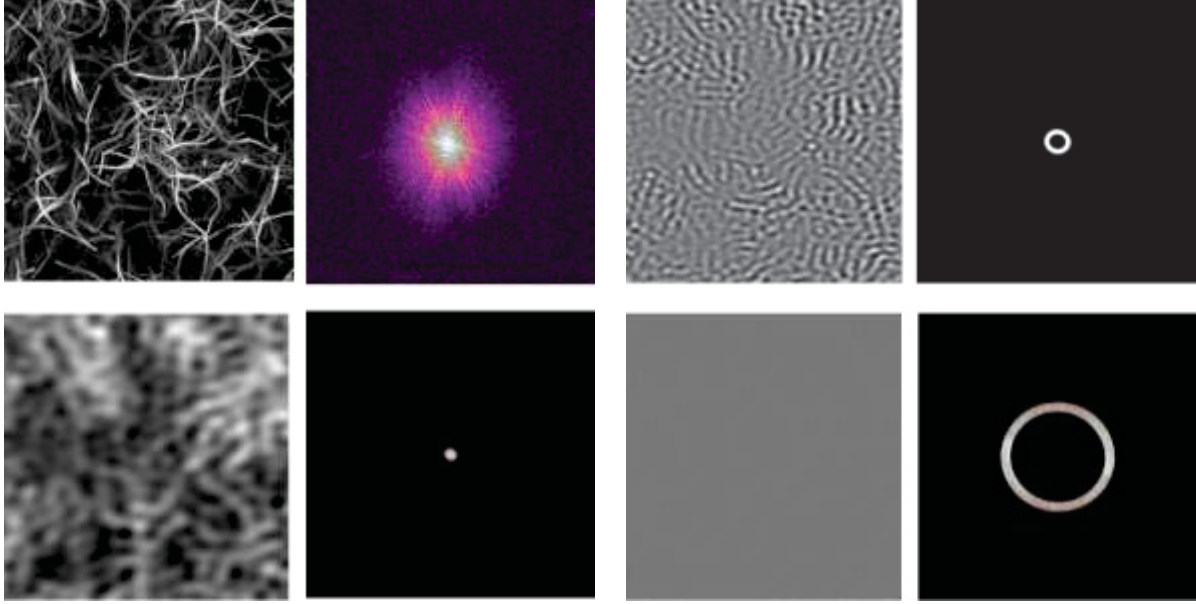
$$F(N_f) = \frac{1}{2}Y \quad (45)$$

where  $Y$  is the sampling rate. In the case of analyzing a 360 x 360 pixel image, the sampling rate is 360 and the Nyquist frequency is 180. Therefore 180 Fourier components are necessary to describe the original image in terms of 180 spatial frequencies. The 180 frequencies within the 2D PSD of the 360 x 360 pixel image can each be represented as a ring in figure 10.



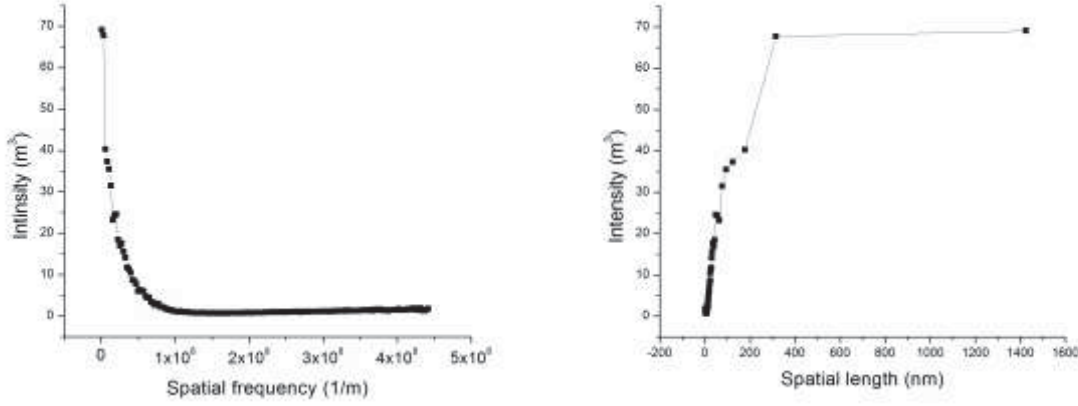
**Figure 10.** *Representation of the PSD in terms of spatial rings.*

The distance from the origin represents the spatial frequency with higher frequency components near the origin and low spatial frequency components near the outer edge. This relationship is shown below in figure 11. In this case, the image of sample 5 from Study One was used [5]. Higher spatial frequency components correspond to finer detail in the images of the generated fBm surface. Notice that the frequencies nearest to the center of 2D PSD correspond to the spatial lengths that contain the information relevant to SWCNT dispersion. Furthermore, all frequency components corresponding to a length greater than one pixel is located near the origin.



**Figure 11.** The a) FFT generated image and the corresponding full 2D PSD for sample 5 of Study One, b) – d) FFT generated image from the bounded 2D PSD containing components of decreasing spatial frequency.

When a 360 by 360 pixel image is sampled at the Nyquist frequency, the plot of the 1D RPSD is a measure of 180 spatial frequencies in relation to their intensity, as determined by equation 44. The intensity is a measure of how often a given spatial frequency is present in each slice of the image. The inverse of the spatial frequency yields the spatial length and, as has been demonstrated, the logarithmic slope of the spatial frequency or spatial length PSD and the intensity of each component in either domain (spatial or frequency) is preserved. The RPSD of the representative original image from figure 11 is presented below in terms of both spatial frequency and spatial length. In terms of spatial length, the RPSD can be used to describe dominant lengths in an image and was utilized in Study One [5]. In Study One, the symbol  $W$  was used in figure 5 to denote intensity on the RPSD. Here, in Study Two the symbol  $I$  is used to indicate intensity. Notice that the intensity is plotted on the  $y$ -axis in units of length cubes, as described in equation 44, and the 180 spatial components are plotted on the  $x$ -axis. Also, notice how the spectrum components are more heavily weighted in the high spatial frequency (low spatial length) region.



**Figure 12.** RPSD generated from sample 5 in Study One in terms of a) spatial frequency and b) spatial length.

In summary, the 3-D volume containing SWCNT dispersion is captured in 2-D high-contrast images that can be broken down into its periodic structures, and the length versus intensity information can be analyzed in 1-D. Therefore, direction independent structural information, in term of the fractal dimension, can be extracted and analyzed.

### 2.2.2 Fitting the data and statistical weighting

Fittingly, the classical Freundlich equation, which is famous for its use in describing allometry, or the study of relationship between body shape, size and function, is utilized to fit the data. The classical Freundlich equation utilized to fit the data is:

$$F(k) = Ak^B \quad (46)$$

where  $k$  is the spatial frequency,  $A$  is a constant coefficient associated with the contrast and SEM instrumentation and  $B$  is the scaling parameter. In the spatial domain, this equation can be represented by the fitting function:

$$F(x) = Cx^B \quad (47)$$

where  $x$  is the spatial length,  $C$  is a new constant coefficient and  $B$  is the same scaling parameter. Thus the data can be fit in either the spatial length or spatial frequency domain, shown

previously in figure 12. If we assume a negative scaling parameter,  $-B$ , the fitting equation shows the familiar form:

$$F(k) = Ak^{-B} \quad (48)$$

Reducing the chi-square function is a measure of the quality of the fit of the data using an appropriate power law function, such as the Freundlich equation. The chi-square function quantifies the deviation of the actual values with values predicted using the appropriate fitting equation, in this case equation 48. The probability, PG, of predicting the actual intensity value,  $S(k_i)$ , for the given  $k_i$ , and assuming Gaussian distribution is given by:

$$PG(k_i) = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\left(\frac{1}{2}\left(\frac{S(k_i)-F(k_i)}{\sigma_i^2}\right)^2\right)} \quad (49)$$

where,  $S(k_i)$  is the observed mean intensity for the given spatial frequency given by equation 48,  $\sigma_i^2$  is the variance of the measurement error for  $S(k_i)$ , and  $F(k_i)$  is predicted relationship (equation 48). The assumption of Gaussian distribution is appropriate because the data was obtained by modeling the SWCNT network as a fBm surface. A data set of  $N(x_i, y_i)$  elements is defined in terms of the total probability, PTG, as the product of the probability at each individual element:

$$PTG(k, F(k)) = \prod_N \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{1}{2}\sum_{i=1}^N \left(\frac{S(k_i)-F(k_i)}{\sigma_i^2}\right)^2} \quad (50)$$

where  $N$  is the number of data points and the data set  $(k, F(k))$  is the result of equation 48 over all spatial frequencies,  $k_i$ . The chi-square function,  $\chi^2$ , is defined as the sum operation in the previous equation:

$$\chi^2 \equiv \sum_{i=1}^N \left(\frac{S(k_i)-F(k_i)}{\sigma_i^2}\right)^2 \quad (51)$$

The variables in the chi squared equation are  $k_i$ , the independent data set (spatial frequency or spatial length),  $k_i$ , the dependent data set (intensity of occurrence),  $S(k_i)$  from equation 44 and  $F(k_i)$ , the fitting function (equation 48) with 2 fitting parameters ( $A$  and  $B$ ). The term reduced chi-square value is the value of the chi-square value divided by the degrees of freedom,  $\nu = N - P$ :

$$\frac{\chi^2}{\nu} \equiv \frac{1}{\nu} \sum_{i=1}^N \left( \frac{S(k_i) - F(k_i)}{\sigma_i^2} \right)^2 \quad (52)$$

where  $N$  represents the number of data points and  $P$  represents the number of fitting parameters. Solving the reduced chi-square function is essentially performing a weighted ordinary least squares approach to regression analysis with weighting factor,  $w_i$ :

$$\chi^2 \equiv \sum_{i=1}^N w_i (S(k_i) - F(k_i))^2 \quad (53)$$

where:

$$w_i = \frac{1}{\sigma_i^2} \quad (54)$$

To better understand how to use these weighting functions, a quick observation how spectrophotometric measurements are determined is necessary. Spectrophotometry measures the transmission and reflection of a material by quantitatively characterizing electromagnetic radiation (light) intensity as a function of the wavelength of the light source. For example, spectrophotometric data is said to show heteroscedastic properties when the variance of measuring small objects is less than the variance of measuring large objects in a given image and is observed when different wavelengths are scattered or absorbed differently. The word heteroscedastic originates from the Greek terms "hetero" and "scedasis" meaning “different” and “dispersion”, respectively. Here, the heteroscedasticity originates from the fact that the large spatial length (or frequency) components are more poorly sampled in the limited region contained in each HR-SEM image when compared to smaller length (or larger frequency) components.

A heteroscedastic data set can affect the values of constants when fitting the data to an equation and assuming that the error term is homoscedastic, or has zero variance. Applying the weighting operator of the reduced chi-square function may counteract this discrepancy. Alternatively, other weighting functions, such as the statistical weighting function, can be utilized. The statistical weighting function will reduce bias associated with  $X$ - or  $Y$ -values and is a technique used when analyzing spectral information in spectrophotometry [54]. Performing the logarithmic function on a data set effectively removes some of the heteroscedasticity, although in this case further stabilization of the variance between the coordinates  $X$  and  $Y$  may be

advantageous. The RPSD data can be fit to the non-linear Freundlich function, equation 48, by minimizing the weighted function in equation 53 where  $w_i$  in this case is the statistical weighting function:

$$w_i = \frac{1}{S(k)} \quad (55)$$

By applying a statistical weighting function when fitting the RPSD data with the power law one can set the  $Y$ -values,  $S(k)$ , to be the arbitrary intensity factor and therefore place more “weight” on the  $X$ -values, which are the dominant spatial frequencies in the image,  $k$ .

The quality of the fit can be measured utilizing the coefficient of determination ( $R^2$ ). The coefficient of determination is a measure of the closeness of fitting the data with the particular parameters  $A$  and  $B$  of equation 48. A coefficient of determination closer to 1 indicates a better fit. Monitoring the coefficient of determination is a method often used in statistics when investigating how well a given function predicts future occurrence by measuring how well a function accounts for the variance in a data set [55]. A coefficient of determination closer to 1 indicates a better fit.

### *2.2.3 Specimen characterization*

A field emission Hitachi S-5200 high resolution scanning electron microscope, with a through the lens (TTL) detector, was utilized to capture high-contrast images as described in the previous study and in Appendix A.

## *3. Results*

### *3.1 Concerning dispersion within HR-SEM images*

The aim of this study is to demonstrate that the high-contrast HR-SEM images do not all scale with the same power, as is the case with most natural images under Benford’s law [20]. Alternatively it is proposed here that the HR-SEM images of dispersion are specimen specific and that a parameter directly proportional to the fractal dimension describing SWCNT dispersion can be obtained from the slope of the RPSD of the HR-SEM images of dispersion.

The following subsections describe the application of the proposed methods to the HR-SEM high-contrast images of dispersion.

### *3.1.1 The fractal properties of dispersion*

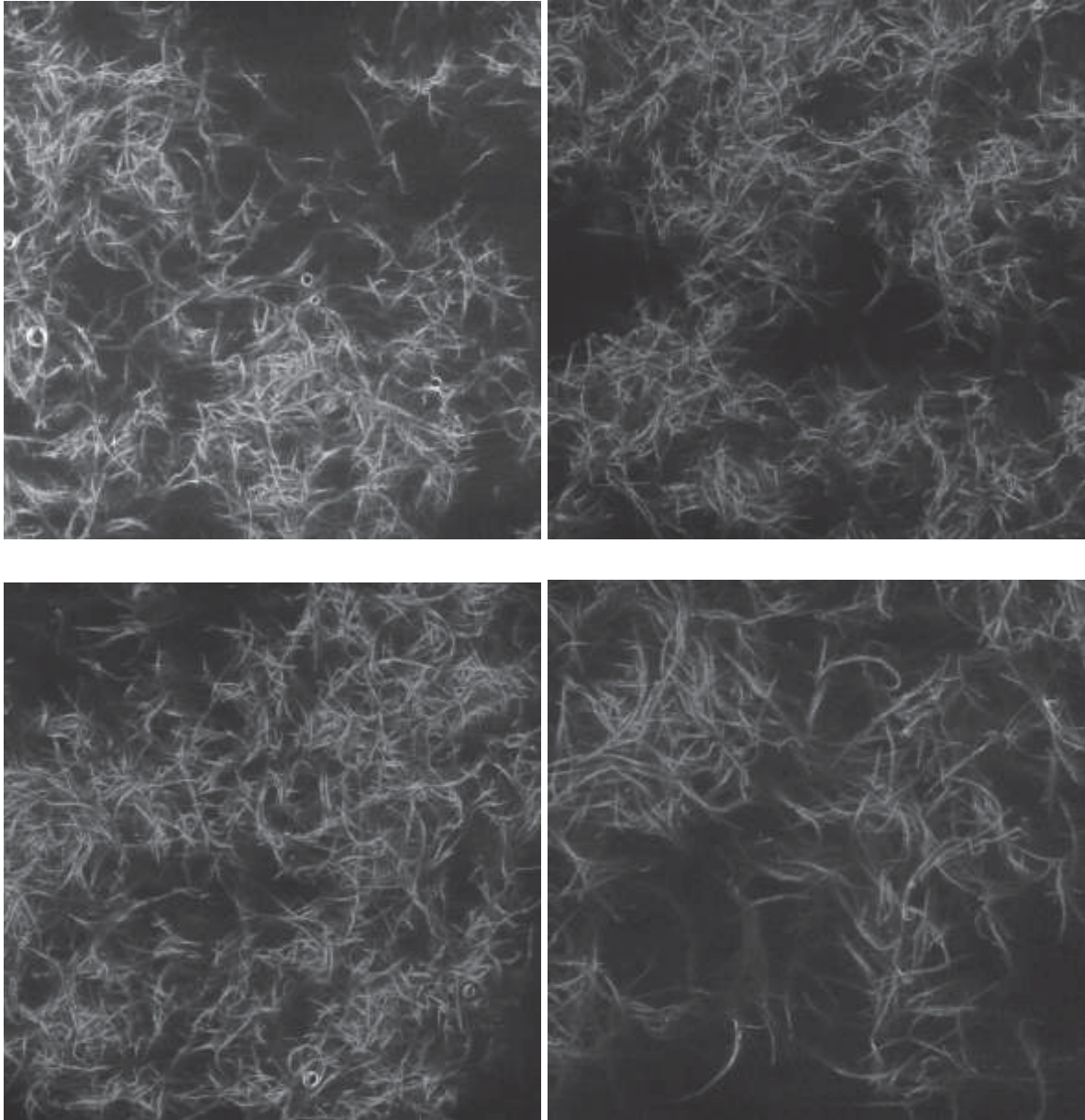
Notice the similarity between all the above equations. Many show similar scale invariant behavior that can be approximated with a power law function of the form:

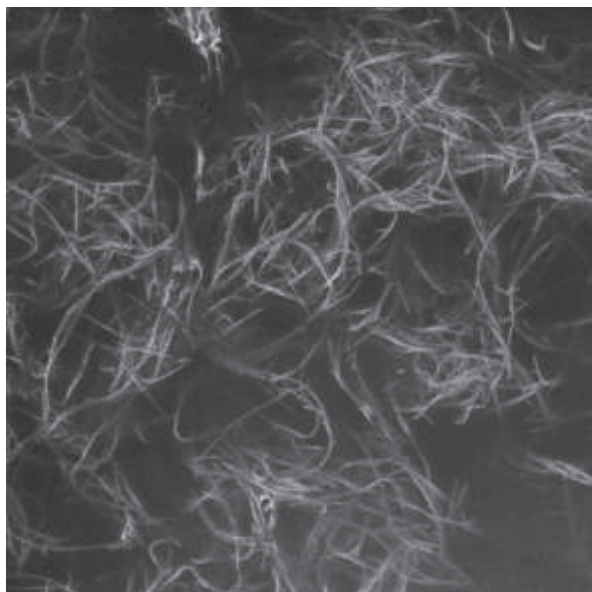
$$F(x) = Ax^{-B} \quad (56)$$

Where  $A$  is a constant  $B$  is the scaling parameter, represented by a straight line on a logarithmic power spectrum. The scaling parameter  $B$  is related to a fractal measurement,  $Df$ , of the structure of dispersion through equation 34. It is hypothesized here that the constant  $A$  is related to the contrast in the image, similar to image analysis using Benford's Law, and the effect of SEM instrumentation. Thus the information pertaining to the structure of the network should be contained in the scaling parameter,  $B$ .

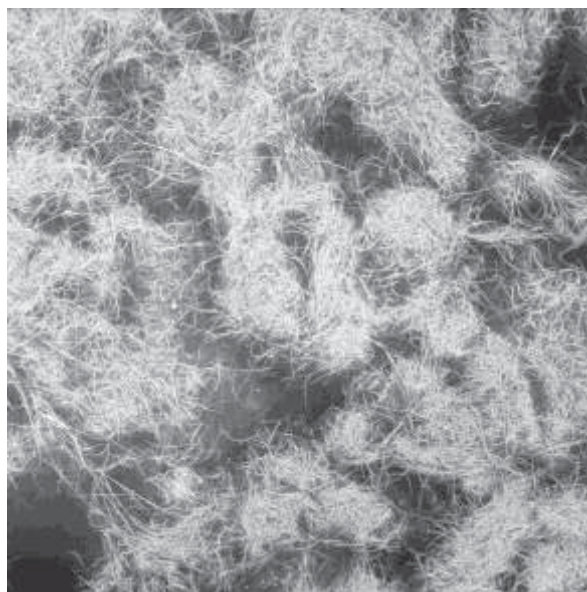
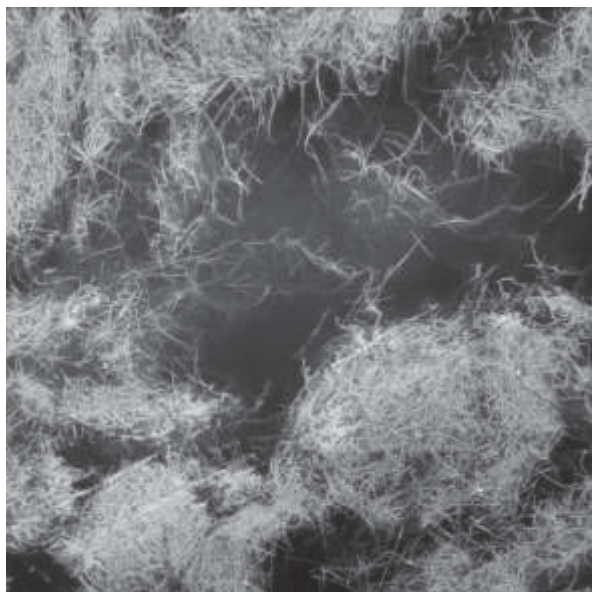
The RPSD is determined by first analyzing the static high-contrast HR-SEM image as a stochastic process, or random field, where each pixel is assigned a value proportional to the intensity at each point image. Again, the image is effectively analyzed as signals that represent radial slices of the 2D image. The PSD of the image is evaluated to describe how the power, or pixel intensities, of the image are distributed in terms of spatial frequency and effectively identify the periodic structures in the image. The inverse of the spatial frequencies represent lengths present in the high-contrast image. The radial power spectral density is the collapsed PSD obtained by averaging all possible directional spectra and creating an independent mean power spectrum. HR-SEM high-contrast images of the PMMA and PS/PMMA based nanocomposites are provided below in figures 13 to 21. Figures 13 to 17 show the high resolution images (1792 x 1792 pixel) and figures 18 to 21 depict the lower resolution images (896 x 896 pixel).

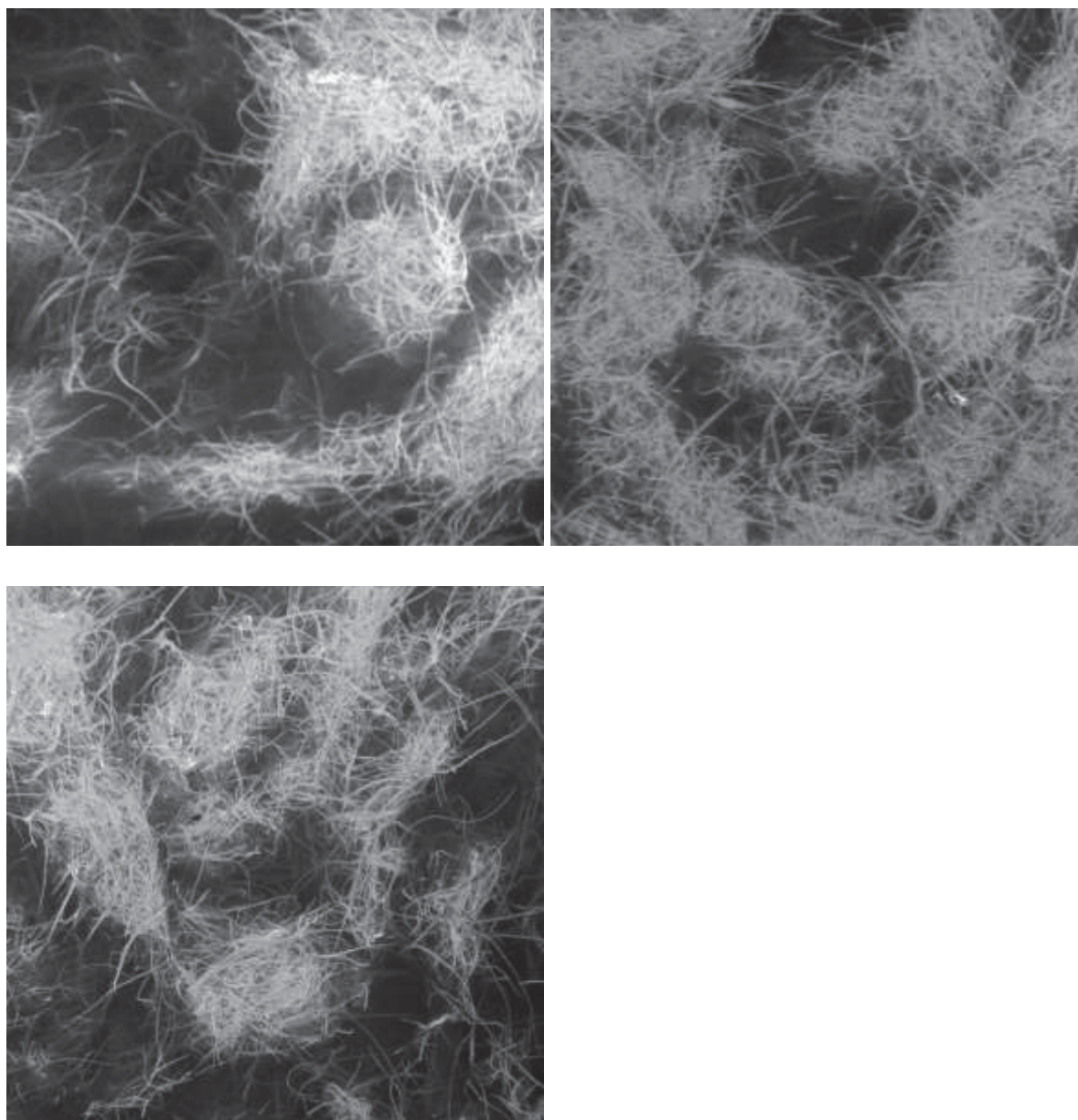
### *3.1.2 High-contrast images of dispersion*



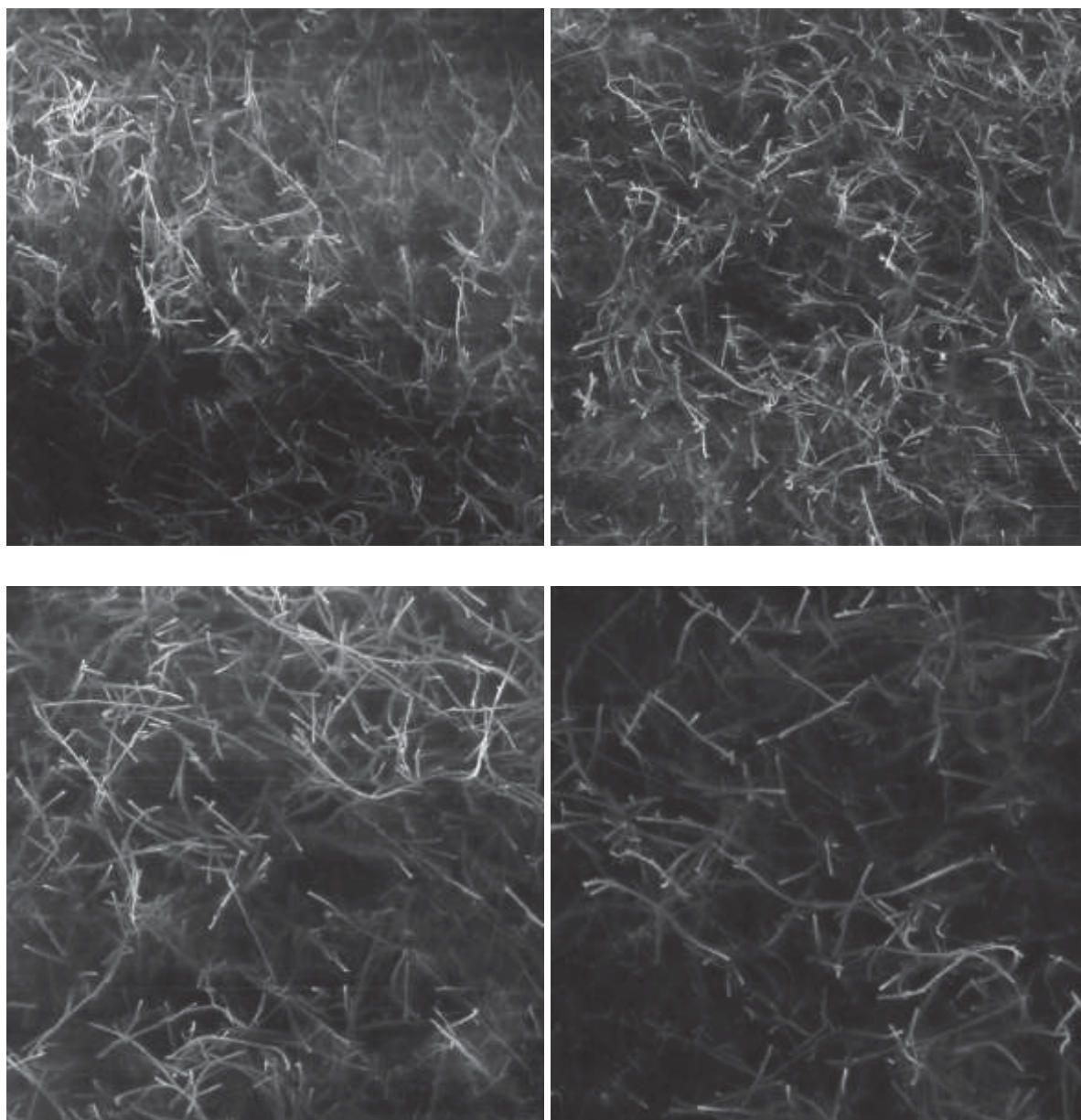


**Figure 13.** HR-SEM high-contrast images (1792 x 1792 pixel) of 1.0 wt% SWCNT dispersion within PMMA nanocomposites at a) – c) 5000 ( $17.92\ \mu\text{m} \times 17.92\ \mu\text{m}$ ) and d) – e) 10000 times magnification ( $8.96\ \mu\text{m} \times 8.96\ \mu\text{m}$ ). The imaging technique allows for the imaging of the SWCNT network within the hosting polymer.

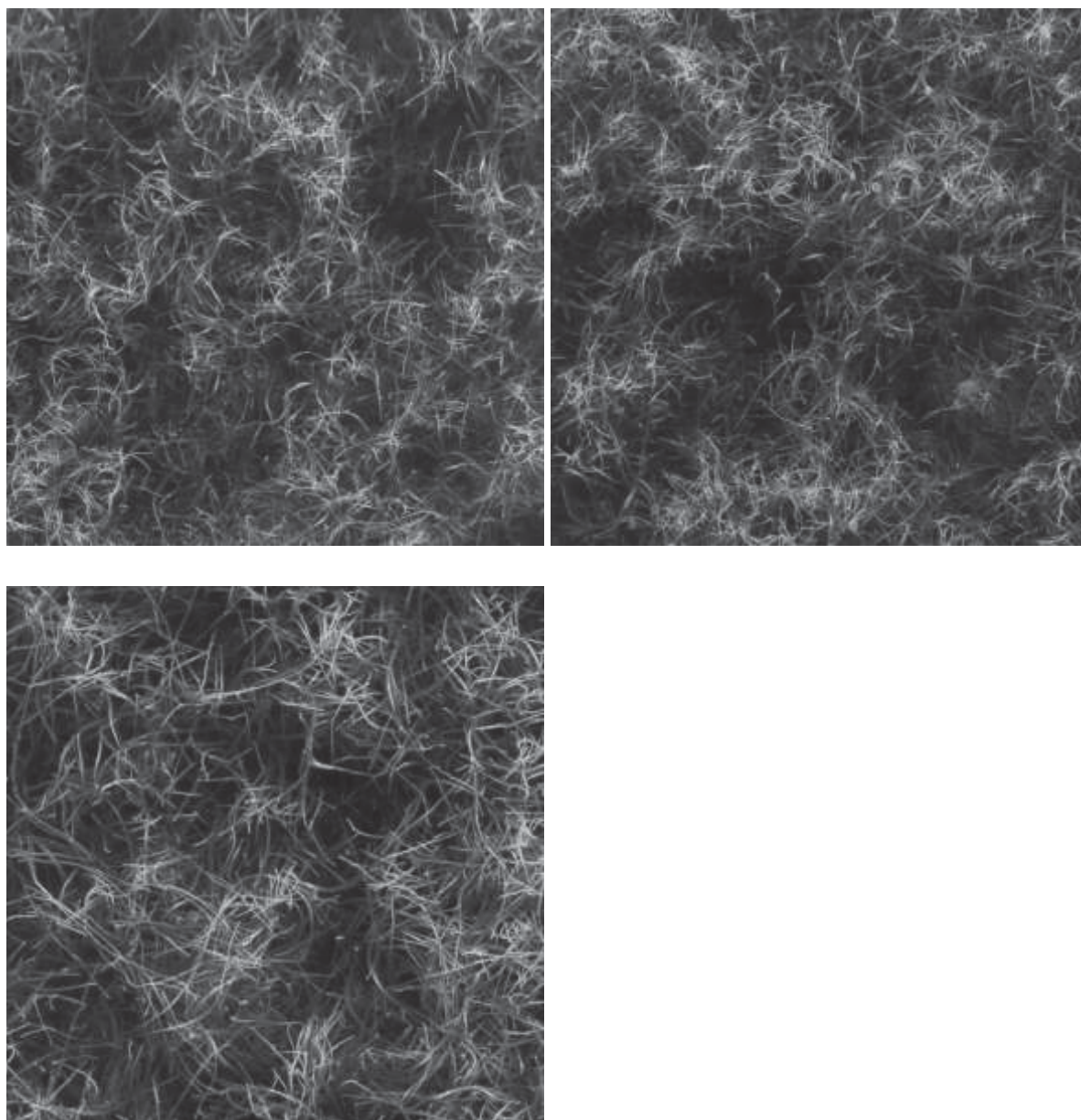




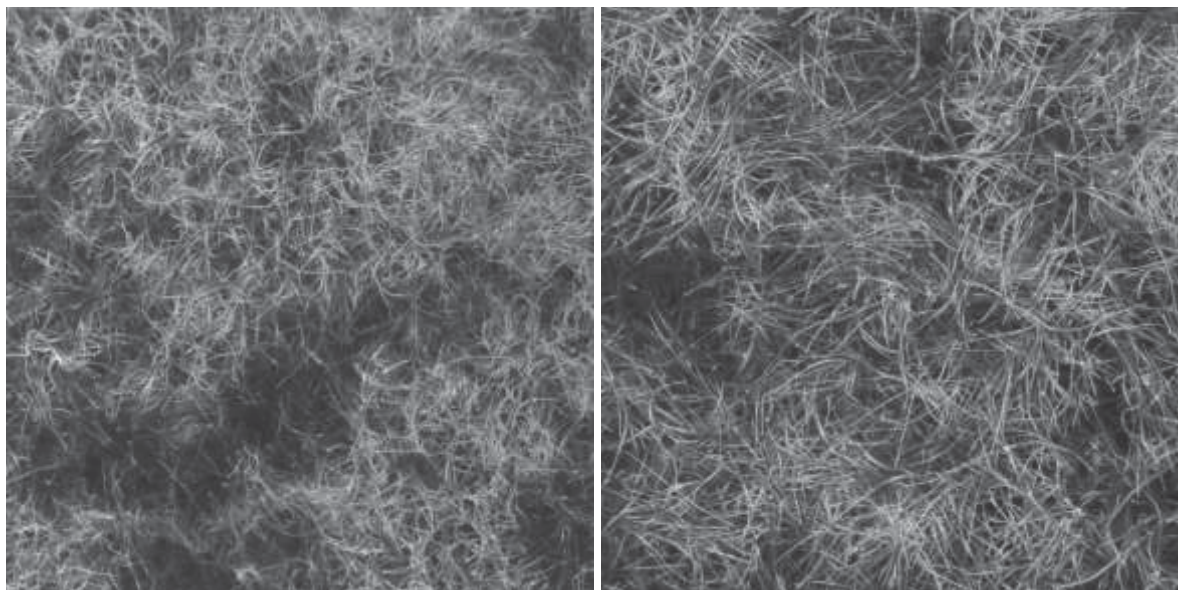
**Figure 14.** HR-SEM high-contrast images (1792 x 1792 pixel) of 5.0 wt% SWCNT dispersion within PMMA nanocomposites at a) – b) 5000 (17.92  $\mu\text{m}$  x 17.92  $\mu\text{m}$ ), c) – d) 10000 times magnification (8.96  $\mu\text{m}$  x 8.96  $\mu\text{m}$ ) in a poor imaging area, e) 10000 times magnification (8.96  $\mu\text{m}$  x 8.96  $\mu\text{m}$ ) in a good imaging area.



**Figure 15.** HR-SEM high-contrast images (1792 x 1792 pixel) of 0.1 wt% SWCNT dispersion within PS/PMMA nanocomposites at a) – b) 5000 ( $17.92\ \mu\text{m} \times 17.92\ \mu\text{m}$ ) and c) – d) 10000 times magnification ( $8.96\ \mu\text{m} \times 8.96\ \mu\text{m}$ ).



**Figure 16.** HR-SEM high-contrast images of (1792 x 1792 pixel) 0.5 wt% SWCNT dispersion within PS/PMMA nanocomposites at a) – b) 5000 ( $17.92\ \mu\text{m} \times 17.92\ \mu\text{m}$ ) and c) 10000 times magnification ( $8.96\ \mu\text{m} \times 8.96\ \mu\text{m}$ ).



**Figure 17.** HR-SEM high-contrast images of (1792 x 1792 pixel) 1.0 wt% SWCNT dispersion within PS/PMMA nanocomposites at a) 5000 (17.92  $\mu\text{m}$  x 17.92  $\mu\text{m}$ ) and b) 10000 times magnification (8.96  $\mu\text{m}$  x 8.96  $\mu\text{m}$ ).

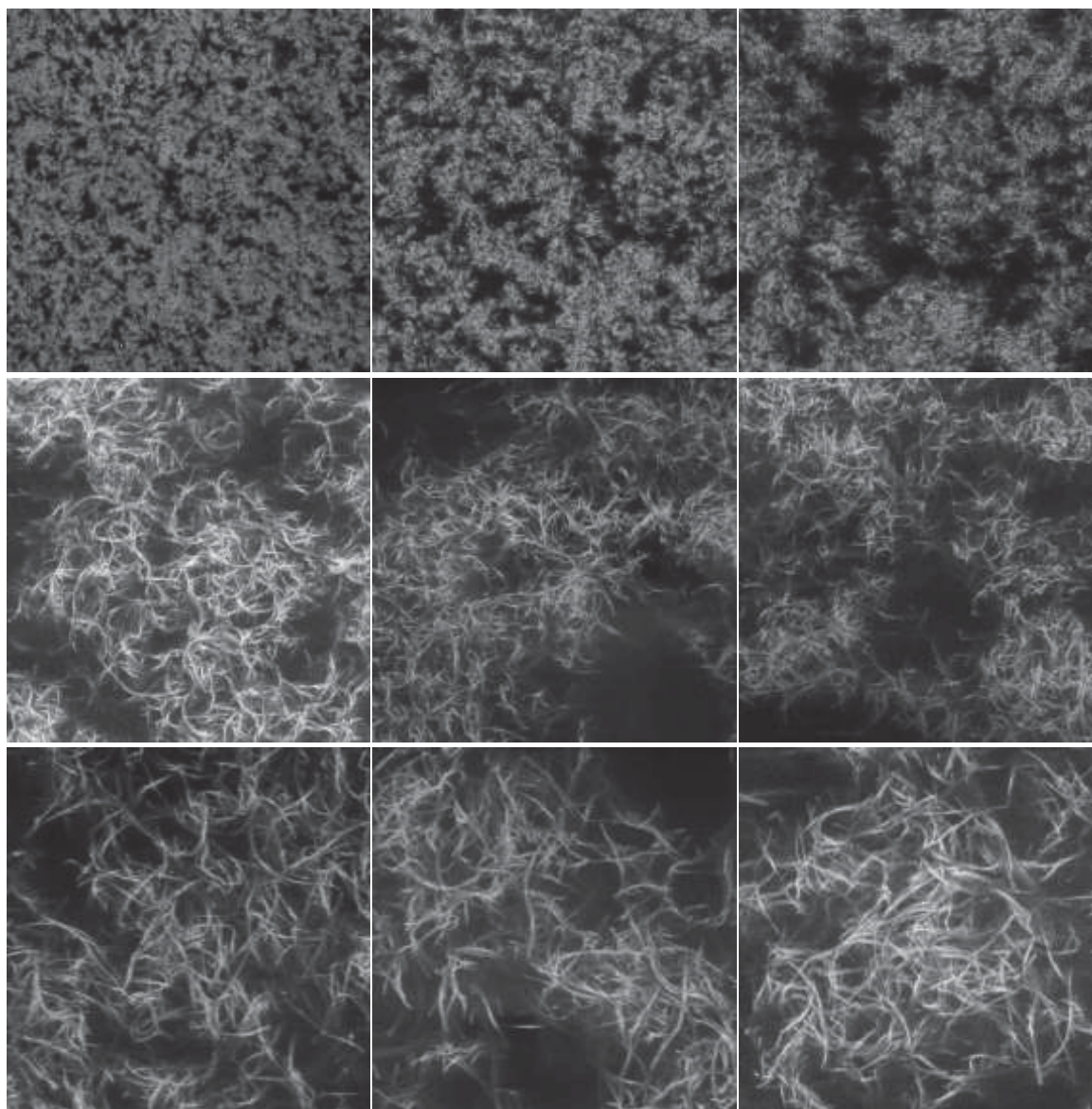
Notice how the high-contrast imaging technique reveals that each specimen type has a distinct state of dispersion and that the PMMA/PS copolymer yields perceived better dispersion. The PMMA and PMMA/PS nanocomposites were more susceptible to beam damage during high-contrast imaging than the samples imaged in Study One. In fact, the images of the 0.1 wt % SWCNT PMMA/PS nanocomposite were captured at the limit of the microscope's operational capabilities. In order to capture the 0.1 wt% SWCNT images, maximum settings for current and voltage (50  $\mu\text{A}$  and 30 kV) were used at highest resolution (1792 x 1792 pixel) during the slowest scan speed possible (80 seconds per image). The effect of the intense electron beam on the specimen can be seen most prevalently in the 0.1 wt% SWCNT PMMA/PS images. Notice how some regions of polymer in figure 15 are visible and begin to overshadow the contrast between the light color SWCNT and dark background. This effect, which greatly diminishes the visualization depth, occurs during the capture of the image. In fact, the microscope was focused over an adjacent area then quickly positioned over the areas in figures 13 to 17 to immediately capture the images. More than one scan (slow and intense enough to visualize the SWCNT network via the high-contrast imaging technique) irreversibly damaged the sample to the point

where subsequent images over the same location proved only to capture regions of electrically saturated polymer. The same trend has been noticed in every high-contrast image; however, the unfavorable consequences are most prevalent in the specimens with low SWCNT concentration or poor dispersion. Thus, the ability to simply capture high-contrast images is in itself is a crude measure of the quality of dispersion.

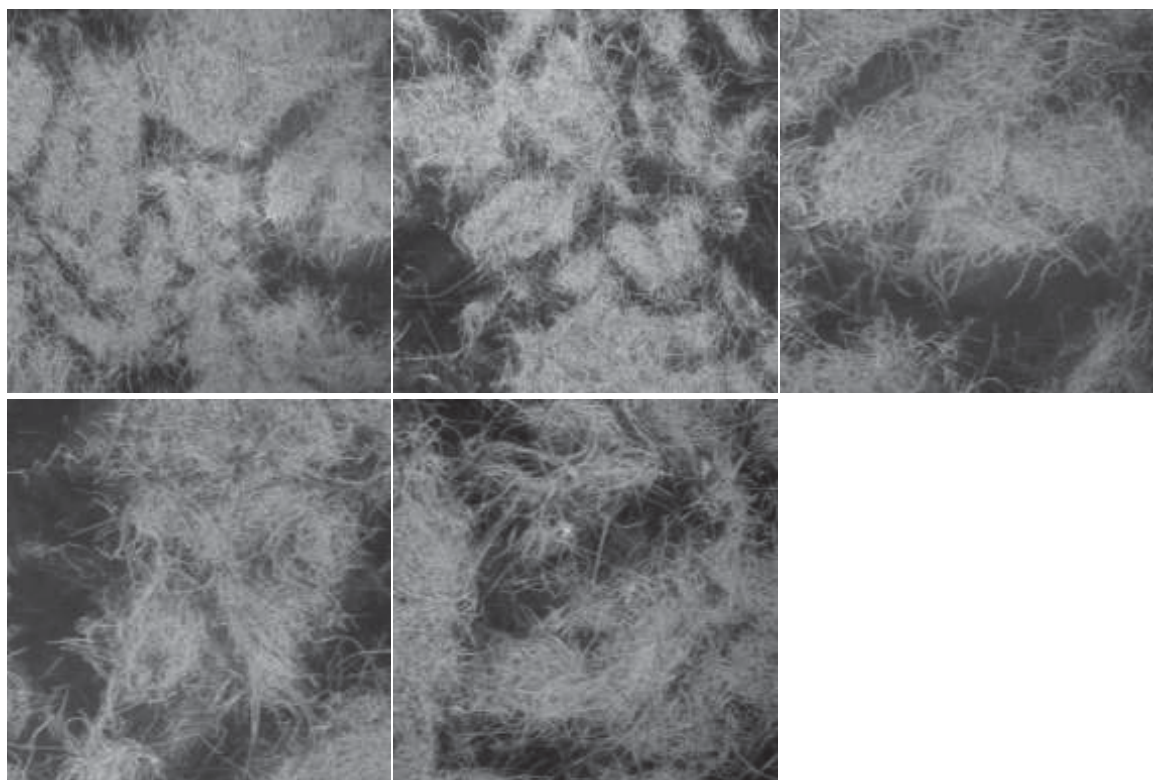
Essentially, the electron beam can be conceptualized as traveling through the thickness of the specimen along the conductive SWCNT network. With an adequate electrical percolation network, the specimen can be subjected to high-contrast imaging with negligible damage. However without an adequate network, the quality of the path to electrical ground is reduced and results as leakage current into the polymer. The regions with extremely poor dispersion or without an adequate amount of nanofiller for the given imaging area will experience more degradation from beam damage and can contaminate the microscope's chamber. In such cases, the imaging conditions should be altered to avoid seriously damaging the specimen or contaminating the chamber. One method is to take faster images at lower resolution. Others can be found in the high-contrast imaging procedure in Appendix A.

Without an adequate conductive SWCNT network dispersed throughout the sample, the energy from the electron beam essentially cannot travel to ground faster than the polymeric regions reluctantly absorb the additional energy. The additional energy resulting from dielectric absorption causes various reactions in the specimen including polymer saturation (charging) even polymer melting (causing the HR-SEM image to move and contort). Samples with good dispersion but low conductive filler content often suffer from polymer saturation while samples, regardless of the filler content, suffer from polymer saturation and degradation in areas without the necessary electrically conductive percolation network as can be seen in the 0.1 wt % SWCNT PMMA/PS specimen. This effect can also be seen in the images of the 5.0 wt% SWCNT PMMA specimen in figure 14c and d. During the image capture, the polymer in these regions physically deformed. The melting was very minimal, but at 10000 times magnification with an 80 second image capture speed, the movement of the sample surface distorts the image. Notice that this did not occur in images (figure 14e) where it is assumed that the imaged area contains a SWCNT network better connected to the electrical ground. Magnifications below 5000 times resulted in excessive polymer charging in the 5.0 wt % SWCNT PMMA specimen and unusable images.

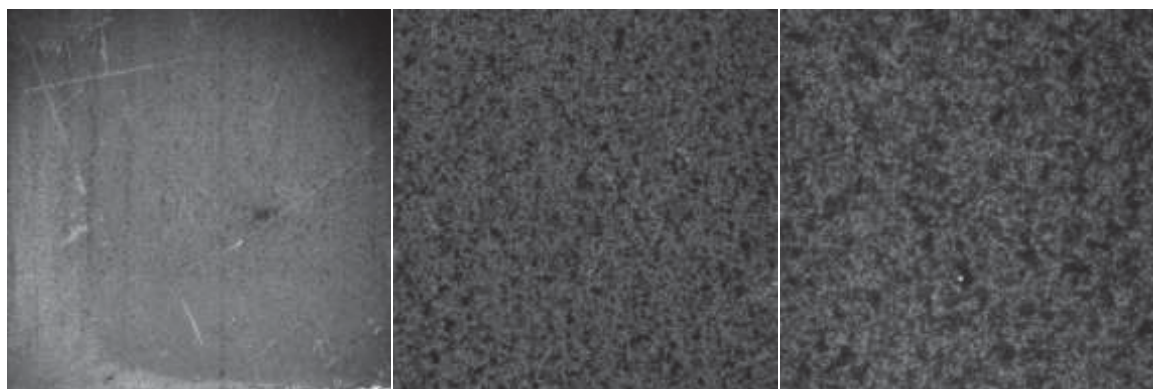
On the other hand, the 1.0 wt% SWCNT PMMA, 0.5 wt% SWCNT PMMA/PS and 1.0 wt% SWCNT PMMA/PS higher resolution images (1792 x 1792 pixel) proved to produce exceptional high-contrast images, provided they were obtained during the first scan over the captured area. The polymeric saturation after multiple scans, although evident, was not as noticeable when compared to the previously mentioned samples. The higher resolution 1792 x 1792 pixel images in figures 13 to 17 contain a limited set of images due to the evident beam damage. All the higher resolution images were captured at 30 kV with an 80 second scan speed in an effort to standardize the process for subsequent image analysis. The current of the electron beam was kept at 20  $\mu$ A for all images except those of the 0.1 wt% SWCNT PMMA/PS specimen. In practice, it is perhaps more effective to tailor the setting for each sample, as was the case for the samples in Study One, in order to minimize the damage to the specimens [5]. Here, in an attempt to standardize the image capture process, additional images were captured at lower resolution (896 x 896 pixel) with faster scan rate (40 seconds per image) but also at 30 kV and 20  $\mu$ A in order to collect a larger sample set for analysis while limiting contamination to the microscope and damage to the imaged surfaces. Figures 18 through 21 provide the lower resolution images (896 x 896 pixel) captured at a faster scan speed (40 seconds per image).

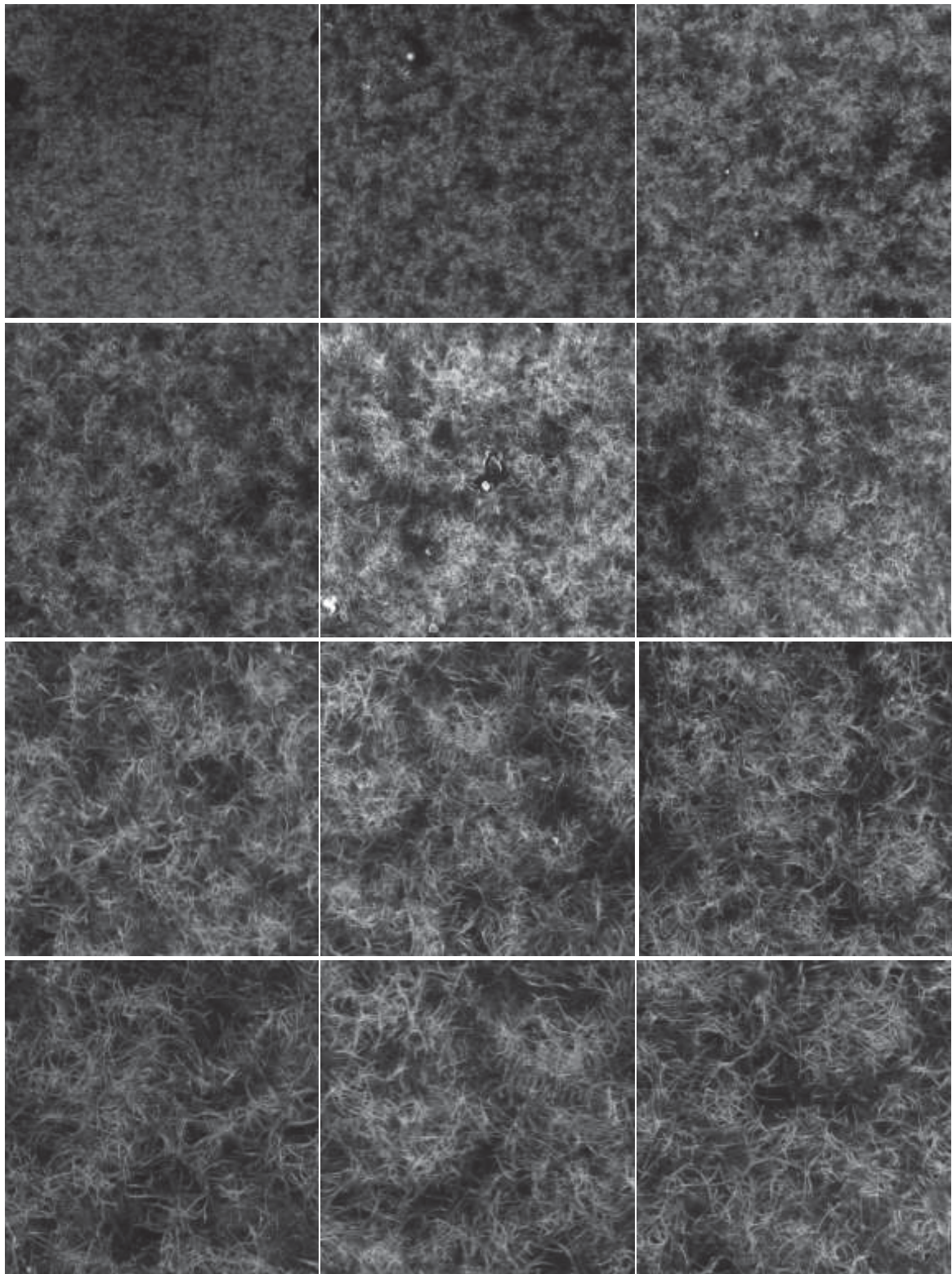


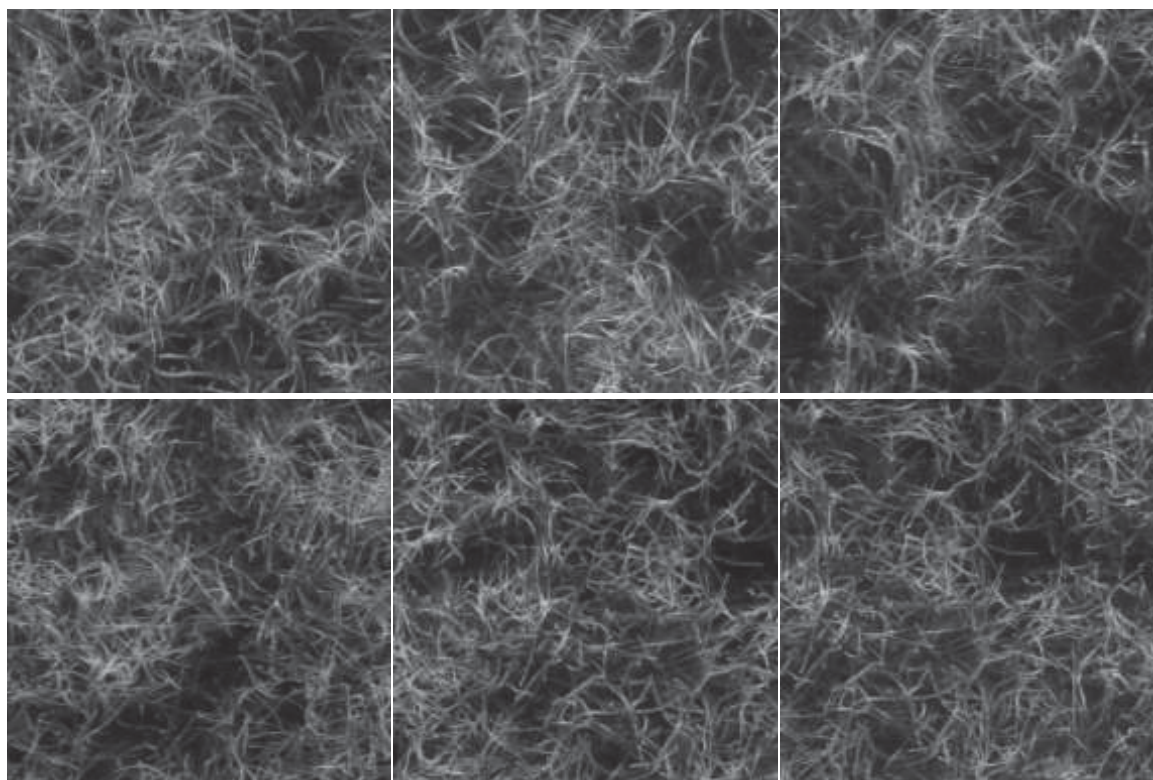
**Figure 18.** HR-SEM high-contrast images (896 x 896 pixel) of 1.0 wt% SWCNT dispersion within PMMA nanocomposites at a) 250 times magnification (358.4  $\mu\text{m}$  x 358.4  $\mu\text{m}$ ), b) 500 times magnification (179.2  $\mu\text{m}$  x 179.2  $\mu\text{m}$ ), c) 1000 times magnification (89.6  $\mu\text{m}$  x 89.6  $\mu\text{m}$ ), d) – f) 5000 times magnification (17.92  $\mu\text{m}$  x 17.92  $\mu\text{m}$ ) and g) – i) 10000 times magnification (8.96  $\mu\text{m}$  x 8.96  $\mu\text{m}$ ).



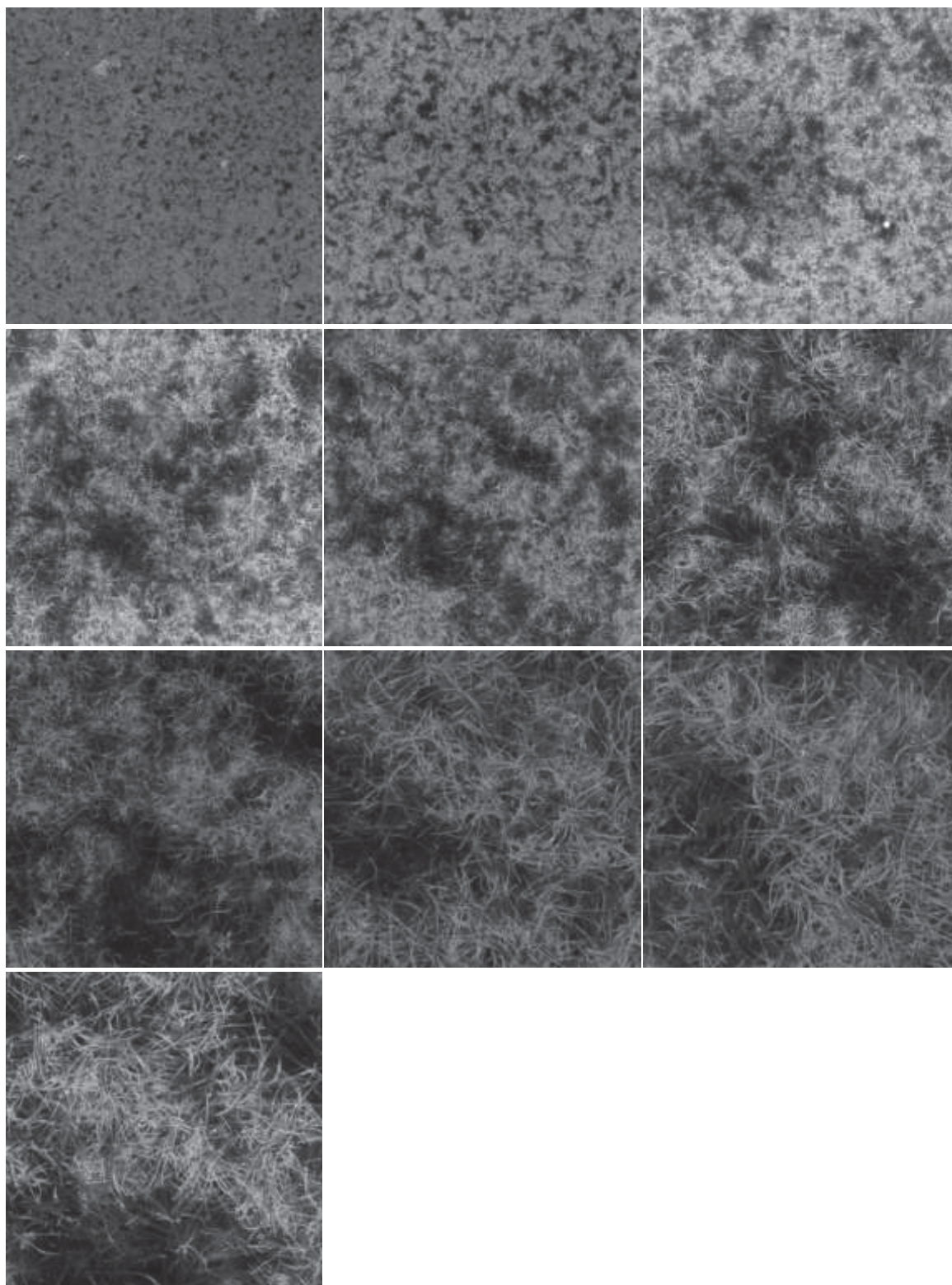
**Figure 19.** HR-SEM high-contrast images (896 x 896 pixel) of 5.0 wt% SWCNT dispersion within PMMA nanocomposites at a) – b) 5000 times magnification ( $17.92\ \mu\text{m} \times 17.92\ \mu\text{m}$ ), c) – d) 10000 times magnification ( $8.96\ \mu\text{m} \times 8.96\ \mu\text{m}$ ) in a poor imaging area and e) 10000 times magnification ( $8.96\ \mu\text{m} \times 8.96\ \mu\text{m}$ ) in a good imaging area.







**Figure 20.** HR-SEM high-contrast images (896 x 896 pixel) of 0.5 wt% SWCNT dispersion within PS/PMMA nanocomposites at a) 100 times magnification (896  $\mu\text{m}$  x 896  $\mu\text{m}$ ), b) 250 times magnification (358.4  $\mu\text{m}$  x 358.4  $\mu\text{m}$ ), c) – d) 500 times magnification (179.2  $\mu\text{m}$  x 179.2  $\mu\text{m}$ ), e) 1000 times magnification (89.6  $\mu\text{m}$  x 89.6  $\mu\text{m}$ ), f) 1500 times magnification (59.73  $\mu\text{m}$  x 59.73  $\mu\text{m}$ ), g) – i) 2500 times magnification (35.84  $\mu\text{m}$  x 35.84  $\mu\text{m}$ ), j) – l) 5000 times magnification (17.92  $\mu\text{m}$  x 17.92  $\mu\text{m}$ ), m) – o) 7000 times magnification (12.8  $\mu\text{m}$  x 12.8  $\mu\text{m}$ ) and p) – u) 10000 times magnification (8.96  $\mu\text{m}$  x 8.96  $\mu\text{m}$ ).



**Figure 21.** HR-SEM high-contrast images (896 x 896 pixel) of 1.0 wt% SWCNT dispersion within PS/PMMA nanocomposites at a) 250 times magnification ( $358.4\ \mu\text{m} \times 358.4\ \mu\text{m}$ ), b) 500

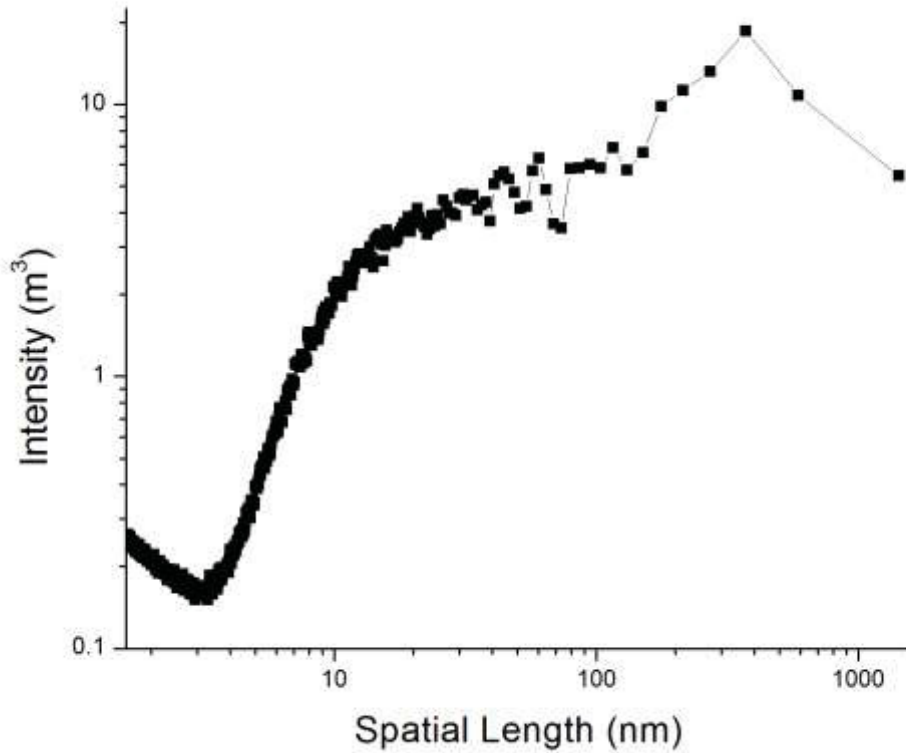
*times magnification (179.2  $\mu\text{m}$  x 179.2  $\mu\text{m}$ ), c) 1000 times magnification (89.6  $\mu\text{m}$  x 89.6  $\mu\text{m}$ ), d) – e) 2500 times magnification (35.84  $\mu\text{m}$  x 35.84  $\mu\text{m}$ ), f) – g) 5000 times magnification (17.92  $\mu\text{m}$  x 17.92  $\mu\text{m}$ ), and h) – j) 10000 times magnification (8.96  $\mu\text{m}$  x 8.96  $\mu\text{m}$ ).*

The faster scan rate and lower resolution reduces the time the beam interacts with the sample and the resulting image degradation, although evidence of poor imaging conditions is still present in some of the captured images. Specifically, the deformation observed in the 5.0 wt % SWCNT PMMA specimen (figure 14c and d) is again observed during the capture of the lower resolution images (figure 19c and d). Conversely, the lower resolution images obviously do not contain equivalent information at finer detail and the faster scan rate may limit the depth of visualization. The ability to capture relevant information on SWCNT dispersion will be compared for each specimen as well as for a variety of situations. Such situations include the comparison between imaging at high (with slower scan rate) and low (with faster scan rate) resolution, different specimen locations, different specimen surfaces, different magnifications and poor (figure 14c and d) versus good imaging areas (figure 14e).

### *3.1.3 Generating the power spectrum*

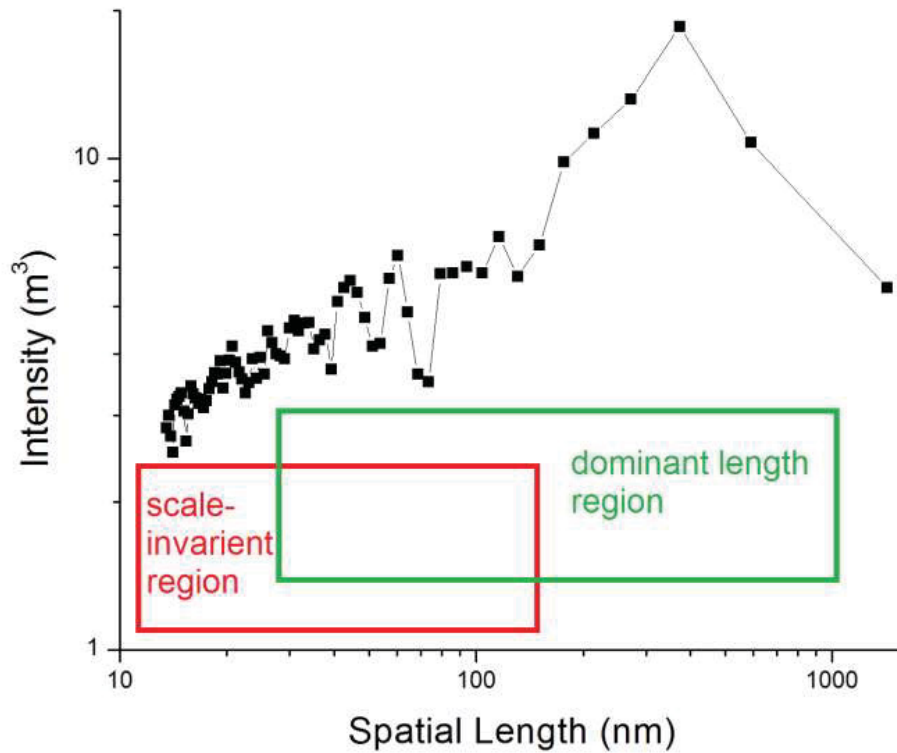
Again, it is proposed to use the scaling parameter of the 1D RPSD to determine the fractal dimension that describes the structure of SWCNT dispersion within HR-SEM images, which capture a 3D volume projected onto a 2D plane. Each image of dispersion will be analyzed as a self-affine fractal-like 2D surface representing the projected SWCNT network. The images will be analyzed in radial slices to produce a RPSD that presents the direction independent spectrum of the dominant lengths in a 1D plot to determine the scaling parameter. Equation 35 can then be used to determine the fractal dimension from the scaling parameter.

The images of dispersion here consist of 896 x 896 pixels and are therefore appropriately sampled at a Nyquist frequency of 448 to create 448 frequency components. The HR-SEM images would require 896 wedges and 448 rings to recreate figures 8 and 10, respectively. The full RPSD for the 1.0 wt% SWCNT PMMA/PS nanocomposite corresponding to the HR-SEM high-contrast image in figure 17d is below in figure22.



**Figure 22.** *Logarithmic RPSD of the 1.0 wt% SWCNT PMMA/PS nanocomposite in terms of spatial length. The 10,000 times magnification image shown in figure 17b is 8.96  $\mu m$  by 8.96  $\mu m$ . At 1792 x 1972 pixels, the pixel size is 5nm by 5nm.*

The limited range highlighted in the logarithmic plot of the spatial density shown below in figure 23 displays a region of constant slope, similar to the Richardson plot in figure 4. The scale invariant nature again reveals itself on a logarithmic plot. Notice the similarity between the plot of the self-affine function, pink noise and spectral density plotted in figures 5, 6 and 23, respectively.



**Figure 23.** Logarithmic RPSD of the 10k magnification image of the 1.0 wt% PMMA/PS nanocomposites in figure 17b highlighting the general regions to analyze scale invariance and dominant lengths.

Examining the features (dominant lengths) in spatial terms represented in the RPSD is analogous to describing a musical chord by examining the individual notes played. The previous study called upon the RPSD to wash out information concerning the dominant lengths present in the high-contrast images, which reveal themselves as peaks in the RPSD plotted in terms of length rather than spatial frequency, as described in Study One [5].

Alternatively, information can be garnered by also examining the variance of the intensity of all lengths present in the image. As previously stated, it is proposed to analyze HR-SEM images of dispersion assuming SWCNT dispersion has self-affine properties with the power spectrum method derived from the self-affine fBm model.

The RPSD in figure 22 contains the full power spectrum (all 896 frequency components) before filtering the non-scale-invariant data and noise. The region utilized to determine the prominent peaks is apparent from figures 22 and 23. The method to analyze the peaks is presented in Study One [5]. The region of self-affine and scale-invariant behavior is not necessarily obvious but must be determined and bounded in order to suitably measure the slope. The following section will provide a standardized method to determine the upper and lower cutoff limits for determining the RPSD slope regardless of the given image type or magnification.

#### *3.1.4 Fractal length and magnification windows*

From the power spectrum in figure 22 it is apparent that the system does not display monofractal behavior due to the lack of a region of constant slope across the entire spectrum. The power spectrum shows obvious noise at the very high frequency range and evidence of limited sampling at the low spatial frequency range. Additionally, the logarithmic slope within those ranges is not constant indicating that the system is either multifractal or monofractal of limited range. Within the power spectrum, the range of reliable data falls within certain fractal analysis windows, of length and magnification to determine either multiple bounded fractal regions in the case of a multifractal system or a single bounded fractal region in the case of a monofractal system. This study will focus on describing a single fractal region within the power spectrum of the high-contrast images of dispersion.

In order to determine the scaling parameter, the RPSD data over an appropriate fractal window is fit using a power law function. The closeness of fit when fitting the data with the power law can be used as a tool to determine the appropriate fractal length window. A close fit corresponds to an appropriate fractal window.

Notice the region of constant slope in figure 23 above. This region, described here as the fractal analysis length window is bounded by the small length scale features corresponding to either the limit of resolution in the image or the smallest length feature able to be measured in the image. In an ideal case, the lower bound is constrained by dominant nanotube diameters or nanotube to nanotube separation distances. In actuality, the lower bound is constrained by the resolution and instrumentation of the microscope. Obviously, the absolute lower bound could be

defined by the pixel size, but the specific components of the microscope affect the image and can be assumed to take the form of a transfer function of the form:

$$S(f)' = S(f) \cdot MTF^2 \quad (57)$$

where  $S(f)$  is the actual spectral density and the modulation transfer function (MTF) contains the effects of the specific microscope [2]. The MTF bias affects the power spectrum at high frequency and can either be directly filtered or removed thorough comparison of the power spectrum generated from high-contrast images produced from imaging the same volume with multiple microscopes. The noise, present at lengths below the pixel length of 5 nm in figure 22 is effectively filtered when accounting for the MTF bias.

The upper bound of the fractal length window corresponds to limited sampling of low frequency components (the non-scale-invariant region); described as the point where the periodic or fractal behavior measured with the RPSD is overcome by the larger dominant length features, and is often associated with large-scale agglomeration of polymer or SWCNT. Furthermore, when conceptualized in terms of spatial length the upper limit should be less than the crossover scale, which is the persistence length of the length feature analyzed, or the point where vertical and horizontal displacements are equal. In the previous analogy utilizing mountain terrain, the crossover length scale would correspond to the tallest peak heights in the 2D projection of mountain ridgeline. A measure similar to the crossover scale is represented as the quantified SWCNT dispersion parameter defined as persistence length in Study One. Thus, from table 1 in Study One, it is shown the SWCNT persistence length, and therefore the crossover scale, is dependent upon the type SWCNT-polymer composite and the processing conditions [5]. Furthermore, the variance of the crossover scale from sample to sample may be garnered from analyzing the Minkowski connectivity's estimation of cylindrical structure length, as described in Study One [5, 56-59].

The fractal magnification window is determined by capturing a series of HR-SEM images at various magnifications. At the upper limit of the fractal magnification window the fractal length window will be too narrow to reliably determine the scaling parameter. At the lower limit of the fractal magnification window, the magnification will be too small to discern the features of the nanofiller (such as nanotube diameter, bundle size, bundle separation distance, etc.) and any

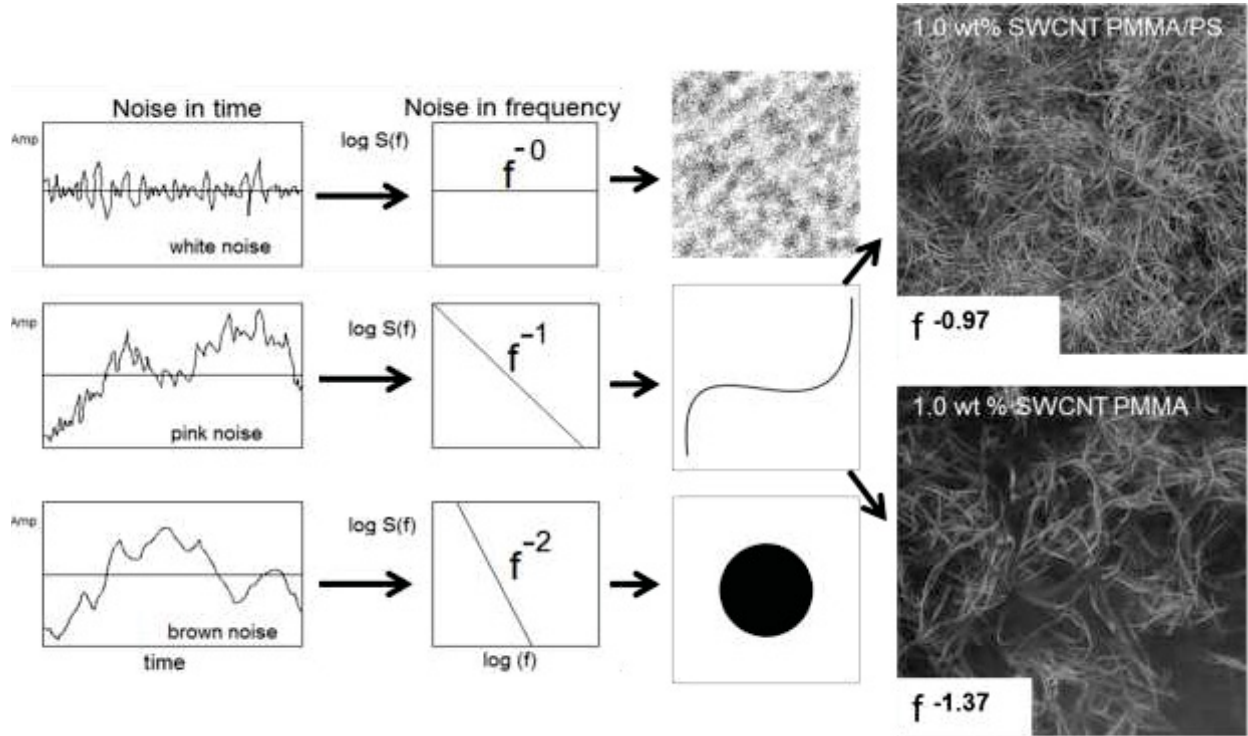
periodic or fractal behavior present in the image is overtaken by large-scale dominant length features. The scaling parameter of the RPSD over appropriate fractal length windows for a series of magnifications can be compared to determine the appropriate fractal magnification window. The measured fractal dimension will deviate as the scale (magnification) is decreased (or increased) at the point edge of the fractal region for a bounded monofractal or multifractal system if the spectrum is not first altered by the imaging limitations of the SEM.

The fractal length window can be interpreted as one of the rings in figure 10, which represents a region of interest relevant to SWCNT dispersion on the 2D PSD (such as the area bounded in figure 11b and c). The fractal window should be as expansive as possible without deteriorating the quality of the fit and without encroaching on the upper and lower limits or the regions constrained by the crossover scale or the MTF at very low spatial lengths. Detailed instructions for filtering the data and determining the slope of the spectral density is provided in the latter sections.

### *3.1.5 The fractal dimension and RPSD scaling parameter of SWCNT dispersion*

Analyzing the scaling parameter of the RPSD is an intuitive measure of the dispersion characteristic because the slope of the RPSD can be examined to glean the structure of a 3D network in terms of a single number. As defined in equation 25, a scaling parameter,  $b$ , with a range from  $1 < B < 3$  is related to the Hurst parameter,  $H$ , and utilized to characterize a fractal. In actuality, the slope,  $B$ , ranges from 0 for a single rod or white noise through a region useful to analyze the SWCNT dispersion (approximately 0.5 to 2.5) to 3 for images of detailed 2D objects or 3D projections. Ideally, a steeper slope corresponds to SWCNT dispersion with a greater amount of large dominant lengths and fewer small dominant lengths indicating more SWCNT agglomeration on a larger scale and less single separated tubes at a smaller scale. Conceptually, the SWCNTs represent many individual 1D rods. As the SWCNTs increasingly agglomerate the slope will become steeper and approaches a scaling parameter of 3, the network becomes better represented by a 3D object. A shallower slope describes SWCNT dispersion with a greater amount of small length scale features and less large length scale features indicating less agglomeration on a larger scale and more debundling of SWCNT at smaller scales. As the agglomerations are minimized overall, the slope of the PSD approaches 1, and the improved dispersion is modeled better as a network of 1D rods. Thus, a steeper slope originating from

poorer dispersion is revealed by a larger absolute value of the scaling parameter. Alternatively, a shallower slope resulting from better dispersion is revealed by a lower absolute value. As the SWCNT dispersion improves the system becomes more periodic and the slope of the power law fit of the RPSD would decrease as is indicated in figure 24 below.

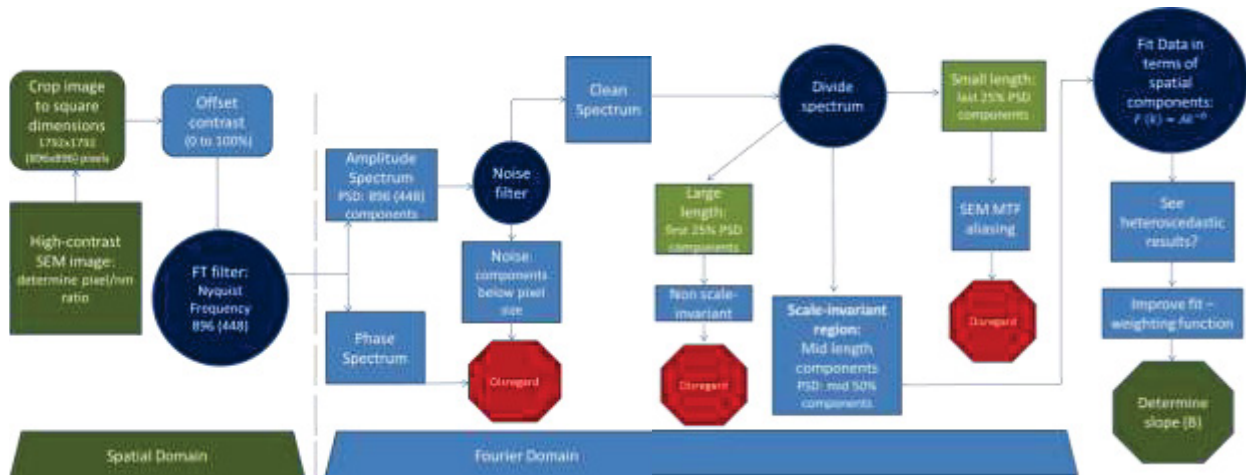


**Figure 24.** Schematic showing the conceptual association of noise, dispersion and the measured scaling parameter. The upper and lower 10000 times magnified ( $8.96 \mu\text{m} \times 8.96 \mu\text{m}$ ) HR-SEM high-contrast images represent the 1.0 wt% SWCNT dispersion within PS/PMMA and PMMA nanocomposites.

Different methods to determine the fractal dimension produce a wide variety of results but each method shows similar relative measurements when compared [49]. The direct computation of the fractal dimension of HR-SEM images of SWCNT dispersion produce a wide range of values depending upon the analysis method. Therefore, as an alternative to comparing various analysis methods, it is more important to carefully define the method and assumptions used to select an appropriate fractal length window in order to determine the scaling parameter and the related fractal dimension.

### 3.2 Dispersion quantification procedure

When comparing the scaling parameter of various RPSDs of the same sample, it becomes apparent that the length and magnification windows analyzed directly affect the resulting value of the scaling parameter. Thus, it is important to detail the overall procedure to prepare the images, filter the results and fit the data. In an effort to standardize the overall image analysis methodology, the technique detailed in figure 25 was developed. Figure 25 highlights the general procedure to analyze HR-SEM high-contrast images of dispersion.

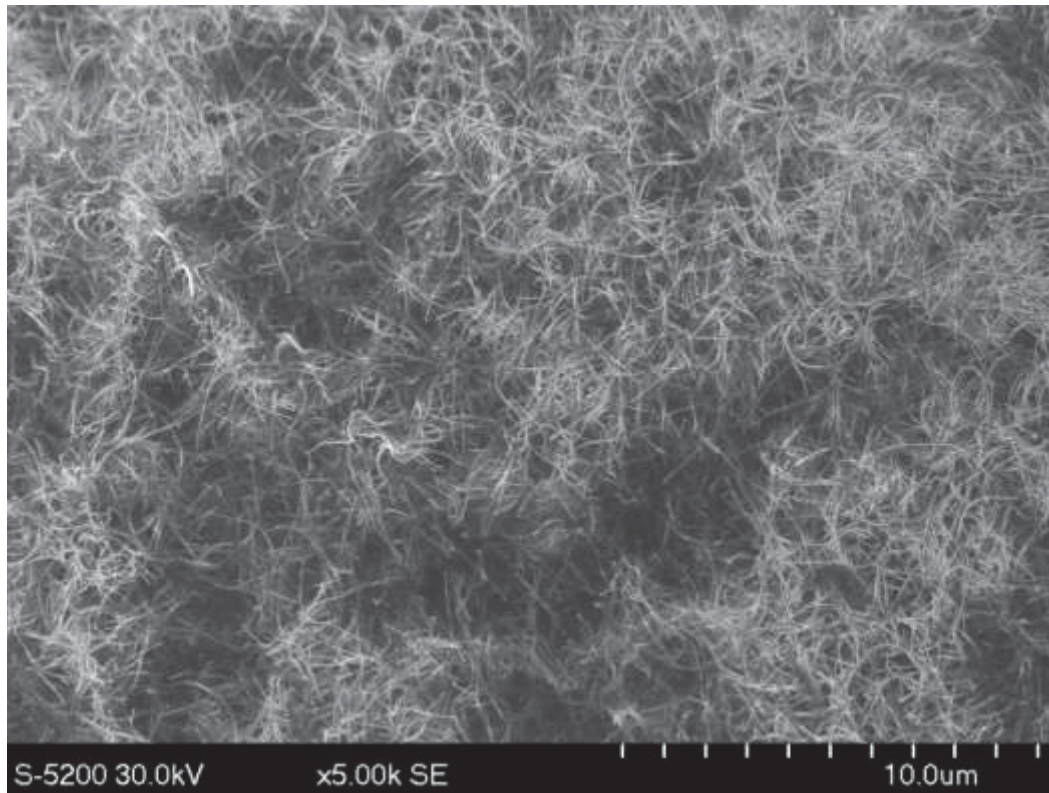


**Figure 25.** Schematic representation of the image analysis process.

Specifically, the image analysis procedure can be broken into the following steps.

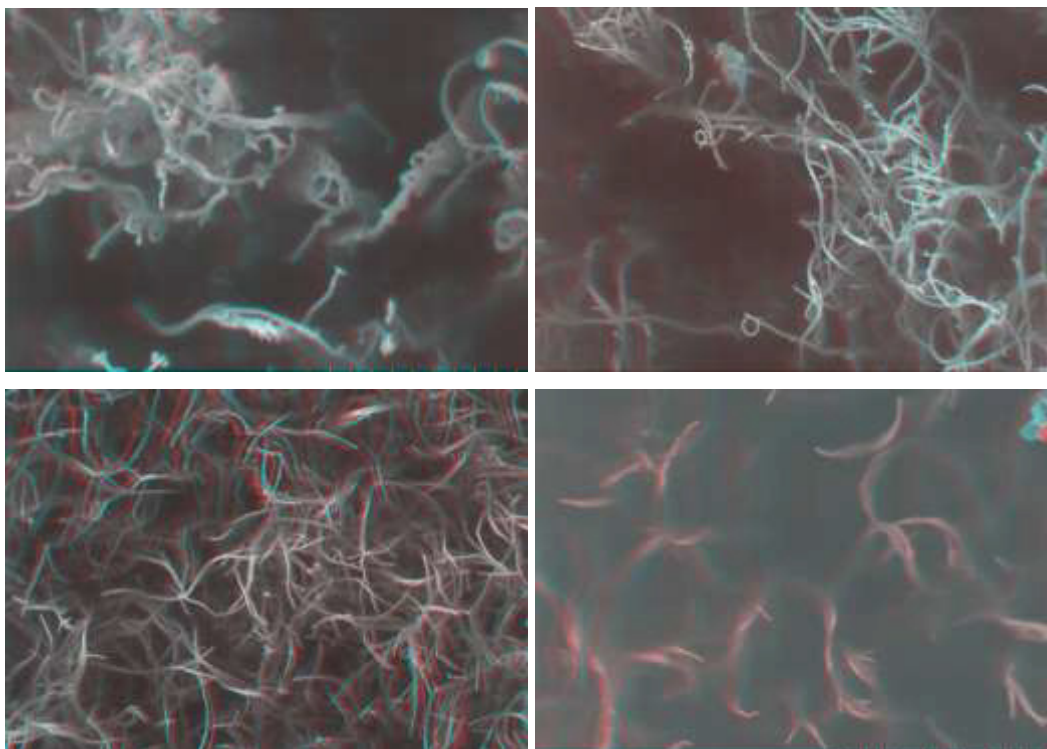
#### 3.2.1 Capturing HR-SEM high-contrast images of dispersion

First, the HR-SEM high-contrast images are obtained following the high-contrast imaging procedure in Appendix A. The Hitachi S-5200 HR-SEM captures images at 2560 x 1920 (or 1280 x 960) pixels when including the status bar (figure 26).



**Figure 26.** Original high-contrast HR-SEM image of the (2560 x 1920 pixel) of the 1.0 wt% SWCNT PMMA/PS specimen.

The imaging depth can be determined using the methodology presented in Study One [5]. Additionally, if the images used to determine the imaging depth are captured at opposing angles (such as  $\pm 25$  degrees), altering the color of the SWCNT to be red in one image and blue in another then recombining produce 3D representational images of dispersion. With red and blue 3D glasses the true nature of the SWCNT dispersion within samples 1, 3, 5 and 6 from Study One reveals itself (figure 27).

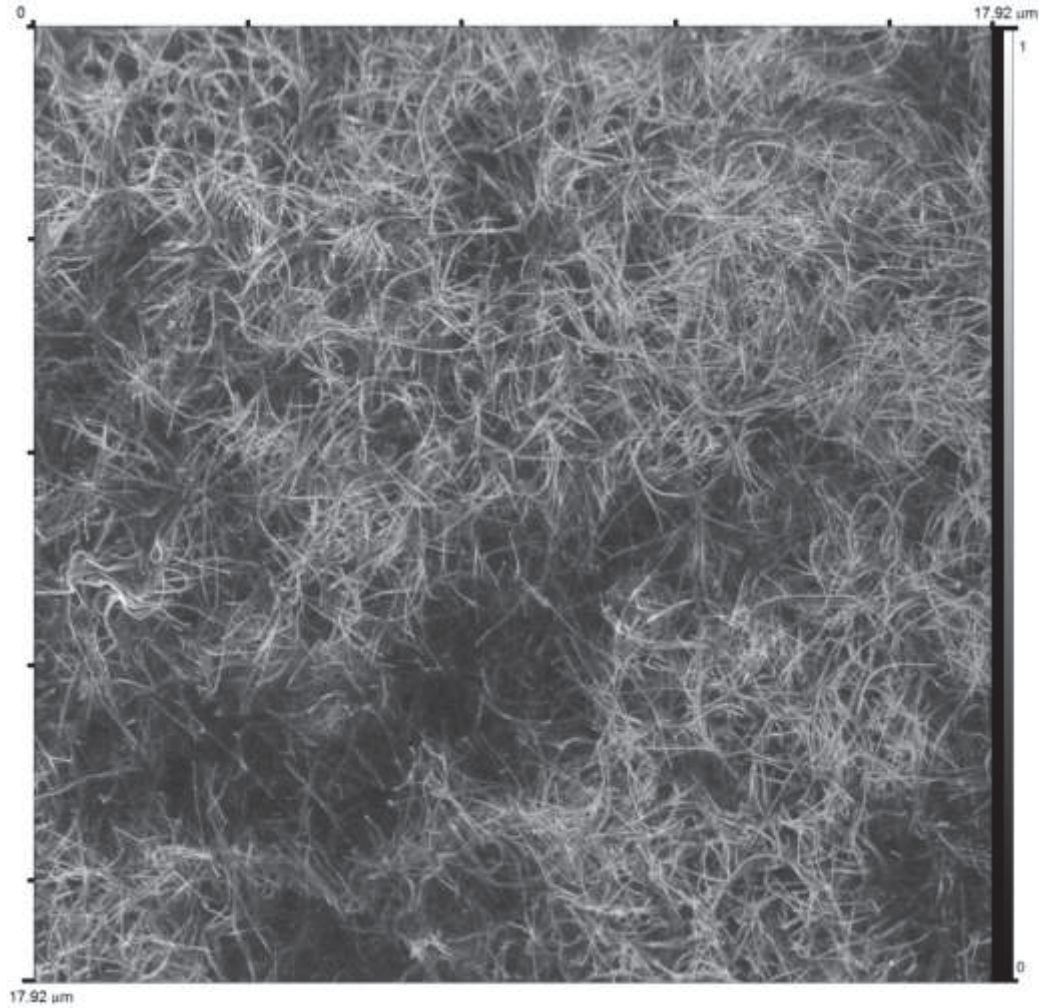


**Figure 27.** 3D images of SWCNT dispersion within nanocomposites for a) sample 1 b) sample 3, sample 5, and sample 6 from Study One. The images were created by combining red and blue tinted images captured at opposing angles ( $\pm 25$  degrees with the red and blue lens covering the left and right eye, respectively). The images are  $12.8 \mu\text{m} \times 8.96 \mu\text{m}$ .

### 3.2.2 Cropping the image and offsetting the contrast

The images are then squarely cropped to remove the SEM status bar and create a  $1792 \times 1792$  (or  $896 \times 896$ ) pixel image. Next, the contrast is offset so the lightest pixel is associated with maximum brightness and the darkest pixel is associated with absolute darkness. The images should also be scaled properly to account for the magnification of the image, thus assigning a length scale to every pixel as well as the overall image in general. For the 5,000 times magnified  $1792 \times 1792$  pixel image below in figure 28 the pixel size is approximately  $10\text{nm} \times 10\text{nm}$ . This relationship can be determined by dividing the length of the image ( $17.92 \mu\text{m}$ ) by the pixel length (1792 pixels) to determine the length/pixel ratio. The same pixel size of  $10 \text{ nm}$  by  $10 \text{ nm}$

can also be obtained with a 10,000 times magnified 896 x 896 pixel image. The relationship between magnification, resolution, pixel size and the range of spatial component lengths is shown in table 2.



**Figure 28.** *The 5,000 times magnification image of the 1.0 wt% SWCNT PMMA/PS nanocomposite after resizing and offsetting the contrast. Each pixel in the 17.92  $\mu\text{m}$  by 17.92  $\mu\text{m}$  area is approximately 10 nm x 10 nm.*

**Table 2.** *The relationship between image resolution, magnification and the resulting parameters.*

| Resolution (pixels) | Mag.  | Image size ( $\mu\text{m}$ ) | Pixel size (nm/pixel) | Full spatial range ( $\mu\text{m}$ ) | Spatial range after filtering (nm) |
|---------------------|-------|------------------------------|-----------------------|--------------------------------------|------------------------------------|
| 896                 | 100   | 896 x 896                    | 1000                  | 0 - 145                              | 1352 – 4087                        |
| 896                 | 250   | 358.4 x 358.4                | 400                   | 0 - 57                               | 540 – 1635                         |
| 896                 | 500   | 179.2 x 179.2                | 200                   | 0 - 29                               | 270 – 817                          |
| 896                 | 1000  | 89.6 x 89.6                  | 100                   | 0 - 14                               | 135 – 409                          |
| 896                 | 1500  | 59.73 x 59.73                | 66.7                  | 0 - 9.5                              | 90 – 272                           |
| 896                 | 2500  | 35.84 x 35.84                | 40                    | 0 - 5.7                              | 54 – 163                           |
| 896                 | 5000  | 17.92 x 17.92                | 20                    | 0 - 2.9                              | 27 – 82                            |
| 896                 | 7000  | 12.8 x 12.8                  | 14.3                  | 0 - 2.0                              | 19 – 58                            |
| 896                 | 10000 | 8.96 x 89.6                  | 10                    | 0 - 1.4                              | 13.5 – 40                          |
| 1792                | 5000  | 17.92 x 17.92                | 10                    | 0 - 2.9                              | 13.5 – 40                          |
| 1792                | 10000 | 8.96 x 8.96                  | 5                     | 0 - 1.4                              | 7 – 20                             |

### 3.2.3 Producing the RPSD at the Nyquist frequency

A 1792 x 1792 (896 x 896) pixel image should be sampled with a Nyquist frequency of 896 (448). Sampling at this Nyquist frequency produces 448 Fourier components corresponding to 448 spatial frequencies. For example, inverting into spatial length provides 448 spatial length components ranging from approximately 1 nm to 1000 nm for a 10,000 times magnification image, shown in figure 12. Inverting into spatial lengths for the higher resolution image produces 896 spatial length components also ranging from approximately 1 nm to 1000 nm as in figure 22.

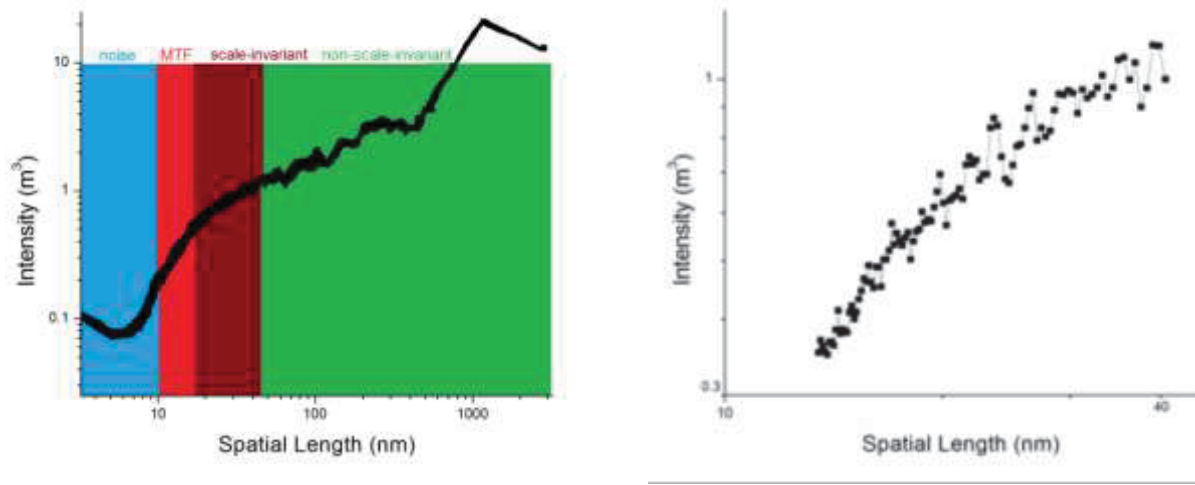
### 3.2.4 Filtering the data and determining the fractal windows

Determining an appropriate fractal analysis window may be specimen specific depending upon the nature of the sample. Generally, the following method produces an appropriate fractal length window to use when fitting the data and analyzing the results. First, the data in the noise regime should be filtered, as shown in figure 25. Filtering the noise regime effectively removes

all components below the pixel size. The remaining components, 200 (100) for the 1796 x 1796 (896 x 896) pixel image, correspond to the lower spatial frequency (larger length) components.

In an effort to standardize the image analysis process the following spectrum splitting procedure is presented. The remaining 200 (100) spatial length components should be divided into four quarters, 1-49, 50-100, 101-150 and 151-200 (1-24, 25-50, 51-75 and 76-100). Next, the areas afflicted by the microscope's MTF at high spatial frequency (small length) and the non-scale-invariant region at low spatial frequency (large length) can be easily filtered by retaining only the intermediate components, 50<sup>th</sup> to 150<sup>th</sup> (25<sup>th</sup> to 75<sup>th</sup>), as described in figure 25. Correspondingly, attempting to filter the high frequency components afflicted by the microscope's MTF may also be accomplished by fixing the lower bound to approximately  $2^{1/2}$  times pixel length, which is the pixel diameter. In the 5,000 times magnified 1792 x 1792 image of figure 28, the 10 nm pixel width corresponds to a pixel-diameter based lower bound of approximately 14 nm. In this example, 14 nm approximately corresponds with the lower bound set by the spectrum splitting method of 13.5 nm, the 150<sup>th</sup> (or 75<sup>th</sup> for a 10000 times magnified 896 x 896 pixel image) component of the spectrum. Utilizing the presented spectrum splitting routine provides a standardized method for comparing high-contrast images of SWCNT dispersion. However, the method may need alteration dependent upon the specific image, scale, imaging conditions and type of nanofiller. Furthermore, this method can be expanded to analyze a wide variety of other material and natural systems.

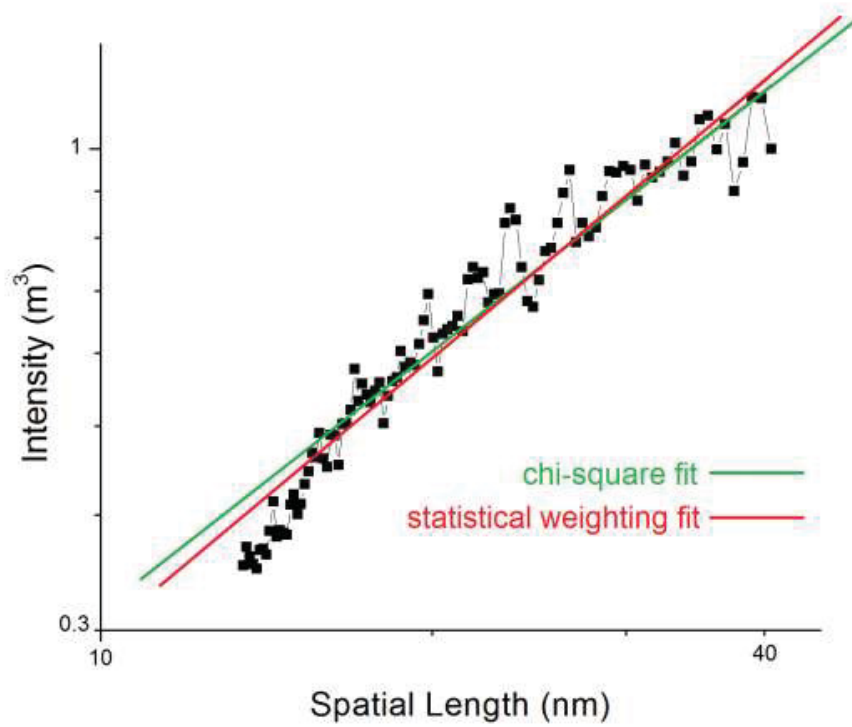
The full spectrum in figure 29a corresponds to the image presented in figure 28 and highlights the four general regions for noise, MFT bias, scale-invariant and non-scale-invariant data. The scale-invariant region represents the approximate fractal length window. Within the non-scale-invariant region the sampling error becomes greater as the spatial length increases. However, the non-scale-invariant region can also be analyzed in the RPSD for the 5000 times magnified image in figure 28 if desired. Alternatively, if the fractal magnification window is large enough, the scaling parameter may be determined from a less magnified image in which the spatial range after filtering contains the region of interest. Filtering for the non-scale-invariant, MTF, and noise regions using the presented approach produces the data shown in figure 29b.



**Figure 29.** The a) full RPSD showing the general noise, MTF bias, scale-invariant and non-scale-invariant regions and b) filtered RPSD of the scale-invariant region for the image in figure 28.

### 3.2.5 Fitting the data to determine the scaling parameter and fractal dimension

The intermediate frequency components of the RPSD should be fit to the classical Freundlich equation with negative exponent as in equation 48 with application of the statistical weighting function in equations 53 and 55. The difference in results determined by using the traditional reduced chi-square approach and the presented statistical weighting approach typically provide similar results. However, samples that produce more heteroscedastic spectral density may provide scaling parameters that correlate from image to image and across various magnifications better when determined using the statistical weighting approach. Fitting the data in figure 29b with equation 44 produces the result in figure 30 below. Table 3 below shows the arbitrary constant ( $A$ ), the slope of the line (scaling parameter  $B$ ) and the coefficient of determination ( $R^2$ ) resulting from reduced chi-square and statistical weighting approaches to fitting the data. Notice in this case the fit from statistical weighting produces slightly different results with a marginally improved value for coefficient of determination, but with a much larger variance when determining the scaling parameter.



**Figure 30.** Effect of weighting function on the resulting parameters and quality of fit for the bounded spectrum from the image in figure 28.

**Table 3.** Comparison of chi-squared and statistical weighting approaches to fitting the data in figure 30.

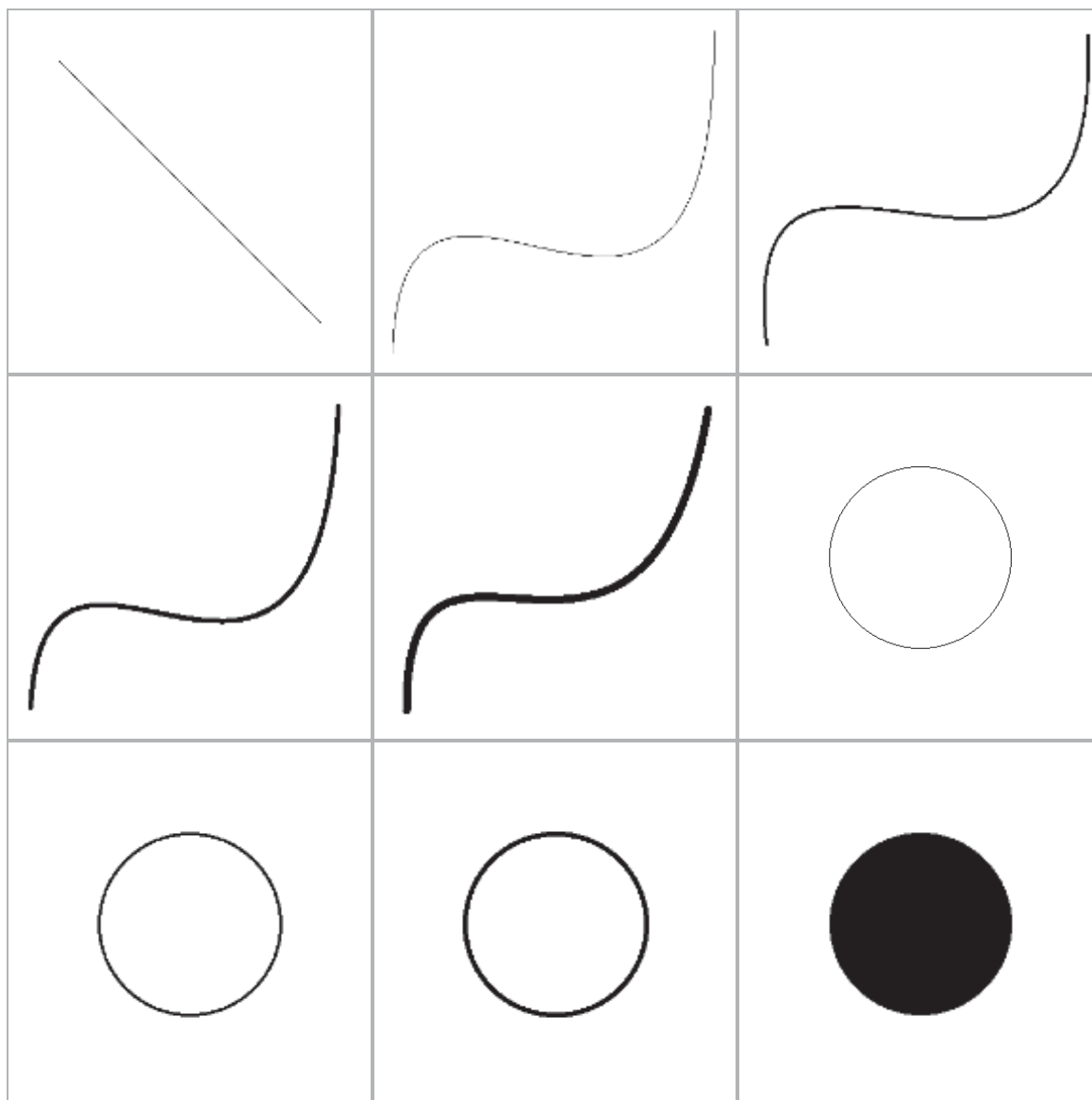
| Fitting function      | Scaling parameter ( $B$ ) |            | $R^2$ |
|-----------------------|---------------------------|------------|-------|
| chi-square            | 0.94                      | $\pm 0.03$ | 0.926 |
| statistical weighting | 0.99                      | $\pm 0.37$ | 0.930 |

Choosing the statistical weighted scaling parameter yields a fractal dimension of 3.01 through equation 35. This value does not describe the dispersion in a straightforward manner due to the fact that many aspects within the images affect the parameters measured from the image, such as the effect from edges, occlusions, pixilation, SWCNT type, SWCNT loading amount and

even the type of polymer. The comparison of scaling parameters of different specimens is most appropriate when equivalent type and concentration of nanofiller is utilized, however, scaling parameters of material systems with different types or amounts of nanofiller can be compared to assess general differences of dispersion qualities. It will be shown that the scaling parameter, and thus the fractal dimension, is indeed determined by the quality of the dispersion and that the scaling parameter is conserved over a fractal magnification window. Furthermore, the measured scaling parameter from multiple HR-SEM high-contrast images of dispersion throughout the specimens (different surfaces and positions) also show reasonable correlation. Thus, the variance of the scaling parameter or fractal dimension can also be used to compare different samples.

### *3.3 Analyzing test images*

In an effort to correlate the scaling parameter with the “shape” of the system being measured, the test images in figure 31 can be analyzed following the procedure in the previous section. The test images include a straight line, a curve of 1, 3, 5 and 8 pixels wide, a line drawn in a circle 1, 3, and 5 pixels wide plus an 18 pixel diameter disk.

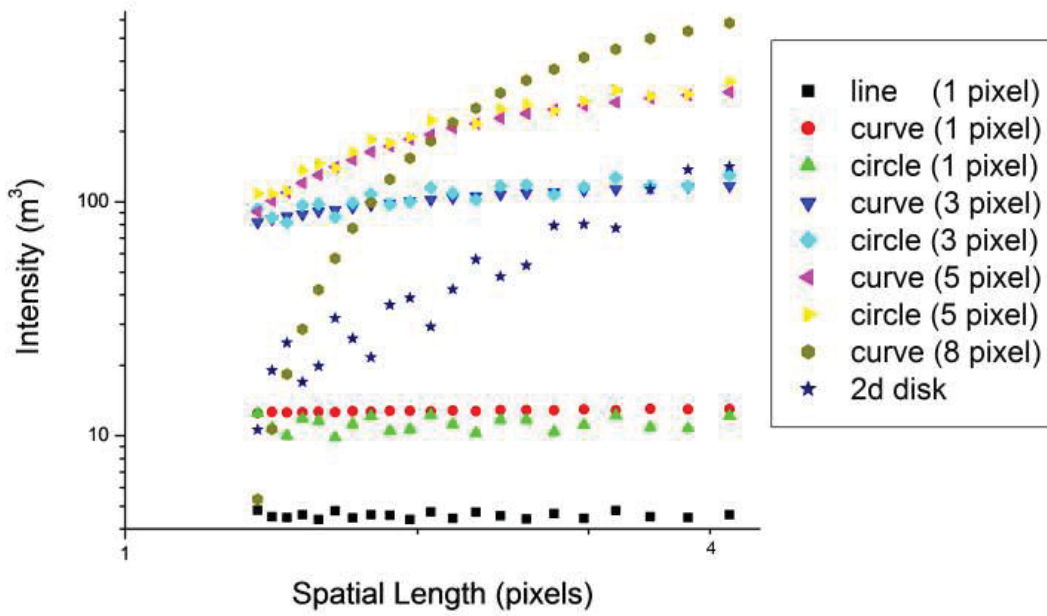


**Figure 31.** Test images consisting of a) 1 pixel wide straight line, b - e) 1, 3, 5 and 8 pixel wide curves, f-h) circle drawn with 1, 3 and 5 pixel wide lines and i) 18 pixel diameter 2D disk.

### 3.3.1 Determining the RPSD

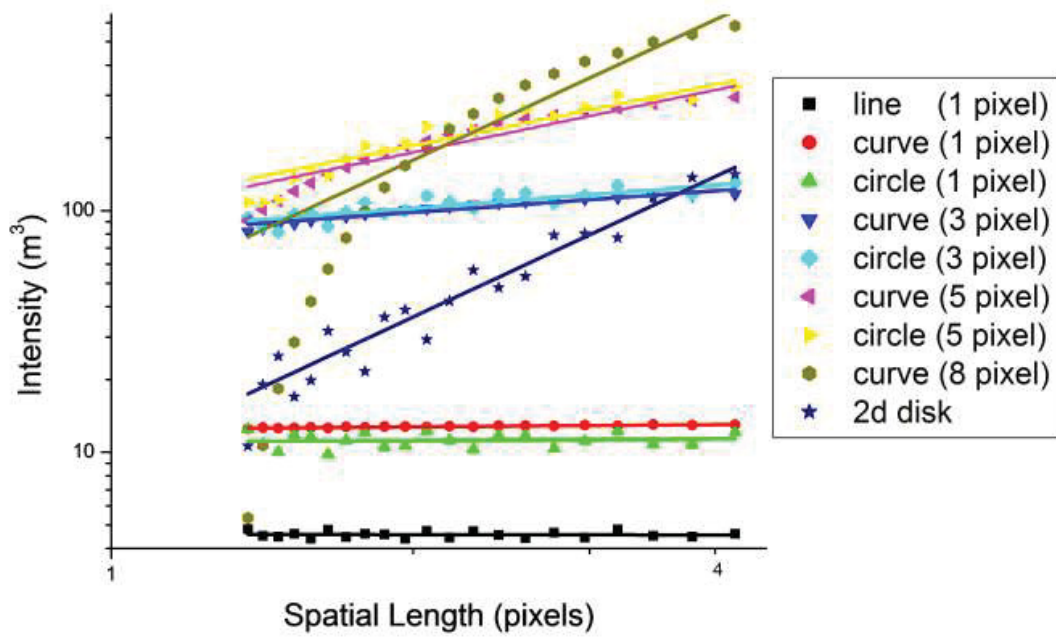
The presented image analysis method applied to these images can also be used to interpret the results of the HR-SEM high-contrast images of dispersion. The images were processed such that 1 pixel equals 1 nm, however, the images will be interpreted in terms of units of pixels. Interpreting these images in terms of pixels will prove useful when analyzing the

images of dispersion. The 360x360 pixel test images sampled at the Nyquist frequency produce 180 frequency components with the pixel length corresponding to the 40<sup>th</sup> component. Dividing into four quarters and retaining the intermediate components yields an analysis window from about 1.4 to 4 pixels as shown in the logarithmic plot of the RPSD in figure 32.



**Figure 32.** *Logarithmic RPSD of the test images of a) 1 pixel wide straight line, b - e) 1, 3, 5 and 8 pixel wide curves, f-h) circle drawn with 1, 3 and 5 pixel wide lines and d) 18 pixel diameter 2D disk.*

Fitting the results with statistical weighting produces the results shown in figure 33 and table 4.



**Figure 33.** *Fitting the RPSD for each test image shows distinct slopes when viewed logarithmically.*

**Table 4.** Results of fitting the RPSD to the Freundlich equation with negative exponent and statistical weighting.

| Shape   | Pixel size | Scaling Parameter ( $B$ ) | $R^2$ |
|---------|------------|---------------------------|-------|
| Line    | 1          | 0                         | 0     |
| Curve   | 1          | 0.03                      | 0.89  |
| Circle  | 1          | 0.02                      | 0     |
| Curve   | 3          | 0.3                       | 0.92  |
| Circle  | 3          | 0.32                      | 0.75  |
| Curve   | 5          | 0.94                      | 0.91  |
| Circle  | 5          | 0.91                      | 0.9   |
| Curve   | 8          | 2.87                      | 0.82  |
| 2D disk | 18         | 2.02                      | 0.95  |

### 3.3.2 Interpreting the RPSD

The test images in figure 31 provide an opportunity to investigate the effect of the width and how different shaped objects are measured. Interpreting the RPSD proves to be complex because it is a product of multiple factors within the image. The dimension of the object plays a large role. For example, consider the noise analogy previously presented. The 1D straight line (or rod) of 1 pixel in figure 31 represents a perfect 1D object of diameter 1 pixel. Because it is perfectly straight, the line will have only two characteristic length features, the width of 1nm and the length which is well outside the bounds of analysis. Furthermore, the methodology of applying an effective analysis window to the HR-SEM images utilized for the test images produces an analysis window of approximately 1.4 – 4 nm. The 1 pixel wide line is outside the lower bound results in the measurement of random white noise for the 1D straight line. The image of the 1 pixel wide curve, however, does not yield a measurement of noise, as is indicated by the value of the coefficient of determination. The coefficient of determination value of 0.87 is much closer to 1 than the value of 0 which was measured not only for the 1 d line of 1 pixel but also for the circle drawn with a 1 pixel line. The PSD of the 1 pixel circle with a center positioned at the origin when analyzed radially also represents a 1 d line and yields the same

measurement of noise as for the 1D line. The 1 pixel wide curve provides a measurable result in the range between 1.3 and 4 pixels because the radial slices not only measure the width of the object, as was the case with the other two 1 pixel wide objects, but will also measure along various angles to effectively measure strings of pixels (between 1.3 and 4 pixels long) that differ in contrast from the background. Thus the RPSD essentially ranks the prevalence of lengths present in the image between 1.3 and 4 pixels, and based upon the slope, the shape of objects measured over the limited analysis window can be measured. The RPSD over this limited analysis window is greatly affected by the pixel width of the imaged object, as is apparent when comparing the results of the curved lines or circles of increasing width. Here, an object width of 3 to 5 pixels produced a useful measurement because it lies within the length window of analysis and results in the measurement of a fractal like object. In terms of the noise analogy, this type of object would correspond to pink, or  $1/f$ , noise. When the line width is increased to a pixel level outside the analysis length window, the RPSD is essentially a measurement of the structure of the edge of the imaged object. In this case, the RPSD would analyze the effect of pixilation along the edge of the drawn line composing the curve and circle. However, as the width of the object is further increased and analyzed over the same length window, the RPSD will increasingly measure lengths of pixels within the width of the object. This thought process is also relevant to the case of HR-SEM images of increasing magnification. As the magnification (or pixel width of the object) is increased, the RPSD measurements will progress from capturing information of the characteristic shape of an object (1 and 3 pixel curve, 3 pixel circle) to the edge shape (5 pixel curve and circle) to measuring lengths contained within the characteristic shape (8 pixel curve and disc). When the width of the characteristic shape is increased to the point of measuring within the shape, the scaling parameter approaches 2 in the case of measuring a perfect 2D object, as can be seen with the test image of the 2D disk. If the 2D disk were to gain surface features to resemble a 3D like object, the scaling parameter approaches 3. The fact that the scaling parameter increased to 2.78 for the 8 pixel curve from 2.02 for the disc can be interpreted as increasing the surface like features through increasing the surface area along the edge of the curve, with the curve itself a 2D object of width outside the upper bound of the analysis length window. When applying the noise analogy, the so-called 2D and 3D measured objects over a given analysis length window can be conceptualized as ordered structures corresponding to brown noise.

Notice that the plot of the 8 pixel curve is not logarithmically linear over the analysis window, thus showing multifractal behavior. The fitting procedure will affect how the scaling parameter is defined over this region. For example, fitting the curve closer to 4 nm will provide a scaling parameter closer to 2 (as shown in figure 33) and fitting the curve closer to 1 nm will provide a scaling parameter closer to 3 (as shown in table 4) because of the observed increase in complexity from pixilation at that scale. Thus interpreting the scaling parameter of the 8 pixel wide curve could be more appropriate over a different analysis window, perhaps between 6 and 10 nm (although the region would be sampled over a non-scale-invariant region due to the limited sampling size). Nevertheless, such multifractal systems often can be characterized by a global scaling parameter that takes into account the various effects within the image. In the case of the 8 pixel curve, the global measure of 2.87 provides an adequate measure of the global scaling parameter as analyzed here.

### *3.3.3 The effect of pixilation*

Understanding the effect of pixilation within the test images should be utilized when analyzing images of dispersion, where pixilation is an unavoidable and inherent within the captured images of SWCNT dispersion. The observation that the 1 pixel wide circle produces a logarithmic power spectrum with a very slight slope and more variance highlights the effect of pixilation. The diagonal 1D line in figure 31d was drawn a 45 degree angle so that the effect of pixilation is minimized. Alternatively, the effect of pixilation is present in the remaining images, including the circle drawn with a 1 pixel line, and produces a measurable effect. The same effect of pixilation may be responsible for yielding the scaling parameter of 2.02 instead of 2.0 for the 2D disc but, like the 1 pixel wide circle, is responsible for the greater variance across the analysis window when compared to the other test images. The variance due to pixilation is more prevalent in RPSD for the 3 pixel wide curve (figure 33) when compared to the images of larger characteristic width because over an 1.4 – 4 nm analysis window, the effect of edges are included within the characteristic shape, rather than add to the description of the characteristic shape, as is the case for objects wider than the analysis window.

The pixilation effect can also be understood in terms of the Fourier components that determine the RPSD. The Fourier transform describes the image in terms of individual frequencies. Subsequently, each Fourier component, determined for the Cartesian PSD from

equation 41, corresponds to a specific spatial length component. Each Fourier component is essentially determined in terms of cosine functions used to convert the image into the frequency domain. Thus the pixilation effect is caused by cosine waves attempting to fit square pixels. Therefore, if the image is captured under conditions where the characteristic size of interest is approximately 3 pixels, the cosine wave used to describe the shape will be less influenced by the square pixels when compared to the case when the characteristic width is larger. When the object of interest is larger than 3 pixels, multiple spatial components will be used to describe the feature; cosine waves which not only represent the characteristic width but also correspond to fitting the square pixels along the edge of the object of interest. Unfortunately, due to complications arising from Gibbs phenomenon, utilizing square wave instead of cosine wave bases Fourier components cannot be implemented to determine the effect upon the RPSD and associated measurements.

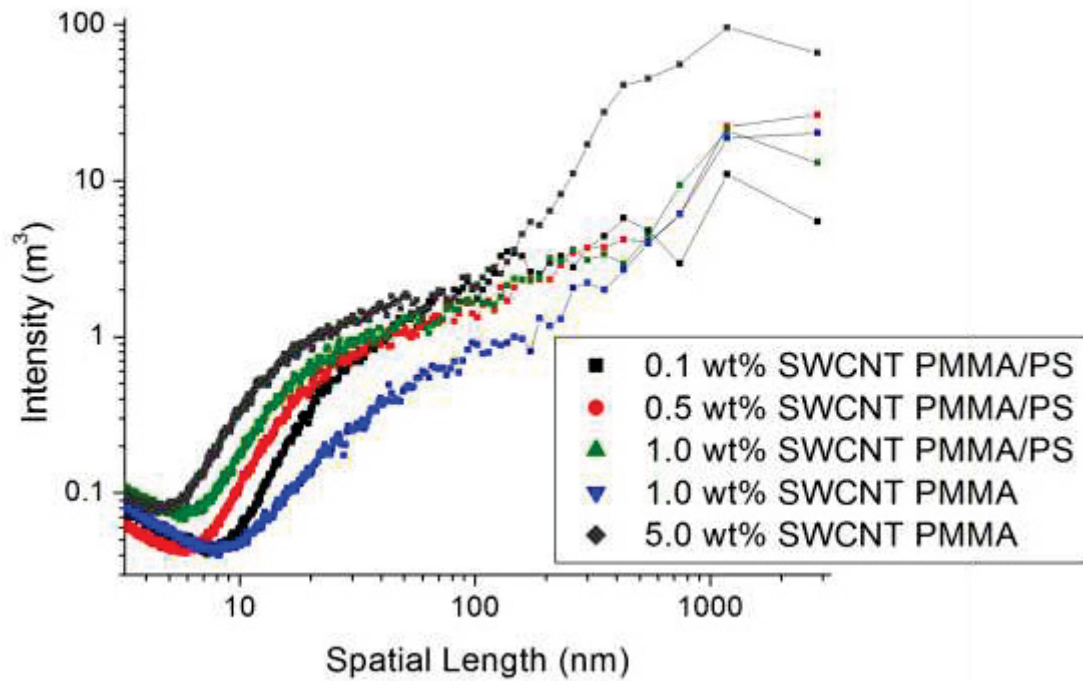
The use of harmonic functions to convert the image leads to the Fourier sampling process to be described as an investigation of the harmonics or periodicities within the image. Furthermore, the harmonic description of features leads to resonance in the PSD. This can be conceptualized with a musical analogy in that the PSD describes music in terms of individual chords. Multiple Fourier components can be used to describe the same feature, similar to how two instruments of different timbre produce musical notes of the same pitch (frequency) and loudness (amplitude). Thus a feature of 25 nm will appear at 25 nm in the PSD but also appear at 50 nm with reduced intensity.

Similar effects, which include the effects of edges, corners and occlusions, also influence the RPSD and will prove relevant when considering the images of SWCNT dispersion. The addition of pixilation, edge effect, corners and occlusions all contribute to more complexity in the image, and thus will result in an increased measurement of the scaling parameter. Furthermore, the RPSD produces a measure of the periodicities or harmonics in the image, such that a large characteristic length will produce resonant harmonics with decreasing spatial length. It is important to note that the culmination of many effects, including object shape, object width, analysis length window, pixilation, edges and others, produce the RPSD. Thus, analyzing images similar in context provides the most effective form of comparison. However with careful analysis, the RPSD can yield useful information across wider sample sets.

### 3.4 Analyzing images of SWCNT dispersion

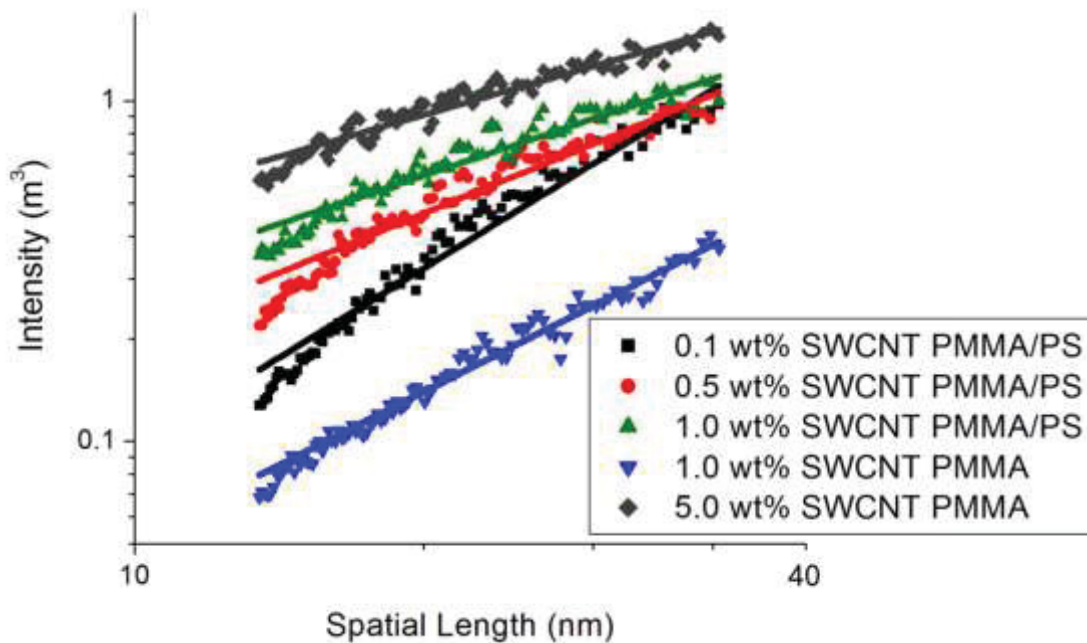
#### 3.4.1 RPSD Results

The images shown in figures 13 – 21 were processed following the developed methodology. The full RPSD for representative 5000 times magnified higher resolution (1792 x 1792 pixel) images are shown below in figure 34.



**Figure 34.** RPSD of representative images (1792 x 1792 pixel) from figures 13 to 17.

Following the presented methodology for developing the analysis length window, the filtered data from figure 34 is provided in figure 35. Notice how each specimen type shows a distinct slope when fit with equation 48.



**Figure 35.** RPSD analysis length window of the spectrum in figure 34.

These slopes, characterized as the scaling parameter of dispersion, can be analyzed and compared as a technique to quantify the SWCNT network. The RPSD results for the 1.0 wt% SWCNT PMMA, 5.0 wt% SWCNT PMMA, 0.1 wt% SWCNT PMMA/PS, 0.5 wt% SWCNT PMMA/PS and 1.0 wt% SWCNT PMMA/PS nanocomposites provided in tables 5, 6, 7, 8 and 9, respectively. Tables below provide information regarding the imaging surface (the side against the glass casting plate or the side exposed to air) in the order presented in figures 13 – 21, magnification, resolution, pixel size, analysis length window (range) as well as the scaling parameter and coefficient of determination obtained from both the traditional chi-squared fit and from statistical weighting.

**Table 5.** RPSD results for the 1.0 wt% SWCNT PMMA samples shown in figures 13 and 18.

|                    | Surf. | Mag.  | Res. | Pixel (nm) | Range (nm) | Scaling Parameter (chi square) | R <sup>2</sup> | Scaling Parameter (statistical weight) | R <sup>2</sup> |
|--------------------|-------|-------|------|------------|------------|--------------------------------|----------------|----------------------------------------|----------------|
| 1.0 wt% SWCNT PMMA | Air   | 250   | 896  | 400        | 540-1635   | 1.49                           | 0.98           | <b>1.51</b>                            | 0.98           |
|                    | Air   | 500   | 896  | 200        | 270-817    | 1.12                           | 0.95           | <b>1.1</b>                             | 0.96           |
|                    | Air   | 1000  | 896  | 100        | 135-409    | 1.21                           | 0.91           | <b>1.14</b>                            | 0.91           |
|                    | Glass | 5000  | 896  | 20         | 27-82      | 1.12                           | 0.89           | <b>1.15</b>                            | 0.9            |
|                    | Air   | 5000  | 896  | 20         | 27-82      | <b>0.87</b>                    | <b>0.84</b>    | <b>0.92</b>                            | <b>0.86</b>    |
|                    | Air   | 5000  | 896  | 20         | 27-82      | 0.977                          | 0.9            | <b>1</b>                               | 0.91           |
|                    | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.52                           | 0.98           | <b>1.54</b>                            | 0.98           |
|                    | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.43                           | 0.97           | <b>1.46</b>                            | 0.97           |
|                    | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.51                           | 0.97           | <b>1.58</b>                            | 0.97           |
|                    | Glass | 10000 | 896  | 10         | 14 - 40    | 1.6                            | 0.97           | <b>1.72</b>                            | 0.96           |
|                    | Air   | 10000 | 896  | 10         | 14 - 40    | 1.7                            | 0.95           | <b>1.84</b>                            | 0.95           |
|                    | Air   | 10000 | 896  | 10         | 14 - 40    | 1.68                           | 0.97           | <b>1.77</b>                            | 0.97           |
|                    | Air   | 10000 | 1792 | 5          | 7 – 20     | 1.52                           | 0.98           | <b>1.49</b>                            | 0.98           |
|                    | Air   | 10000 | 1792 | 5          | 7 – 20     | 1.73                           | 0.98           | <b>1.74</b>                            | 0.98           |

**Table 6.** RPSD results for the 5.0 wt% SWCNT PMMA samples shown in figures 14 and 19.

|                    | Surf. | Mag.  | Res. | Pixel (nm) | Range (nm) | Scaling Parameter (chi square) | R <sup>2</sup> | Scaling Parameter (statistical weight) | R <sup>2</sup> |
|--------------------|-------|-------|------|------------|------------|--------------------------------|----------------|----------------------------------------|----------------|
| 5.0 wt% SWCNT PMMA | Air   | 5000  | 896  | 20         | 27-82      | <b>0.72</b>                    | <b>0.88</b>    | <b>0.71</b>                            | <b>0.88</b>    |
|                    | Air   | 5000  | 896  | 20         | 27-82      | <b>0.56</b>                    | <b>0.82</b>    | <b>0.58</b>                            | <b>0.82</b>    |
|                    | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.06                           | 0.95           | <b>1.09</b>                            | 0.96           |
|                    | Air   | 5000  | 1792 | 10         | 14 - 40    | 0.81                           | 0.95           | <b>0.84</b>                            | 0.94           |
|                    | Air   | 10000 | 896  | 10         | 14 - 40    | 1.3                            | 0.92           | <b>1.4</b>                             | 0.93           |
|                    | Air   | 10000 | 896  | 10         | 14 - 40    | 1.21                           | 0.94           | <b>1.26</b>                            | 0.94           |
|                    | Air   | 10000 | 896  | 10         | 14 - 40    | 1.07                           | 0.93           | <b>1.11</b>                            | 0.93           |
|                    | Air   | 10000 | 1792 | 5          | 7 - 20     | 2.78                           | 0.98           | <b>2.9</b>                             | 0.97           |
|                    | Air   | 10000 | 1792 | 5          | 7 - 20     | 2.42                           | 0.99           | <b>2.48</b>                            | 0.98           |
|                    | Air   | 10000 | 1792 | 5          | 7 - 20     | 2.37                           | 0.98           | <b>2.49</b>                            | 0.98           |

**Table 7.** RPSD results for the 0.1 wt% SWCNT PMMA/PS samples shown in figure 15.

|                       | Surf. | Mag.  | Res. | Pixel (nm) | Range (nm) | Scaling Parameter (chi square) | R <sup>2</sup> | Scaling Parameter (statistical weight) | R <sup>2</sup> |
|-----------------------|-------|-------|------|------------|------------|--------------------------------|----------------|----------------------------------------|----------------|
| 0.1 wt% SWCNT PMMA/PS | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.74                           | 0.96           | <b>1.86</b>                            | 0.96           |
|                       | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.6                            | 0.96           | <b>1.74</b>                            | 0.96           |
|                       | Air   | 10000 | 1792 | 5          | 7 - 20     | 2.24                           | 0.99           | <b>2.3</b>                             | 0.99           |
|                       | Air   | 10000 | 1792 | 5          | 7 - 20     | 3                              | 0.99           | <b>3.26</b>                            | 0.99           |

**Table 8.** *RPSD results for the 0.5 wt% SWCNT PMMA/PS samples shown in figures 16 and 20.*

|                       | Surf. | Mag.  | Res. | Pixel (nm) | Range (nm) | Scaling Parameter (chi square) | R <sup>2</sup> | Scaling Parameter (statistical weight) | R <sup>2</sup> |
|-----------------------|-------|-------|------|------------|------------|--------------------------------|----------------|----------------------------------------|----------------|
| 0.5 wt% SWCNT PMMA/PS | Glass | 100   | 896  | 1000       | 1352-4087  | <b>0.18</b>                    | <b>0.27</b>    | <b>0.17</b>                            | <b>0.24</b>    |
|                       | Glass | 250   | 896  | 400        | 540-1635   | 1.03                           | 0.93           | <b>1.08</b>                            | 0.94           |
|                       | Glass | 500   | 896  | 200        | 270-817    | 1.22                           | 0.96           | <b>1.21</b>                            | 0.95           |
|                       | Air   | 500   | 896  | 200        | 270-817    | 1.22                           | 0.94           | <b>1.24</b>                            | 0.95           |
|                       | Glass | 1000  | 896  | 100        | 135-409    | 1.03                           | 0.94           | <b>1.03</b>                            | 0.94           |
|                       | Air   | 1500  | 896  | 66.7       | 90-272     | 1.02                           | 0.94           | <b>1</b>                               | 0.94           |
|                       | Glass | 2500  | 896  | 40         | 54-163     | <b>0.83</b>                    | <b>0.87</b>    | <b>0.82</b>                            | <b>0.88</b>    |
|                       | Air   | 2500  | 896  | 40         | 54-163     | 1                              | 0.93           | <b>1.01</b>                            | 0.92           |
|                       | Air   | 2500  | 896  | 40         | 54-163     | <b>0.79</b>                    | <b>0.88</b>    | <b>0.82</b>                            | <b>0.89</b>    |
|                       | Glass | 5000  | 896  | 20         | 27-82      | 1.27                           | 0.92           | <b>1.34</b>                            | 0.96           |
|                       | Air   | 5000  | 896  | 20         | 27-82      | 0.98                           | 0.9            | <b>1.02</b>                            | 0.9            |
|                       | Air   | 5000  | 896  | 20         | 27-82      | 0.87                           | 0.85           | <b>0.93</b>                            | 0.86           |
|                       | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.21                           | 0.94           | <b>1.29</b>                            | 0.94           |
|                       | Air   | 5000  | 1792 | 10         | 14 - 40    | 1.16                           | 0.95           | <b>1.23</b>                            | 0.94           |
|                       | Glass | 7000  | 896  | 14.3       | 19-58      | 1.13                           | 0.89           | <b>1.22</b>                            | 0.9            |
|                       | Air   | 7000  | 896  | 14.3       | 19-58      | 1.3                            | 0.96           | <b>1.37</b>                            | 0.95           |
|                       | Air   | 7000  | 896  | 14.3       | 19-58      | <b>1.08</b>                    | <b>0.87</b>    | <b>1.17</b>                            | <b>0.88</b>    |
|                       | Glass | 10000 | 896  | 10         | 14-40      | 1.5                            | 0.89           | <b>1.7</b>                             | 0.9            |
|                       | Glass | 10000 | 896  | 10         | 14-40      | 1.42                           | 0.93           | <b>1.6</b>                             | 0.93           |

|  |       |       |      |    |        |      |      |             |      |
|--|-------|-------|------|----|--------|------|------|-------------|------|
|  | Glass | 10000 | 896  | 10 | 14-40  | 1.66 | 0.94 | <b>1.82</b> | 0.95 |
|  | Air   | 10000 | 896  | 5  | 7 - 20 | 1.39 | 0.9  | <b>1.55</b> | 0.91 |
|  | Air   | 10000 | 896  | 5  | 7 - 20 | 1.58 | 0.91 | <b>1.82</b> | 0.91 |
|  | Air   | 10000 | 896  | 5  | 7 - 20 | 1.5  | 0.95 | <b>1.64</b> | 0.94 |
|  | Air   | 10000 | 1792 | 5  | 7 - 20 | 1.61 | 0.96 | <b>1.76</b> | 0.96 |

**Table 9.** RPSD results for the 1.0 wt% SWCNT PMMA/PS samples shown in figures 17 and 21.

| 1.0 wt%<br>SWCNT<br>PMMA/PS | Surf. | Mag.  | Res. | Pixel<br>(nm) | Range<br>(nm) | Scaling<br>Parameter<br>(chi<br>square) | R^2         | Scaling<br>Parameter<br>(statistical<br>weight) | R^2         |
|-----------------------------|-------|-------|------|---------------|---------------|-----------------------------------------|-------------|-------------------------------------------------|-------------|
|                             | Air   | 250   | 896  | 400           | 540-<br>1635  | 1.43                                    | 0.96        | <b>1.45</b>                                     | 0.96        |
|                             | Air   | 500   | 896  | 200           | 270-<br>817   | 1.43                                    | 0.96        | <b>1.39</b>                                     | 0.95        |
|                             | Air   | 1000  | 896  | 100           | 135-<br>409   | 0.98                                    | 0.96        | <b>0.99</b>                                     | 0.95        |
|                             | Air   | 2500  | 896  | 40            | 54-163        | <b>0.8</b>                              | <b>0.88</b> | <b>0.77</b>                                     | <b>0.87</b> |
|                             | Air   | 2500  | 896  | 40            | 54-163        | <b>0.62</b>                             | <b>0.84</b> | <b>0.64</b>                                     | <b>0.85</b> |
|                             | Air   | 5000  | 896  | 20            | 27-82         | <b>0.67</b>                             | <b>0.86</b> | <b>0.68</b>                                     | <b>0.86</b> |
|                             | Air   | 5000  | 896  | 20            | 27-82         | <b>0.79</b>                             | <b>0.9</b>  | <b>0.82</b>                                     | 0.91        |
|                             | Air   | 5000  | 1792 | 10            | 14 - 40       | 0.94                                    | 0.93        | <b>0.99</b>                                     | 0.93        |
|                             | Air   | 10000 | 896  | 5             | 14 - 40       | 1.2                                     | 0.93        | <b>1.25</b>                                     | 0.93        |
|                             | Air   | 10000 | 896  | 5             | 14 - 40       | 1.24                                    | 0.89        | <b>1.33</b>                                     | 0.9         |
|                             | Air   | 10000 | 896  | 5             | 14 - 40       | <b>1.06</b>                             | <b>0.87</b> | <b>1.17</b>                                     | <b>0.88</b> |
|                             | Air   | 10000 | 1792 | 5             | 7 - 20        | 1.15                                    | 0.93        | <b>1.24</b>                                     | 0.93        |

As previously discussed, the spectral density of the 8 pixel curve shows multifractal behavior with multiple regions that could be fit with equation 48. Ideally, the windowed region to analyze the SWCNT composites is specified to contain a monofractal region, but often such a

region produces an ambiguous scaling parameter. The coefficient of determination, shape of the logarithmic curve and result for the scaling parameter are often enough to determine if a direct interpretation of the bounded RPSD is applicable. Additionally, the increase in the amount of variance at larger lengths often produces a poor fit and possibly a poor representation of the true scaling parameter. In the tables above, any scaling parameter determined with a coefficient of determination below 90% is shown in red text.

Notice, in general, that each specimen type is described by a scaling parameter that is reasonably conserved for each sample over a magnification window between 1000 and 5000 times magnification, and/or another between 5000 and 10000 times magnification. Also, the results from both fitting techniques (chi-square and statistical weighting) show reasonable correlation. Essentially, either fitting technique can be utilized to determine the scaling parameter over the defined analysis window. However, if the data shows greater variance at the larger length range (near the dominant feature region in figure 23), fitting with statistical weighting yields more accurate correlation and will be utilized throughout the remainder of the study.

Notice that the scaling parameters show relatively consistent trends that are specific to each sample, particularly when taking into account the coefficient of determination. The 1.0 wt% SWCNT PMMA/PS specimen is found to contain the lowest scaling parameter of the sample set. The value for the scaling parameter is progressively followed by the 0.5 wt% SWCNT PMMA/PS, 1.0 wt% SWCNT PMMA, 5.0 wt% SWCNT PMMA and 0.1 wt% SWCNT PMMA/PS specimens, respectively.

The overall trend is not very intuitive because of the effect of all the variables involved in determining the spectral density slope. However, with careful analysis the results can be adequately interpreted. First, notice that the 0.1 wt% SWCNT PMMA/PS specimen shows the highest overall trend of the measured scaling parameter with increasing magnification. This is counterintuitive to the expected result based upon the images of dispersion in figure 15. Figure 15 shows well dispersed straight tubes and thus should correspond to a lower scaling parameter. However, the low SWCNT loading does not provide a conductive nanotube network adequate for unblemished high-contrast imaging. As previously mentioned, the images of the 0.1 wt% SWCNT PMMA/PS specimen were captured at the absolute limit of the microscopes operational range. This proved to inadequately deliver the resolution necessary for dispersion analysis

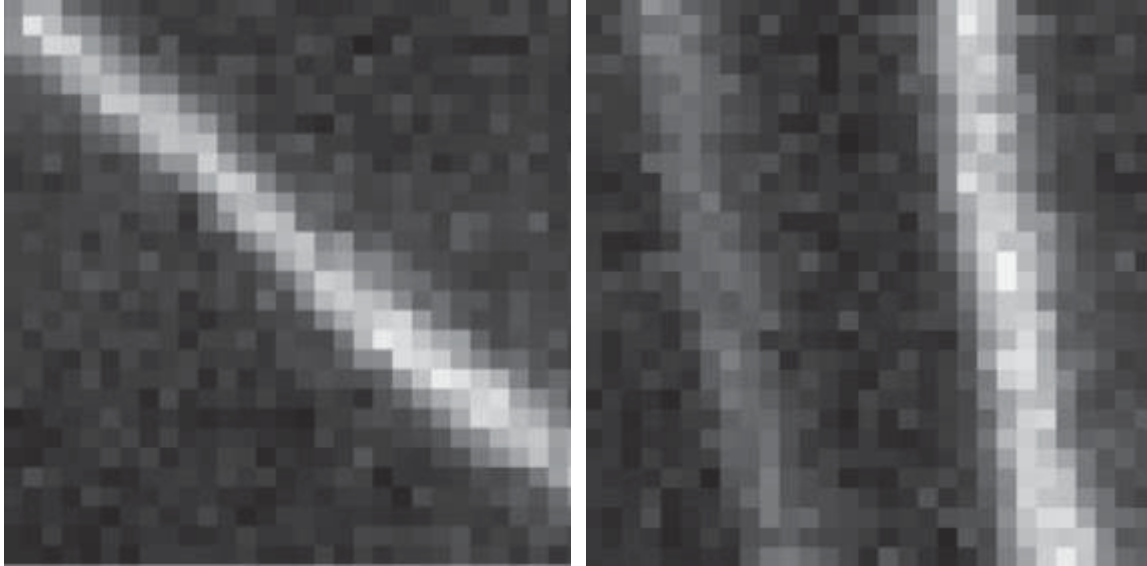
because the lack of a thorough conductive network yields to electrical saturation of the polymeric regions surrounding a single SWCNT or bundle of SWCNT. As the polymer saturates, it increasingly stores electrical charge as the area progressively materializes within HR-SEM high-contrast images. This effect can be seen in the images of figure 15. Notice how the polymeric regions surrounding the nanotubes are more visible than the rest of the specimens and begin to represent the surface of a 3D object. The tubes are analyzed in this case as surface features of a rough 3D agglomeration of polymer and SWCNT and therefore cannot directly be compared to the other specimens. The 5.0 wt% SWCNT PMMA specimen also shows unintuitive results. Again, a thorough investigation yields an appropriate interpretation of the image. Upon closer analysis, the analysis length window (the range in the figures above) for the 5.0 wt% SWCNT PMMA specimen (7 - 87 nm) does not adequately capture information on large agglomerated structures.

Alternatively, the 1.0 wt% SWCNT PMMA/PS, 0.5 wt% SWCNT PMMA/PS and 1.0 wt% SWCNT PMMA specimens provide an excellent opportunity not only to measure and describe dispersion within these images, but also investigate the ability to compare scaling parameters over different specimens. However, first it is advantageous to investigate the transition in the scaling parameter between the general regions of 1000 to 5000 times magnification and the scaling parameter obtained from the majority of images above 5000 times magnification.

#### *3.4.1.1 Determining the length window for analysis*

Determining the appropriate analysis length window is a factor of many variables, including magnification, resolution, imaging conditions and the characteristic size of the object of interest. The test images have shown that the presented methodology for image analysis and the spectrum splitting technique that optimal measurements of the scaling parameter are obtained when the characteristic length is approximately 3 pixels wide. From the higher resolution (1792 x 1792 pixel) images, we can determine the approximate width of the imaged characteristic tube or bundle width in terms of nanometers or pixels. In order to investigate the ability for the PMMA and PMMA/PS polymers to interact with and disperse individual SWCNT, the characteristic length (and thus the focus of the analysis length window) will be set to what appear to be the width of single SWCNT. High-contrast imaging of conductive nanofiller with an

insulating material proves to greatly exaggerate the size. The difference in the imaged size of the SWCNT (assuming the tubes are individually dispersed) can be determined by enlarging the image to determine the characteristic width of the imaged SWCNT in terms of pixels. Figure 36 below shows enlarged SWCNT within the 5000 times magnified 0.5 wt% SWCNT PMMA/PS and 10000 times magnified 1.0 wt% SWCNT PMMA/PS (1792 x 1792 pixel) images, respectively. Equivalent results are obtained for the PMMA based nanocomposites.



**Figure 36.** *The effect of high-contrast imaging: enlarged SWCNT within the a) 5000 times magnified 0.5 wt% SWCNT PMMA/PS and b) 10000 times magnified 1.0 wt% SWCNT PMMA/PS (1792 x 1792 pixel) images. Each pixel is a) 10nm and b) 5nm wide.*

From figure 36a, the width of the SWCNT bundle at (1792 x 1792 pixel) 5000 times magnification is approximately 3 pixels depending upon angle of measurement with respect to the square shaped pixels. From figure 36b, the width of the SWCNT bundle at (1792 x 1792 pixel) 10000 times magnification is approximately 5 to 6 pixels. From table 2 the characteristic SWCNT width within the high-contrast images can be estimated to be approximately 25 to 30 nm. The manufacturer claims the tubes are  $1 \pm 0.3$  nm in diameter. Thus, the high-contrast imaging process is assumed to enlarge the width of SWCNT bundles within the PMMA/PS copolymer almost 30 times the diameter of an individual SWCNT. This either indicates high-

contrast imaging causes the individual SWCNTs to appear over 30 times larger, or more realistically, that individual bundles of SWCNT appear 25 – 30 nm in diameter.

Therefore, to measure the characteristic length of SWCNT dispersion within the images specimens, an appropriate analysis length window would center around 25 – 30 nm. The previous tables providing the results of PRSD analysis, it can be seen that the analyzed length range between 7 – 20 nm for the higher resolution (1792 x 1792 pixel) 10000 times magnified images is too limited to capture information relevant to SWCNT dispersion and, in fact, is weighted by pixilation information (as was the case with the test images constructed with thicker lines). Therefore, the appropriate analysis window for these samples is better captured with lower resolution or lower magnification (when compared to the higher resolution 10000 times magnified images) in order to capture a length window which contains the characteristic length, which in this case is the apparent SWCNT bundle diameter of 25 – 30 nm.

Interestingly, even though the 10000 times magnified lower resolution (896 x 896 pixel) and 5000 times magnified higher resolution (1792 x 1792 pixel) images contain the same pixel to length ratio (with the exception of the 1 wt% SWCNT PMMA/PS specimen), the 10000 times magnified lower resolution (896 x 896 pixel) images follow the same trend as the higher resolution (1792 x 1792 pixel) 10000 times magnified images. Similarly, the 5000 times magnified higher resolution (1792 x 1792 pixel) images follow the trend of the 5000 times magnified lower resolution (896 x 896 pixel) images. From the RPSD results, the 5000 times magnified higher and lower resolution images appear to provide the most appropriate measure for the local scale parameter at the microscopic level for SWCNT dispersion without noticeable influence of measuring pixilation along the edge of an object considerably wider than 3 pixels. The higher resolution (1792 x 1792 pixel) 10000 times magnified images prove to contain too limited of a range of information relevant to local SWCNT dispersion and should be omitted. The potential of expanding the large scale boundary of the analysis length window for the 10000 times magnified (896 x 896 pixel) images to attempt capturing the same information as the 5000 times magnified images is examined in the following section.

### 3.4.1.2 Expanding the length window of analysis

It is of interest to investigate the limits of the upper bound of the fractal length window in order to determine if it is possible to capture information that is perhaps more descriptive of SWCNT dispersion in the higher magnification images, such as the images above 5000 times magnification that yield an increased measurement of the scaling parameter due to the unavoidable effect of pixilation. Expanding the analysis window of higher magnified images will allow for comparison with the measured scaling parameter over an equivalent analysis window for an image of lesser magnification. The results for expanding the magnification window of the lower resolution (896 x 896 pixel) 10000 times magnified images are provided in table 10 below. This test provides insight into the overall scale invariant nature of the imaged dispersion and the potential to measure the scaling parameter over the non-scale-invariant region.

**Table 10.** Comparison of the scaling parameter obtained over various analysis length windows for the 896 x 896 pixel 10000 times magnified images in figures 18 – 21.

| Sample             | Surface | Range (nm) | Scaling Parameter (statistical weight) | R <sup>2</sup> |
|--------------------|---------|------------|----------------------------------------|----------------|
| 1.0 wt% SWCNT PMMA | Glass   | 14-40      | <b>1.72</b>                            | 0.96           |
|                    |         | 27-80      | <b>0.93</b>                            | 0.88           |
|                    |         | 20-60      | <b>1.22</b>                            | 0.91           |
|                    |         | 14-80      | <b>1.37</b>                            | 0.92           |
|                    | Air     | 14-40      | <b>1.84</b>                            | 0.95           |
|                    |         | 27-80      | <b>0.94</b>                            | 0.86           |
|                    |         | 20-60      | <b>1.32</b>                            | 0.94           |
|                    |         | 14-80      | <b>1.33</b>                            | 0.92           |
|                    | Air     | 14-40      | <b>1.77</b>                            | 0.97           |
|                    |         | 27-80      | <b>1.11</b>                            | 0.94           |
|                    |         | 20-60      | <b>1.19</b>                            | 0.97           |

|                            |       |       |             |      |
|----------------------------|-------|-------|-------------|------|
| 5.0 wt%<br>SWCNT<br>PMMA   | Air   | 14-80 | <b>1.38</b> | 0.95 |
|                            |       | 14-40 | <b>1.4</b>  | 0.93 |
|                            |       | 27-80 | <b>0.61</b> | 0.75 |
|                            |       | 20-60 | <b>0.91</b> | 0.85 |
|                            | Air   | 14-80 | <b>1.02</b> | 0.89 |
|                            |       | 14-40 | <b>1.11</b> | 0.93 |
|                            |       | 27-80 | <b>0.5</b>  | 0.7  |
|                            |       | 20-60 | <b>0.67</b> | 0.81 |
|                            | Air   | 14-80 | <b>0.8</b>  | 0.89 |
|                            |       | 14-40 | <b>1.26</b> | 0.94 |
|                            |       | 27-80 | <b>0.55</b> | 0.66 |
|                            |       | 20-60 | <b>0.79</b> | 0.81 |
|                            |       | 14-80 | <b>0.91</b> | 0.88 |
| 0.5 wt%<br>SWNT<br>PMMA/PS | Glass | 14-40 | <b>1.7</b>  | 0.9  |
|                            |       | 27-80 | <b>0.87</b> | 0.87 |
|                            |       | 20-60 | <b>1.16</b> | 0.91 |
|                            |       | 14-80 | <b>1.24</b> | 0.92 |
|                            | Glass | 14-40 | <b>1.6</b>  | 0.93 |
|                            |       | 27-80 | <b>0.57</b> | 0.79 |
|                            |       | 20-60 | <b>0.99</b> | 0.89 |
|                            |       | 14-80 | <b>1.23</b> | 0.85 |
|                            | Glass | 14-40 | <b>1.82</b> | 0.95 |
|                            |       | 27-80 | <b>0.61</b> | 0.78 |
|                            |       | 20-60 | <b>0.9</b>  | 0.83 |
|                            |       | 14-80 | <b>1.14</b> | 0.88 |
|                            | Air   | 14-40 | <b>1.55</b> | 0.91 |
|                            |       | 27-80 | <b>0.5</b>  | 0.53 |
|                            |       | 20-60 | <b>1</b>    | 0.83 |
|                            |       | 14-80 | <b>1.14</b> | 0.82 |

|                                      |     |       |             |      |
|--------------------------------------|-----|-------|-------------|------|
|                                      | Air | 14-40 | <b>1.82</b> | 0.91 |
|                                      |     | 27-80 | <b>0.67</b> | 0.73 |
|                                      |     | 20-60 | <b>1.06</b> | 0.93 |
|                                      |     | 14-80 | <b>1.15</b> | 0.86 |
|                                      | Air | 14-40 | <b>1.64</b> | 0.94 |
|                                      |     | 27-80 | <b>1.4</b>  | 0.88 |
|                                      |     | 20-60 | <b>1.05</b> | 0.88 |
|                                      |     | 14-80 | <b>1.4</b>  | 0.93 |
| <b>1.0 wt%<br/>SWCNT<br/>PMMA/PS</b> | Air | 14-40 | <b>1.25</b> | 0.93 |
|                                      |     | 27-80 | <b>0.5</b>  | 0.51 |
|                                      |     | 20-60 | <b>0.84</b> | 0.83 |
|                                      |     | 14-80 | <b>0.88</b> | 0.84 |
|                                      | Air | 14-40 | <b>1.33</b> | 0.9  |
|                                      |     | 27-80 | <b>0.33</b> | 0.48 |
|                                      |     | 20-60 | <b>0.68</b> | 0.79 |
|                                      |     | 14-80 | <b>0.88</b> | 0.82 |
|                                      | Air | 14-40 | <b>1.17</b> | 0.88 |
|                                      |     | 27-80 | <b>0.35</b> | 0.51 |
|                                      |     | 20-60 | <b>0.4</b>  | 0.63 |
|                                      |     | 14-80 | <b>0.78</b> | 0.82 |

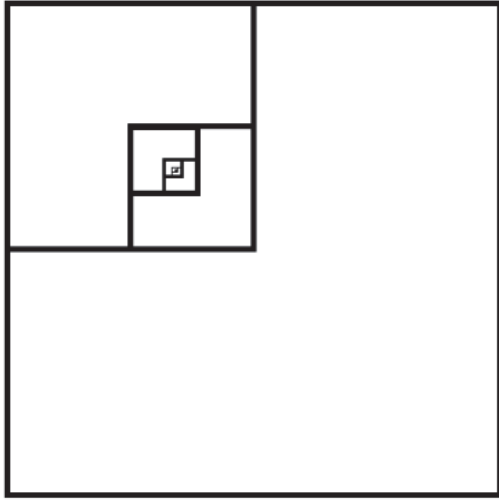
The results from table 10 show that the scaling parameter determined over equivalent length regions that do not necessarily contain the so-called scale invariant region can be reasonably compared from sample to sample when the captured images contain relevant information at characteristic lengths of approximately 5 to 6 pixels. The best coefficient of fit for the 10000 times magnified (896 x 896 pixel) images is obtained when including only the scale invariant region (14 nm – 40 nm) within the length range, followed by the largest overall length region containing the full scale invariant region (14 nm – 80 nm). Thus, as expected the coefficient of determination decreases as the amount of scale invariant length components are removed. Furthermore, the results obtained when expanding the upper end of the analysis length

window show more similarity with the images of lower magnification. Thus expanding the length range for analysis effectively reduces the effect of pixilation for these images and produces more relevant results.

Similarly notice that the expanded length range can account for the discrepancy in the scaling parameter measured between the poor and good quality images the 10000 times magnified images (896 x 896 pixel) of the 5 wt% SWCNT PMMA specimen (figure 19 and table 6). Thus, expanding the length range for analysis in an effective method to remove some of the ambiguity produced from certain imaging effects as well as from the increased effects of pixilation as the characteristic size of the object increases. This technique can also be utilized to account for poor focus at the finer length scales and compare high-contrast images taken over different magnifications, with different microscopes or of different material systems (due to the fact that a given type of polymer may impart specific characteristics, such as the apparent nanotube thickness, electron saturation and the associated limitations in resolution, into the image).

#### *3.4.1.3 Investigation of self-affinity*

Essentially, the images have been captured following the schematic representation of capturing images over the same surface at increasing magnification shown below in figure 37.



**Figure 37.** *Schematic representation of capturing images of dispersion at increasing magnification in order to investigate the self-affine nature.*

Sets of images captured in this manner provide an opportunity to test the self-affine nature of the imaged dispersion by comparing the result over a range of magnification. Attempting to prove that the dispersion is self-affine by is an important consideration during the analysis of these images. This is important because the power spectrum method and fBm are both built upon the assumption that the system being measured is self-affine. If the scaling parameter is reasonably stable over appropriate fractal length and magnification windows but different from specimen to specimen analyzed, the assumption of measuring a scaling parameter describing a self-affine system is further supported. Similar to observing that a similar scaling parameter can be measured across various magnifications, the scaling parameter at various locations along a surface can also be investigated for consistency. The final investigation of self-affinity involves comparing the scaling parameter determined from a 1D PSD obtained when slicing the image in 3 different ways; radially, horizontally and vertically.

The results from the previous sections show that the scaling parameter on both the glass and air surface for multiple locations and magnifications is relatively consistent when following the presented methodology and taking into account the coefficient of determination, omitting the

1792 x 1792 pixel 10000 times magnified images and expanding the length range for analysis of the 896 x 896 pixel 10000 times magnified images. Thus a somewhat consistent scaling parameter can be obtained over the appropriate analysis windows across different surfaces, positions, magnifications and combinations of the three which indicates self-affinity. Furthermore, the scaling parameters are shown to be relatively specimen specific, signifying the usefulness of the presented dispersion analysis technique.

Notice that overall the scaling parameter numerically increases with increasing magnification, especially between 5000 and 10000 times magnification. The trend shows an increasing scaling parameter with increasing magnification and associated pixilation effects, a result expected from the previous investigation of the test images. The absence of this trend over the 1000 to 5000 times magnified images indicates that the imaged dispersion is a self-affine system over this magnification window.

In an effort to further validate the self-affine assumption of the fBm, the scaling parameters from the radial 1D PSD (RPSD) and the standard 1D are compared. Table 11 below shows the relationship between the scaling parameters obtained from two standard 1D PSDs, determined from the averages of horizontally, vertically or radially slicing the image.

**Table 11.** *The scaling parameters obtained from the 1D horizontal, vertical and radial PSDs for the 5000 times magnified images in figures 13 – 21.*

| Sample             | Surface | PSD direction | Scaling Parameter (statistical weight) | R <sup>2</sup> |
|--------------------|---------|---------------|----------------------------------------|----------------|
| 1.0 wt% SWCNT PMMA | Air     | radial        | <b>1.54</b>                            | 0.98           |
|                    |         | horizontal    | <b>1.3</b>                             | 0.99           |
|                    |         | vertical      | <b>1.34</b>                            | 0.98           |
|                    | Air     | radial        | <b>1.46</b>                            | 0.97           |
|                    |         | horizontal    | <b>1.31</b>                            | 0.99           |
|                    |         | vertical      | <b>1.21</b>                            | 0.98           |

|                                      |     |            |             |      |
|--------------------------------------|-----|------------|-------------|------|
|                                      | Air | radial     | <b>1.58</b> | 0.97 |
|                                      |     | horizontal | <b>1.37</b> | 0.98 |
|                                      |     | vertical   | <b>1.31</b> | 0.98 |
| <b>5.0 wt%<br/>SWCNT<br/>PMMA</b>    | Air | radial     | <b>1.09</b> | 0.96 |
|                                      |     | horizontal | <b>1.19</b> | 0.97 |
|                                      |     | vertical   | <b>1.06</b> | 0.97 |
|                                      | Air | radial     | <b>0.84</b> | 0.94 |
|                                      |     | horizontal | <b>0.99</b> | 0.96 |
|                                      |     | vertical   | <b>0.94</b> | 0.97 |
| <b>0.1 wt%<br/>SWCNT<br/>PMMA/PS</b> | Air | radial     | <b>1.86</b> | 0.96 |
|                                      |     | horizontal | <b>1.58</b> | 0.97 |
|                                      |     | vertical   | <b>1.75</b> | 0.97 |
|                                      | Air | radial     | <b>1.74</b> | 0.96 |
|                                      |     | horizontal | <b>1.59</b> | 0.98 |
|                                      |     | vertical   | <b>1.56</b> | 0.97 |
| <b>0.5 wt%<br/>SWCNT<br/>PMMA/PS</b> | Air | radial     | <b>1.29</b> | 0.94 |
|                                      |     | horizontal | <b>1.36</b> | 0.97 |
|                                      |     | vertical   | <b>1.34</b> | 0.98 |
|                                      | Air | radial     | <b>1.23</b> | 0.94 |
|                                      |     | horizontal | <b>1.19</b> | 0.97 |
|                                      |     | vertical   | <b>1.22</b> | 0.97 |
| <b>1.0 wt%<br/>SWCNT<br/>PMMA/PS</b> | Air | radial     | <b>0.99</b> | 0.93 |
|                                      |     | horizontal | <b>1</b>    | 0.97 |
|                                      |     | vertical   | <b>1.06</b> | 0.97 |

This relative stability of the scaling parameter for each image and for different images of each specimen also validates the assumption that the proposed method is characterizing a self-affine surface. Notice that the horizontal streaking in the 0.1 wt% SWCNT PMMA/PS images in figure 15b does not appreciably affect the resulting scaling parameter. As was the case with

previous investigation of self-affinity, it is assumed that the slight discrepancies between the results is not due to the inappropriate application of self-affinity, but rather can be attributed to the fact that the images imperfectly represent a partially captured fractal-like self-affine network. The relative stability of scaling parameter regardless of position, magnification or computation orientation reinforces the validity of a self-affine surface and characterizing SWCNT dispersion in terms of a fractal nature. Therefore, the scaling parameters determined for different specimens can be considered representative of the overall dispersion within the nanocomposite and compared.

#### *3.4.1.4 Interpretation of the RPSD results*

In the case of the 0.1 wt% PMMA/PS specimen, the nanotubes are analyzed as surface features of a rough 3D agglomeration of polymer and SWCNT resulting from and inadequate high-contrast electrical percolation network. Therefore the nature of dispersion, in very general terms, may be compared with the other samples by conceptualizing the dispersed SWCNT as surface features captured in a 2D projection of a 3D object and comparing the measured fractal dimension as if it was determined for a 3D object. This is accomplished by simply determining the fractal dimension of the conceptualized 3D object in three Euclidian dimensions, using equation 34, rather than two Euclidian dimensions (equation 35). Thus the scaling parameters provided in table 7 can be compared with the others by simply subtracting 1. A more intuitive overall trend with respect to all specimens is observed when the adjusted scaling parameter is used for images that suffer from so-called saturation caused from low filler loading. Alternatively, such images can be adjusted in order to remove the saturated areas to retain information on the SWCNT only. However, the purpose here is to standardize the image analysis process without individual image modification.

Lower magnification 5.0 wt% SWCNT PMMA images (2500 times magnified and below) indicated a strong measure of white noise due to excessive charging of the polymer in the captured area and did not produce measurable results. This affliction, to a lesser degree, is also present in the lower resolution (896 x 896 pixel) 5000 times magnified images, as indicated by the lower values for coefficient of determination. The higher resolution (1792 x 1792 pixel) 5000 and 10000 times magnified images of the 5.0 wt% SWCNT PMMA specimen only capture information relevant to the straight SWCNT present outside the agglomerated regions, as can be

seen in figure 14e. Thus the observed scaling parameter for the 5.0 wt% SWCNT PMMA specimen is adequately measuring dispersion, just not over the length scale necessary to quantify the dispersion of higher weight percent SWCNT specimen and compare with the other samples.

The 1.0 wt% SWCNT PMMA, 0.5 wt% SWCNT PMMA/PS and 1.0 wt% SWCNT PMMA/PS specimens produce relevant scaling parameters for direct comparison. The average scaling parameter with a coefficient of determination above 0.90 from the 5000 times magnified images from tables 5 to 9 and 11 with the associated fractal dimension (equation 34) is provided below in table 12.

**Table 12.** *Average scaling parameter and fractal dimension from the high-contrast 5000 times magnified PMMA and PMMA/PS nanocomposite images.*

| Sample                | Average Scaling Parameter (stat. weight) | Standard Deviation of Scaling Parameter | Average Fractal Dimension |
|-----------------------|------------------------------------------|-----------------------------------------|---------------------------|
| 1.0 wt % SWCNT PMMA   | 1.37                                     | 0.17                                    | 2.82                      |
| 0.5 wt% SWCNT PMMA/PS | 1.22                                     | 0.14                                    | 2.89                      |
| 1.0 wt% SWCNT PMMA/PS | 0.97                                     | 0.09                                    | 3.01                      |

The higher resolution 5000 times images were compared in order to sample the spectrum around the high-contrast influenced SWCNT characteristic width of 25 – 30 nm with limited pixilation effect. The average scaling parameters determined from the PSDs are shown to fall from the highest average value of 1.37 for the 1.0 wt% SWCNT PMMA specimen followed by 1.22 for the 0.5 wt% SWCNT PMMA/PS specimen to 0.97 for the 1.0 wt% SWCNT PMMA/PS specimen. Through equation 35, these values correspond to fractal dimensions of 2.82, 2.89 and 3.01 for the 1.0 wt% SWCNT PMMA, 0.5 wt% SWCNT PMMA/PS and 1.0 wt% SWCNT PMMA/PS specimens, respectively. The addition of PS to PMMA is shown to improve the resulting dispersion as a result of the addition of an aromatic moiety along a side chain.

The scaling parameter of the 0.5 wt% PMMA/PS specimen was higher than the 1.0 wt% PMMA/PS specimen. The effect of percentage filling material upon the measured scaling parameter is a difficult trend to define. Therefore, an interpretation based upon the given results is presented. The percent-filler trend from 0.5 to 1.0 wt% SWCNT can perhaps be attributed to the observation that a larger percentage of filler material within the same imaged volume yields more occlusion which is reflected in the power spectrum. As the percent filling material increases from 0.5 to 1.0 wt% SWCNT in PMMA/PS, additional occlusion gives rise to surplus information regarding corners, pixilation and edge effects but also relatively more information regarding the nature of the characteristic length of interest and the associated self-affinity. Thus the RPSD is less weighted by the effects of pixilation, edges and corners with additional filling material. This trend is specific to SWCNT (due to the large aspect ratio) and only appropriate over a given range of filling material. The trend will reverse before 5.0 wt% SWCNT filler is reached and is observed as further occlusion produces larger imaged agglomerations. The measured scaling parameter will begin to increase at some point between 1.0 and 5.0 wt % SWCNT when the power spectrum becomes more weighted by pixilation, edges and corners than information pertaining to the characteristic width and related self-affinity. As the percent filler is further increased the sizes of agglomerations amass to an extent outside the range of analysis for the 5000 times magnified images and the trend is again reversed, as indicated in the analysis of the 5 wt% SWCNT PMMA specimen. Also, the effect of saturation and imaging induced damage results in the additional measurement of white noise. These two effects both effectively lower the measured scaling parameter after a given threshold between 1.0 and 5.0 wt% SWCNT has been reached. Therefore, comparison between specimens of different loading amounts can be accomplished after taking the intricate percentage-filler trend into account. The measured scaling parameter indicates an improvement of SWCNT dispersion originating from the favorable interaction between SWCNT and PMMA/PS copolymer over the PMMA homopolymer, a trend visually observed in the images dispersion.

#### *4. Summary*

The standardized procedure developed for analyzing high-contrast images of dispersion provides an essential tool not only to quantitatively measure and compare dispersion within formed nanocomposites but to do so without bias. The measured shape of dispersion, in terms of

the scaling parameter, for these materials was shown to meet the requirement of self-affinity in order to employ the proposed method. Finally, the techniques developed to describe SWCNT dispersion with scaling parameters (Study Two) are consistent with the characteristic lengths (Study One). This in turn will facilitate the modeling and processing of these and similar materials as well as enable the formation of nanocomposites with enhanced physical properties.

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#### 4.0 CHAPTER FOUR: STUDY THREE

##### *“Carbon Nanotube Dispersion within Polymer Nanocomposites: Validation of the Fractal Quantification Method and the Relationship with Enhanced Physical Properties”*

###### *Abstract*

The previous studies provide innovative methods to consistently measure single wall carbon nanotube (SWCNT) dispersion within a hosting material, given that the nanocomposite is susceptible to high-contrast (poly-transparent, high kV or voltage-contrast) imaging and contains relatively low filler content. In an effort to improve the usefulness of those dispersion analysis techniques, the dispersion measured directly from high resolution scanning electron microscopy (HR-SEM) high-contrast images is compared to the measurement of dispersion determined from one state-of-the-art techniques in SWCNT dispersion characterization: small angle neutron scattering (SANS). The approach presented in Study Two provides a measurable quantity proportional to the fractal dimension of the dispersion measured directly from the power spectrum of the high-contrast HR-SEM images and produces an intuitive method and measurement of the SWCNT dispersion quality. This method will be compared to one of the only available methods to measure SWCNT dispersion within a formed composite, SANS. Subsequently, the relationship between the dispersion quality and resulting physical property improvements (Young's modulus and glass transition temperature) as a function of SWCNT content will be investigated for SWCNT-nanocomposites composed of two different hosting polymers; a homopolymer and its copolymer with a monomer containing an aromatic moiety, which is hypothesized to improve the dispersion interaction between polymer and nanotube. The hosting polymer with better theorized SWCNT dispersion qualities is shown to more readily benefit from the addition of SWCNT and indicates that SWCNT dispersion is achieved at the microscopic level.

## *1. Introduction*

The novel dispersion quantification methods previously described would benefit from the validation from one state-of-the-art technique in dispersion characterization, small angle scattering analysis. Similar comparisons have been made to compare dominant length feature measurements between small angle x-ray scattering (SAXS) and Fourier analysis of both TEM images of nanoparticle assemblies [1] and scanning transmission electron microscopy of nanoclay-polymer nanocomposites [2]. Small angle studies have also been used to characterize the fractal dimension SWCNT dispersion in suspensions [3-5], within formed epoxy and ceramic based nanocomposites [6, 7] plus differentiate the characteristic size of colloidal dispersed silica particles [8]. Here, the measured dispersion quality obtained from the method presented in Study Two and small angle neutron scattering (SANS) analysis of the series of thin film SWCNT-polymer nanocomposites are compared.

One motivation to provide and validate a SWCNT dispersion quantification method is to investigate the potential to improve the material properties of a nanocomposite through the selection of hosting materials with traits that encourage improved dispersion [9-15] and physical kinetic mixing [16-21]. Thus the risk of damage to individual SWCNT through excessive kinetic based mixing methods or the addition of catalysts/surfactants intended to produce enhanced dispersion is curtailed [22-48]. The relationship between polymer chemistry, nanofiller and fabrication method with the resulting SWCNT dispersion can be utilized as a tool to evaluate the potential for designing nanocomposites with favorable or tailored physical properties measured at the macro level through attempting to control dispersion at the microscopic level. Furthermore, certain material characteristics of SWCNT nanocomposites, such as the ability to resist dielectric breakdown, may only be realized when dispersion between the nanotubes and individual polymer chains is accomplished at the microscopic (local, nano or molecular) level.

In an effort to correlate dispersion with resulting material properties and investigate the potential to achieve SWCNT dispersion at the microscopic level, the relationship between dispersion quality and material property improvement is investigated for the samples presented in Study Two. Correlating SWCNT dispersion with measured physical properties is inherently difficult when considering nanocomposites composed of percolated networks in which the amount of the hosting material vastly surpasses the counterpart, particularly when the less

prevalent counterpart influences the material properties of interest. Thus, it is desirable to present the relationship between the quantified dispersion and measured physical properties through considering material properties that are conceivably altered directly by the SWCNT dispersion quality and can be measured utilizing methods which adequately correlate a measured parameter with dispersion at the appropriate level.

Here, the relationship between SWCNT content, dispersion quality at the local level and the relative global improvements in glass transition temperature and stiffness are investigated in an attempt to provide a straightforward and fundamental analysis. An improvement in the stiffness, measured in terms of Young's modulus, indicates enhanced reinforcement obtained through inclusion of the structural filler. An improvement in the globally measured Young's modulus may indicate that the SWCNT rather than the polymer chains more prevalently distribute the mechanical load to help retain the thin film nanocomposite's structural integrity. The improvement in the glass transition temperature at low SWCNT loadings can indicate that the SWCNT are readily dispersed through appreciating that the SWCNT efficiently absorb additional thermal energy and store the energy within the sp<sup>2</sup> bonding structure of SWCNT instead of the individual copolymer chains. The ability for the nanocomposite to store this thermal energy as vibrations rather than allow the thermal energy to heat individual polymer chains safely allow the nanocomposite to experience higher temperatures without melting and thus realize an improvement in the global glass transition temperature.

## *2. Materials and Methods*

### *2.1 Materials*

#### *2.1.1 PMMA and PMMA/PS nanocomposites*

The sample set contains the same sample set as analyzed in sample 1. The thin film nanocomposites were created with varying amounts of nanotubes with a polymer and its copolymer, which is hypothesized to result in improved dispersion thorough the addition of an aromatic moiety in the form of a phenyl ring. Polymethylmethacrylate (PMMA), polystyrene (PS) and the copolymer of both (PMMA/PS), shown in figures 1, 2 and 3 of Study Two, were combined with varying amounts of single-walled carbon nanotubes in hopes of creating

nanocomposites with enhanced properties. The two matrices were chosen due to their different hypothesized interaction with SWCNT and the resulting dispersion.

Several thin film nanocomposite samples were fabricated along with the corresponding neat polymers. These samples are summarized in table 1 below.

**Table 1.** *PMMA and PMMA/PS nanocomposite thin films compositions.*

| Sample      | Polymer composition | Percent SWCNT (weight %) |
|-------------|---------------------|--------------------------|
| PMMA 0      | 100 % PMMA          | 0                        |
| PMMA 1      | 100 % PMMA          | 1.0                      |
| PMMA 5      | 100 % PMMA          | 5.0                      |
| PMMA/PS 0   | 70 % PMMA - 30% PS  | 0                        |
| PMMA/PS 0.1 | 70 % PMMA - 30% PS  | 0.1                      |
| PMMA/PS 0.5 | 70 % PMMA - 30% PS  | 0.5                      |
| PMMA/PS 1   | 70 % PMMA - 30% PS  | 1.0                      |

The PMMA and PMMA/PS batches were purchased from Polyscience Inc. and purified high pressure carbon monoxide (HiPCO) SWCNTs (diameter ~0.7 – 1.3 nm) were purchased from Carbon Nanotechnologies, Inc., Houston, Texas. PMMA or PMMA/PS were directly dissolved in a dilute (0.075 wt%) SWCNT- dimethylformamide (DMF) solution within a round bottom flask equipped with a mechanical shear stirring rod and nitrogen gas flowing in and out thorough calcium sulfate drying tubes. The SWCNT-DMF solution was not pre-sonicated before addition to the flask but rather mechanically stirred for 5 minutes before directly mixing the PMMA or PMMA/PS and mechanically stirred for an additional 5 minutes before sonication. The flask was submerged in a water bath and subjected to ultrasonic sonication (40 kHz) during the first four hours of mixing. Additional stirring under nitrogen gas occurred until the presence of moisture was absent within the flask, approximately 24 hours. The solid content of the SWCNT-polymer solution was 15% in DMF. The mixture was then cast onto glass plates and

dried in a dry nitrogen-flowing chamber for 48 hours. Finally, the mixture was cured under vacuum for 5 hours at 60 °C to remove the DMF and acquire self-supporting films.

### *2.1.2 Motivation for PMMA and PS nanocomposite study*

The homopolymer PMMA and copolymer PMMA/PS were chosen for this material study to investigate the potential of selecting a matrix with traits to encourage SWCNT dispersion. PMMA was chosen due to its optical clarity, use as “bone cement” in orthopedic surgery and the hypothesized molecular attraction between the carbonyl group ( $O - C = C$ ) of PMMA and both the open ends of the SWCNT and defect locations along the surface of the SWCNT [49,50]. The copolymer with PS was chosen due the enhanced dispersibility of SWCNT instigated by the intermolecular attraction between the 6 member  $sp^2$  bonded ring on the SWCNT surface and the aromatic moiety in the form of a benzene ring side chain [50]. A benzene ring also contains a 6 member  $sp^2$  bonded carbon ring which is attracted to the six-member  $sp^2$  bonded carbon rings along the SWCNT surface. The 70/30 PMMA/PS concentration was chosen due to the unique ability to disperse SWCNT. The more prevalent PMMA will attract the ends of the SWCNT and the less prevalent PS attracts the surface of the SWCNT. Thus, the ends of SWCNT will preferentially be seated in the more prevalent PMMA and be drawn to seek PS in relatively more localized regions within the copolymer.

## *2.2 Methods*

### *2.2.1 Measuring Dispersion with SANS*

SANS has been effectively employed to approximate the fractal dimension of dispersion for nanotube-solvent suspensions by evaluating the region of constant slope of the SANS logarithmic scattering spectrum. SANS effectively probes the microstructure of materials over the length range of tens of Angstroms to hundreds of nanometers, but access is limited due to cost and accessibility [51]. Dimensional power laws, also known as dimensional scattering laws, are well defined for small angle scattering studies and describe how a given network causes an input signal (a neutron beam in the case of SANS) to scatter with a pattern proportional to the structure of the network. The structure is identified in terms of characteristic dimensional shapes

that form the network and scatter the beam [52]. The shapes are described by the dimension such that a rod is 1D, a disk is 2D and a sphere is 3D. This implies that an object can be characterized by a relation proportional to the characteristic size of the objects composing the network raised to the dimension of the shape. The power law scattering that results is thus defined by the dimension of the scattering objects in terms of a relationship between the scattering angle and scattering intensity  $I(q)$  as a function of Bragg size,  $r$ :

$$I(q) = N(q^{-1}) \cdot n^2(q^{-1}) \quad (1)$$

at a given scattering angle,  $2q$ , where  $q$  is  $r^{-1}$ ,  $N$  is the number of scattering domains,  $[N(q^{-1})]$  is the number of individual scattering elements in a volume and  $[n^2(q^{-1})]$  is the number of electrons in an atom at low angles squared. The Bragg size of the object originates from Bragg's law and can be conceptualized as the characteristic size of the scattering object,  $r$ . The scattering of a rod with characteristic size  $r$  is a function of the diameter,  $D$  and length,  $L$ . The number of scattering elements in a rod is  $L/r$  and the number of electrons per scattering element is  $rD^2$ .

Converting to  $q$  and inputting into equation 1 yields:

$$I(q) = LD^4 \cdot (q^{-1}) \quad (2)$$

Thus, the scattering intensity follows a  $q^{-1}$  decay in intensity for a 1D object. The scattering of a disk with characteristic size  $r$  is a function of the diameter,  $D$ , length,  $L$ , and thickness,  $t$ . The number of scattering domains,  $N$ , is  $rD^2$  and the number of electrons per scattering domain is the volume of the domain,  $tr^2$ . Converting to  $q$  and inputting into equation 1 yields:

$$I(q) = (Dt)^2 \cdot (q^{-2}) \quad (3)$$

The scattering intensity follows a  $q^{-2}$  decay in intensity for a 2D object. The same trend can be shown for 3D objects. Therefore, small angle scattering studies approximate the fractal dimension thorough the following relation:

$$I(q) \approx (q^{-Df}) \quad (4)$$

where  $Df$  is the fractal dimension of the individual scattering objects. Generally accepted fractal exponents for various morphologies and networks used to analyze small angle scattering data is shown below in table 2.

**Table 2.** *Fractal exponents associated with different shapes used to describe SWCNT dispersion with SANS.*

| Fractal exponents for “shapes” in SANS |     |
|----------------------------------------|-----|
| 1D rigid rod                           | 1   |
| Chain with excluded volume             | 5/3 |
| 2D object                              | 2   |
| 3D objects                             | 3   |

### 2.2.2 Specimen characterization

SANS measurements were obtained at the NIST Center for Neutron Research with an 8 meter SANS instrument with incident neutron wavelengths of 10 Angstroms and a target to detector distance of 3.84 meters. After passing through the thin films, the scattered neutrons were summated with a 2D neutron detector. The intensity of the scattered neutrons were radially averaged to produce the total scattering cross section for each specimen.

The tensile properties of the films were evaluated at room temperature and humidity using an Instron 5848 MicroTester outfitted with a 1000 Newton load cell. In an attempt to control the variance in temperature and humidity, the samples were tested sequentially in a closed room. The samples were carefully cut into 3 mm wide rectangular strips using Thwing-Albert Instrument’s JDC precision sample cutter. The specimens were tested according to ASTM 882 with a 30 mm gauge length and an extension rate of 3mm/min. However, only 3 specimens were tested for each composite film due to the limited supply of material also analyzed with SANS. The glass transition temperatures were determined using differential scanning calorimetry (DSC). Three DSC scans were performed on six mg samples with a Setaram DSC 131 in nitrogen atmosphere from room temperature to 120 °C at a rate of 2 °C/min.

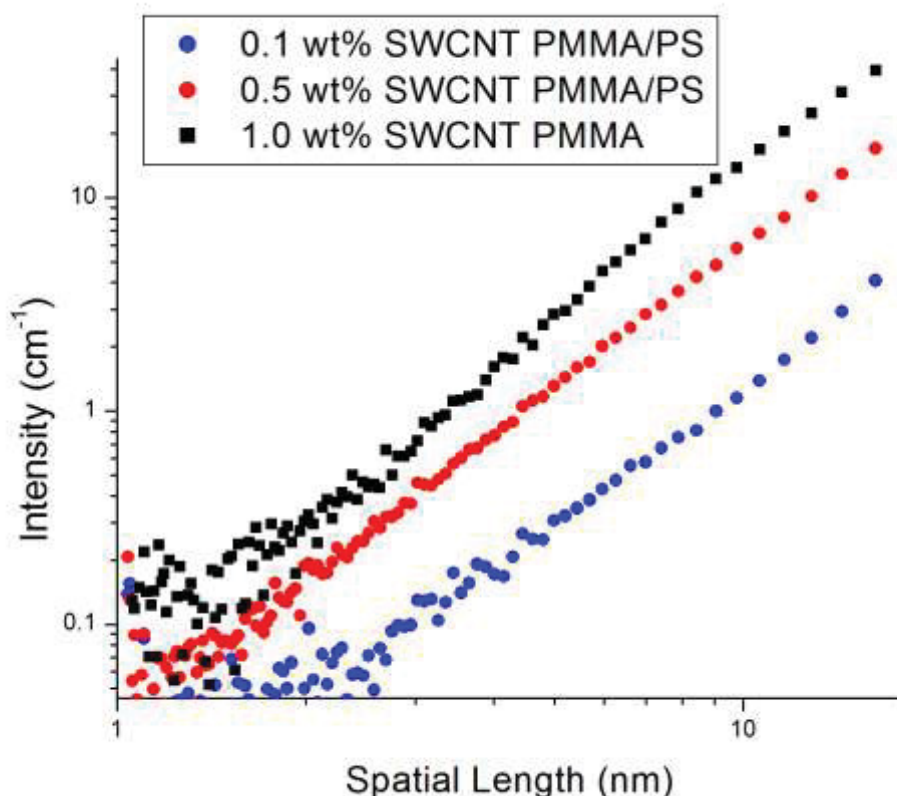
### 3. Results

#### *3.1 Determining the Fractal Dimension from SANS*

As previously discussed, SWNTs thoroughly dispersed in surfactant solutions have been shown to represent rigid rods, as reflected in the power spectrum of the SANS scattering spectrum [3-5]. Furthermore, most scattering measurements of SWNT/polymer composites yield power law dependence with a scaling exponent ranging from 2 to 3 and ascribed to SWNT bundles with a varied distribution of sizes and structures [3-5]. Similar to the RPSD's measurement of a scaling parameter, a lower absolute value for the scaling parameter corresponds to improved dispersion. The neutron scattering intensity as a function of momentum transfer is typically reported in units of inverse Angstroms. Here, the neutron scattering intensity is presented as a function of spatial length to facilitate direct comparison with the previous RPSD plots. The spatial length is expressed here as the inverse of the momentum transfer.

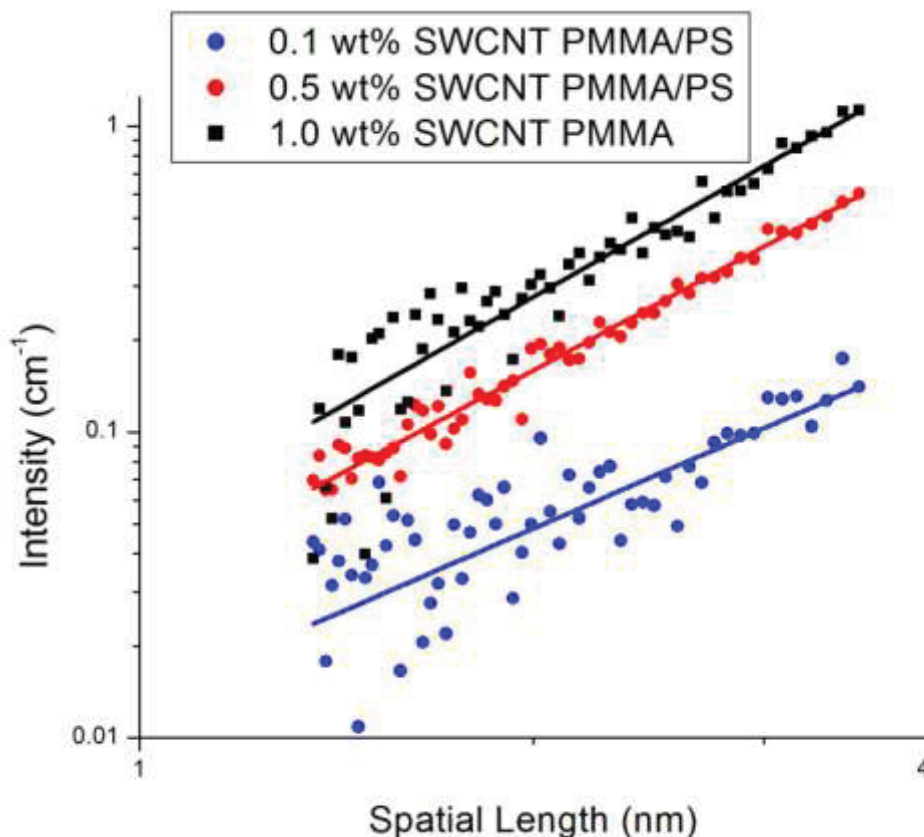
##### *3.1.1 Systematic measurement of the fractal dimension*

The neutron scattering intensity as a function of spatial length over the entire measured spectrum after removal of incoherent background data and correcting for detector efficiency for the samples measured with SANS (0.1 wt% SWNT PMMA/PS, 0.5 wt% SWNT PMMA/PS and 1.0 wt% SWNT PMMA) are shown in figure 1 below.



**Figure 1.** *The neutron scattering intensity as a function of spatial length (inverse of momentum transfer) over the entire measured spectrum for the 0.1 wt% SWNT PMMA/PS, 0.5 wt% SWNT PMMA/PS and 1.0 wt% SWNT PMMA specimens.*

In an effort of standardization, the analysis length window developed to measure the PSD will be utilized to determine the scaling parameter from the SANS scattering spectrum. The full spectrum (112 components) was quartered and the intermediate components (components between 28 to 84). This yields an analysis length window between 1.35 to 3.55 nm. The slope was fit with the same power law function and determined through statistical weighting in the manner utilized for the PSD of the high-contrast images. The SANS scaling parameters (defined as the fractal dimensions of the scattering networks) are determined from the bounded region in figure 2 below to be 1.86, 2.29 and 2.64 for the 0.1 wt% SWNT PMMA/PS, 0.5 wt% SWNT PMMA/PS and 1.0 wt% SWNT PMMA specimens, respectively.



**Figure 2.** *The neutron scattering intensity as a function of spatial length (inverse of momentum transfer) for the 0.1 wt% SWNT PMMA/PS, 0.5 wt% SWNT PMMA/PS and 1.0 wt% SWNT PMMA specimens over a bounded spectrum obtained following the procedure developed for PSD analysis from high-contrast images.*

### 3.1.2 Comparison of SANS and RPSD results

To aid in the interpretation of the relationship between dispersion and material property improvement, the dispersion within the 10,000 times HR-SEM high-contrast images for the 1 wt% SWCNT PMMA homopolymer and PMMA/PS copolymer in terms of the dispersion parameters presented in Study One (table 3).

The resulting trends between specimen and the dispersion parameters measured using HR-SEM RPSD image analysis (from the images analyzed in table 12 of Study Two) and SANS show direct similarities, as demonstrated in table 3.

**Table 3.** *Average RPSD scaling parameter from the high-contrast 5000 times magnified HR-SEM images in Study Two and the fractal dimension determined from SANS.*

| Sample      | Polymer composition | Percent SWCNT (weight %) | Scaling Parameter (RPSD avg.) | Fractal Dimension (SANS ) |
|-------------|---------------------|--------------------------|-------------------------------|---------------------------|
| PMMA 0      | 100 % PMMA          | 0                        | —                             | —                         |
| PMMA 1      | 100 % PMMA          | 1.0                      | 1.37                          | 2.64                      |
| PMMA 5      | 100 % PMMA          | 5.0                      | —                             | —                         |
| PMMA/PS 0   | 70 % PMMA - 30% PS  | 0                        | —                             | —                         |
| PMMA/PS 0.1 | 70 % PMMA - 30% PS  | 0.1                      | —                             | 1.86                      |
| PMMA/PS 0.5 | 70 % PMMA - 30% PS  | 0.5                      | 1.22                          | 2.29                      |
| PMMA/PS 1   | 70 % PMMA - 30% PS  | 1.0                      | 0.97                          | —                         |

The scaling parameter rather than the fractal dimension derived from the scaling parameter as described in Study Two is utilized for comparison with the fractal dimension derived from the SANS scattering spectrum. As discussed in Study Two, the measured value of fractal dimension can only be interpreted as a measure specific to the given definition for fractal dimension. For example, the fractal dimension described in Studies One and Two describe the order of randomness within the HR-SEM images of SWCNT dispersion with an increase in randomness, as indicated by an increased value of fractal dimension, indicating improved dispersion. Alternatively, the scaling parameter in Study Two describes the dimensionality within the image, with a lower dimension indicating better dispersion in terms of straight nanotube lengths and minimal agglomeration.

Study Two proved that the interpretation of the measured values along with a thorough understanding of the analysis method is required to adequately interpret the RPSD results. The

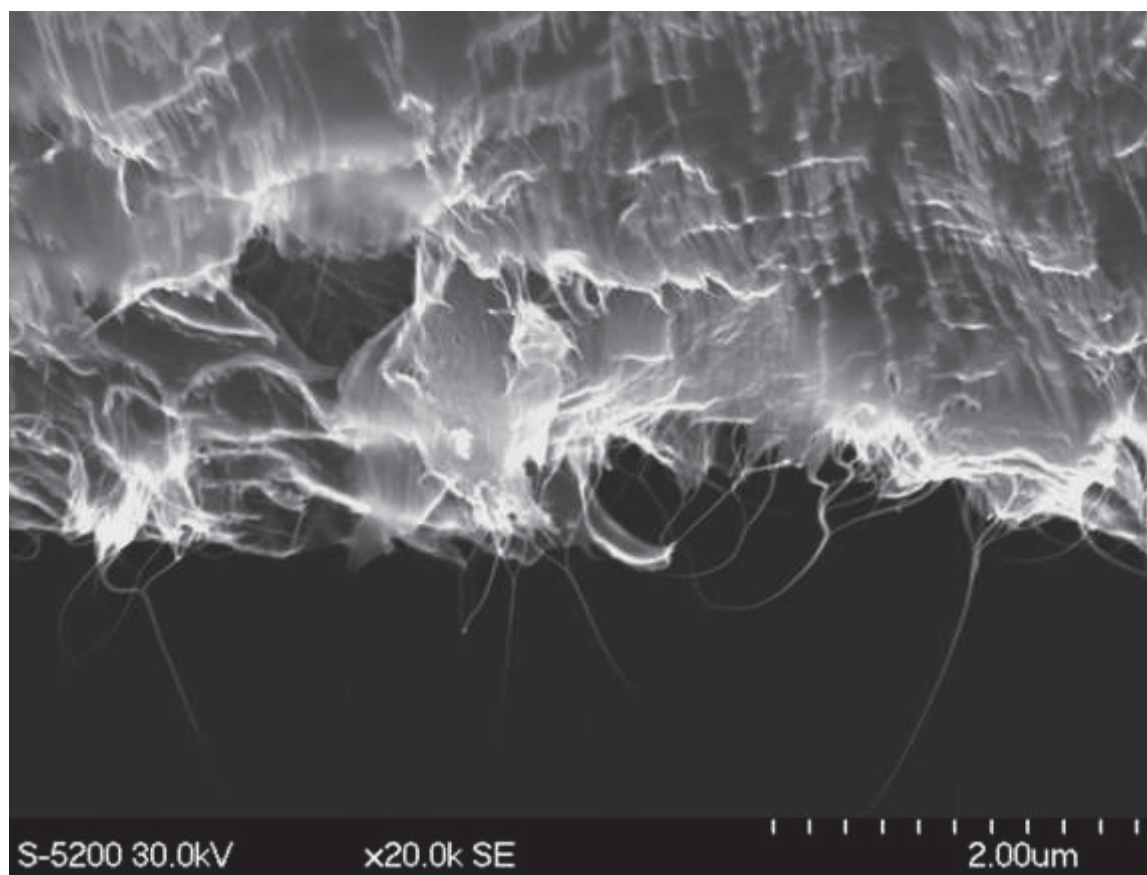
SANS fractal dimension, like the RPSD scaling parameter derived from the HR-SEM images, is a measure of the dimensionality of the structure within the sampled volume, where an improvement in dispersion is reflected by a lower numerical measure. Therefore, the scaling parameter from the RPSD and the fractal dimension determined from the SANS scattering spectrum, or perhaps more appropriately termed as the SANS scaling parameter, will be utilized here for comparison.

The RPSD derived scaling parameter of the 0.5 wt% SWCNT PMMA/PS specimen was observed to be lower than the 1.0 wt% SWCNT PMMA specimen, a trend also seen in the SANS measurements for fractal dimension. Notice the discrepancies between the percent-filler trends between the RPSD scaling parameter and the SANS fractal dimension. As described in Study Two, the percent-filler trend from 0.5 to 1.0 wt% SWCNT in PMMA/PS is attributed to the observation that a larger percentage of filler material within the same imaged volume yields more occlusion contained within the power spectrum of the HR-SEM images. As the percent of the filling material increases, additional occlusion gives rise to surplus information regarding corners, pixilation and edge effects but also relatively more information regarding the nature the SWCNT dispersion. The RPSD is therefore less weighted by the effects of pixilation, edges and corners with additional filling material, a trend specific to SWCNT due to the large aspect ratio and only appropriate over a given range of filling material. The trend will reverse before 5.0 wt% SWCNT filler is reached and is observed as further occlusion produces larger agglomerations contained in the HR-SEM images. The measured scaling parameter will begin to increase at some point above 1.0 wt % SWCNT when the RPSD power spectrum becomes more weighted by pixilation, edges and corners than information pertaining to the characteristic width and related self-affinity. As the percent filler is further increased the sizes of agglomerations amass to an extent outside the range of analysis and the trend is again reversed.

Comparison of the dispersion measured from HR-SEM images between specimens of different loading amounts can be accomplished after taking the intricate percentage-filler trend into account. SANS is not effected by occlusion in the same manner because HR-SEM images contain the 2D projection of a 3D network while SANS probes the actual 3D volume. Accounting for this observation reinforces the result obtained through RPSD analysis of the HR-SEM images in Study Two; that applying the dispersion argument leads to the conclusion that

PMMA/PS copolymer yields more effective SWCNT dispersive properties than the PMMA homopolymer. Furthermore, the results, when taking into account the effects of occlusion, indicate that low SWNT loading favors better dispersion. The SANS data from the 0.1 wt % SWCNT PMMA/PS specimen demonstrates a consistent trend with RPSD results obtained after assuming the SWCNT for this particular specimen represent features upon a three dimensional surface (as previously described in Study Two). The average scaling parameter from the 5000 times magnified high-resolution images is 1.8. Applying the previous argument could allow for interpretation of the scaling parameter as representative of surface features yields a value of 0.8. Consequently, the scaling parameters obtained through SANS follow the same trend as and validate the proposed RPSD method after accounting for the difference in the percentage-filler trends associated with each dispersion quantification method.

Interestingly, the SANS length region containing the assumed characteristic width of the SWCNT (diameter  $\sim 0.7 - 1.3$  nm) in figure 38 indicates the measurement of white noise. Thus, bounding the length analysis region again removes components afflicted by noise. The analysis length window of  $1.35 - 3.55$  nm measures the scattering regime above the assumed characteristic length. This is an option available with the proposed RPSD method when the appropriate image is analyzed. In this case, the most appropriate scaling parameters for comparison are attained from lower resolution 5000 times magnified images with an associated analysis length window of  $27 - 84$  nm (from table 2 of Study Two) for an apparent high-contrast characteristic width between  $25 - 30$  nm. The difference in the characteristic width between the actual SWCNT and the apparent high-contrast characteristic width is emphasized in the cross-section image below.



**Figure 3.** *Cross-section image showing the typical difference in apparent SWCNT diameter between SWCNT pulled out of the specimen and those located within the polymer captured through high-contrast imaging.*

The exposed SWCNT in figure 3 are also artificially swollen due to the effect of HR-SEM imaging and the presumptive coating of crystalized polymer surrounding the extracted SWCNT. Additionally, notice that after extraction individual SWCNTs immediately rebundled with one another. Although the intrinsic rebundling was encouraged by the energy input from the electron beam of the SEM, this highlights the difficulty of separating individual SWCNTs and keeping them separated.

To support the previous results and aid in the interpretation of the relationship between SWCNT network structure and material property improvement, the dispersion within the 1 wt% SWCNT PMMA homopolymer and PMMA/PS copolymer specimens in terms of the dispersion

parameters presented in Study One. The 10,000 times HR-SEM high-contrast images were analyzed following the methodology presented in Study One and the results are shown in table 4 below.

**Table 4.** *Dispersion parameters for the 1 wt% SWCNT PMMA and PMMA/PS specimens.*

| Sample              | Bundle diameter (nm) | Segment length (nm) | Bundle spacing (nm) |
|---------------------|----------------------|---------------------|---------------------|
| 1 wt% SWCNT PMMA    | $73 \pm 45$          | $205 \pm 162$       | $483 \pm 138$       |
| 1 wt% SWCNT PMMA/PS | $34 \pm 17$          | $372 \pm 135$       | $115 \pm 15$        |

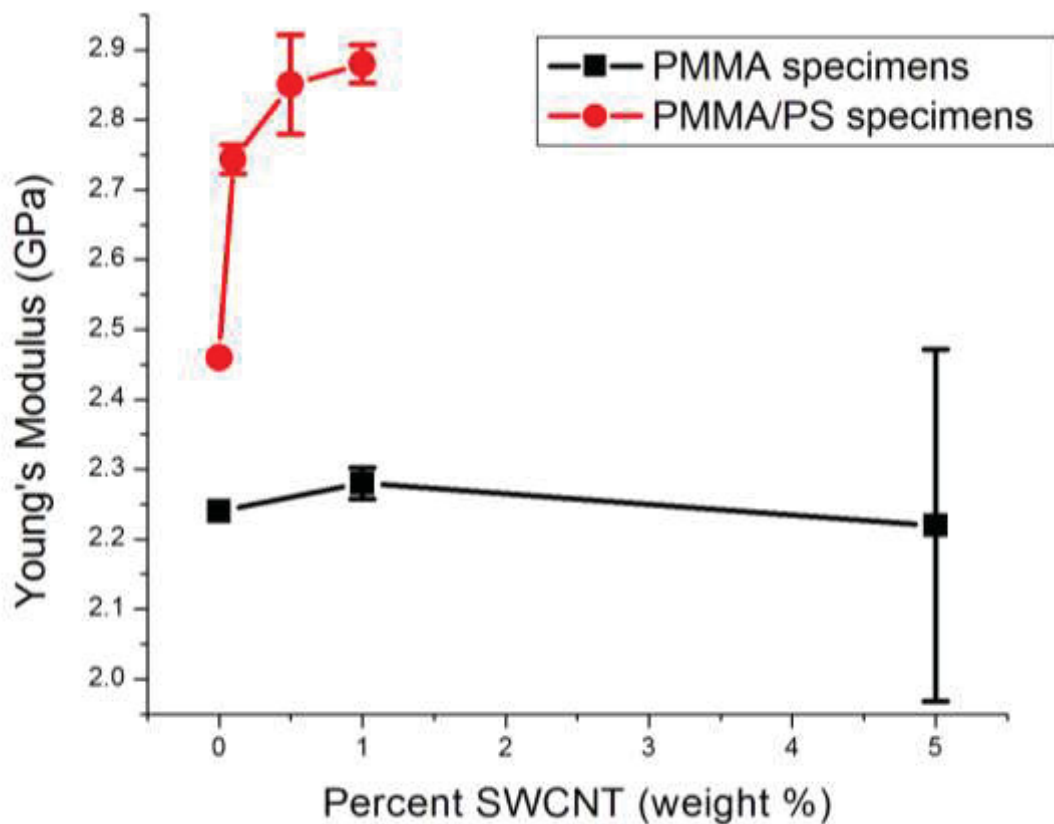
The results from table 4 support the previous results and show that the copolymer yields dispersion parameters which indicate much better dispersion than the homopolymer. The smaller bundle diameter associated with the copolymer indicates better SWCNT separation. The segment length measured from the copolymer system indicates a SWCNT network with straighter and longer SWCNT. The copolymer's ability to resist the agglomeration and produce uniform dispersion is demonstrated by the lower bundle spacing and smaller overall variance for the parameters measured in table 4. Finally, the stability in the parameters measured from HR-SEM images of dispersion captured over a period of 4 years indicates that the composites are thermodynamically stable overtime when exposed to standard room conditions.

### *3.2 Material properties*

#### *3.2.1 Tension test*

Determining the mechanical properties of the PMMA and PMMA/PS polymer nanocomposites were limited by premature failure. The integration of SWCNT into a copolymer of PMMA/PS and evaluating their mechanical properties with a tension test proved difficult due to the severe brittleness of the samples. Cracks would often form during fabrication of the PMMA/PS copolymer samples compounding the difficulty of handling associated with loading

the specimens into the testing module. Conversely, cracks did not form in the fabrication of the homopolymer, PMMA, and the tensile strength was revealed to remain relatively constant with increasing carbon nanotubes percentages, hovering around 50 MPa. Premature failure as a result of handling difficulty due to brittleness can underestimate the ultimate tensile strength and failure strain. The tensile strength and strain measurements of the copolymer specimens produced erratic results due to the limited amount of sample material available for tensile testing (three samples of each specimen). Therefore, only the Young's modulus in terms of SWCNT percent filler by weight is presented for both PMMA and PMMA/PS based nanocomposites (figure 4).



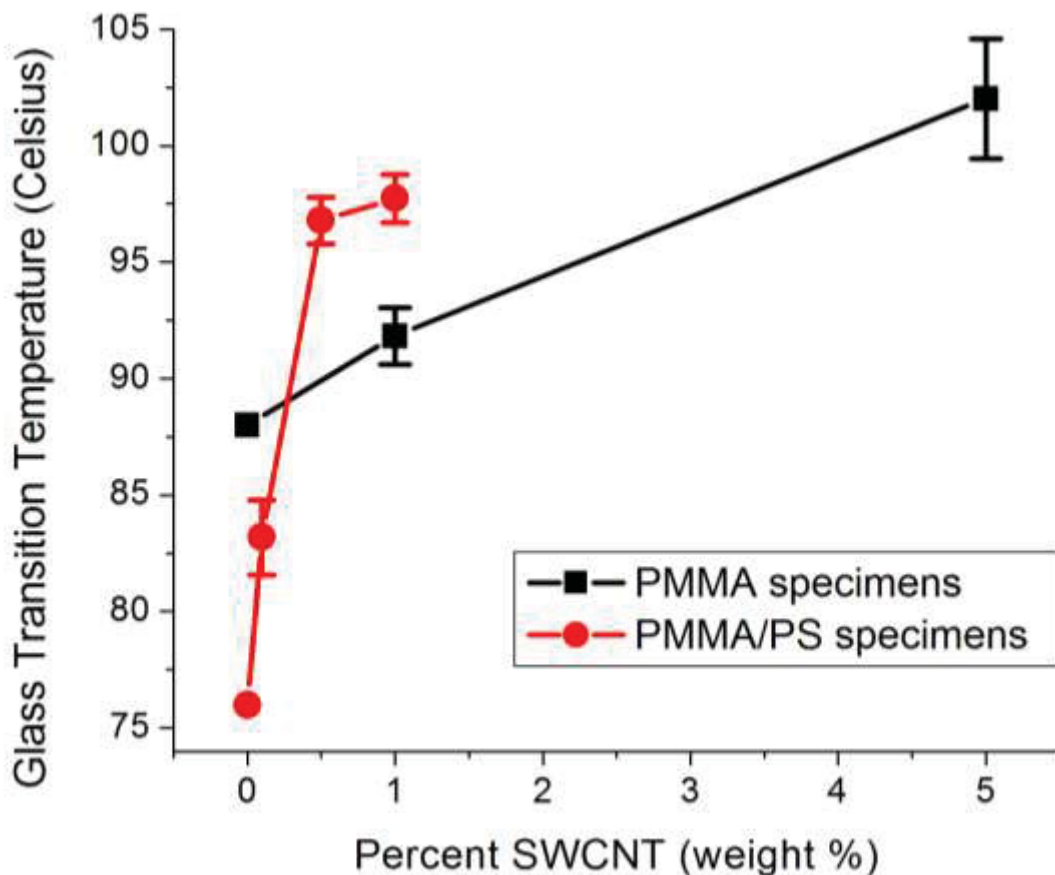
**Figure 4.** Young's modulus as a function of SWCNT content (weight percent) for the PMMA and PMMA/PS nanocomposites.

The Young's modulus of the PMMA-based specimens gradually increased 1.8% through the addition of 1.0 wt% SWCNT, but remained rather stagnant as the percentage of SWCNT was increased to 5.0 wt%. Notice the variance in the measurements for the 5.0 wt% sample. This observation, along with the fact that the overall modulus dropped, can be attributed to the agglomerations and associated inconsistency of SWCNT dispersion within PMMA at higher loading (5.0 wt%). Alternatively, the Young's modulus of the PMMA/PS-based specimens increased dramatically (11.5%) from 0 wt% to 0.1 wt% SWCNT and reached an overall increase of 17% for the 1.0 wt% SWCNT PMMA/PS specimen.

The interaction between hosting polymer and SWCNT can be generalized as the mechanism which allows the transfer of some properties of the nanomaterial to the bulk nanocomposite. Accordingly, the improvement in Young's modulus can be attributed to the notion that enhanced dispersion of SWCNT within the hosting polymer increases the interfacial area and yields superior energy transfer between individual SWCNTs and polymer chains. Thus, the results from tension testing also indicate that the PMMA/PS copolymer is dispersing the SWCNT better than the PMMA homopolymer.

### *3.2.2 Glass transition temperature analysis*

The change in glass transition temperature ( $T_g$ ) as a function of the SWCNT filler content is shown below in figure 5.



**Figure 5.** Glass transition temperature as a function of SWCNT content (weight percent) for the PMMA and PMMA/PS nanocomposites.

The glass transition temperature of the homopolymer PMMA increased over 16% from 88 °C to 102 °C through the addition of 5 wt% SWCNT. The copolymer PMMA/P showed dramatic glass transition temperature increase of almost 29%, increasing from 76 °C to almost 98 °C through the addition of 1 wt% SWCNT. Notice that the largest variance is present in the 5.0 wt% SWCNT PMMA specimen, again indicating the largest global variance in SWCNT dispersion and the associated agglomerations of polymer and SWCNT.

The dramatic increase in the glass transition temperature at low SWCNT loadings within PMMA/PS copolymer indicates that the SWCNT are dispersed better at the microscopic level. The glass transition temperature is considered as the temperature at which the glassy regions of

the polymer lose their rigidity. This transition occurs when the molecules composing the polymer in the glassy regions begin to rotate about their backbone. The addition of the SWCNT into the polymer inhibits the rotational motion of the polymer molecules and increases the glass transition temperature. Thus, the glass transition temperature results also indicate that the copolymer PMMA/PS copolymer disperses SWCNT better than the PMMA homopolymer.

#### *4. Summary*

The scaling parameters measured from high-contrast images were validated with a current state of the art SWCNT dispersion analysis method, SANS, but in a very rapid manner that is not as limited by cost or availability. The results from the tension and glass transition temperature experiments show correlation of superior dispersion not only with improved Young's modulus and glass transition temperature but with much more rapid improvement with much less nanofiller. The measured scaling and dispersion parameters, results of physical property characterization and the observation that the copolymer-based nanocomposite realized a dramatic increase in glass transition temperature with an order of magnitude less SWCNT filler content when compared to the homopolymer-based nanocomposite, equivalent in terms of fabrication method and SWCNT amount, indicates that SWCNTs are dispersed within the copolymer at the microscopic level. This can be conceptualized by attributing the polymer's resistance to melting at the molecular level to the SWCNT's ability to inhibit the motion of the polymer backbone. Accordingly, the effect of dispersion upon the glass transition temperature is an effective experimental method to validate SWCNT dispersion at the microscopic level.

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## 5.0 CHAPTER FIVE: CONCLUSIONS

The numerous motivations and effectiveness of incorporating nanotubes into polymers to form unique nanocomposites with material properties derived from both constituents have been well documented. The relationship between the fabrication methods and resulting materials properties has also been investigated. However, understanding the influence of dispersion upon the resulting material properties of the nanocomposites has been hindered by the lack of an appropriate imaging technique to visualize the SWCNTs and the ability quantify dispersion in terms of parameters descriptive characteristic features. The incorporation of high-contrast imaging and the quantification techniques presented here facilitates the assessment of the nanostructure's influence upon the material properties. Analyzing the power spectrum of SWCNT polymer nanocomposites obtained from high-contrast HR-SEM images provides a unique method to quantitatively assess SWCNT dispersion in terms of descriptive length parameters.

Evaluating the scaling parameters associated with the images of dispersion within formed nanocomposites allows for a measurement describing the shape of SWCNT dispersion. A relatively consistent scaling parameter obtained over numerous locations provides a single descriptive measure of the bulk dispersion, and the variance of scaling parameters is suitable to interrogate the variance of dispersion throughout the material. The technique to measure the scaling parameters was validated with one of the state of the art dispersion quantification techniques, SANS. Notably, analogous information was obtained from high-contrast HR-SEM images of dispersion collected from electrons emitted from the SWCNT network and neutrons scattered by the SWCNT network as they traveled through bulk nanocomposite material. The developed method's inclusion of images with the analysis of dispersion may prove to corroborate dispersion analysis methods that, similar to SANS, do not have the ability to visualize the interrogated system and therefore may aid in the interpretation of results.

The utilization of the presented quantification methods will facilitate measuring the dispersion of other types of nanomaterials, quantifying alignment and analyzing other forms of data. These methods may also prove useful in validating models that describe such nano-

percolated composites near the percolation threshold in terms of characteristic lengths, such as bundle width and separation distance, and a measure of the scaling parameter. Such models would further the effectiveness of other dispersion interrogation techniques which to not include a method to visualize the nanostructure, such as ellipsometry or nuclear magnetic resonance imaging.

The relationship between the dispersion quantified using the proposed methods and experimentally measured physical property improvement as a function of SWCNT amount was investigated. It was shown that the developed quantification methods adequately represent SWCNT dispersion quality and superior dispersion parameters correlate with enhanced material property improvement for the sampled nanocomposites.

## APPENDIX A: High-Contrast Imaging Procedure

### *A.1. General HR-SEM Procedure – Specific to Hitachi S-5200 High Resolution Scanning Electron Microscope.*

The following is the general procedure to operate the Hitachi S-5200 high-resolution scanning electron microscope, originally written by Peter T. Lillehei of NASA Langley Research Center in and slightly modified here to account for operational changes since 2007.

1. Prepare sample.
  - Mount on specimen stub using silver paste or load a thin film specimen into the TEM grid holder.
  - If the sample has silver and you need to do EDS use gold paste.
  - Do not use graphite paste, or conductive carbon tape.
  - Use the appropriate specimen stub for the sample. The various stubs have starting heights from - 2.0 mm to +1 mm.
  - Maximum sample height is +2.0 mm.
  - Use a thin sample stub if your sample is thick to prevent losing the sample in the exchange or vacuum chamber
  - All paste must dry for a minimum of 24 hours prior to use.
2. Record sample height from height gauge.
3. Insert sample into sample rod.
  - Shake the sample rod to make sure the sample is secure.
  - If anything is loose at this point stop.
  - Give the sample a puff of air to make sure it will not dislodge. This step is especially important on powder samples.
4. Fill the LN2 trap with liquid nitrogen following appropriate safety protocol.
5. Log into the computers.

6. Start the software on the main computer.
7. Open the Stage Control window.
8. Set the restriction to the appropriate holder.
  - STD Holder = S-5200 Standard, S-5200 STEM, S-5200 FIB.
  - Cross-Sect Holder = S-5200 Cross Section.
9. Set tilt on the Restriction if necessary.
  - Maximum T for STD = +/- 35 <- NOTE: MAXIMUM LIMITS FOR SAFE OPERATION. It is possible to set +/- 40 but may result in an electrical short and automatic shutdown.
  - Maximum T for Cross-Sect = +/- 10.
10. Make sure the Stage is in the Home position.
  - Press the home icon on the main panel.
  - Alternatively, press the Go to Home button on the Stage Control.
11. Insert sample rod.
  - Remove shipping rod - gently pull straight back, turn clockwise, pull straight back more, turn counter clockwise, wait for evacuation (evac) light to flash, toggle switch to air, wait for pressure to equalize, remove the shipping rod.
  - Inset sample rod, toggle switch to evac, wait for light to flash, turn clockwise, gently guide rod into the chamber, turn counter clockwise, and move rod to final position.
  - If the evac light stops flashing while at the exchange position toggle to air and then back to evac to start the process again. The light must be flashing to make the clockwise turn.
  - If any alarms sound during this process please stop.
12. Open the Column Set-Up
  - Enter the height of the sample.

- Select the appropriate Lens combinations.
- 7,2 good for most imaging (best for STEM).
- 12,2 good for high resolution imaging in SE.
- Higher Lens numbers mean smaller beam spot sizes and better resolution, but a less intense beam and more tedium when adjusting the focus and stigmatism.

### 13. Check the remaining settings

- Image Set-Up: Set Capture Speed/Integration to desired parameters, make sure auto increment is checked.
- Data Display: Time, Auto Increment, Back Ground Image, “For photograph” should not be checked, all others should.
- Signal Select: All dropdown menus should read SE (select TE here later if doing STEM).
- Signal Processing: 8, 256, SE, Off.
- If using Energy-dispersive X-ray spectroscopy (EDAX), Enable Analysis mode: then check DBC box.

### 14. Click in the Vacc box to bring up the HV Control

- Flash now if needed (check log book for error messages).

### 15. Select appropriate Vacc and Ie settings.

- NT/poly: 0.5 - 1.5 keV, 10 - 30 uA. Best for E-field imaging.
- Conductive samples: 5 keV - 15 keV, 10 - 30 uA.
- Non-conductive samples: < 1 keV, 5 - 30 uA (sometimes low voltage high current works).
- EDAX: find heaviest element's spectral line of interest and multiply by at least 2 to set Vacc, use as high of a current as the sample will tolerate. For most samples normal probe current is sufficient, this is set in the Column Set-Up.
- STEM: 20 - 30 keV, 10 - 30 uA.

### 16. Turn the high voltage (HV) on.

- Verify the settings on the warning box and note the operating limits.
  - Notice the HV light is lit on the column of the HR-SEM (always ensure this light is off when changing samples).
17. Record all data in the log book.
18. Open the Alignment window.
19. Set focus and stigmatism as best as possible then select Beam Align.
20. Center beam spot in lens aperture (not necessarily aligned with software target).
21. Select Aperture Align.
- Adjust settings until image movement is as small as possible.
22. Select off and re-adjust focus and stigmatism.
23. Select Stigma Align X.
- Adjust settings until image movement is as small as possible.
24. Repeat for Stigma Align Y.
25. Select Off.
26. Adjust focus and stigmatism at a magnification higher than the max you will be using.
27. Start imaging:
- Use the track ball to move to new locations.
  - Use the image shift if the motor's movement is too large.
  - Use the Raster Rotation to rotate the image.
  - Use the Signal Select to select TE for STEM imaging.

- Use the Signal Control for COMPO imaging or to filter the SE.
- Use the Set Detectors to select the main SE/BSE detector, the dedicated YAG-BSE, or to mix the detectors (Note: the main SE detector collects BSE as well and this is used for the COMPO and filtered SE).
- Monitor the current, which will vary after flashing (this will happen for the first few hours after a flash) re-adjust as necessary.
- Note: Do not click the 'Preset' button above the 'H/L' button. It will destroy all the current alignment parameters and they will all have to be re-aligned. Also, do not change mechanical apertures for alignment except the STEM aperture. If you think they need adjusting please stop and notify the person in charge of the equipment.

28. Start taking lots of pictures.

- Save pictures to your directory.
- Use an appropriate file name, preferably using less than 8 characters (do not use the underscore "\_" in the name).
- Don't close the Captured Image window until files are saved to the disk, the images will be lost.

29. When finished turn off HV.

30. Return to the home position.

31. Remove the sample rod.

- Gently pull straight back, turn clockwise, pull straight back more, turn counter clockwise, wait for evac light to flash, toggle switch to air, wait for pressure to equalize, remove the sample rod.

32. Inset Shipping rod

- Toggle switch to evac, wait for light to flash, turn clockwise, gently guide rod into the chamber, turn counter clockwise, and move rod to final position.

- If the evac light stops flashing while at the exchange position toggle to air and then back to evac to start the process again. The light must be flashing to make the clockwise turn.
- If any alarms sound during this process please stop and notify the person in charge of the equipment.

33. Remove sample from the sample rod.

34. Make sure all images are saved.

35. Close the SEM software.

36. Log out of the computer

37. Record any comments in the log book.

38. Clean up

*A.2. High-contrast (high-kV or voltage-contrast) Imaging Procedure - Procedure for high-contrast imaging builds off of the previous HR-SEM Procedure*

High-contrast (high kV or voltage-contrast) imaging is a method to observe embedded nano-structures, such as Single Wall Carbon Nanotube (SWNT) networks, within a polymer matrix. Imaging the interior of a nano-composite housing a conductive nano-array within a polymer matrix can be achieved by means of a Hitachi S-5200 High Resolution Scanning Electron Microscope (HR-SEM). High-contrast imaging allows one to see through the polymer matrix as if it were invisible making the SWNT network clearly observable deep within the composite. Under optimum conditions, it is feasible to image the nano-structure as deep as roughly 1 micron into the host polymer. High-contrast imaging yields a much more accurate depiction of actual SWNT dispersion when compared with more traditional HR-SEM electric

field imaging. This procedure has been repeated on a variety of other scanning electron microscopes.

1. Follow the procedure for mounting the sample and calibrating the HR-SEM software as described procedures for high resolution scanning electron microscopy.
  - For most situations, the operator should select 7 for the first lens option and 2 for the second.
  - Additionally, a 160 second scan will yield the clearest, deepest images.
2. The nano-composite conductive substructure will be visible under a narrow range of voltage settings.
  - The conductivity of the material is a controlling factor for the required voltage.
  - The voltage that will be necessary to image the substructure increases with the resistivity of the composite.
3. Tune the HR-SEM to a current of 20  $\mu\text{A}$  and the approximate high-contrast viewing voltage – between 15 kV – 30kV – depending upon your sample.
  - If the sample is not thoroughly conductive it will burn in the chamber so be careful when imaging a new material.
  - Turn on the electron beam.
4. Select a slow scan option to slow the beam down and increase your intensity/area.
  - Before aligning the beam attempt to roughly focus the image.
  - The conductive substructure will appear white and the polymer will appear black.
5. Aligning the beam and tuning the stigmatism is difficult under the high voltages necessary for high-contrast imaging.
  - After roughly focusing the image as best as possible at a low magnification, navigate to either a visible surface feature, such as a particle of debris, or some other visual component of the nano-component such as a nano-structure element located upon or near the surface.

6. Under the fast scan viewing option, tune the alignment and stigmatism so that visible feature comes to rest.
  - This may be difficult because the conductive structural feature will not be easily recognizable because it may does not emit many secondary electrons under the fast scan setting.
  - In general, as the electron beam voltage increases, the amount of secondary electrons generated decreases.
  - Therefore, it is a better to first tune the alignment and stigmatism using a particle of debris before navigating to a conductive structural component.
7. Now that some structural component is aligned and the beam is stable, it is time to focus upon the object.
  - Select the slow scanning option and adjust the focus until the conductive subsurface objects become visible as white features within a black host polymer.
  - The polymer should appear as invisible allowing one to see relatively deep into the nano-composite.
8. If the polymer is still visible and effectively blocks the operator from imaging the sub-surface features, try a higher voltage or current and repeat the previous steps.
  - If the substructure is not distinctly visible or the polymer rich areas are saturated with trapped electrons causing the polymer rich areas to fade to gray and eventually block the visualization of the subsurface components, try to decrease the voltage or current and repeat the above steps until the subsurface features become distinct.
  - In order to utilize high-contrast imaging an optimum setting for voltage and, to a lesser extent, current for each sample must be determined.
  - The optimum settings lie somewhere between imaging the polymer surface and imaging a gray, fuzzy, electron saturated polymer.

9. After successfully imaging of some subsurface feature at a relatively low magnification the operator should increase the magnification to about twice the desired imaging magnification and repeat the steps for tuning the alignment, stigmatism, and focus.
10. Before capturing any pictures, the operator should use the auto contrast and brightness command to capture the entire range of contrast over the imaging window, which will ensure that deepest subsurface features can be recognized.
  - However, the auto contrast and brightness command should be utilized over an area of which the operator is not capturing pictures and that contains no particles of debris.
  - This command can quickly saturate the polymer material with electrons creating a gray, fuzzy image as the polymer becomes somewhat visible.
  - Using this command while a particle of debris is located in the imaging window will effectively set the brightest element in the frame to the particle and not the nearest, most conductive subsurface element.
  - The auto contrast and brightness command should be employed during the slowest of the slow scans.
11. Capturing images of the subsurface material is best accomplished by means of the slowest slow scan and may take a few minutes.
  - However, if the polymer becomes saturated with electrons and fades to gray, the voltage or current may need to be reduced.
  - This is a sign that the sample is too resistive for the current electron beam.
  - Alternatively, the operator can choose to capture an image using a faster slow scan but will sacrifice picture quality.
  - Sometimes it may be desired to image the surface characteristics as well as the uppermost subsurface features. This can be accomplished by using the slower fast scan where the image slowly materialized into the imaging window.
  - Finally, be sure not to perform the fine-tuning of the alignment, stigmatism, and focus on the desired screenshot area in order to prevent polymer saturation. It is

recommended that the fine-tuning of the alignment, stigmatism, and focus be carried out over an adjacent area that is of the same general height.

#### *A.2.1. Considerations*

In order to capture the clearest high-contrast images, it is important to realize that the time the electron beam is aimed on an imaging area and the voltage/current of the electron beam directly relate to the amount of electrons absorbed by the polymer over that given area. As the scanning time, voltage or current of the electron beam increases, the polymer increasingly absorbs electrons that have no channel to ground. As the electron saturation of the polymer increases, the polymer becomes progressively more opaque and the image will gradually lose focus. The ability to observe the nano-structures within the sample will be seriously limited as the polymer saturates. The operator must then move to another location or remove the sample from the HR-SEM for a given period of time (hours) and let the polymer naturally de-saturate in order to capture clear images.

The high voltage electron beam necessary to permit high-contrast imaging is directly related to the conductivity of the sample. If the subsurface structural component is not adequately conductive, dispersed throughout the composite, or connectively networked to ground, it may not be possible to utilize high-contrast imaging with the present maximum electron beam voltage and current limitations of HR-SEM.

#### *A.3. Procedure for Constructing Three Dimensional High-contrast Images*

3-D imaging of the subsurface network is accomplished by means of HR-SEM with stage tilting capabilities. Two images captured at opposite tilt incidences, painted appropriately and morphed together will yield a picture that can be viewed three dimensionally using the appurtenant 3-D viewing device.

1. Follow the procedure for high-contrast imaging in order to view the subsurface structure of a selected area.

2. Choose an area to reconstruct as a 3-D image.

- Be sure to choose a magnification large enough to adequately reconstruct the 3-D image.
- A suggestion would be to choose a magnification so that the imaging screen width is about one to five times the maximum imaging depth.
- Choose an area with some recognizable subsurface features.
- It is a good idea to choose an imaging area where at least one of the recognizable features is located in a corner and the center of the viewing window.
- Be sure to capture an image of the desired screenshot area for reference.

3. Using the Raster Rotation, rotate the screen by 90 or  $-90$  degrees.

- This will allow the beam to scan the imaged area in a fashion that is necessary for upright 3-D reconstruction with red/blue or red/green glasses.
- An alternative to rotating the sample is so simply rotate the finished 3-D image by 90 or  $-90$  degrees.
- Rotating the sample prior to capturing the images will yield a wider 3-D image.

4. Using the tilt control function, tilt the sample by some prescribed angle.

- It is recommended to use the same tilt angles ( $25^\circ$  &  $-25^\circ$ ) so that both images are compressed by the same amount, assuming that the surface is relatively level.
- Most 3-D reconstruction literature recommends a total change in tilt of  $7^\circ$ . However, it has been determined that a  $50^\circ$  difference ( $25^\circ$  &  $-25^\circ$ ) creates the most dramatic high-contrast 3-D images.
- A suggestion would be to capture a series of screenshots over a range of tilts in order to determine the optimum difference in tilt for a specific composite.
- As the sample is tilted, the operator must use the scrolling control to keep the desired screenshot area in view.

5. After the stage has been titled, follow the procedure for tuning the alignment, stigmatism, focus, contrast, and brightness as described in the procedure for high-contrast imaging.
  - It is recommended that the center of the image be given the most consideration when focusing.
  - See the considerations within the procedure for high-contrast imaging.
  - Make sure the area utilized for fine-tuning the alignment, stigmatism, focus, contrast, and brightness is adjacent to the desired screenshot area but also is located the same distance from the axis of rotation in order to maintain the same general distance from the final lens and prevent polymer saturation.
  - For best results, capture an image of the desired screenshot using the slowest of the slow scans.
6. Using the tilt control function, tilt the stage by the opposite amount (-25° image was previously captured).
  - Again, as the sample is tilted, the operator must use the scrolling control to keep the desired screenshot area in view.
  - Again, follow the procedure for tuning the alignment, stigmatism, focus, contrast, and brightness as described in the previous step.
  - Capture an image of the desired screenshot.
7. Reconstructing the 3-D picture can be accomplished by means of any number of imaging programs.
  - Most red/blue and red/green glasses position the red lens over the left eye.
  - Therefore the image captured under negative tilt should be painted red while the image captured under the positive tilt should be captured as blue or green.
  - These two images should then be morphed together and aligned to each other.
  - Attention should be given to ensure that the centers of the images are perfectly aligned.
  - The images come to three-dimensional life while wearing the appropriate 3-D optics.

#### *A.3.1. Considerations*

In order to reconstruct paramount 3-D pictures, the electron beam must scan the imaged area minimally in order to curtail the polymer saturation. A 3-D image created from captured images with electron-saturated polymer will appear foggy, out of focus and will dramatically limit the optical depth. Finally, in order to reconstruct the full screenshot, it is important to ensure that some artifact is located in the direct center of both stereo pair images.