

Understanding the Influence of Non-covalent Interactions and Nanoparticle Geometries in Carbon Based Polymer Nanocomposites

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DEDICATION

*To Lesley Paige,
My love, my rock, my green route companion.*

*To Anderson,
Behave or I'll make you read this one day...
...and there will be a quiz.*

I love you both more than you know!

—BC

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ABSTRACT

Low-loading polymer nanocomposites (PNC) are an area of great interest in polymer science. As nanoparticles (NP) are typically expensive in comparison to matrix materials; the low loading regime makes the most efficient use of materials, and represents the optimum for realizing cost effective, high-performance PNCs. However, formulating effective low-loading composites is not without challenges. In addition to the typical requirement of good dispersion for efficient translation of NP properties to the bulk, low-loading composites can sometimes exhibit anomalous (non-classical) dynamics, and unpredictable properties. It is within this context that this thesis aims to examine the effects of NP geometry and softness on the occurrence and nature of anomalous melt dynamics in low-loading PNCs.

The first project presented in this thesis outlines the synthesis and characterization of few-layer graphene (FLG) used in subsequent dynamics studies. From graphite to exfoliated graphite oxide, chemically reduced FLG, and annealed FLG; composition and optoelectric persistence width were tracked through elemental analysis and Raman spectroscopy respectively. A profilometric analysis of some samples was performed using atomic force microscopy. Finally, spectroscopic and compositional information were combined with a geometric growth model to yield a scaled empirical formula that is simultaneously indicative of both compositional purity and optoelectric grade.

Next, PNC melt dynamics were probed for low-loading PNCs filled with fullerenes, carbon nanotubes, and FLG. Graphitic nanoparticles with at least one common dimension, an identical series of styrene-acrylonitrile co-polymers matrices, and identical composite processing conditions were used to form a *ceteris paribus* assessment of the effect of NP geometry on PNC melt dynamics under conditions favorable for anomalous viscoelastic behavior. Rheometry and NMR relaxometry were used to probe the dynamics on both the bulk and local scale. Bulk and local, segmental dynamics were combined to create segmental scale model (with and without attractive NP-polymer interactions) describing the origin of anomalous viscoelastic behavior in the bulk.

Finally, neutron reflectivity was used to probe matrix self-diffusion in low-loading PNCs of polystyrene (PS) filled with novel, PS-based, soft, nanoparticles. The effect of NP softness on the diffusive dynamics in PNCs is examined.

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CHAPTER 1

INTRODUCTION

1.1 Polymer Nanocomposites

1.1.1 Introduction and Background

In the world today there is an ever increasing demand for new and varied high-performance materials. As industry strives to produce goods and technologies that are smaller, lighter, stronger, smarter, and more energy efficient, there is a perpetual need to develop the materials required to achieve these engineering goals. Though early synthetic polymers could not compete with traditional materials like metals, stone, and silicate glasses for most engineering purposes, advances in polymer synthesis, polymer blending, and polymer composites, brought polymers to the forefront of industrially significant engineering materials. Polymer composites consist of a polymer matrix filled or embedded with one or more chemically different fillers, producing a new material with properties different from any individual component. An early example of an industrial significant polymer composite is the use of carbon black filler in tires and other vulcanized rubber products to improve wear resistance.¹ Due to their relative ease of processability and the ability to create materials with widely varied properties, polymer composites have become a ubiquitous part of modern society.

Recent years have brought about the genesis of a new branch of material science focused specifically on nanoscale materials. Nanomaterials or nanoparticles refer any material or particle having at least one dimension on the scale of 1 to 100 nanometers² and can have very interesting properties that are different from those of their macro and micro scale analogs. Nanoparticles vary widely in type and structure and can have favorable optical, electrical, thermal, chemical, or mechanical properties that are unique to the nanoscale. However, these unique properties can be

difficult to translate to the larger scale materials required for most applications. Polymer nanocomposites (PNC) consist of a polymer matrix and nanoscale filler. Relative low cost, versatility, and ease of processing make PNCs an aptly suited vehicle for capturing nanoparticle properties in “application-scale” materials.

1.2 Properties and Composites of Nanoparticles in Study

1.2.1 C₆₀ Fullerenes

Ever since their discovery, C₆₀ fullerenes, and derivatives, have been of great interest to the scientific community due to their thermal, electrical, optical, and photoelectronic properties. The buckminsterfullerene or C₆₀ was first reported by Kroto and Smalley in 1985³. Using time-of-flight mass spectrometry they detected the stable 60 carbon structure from laser vaporized graphite and proposed a 32 face truncated icosahedral cage structure. The first scale synthesis for producing usable quantities of C₆₀ and confirmation of the spheroidal structure was reported in 1990⁴. Extensive work has been done to examine C₆₀ for its non-linear optical properties⁵⁻⁷ and for the possible use of C₆₀ and derivatives in organic photovoltaic polymer films and other organic electronic polymer composite applications⁸⁻¹¹. Additionally, solid C₆₀ is a semiconductor but can be made conductive through doping and even be made to exhibit high-temperature (33K) super-conductivity⁷.

1.2.2 Carbon Nanotubes

Carbon nanotubes are another type graphitic nanoparticle with extremely high aspect ratios. Multi-walled carbon nanotubes (MWNT) were first discovered in 1991 during the arc-evaporation of graphite to synthesize of fullerenes by Ijima¹². The synthetic method involves creating an electrical arc between two graphite electrodes, vaporizing material from the anode which condenses on the cathode as nanotubes and fullerenes. Structurally, MWNTs consist of a

few layers of graphite rolled up into concentric cylinders. In 1993 the synthetic method was refined to yield single-walled carbon nanotubes (SWNT) by intercalating transition metals into the electrodes^{13, 14}. Figure 1.1 illustrates the typical structure of MWNT and SWNTs¹⁵. Today SWNTs are synthesized in bulk by multiple methods each with its own tradeoffs between efficiency and the quality of the product produced¹⁶⁻²⁰. However, regardless of the production method used, all SWNT must go through extensive purification to remove catalyst, amorphous carbon, and unwanted graphitic allotropes. For most modern production methods the purification process can have the biggest impact on both the purity and dispersibility of the end product²⁰. Production of SWNT creates both semi-conducting and metallic type SWNTs depending the direction the graphene sheet was rolled up, and the two types can not be efficiently separated. However, both types of SWNTs have extremely favorable mechanical, electrical, thermal properties, with an elastic modulus as high as 1 TPa and electrical and thermal conductivities as high as $\sim 10,000 \text{ S/cm}$ and $\sim 6000 \text{ Wm}^{-1}\text{K}^{-1}$ ($3500 \text{ Wm}^{-1}\text{K}^{-1}$ experimentally) respectively²¹. These properties make SWNTs an attractive material for many potential nanocomposite applications, especially for organic electronic, thermo-electric, high-strength applications. It has been shown that for many application nanotubes are most effective as a nanocomposite filler when well dispersed²²⁻²⁵. However, because of their high surface area and resulting strong intertube interactions carbon nanotubes form bundles and are difficult to disperse well in a polymer matrix, complicating their use in many arenas.

1.2.3 Graphene

Perhaps the simplest graphitic nanoparticle is single-sheet graphene. Graphene, shown in Figure 1.2, is a two dimensional layer of sp^2 hybridized carbon one atom thick and is equivalent

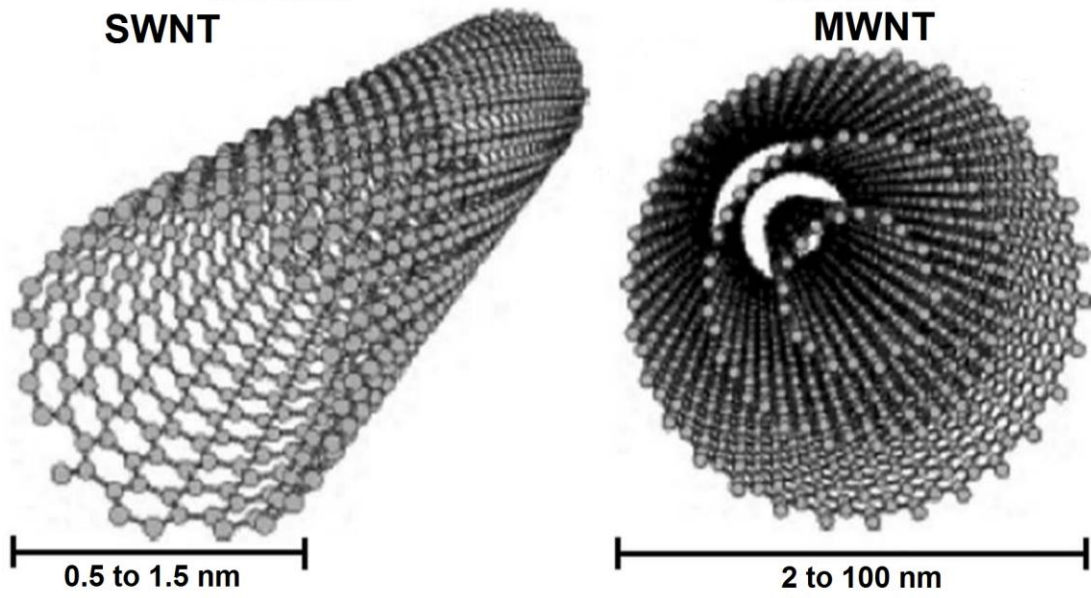


Figure 1.1 Typical structure a single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes.

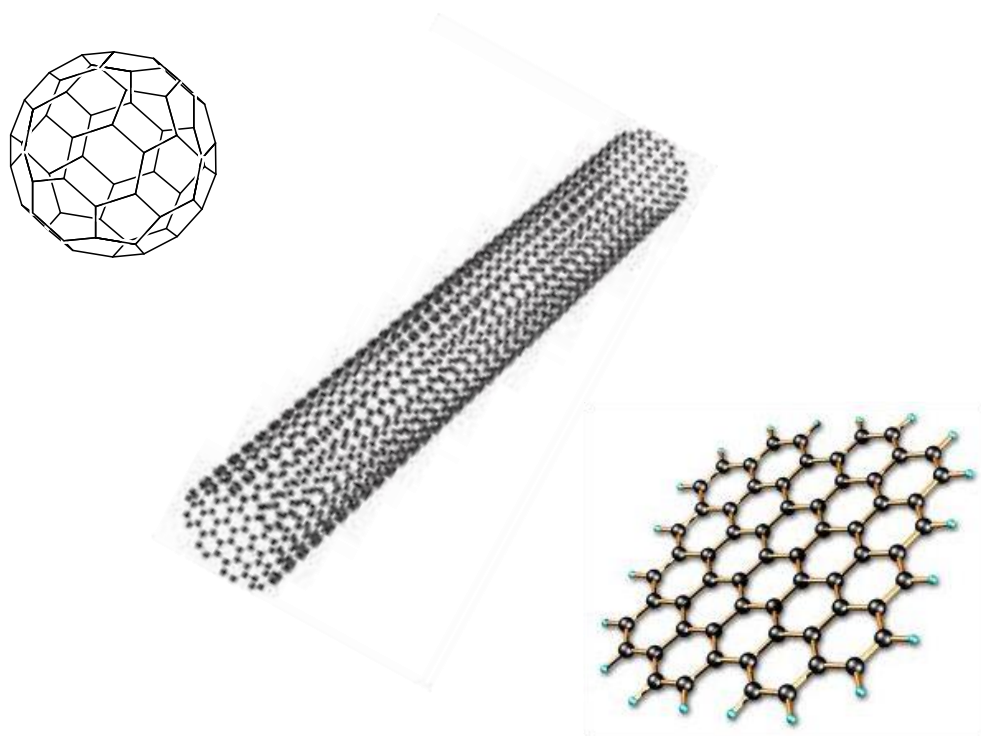


Figure 1.2 From left to right: C₆₀, single-walled nanotube, and a small graphene sheet (not to scale).

to a single layer of graphite. Though considered the building block of all other graphitic carbon allotropes, graphene research is still quite young as single layer graphene was not successfully isolated until 2004²⁶. However, with thermal and electrical properties comparable to those of SWNTs, a Young's modulus of 1 TPa, and stiffness of 130 GPa, graphene is one of the strongest carbon nanoparticles and has become a material of great interest. Large scale commercial production of high-grade single or few layer graphene remains a challenge, therefore most researchers produce their own graphene in house^{27, 28}. The most common scalable production methods produce few-layer graphene exfoliating graphite down to particles a few layers thick²⁷⁻⁴³. Intercalation compounds or oxidation usually aids this process, by expanding the inter-layer spacing and facilitating exfoliation. In the case of oxidation, partial chemical reduction and/or thermal annealing are typically implemented post exfoliation to restore some sp^2 structure. The quality of the produced graphene varies widely based on production method and the starting graphite employed^{44, 45}.

1.2.4 Soft Polymeric Nanoparticles

Soft nanoparticles (SNP), specifically those composed from a single monomer and crosslinker, are unique among nanoparticles. Unlike most nanoparticles, SNPs are soft and generally deformable under flow or stress, and their level of softness/ rigidity can be tuned during synthesis. SNP also have solubility properties similar to their linear polymer analogs and theoretically high miscibility in said linear analogs. Such nanoparticles have been synthesized by multiple researchers recently^{46, 47}, primarily from polystyrene. They can be described as a “fuzzy gel”⁴⁶ having a cross-linked core surround by a softer, less cross-linked, “fuzzy” corona; though the exact geometry and properties varies with conditions and synthetic method. Such NPs are of interest, because when included in a compatible matrix, their tunability and potentially high

miscibility, greatly extend the range to which a composite's visco-elastic flow and mechanical properties can be varied without changing most of the other properties associated with the base polymer.

1.3 Objective of This Dissertation

In recent years, the body of research on polymer nanocomposites has been growing exponentially and the potential applications ever diversifying into all branches of science. However, one important theme keeps reoccurring in the literature: polymer composite containing nano-fillers do not behave as predictably, as those containing micro and macro scale fillers. There has been much research into why some nanocomposites exhibit behavior that classical theory cannot predict while others do not. Several well done studies have identified that barring any chemical difference between particles, the primary source of anomalous polymer nanocomposite behavior is the size ratio of the NP to the polymer chains of the matrix⁴⁸⁻⁵⁴. Above a critical ratio the composite will behave classically, and below this value the composite may exhibit anomalous behavior at low loading if the matrix polymer is sufficiently entangled^{50, 51, 53-55}. Unfortunately, these studies have been ad hoc, as researchers focus on the materials, and conditions that are important and familiar to them. This has left a gap in the knowledge base where there has been no *ceteris paribus* (all else being equal) study of the effect the geometry, specifically dimensionality, of chemically equivalent NPs has on the nature of the observed behavior within this anomalous regime. Additionally, almost all studies use what can be described as 'hard particles', and little attention has been given to the potential effect of particle rigidity or softness within this anomalous regime. Therefore it is the objective of this dissertation to begin filling in these knowledge gaps; studying melt dynamics of composites of different graphitic nanoparticles in a common set of matrix polymers, as well as, polystyrene SNPs of

varied softness in a polystyrene matrix, all under conditions that are permissive to occurrence anomalous melt dynamics.

The first dynamics study in this dissertation (Chapter 4), examines the effect that NP geometry has on polymer chain dynamics in low-loading (1wt%) nanocomposites. For this study, graphitic NPs (C_{60} fullerenes, carbon nanotubes, and few-layer graphene) with one common dimension ($\sim 1\text{nm}$) were compounded with a common set of styrene-acrylonitrile random copolymers (SAN, 0-56mol% acrylonitrile). The goal of the study is to use a common set of matrix polymers, identical preparation methods, and chemically similar NPs to eliminate variables that exists when comparing data from different sources, and directly examine the effect NP geometry has on composite melt dynamics when at least one NP dimension is well below the critical NP:matrix chain size ratio. Melt dynamics in this study were probed in the bulk and local segmental dynamic regimes using rheology and NMR relaxometry respectively.

Chapter 5 is a melt dynamics study designed to examine how SNPs of varied softness affect polymer chain diffusion in low-loading (1wt%) composites with their linear analogs as the matrix. In this study, composites were made by inclusion of two different polystyrene based soft nanoparticles synthesized with different amounts of crosslinker (~ 1 and $2\text{ mol\%}$) embedded in a polystyrene matrix (or its deuterated equivalent). These SNPs were chosen because they are of equivalent radius and mesh size, and can both be described as “fuzzy gel” particles. This difference in crosslinker content only changes the size of the particle’ stiffer core and subsequently overall particle softness. The objective of this study is to examine how the change in overall particle softness affects matrix chain dynamics by monitoring the interdiffusion of symmetrical bilayers of thin-film composites; laying the foundation for further systematic study of composites containing these unique NPs. To accomplish this goal, neutron reflectivity was

employed to monitor bilayer melt diffusion, and from this data, diffusion coefficients were extracted and compared. For the purpose of comparison, an attempt was also made to extract the same information for composite containing the graphitic nanoparticles.

Chapter 3 outlines the synthesis and characterization of the graphene needed for other studies within this dissertation. At the time this work began, commercial availability of quality bulk graphene was poor. What was available in quantities suitable for composites was either of a low grade and purity or so thick that even the term ‘few-layer graphene’ was no longer appropriate. Currently, the quality and quantity of graphene available has risen to meet demand, however, even today few-layer graphene of less than 10 layers is difficult to find in bulk form. For these reasons, and to be dimensionally equivalent to the SWNTs and fullerenes used in this dissertation, the objective of this study was the scale synthesis and characterization of quality graphene keeping the average number of layers as low as possible. Keeping the smallest dimension of each graphitic nanoparticle used, as close as possible is important for a proper *ceteris paribus* study of the overall effect of NP geometry on anomalous melt dynamics in composites. If the graphene used were too thick it could put the composite outside the conditions under which anomalous dynamics are possible and lead to erroneous conclusions. For this reason, it was important that average NP thickness be below 2.5nm (~7 layers) and preferably closer to the 1.2nm average diameter of the fullerenes and nanotubes. This study also largely examines the use of Raman spectroscopy for probing the physical characteristics of few-layer graphene based on opto-electric properties.

As a whole this dissertation aims to provide a deeper understanding of how the often overlooked parameters of nanoparticle geometry and softness effect melt dynamics in polymer nanocomposites. Specific focus is given to composites at low filler loading under conditions that

are favorable for anomalous melt behavior. The low-loading regime is an area of great importance to many working in the nanocomposites field. Using low filler loadings can allow a composite to gain desirable properties imparted by the NP as efficiently and cost effectively as possible without losing many of the matrix polymers favorable characteristics. Gaining better understanding of when, why, and how nanoparticle melt dynamics deviate from traditional theory could be invaluable to compounders both looking to avoid and take advantage of anomalous melt behavior.

CHAPTER 2

INSTRUMENTAL TECHNIQUES

2.1 Raman Spectroscopy

2.1.1 Background and overview

Raman spectroscopy makes use of the Raman effect to probe the rotational and vibrational modes of molecules and bears the name of Sir Chandrasekhara Venkata Raman, who won the 1930 Nobel Prize in Physics for observing the effect in liquids. First observed in 1928 using monochromated sunlight and a crossed filter, the Raman effect is the inelastic scattering of light by matter.⁵⁶ That is, when light impinges upon a sample, a small fraction (typically 1×10^{-8}) of the incident photons spontaneously transfer energy to or from the sample and undergo a shift in wavelength and frequency. More specifically, if an incident photon lacks the energy required to cause a true electronic transition, the associated oscillating electric field can induce an oscillating dipole moment, promoting the molecule to a short-lived virtual excited state. Photons can be scattered elastically (Rayleigh scattering), inelastically with an energy loss (Stokes), or an energy gain (anti-Stokes). The elastically scattered photons have the same wavelength and frequency as the incident beam and their reciprocal wavelength is the center (i.e. 0 cm^{-1}) from which Raman shifts are measured. When Stokes scattering occurs, the electric field of incident photon interacts with the molecules ground rovibronic state. If the induced virtual state is Raman active, a change in the molecule's polarizability occurs, and energy is transferred to the molecule the photons are scattered with a longer wavelength than the incident light. In anti-Stokes scattering, the incident photon interacts with an excited vibrational state and the change polarizability results in energy transfer from the molecular, and the scattered photon has a shorter wavelength.^{57, 58} If no change in polarizability occurs, then there is no energy transfer and

photons are scattered at the incident wavelength (Rayleigh scattering). In this manner, Raman spectroscopy provides a fingerprint of a molecule's active rotational and vibrational modes as the energy difference between the incident and scattered photons, i.e. the energy associated with a given Raman active mode.

Due to the small fraction of photons that undergo Raman scattering under normal conditions (~ 1 in 10^8 photons)^{57, 58}, sensitivity is one of the primary challenges associated with Raman spectroscopy. Therefore, to achieve a good analytical signal in minimal time, high intensity monochromatic incident light is required. For this reason, lasers are used as the incident light source in almost all modern Raman spectroscopy. The high intensity of the monochromatic laser light increases the total amount of scattered photons increasing intensity of Raman scattering to levels that facilitate analytical use.

Modern Raman spectroscopy takes many different forms. One of the more popular spectroscopy setups for analytical use is micro-Raman spectroscopy. Micro-Raman spectrometers couple Raman spectroscopy with visible light microscopes. The typical micro-Raman setup is a 180° back-scattering configuration, where the incident is directed through the microscope objective to a focused point on the sample. The back-scattered light (Raman and Rayleigh) is collected through the objective, the Rayleigh line filter out, and remaining collected light routed into the monochromator and detector. The monochromator, typically a diffraction grating, spreads the constituent wavelengths out spatially so the detector can resolve the intensity of each wavelength. Modern spectrometers typically use charge-coupled device (CCD) imaging or line-array sensors for detection. This allows a range of wavelengths to be measured simultaneously across the width of the detector. Micro-Raman offer several advantages including: measurement on small sample volumes, good spatial resolution of the sampling area,

increased photon flux of the focused incident beam, and visual inspection and selection of the sampled area.

Micro-Raman spectroscopy is particularly useful in the analysis of graphitic NPs and composite materials containing them. Graphitic NPs such as C60, SWNTs, and graphite/graphene have well defined characteristic non-dispersive vibrational modes. Being non-dispersive, these vibrational modes give the same Raman shift regardless of the wavelength of the incident light. This allows for the flexibility to choose the incident wavelength used based on other factors, such as, minimizing sample degradation, minimizing fluorescence, resolution, and sensitivity to modes of interest. For example, in a SWNT PNC, using a longer wavelength provides better sensitivity the radial breathing mode (sacrificing intensity of high energy modes), and the lower energy photons reduce thermal degradation of the sample and possible fluorescence from the matrix. These characteristic modes can be used to probe many structural characteristics of graphitic NPs, such as, SWNT radius and type (metallic vs semiconducting). Examining the ratio of disorder/defect induced dispersive Raman bands to that of the G band (characteristic of continuous sp^2 structure) gives a measure of NP quality. The G band ($\sim 1600\text{ cm}^{-1}$) and 2D or G' band ($\sim 2700\text{ cm}^{-1}$) are characteristic of graphitic materials⁵⁹ and the intensity and structure of the bands varies between materials. One example of this is the difference in the 2D band between pristine CVD grown graphene and graphene produced by exfoliation and chemical conversion of graphite oxide. In single and few layer CVD graphene the 2D band is pronounced and very intense.^{60, 61} In contrast in chemically converted graphene of an equivalent number of layers the 2D band is very weak modulated bump that is convoluted with defect induced second-order dispersive modes.⁴⁵ This can also be seen in CVD graphene that has experienced a high degree of ion bombardment.⁶⁰ The 2D band is a second-order mode of the G

band, and in defect rich samples the G band couples with dispersive modes creating second-order combinational modes, decreasing the probability of G-to-G coupling and reducing the 2D band intensity.⁶⁰ By probing small and visually distinct areas throughout a sample and comparing intensity, micro Raman can be used to measure the level of NP dispersion PNCs.²²

2.2 Nuclear Magnetic Resonance Spectroscopy

2.2.1 Background and overview

First developed as an analytical technique in the 1940s, nuclear magnetic resonance (NMR) spectroscopy has become a very powerful tool for elucidating the structure, dynamics, and chemical environment of molecules. Though the design of NMR experiments and instrumentation (both spectroscopic and imaging) have become quite diverse, they all take advantage of the same basic physics. Fundamentally, any spinning charged particle will generate a magnetic moment parallel to its angular momentum vector. Therefore, any nuclei possessing angular momentum, i.e. non-zero spin quantum number ($I \neq 0$), will possess a magnetic moment oriented along the axis of rotation. When an external magnetic field is applied, a small population of nuclei (a few ppm) will roughly align their spin axes and magnetic moment with the field.⁶²⁻⁶⁴ The actual orientation of the magnetic moments is slightly off axis from the field, with a gyroscopic precession about the field direction. The rate at which the nuclei of an isotope precess is its Larmor frequency, and is dependent on the magnetic field strength. This is probed with a rotating magnetic field (RF pulse) of the same frequency, causing the probed nuclei to resonate. Resonance causes the magnetic dipoles to flip, inducing a minute electric charge in a detector coil.^{65, 66} However, the electron density surrounding nuclei partially shields them from the magnetic field causing a small deviation of their precession from the reference frequency. This requires that either the field strength (or RF pulse frequency) be adjusted to achieve

resonance. By sweeping the field strength (or pulse frequency), nuclei with different degrees of shielding (i.e. different surrounding electron density) resonate separately and can therefore be distinguished by the amount of adjustment to field strength (of pulse frequency) needed to achieve resonance. Since, the amount each nucleus is shielded is dependent on the local electron density, valuable information about their chemical environments and therefore molecular structure can be obtained. This is the basic premise on which all forms of NMR spectroscopy and imaging rely.⁶²⁻⁶⁴

2.2.2 Solid-state proton NMR

There are many different types of NMR instruments and experiments probing many different nuclei to provide information on the structure and dynamics of molecules. The scope of this dissertation pertains specify to probing the transverse (T_2) relaxation of polymer systems using solid-state proton (^1H) NMR (SS-NMR), to provide information on polymer chain dynamics. In SS-NMR anisotropic interactions such as dipolar coupling, which would normally be averaged out in solution phase due to Brownian motion, contribute to strong line broadening of NMR spectra. To prevent line broadening from washing out all structural detail from SS-NMR spectrum, techniques like high-speed spinning are typically used^{62, 63}. However, for relaxometry sample spinning greatly complicates experimental design⁶⁷ and is usually avoided. Alternatively, amorphous thermoplastic samples can be heated to well above their glass-transition temperature (T_g), increasing molecular mobility and regaining some spectral detail.⁶⁶ For vinyl polymers, this allows for the distinction of the ^1H signal of the aliphatic backbone from that of any significant deshielded ^1H on side groups. However, there is still too much line broadening to resolve separate signals from unique but chemically similar hydrogen atoms, as would be possible in solution. An example of this is the in melt phase SS-NMR spectrum of

polystyrene, which exhibits two broad ($\sim 3\text{-}4\text{ppm}$ wide) ^1H signals; one for the aliphatic backbone (centered at $\sim 2\text{ppm}$), and one for the all of the hydrogens on side-chain phenyl ring (centered at $\sim 7\text{ppm}$). This is in contrast to the solution phase ^1H NMR spectrum, where the aliphatic region consists of a quintuplet for the $-\text{CH}-$ and a triplet for the $-\text{CH}_2-$ and the phenyl ring hydrogens are resolved into a doublet, and two triplets for the ortho, and meta and para hydrogens respectively. While this decreased level of spectral detail is not ideal for structural analysis, it is sufficient to allow selective probing of the backbone diffusive dynamics via T_2 relaxometry.

2.2.3 Transverse relaxation in polymer systems

NMR relaxometry can be a powerful tool for probing properties of polymers on the local scale. Transverse or spin-spin (T_2) relaxation has been used for a multitude of applications and probed using a variety of instrumental designs. Spectrometer designs used for probing T_2 relaxation in polymers range from small, low-field, benchtop spectrometers, to large high field spectrometers, and multi-dimensional NMR imaging systems. Low-field systems a find increased use industrial quality control settings for rapid characterization of crosslinking variance in elastomers and composites.^{68, 69} Larger high-field magnets are generally used only in academic settings due to high cost. There are also many a wide variety of pulse sequences used to probe T_2 relaxation,^{65, 66} though most are variations on the standard spin-echo experiment that is used in this work.

Transverse NMR relaxation is the process by which the magnetization in the xy plane (transverse to the field), induced by an RF pulse, decays with time. This is result of decoherence of the nuclear spins, due to random, local fluctuations in the magnetic field. Local field fluctuations are a result of a given nucleus feeling a contribution to the magnetic field from

neighboring nuclei in addition to the static field, and therefore being sensitive to local density fluctuations. The result of local field fluctuation is random dispersion of the precession frequencies of the nuclear spins. This results in an increasing loss of phase coherence of the nuclear spins and eventually no net transverse magnetization. It is the sensitivity to local density fluctuation inducing fluctuations in the local field, that makes T_2 relaxation sensitive to diffusive polymer chain dynamics.⁶⁶

The standard Hahn spin-echo experiment (and variation thereof) is used to probe T_2 relaxation.⁷⁰ A schematic of the standard Hahn spin-echo pulse sequence is shown in Figure 2.3.

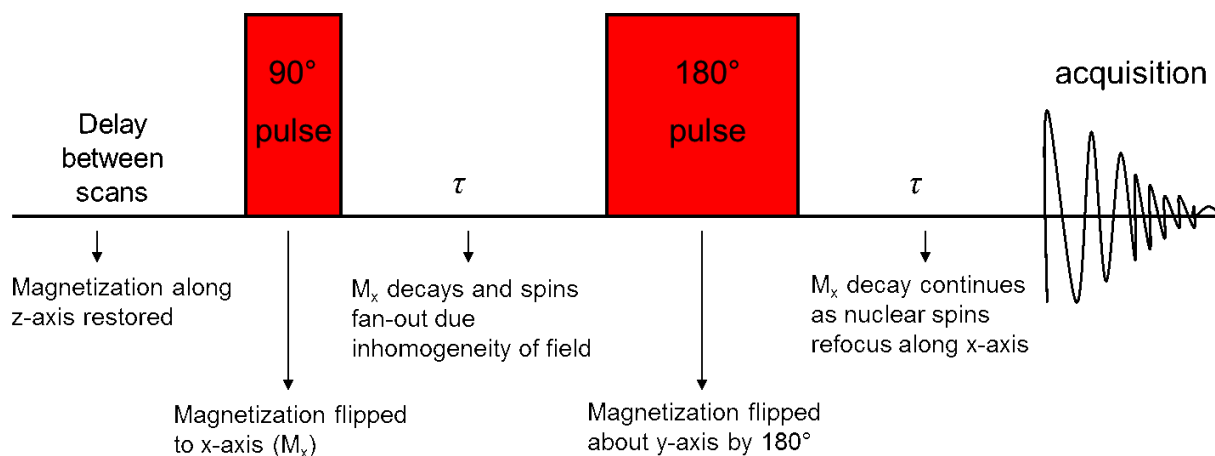


Figure 2.3 Diagram of the standard Hahn spin-echo pulse sequence

The pulse sequence consists of scan delay to restore the equilibrium z-axis (parallel to the field) magnetization, followed by a 90° RF pulse that tips magnetization into the xy plane. This is followed by a delay of time, τ , in milliseconds; during which dephasing of the nuclear spins occurs due to both local field fluctuations, and static field inhomogeneity (systematic and non-random). A subsequent 180° pulse flips the magnetization causing any dephasing from field

inhomogeneity to begin refocusing. After another delay of length τ , dephasing due to static field inhomogeneity has been reversed, leaving only the non-reversible dephasing contribution from local field fluctuations. The free-induction decay (FID) is recorded Fourier transformed to the frequency domain, and the cycle starts again at a new value of τ . Typically, spectra are recorded at several values of τ , to create a decay curve for the determination of T_2 .^{62, 64, 65} Generally, T_2 is defined as the time (2τ) required for the transverse magnetization to decay to $\sim 37\%$ ($1/e$) of the original value. For simple systems, such as small molecules and low MW polymers, a single exponential can typically describe the signal decay. However, for more complicated systems, like entangled or crosslinked polymers, there can be multiple exponential decay contributions corresponding to regions of different average density fluctuation and therefore, different mobility.^{48, 49, 71-74}

2.3 Oscillatory Shear Rheometry

2.3.1 Background and overview

Rheometry is the experimental study of the viscoelastic flow characteristics of materials in response to deformation or stress. Different rheometer designs can be used to probe the flow properties of materials; this dissertation is specifically concerned with rotational rheometry. In rotational rheometry, a sample is placed between two elements (geometries) with a known gap and rotational shear-stress (torque) is applied. The stress (σ), strain (γ , angular displacement), and strain rate are used to examine the solid-like and liquid-like responses of the material. The three most common geometries used in rotational rheometry are, concentric cylinder, cone and plate, and parallel plate; they are pictured in Figure 2.1.⁷⁵ A concentric cylinder geometry consists of a cylindrical cup and concentric cylindrical rotor, with the sample filling the gap between rotor and cup wall. A cone and plate geometry consists of a very shallow ($1-4^\circ$) conical

rotor in close proximity to a stationary plate, with the sample filling the gap between. The parallel plate geometry is similar to the cone and plate, except the rotor is a flat plate parallel to the lower plate.

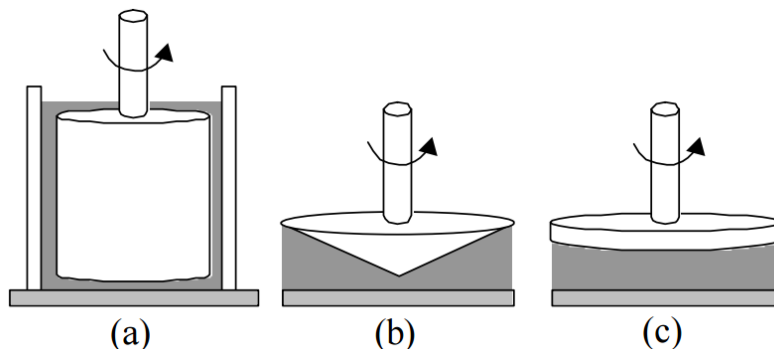


Figure 2.1 Common rotational rheometry tool geometries: (a) concentric cylinder, (b) cone and plate, (c) parallel plate.

The rheometric analysis presented in this dissertation employs oscillatory shear measurements in a parallel plate geometry. In oscillatory shear experiments, shear stress is applied as alternating rotation and counter-rotation. This creates an oscillating sinusoidal stress and resulting sinusoidal strain wave, both having a frequency equal to the strain rate. Any lag between peak amplitude of the stress (σ_0) and strain (γ_0) waves is known as the phase angle (δ), and is reported in degrees. For a purely elastic solid $\delta=0^\circ$, as all energy applied during deformation is recovered in the manner of an ideal Hookean spring. An ideal Newtonian fluid behaves in a purely viscous manner dissipating the applied stress yielding a phase angle of 90° . The phase angle of all polymeric materials falls between 0° and 90° , as polymers possess both viscous and elastic character.⁷⁶ In experiment, the desired amplitude of strain is set, and the necessary torque (stress) is measured at several pre-set strain rates (frequencies of oscillation). The resulting data is given as a function of frequency (ω). Typically, complex viscosity (η^*),

phase angle (δ or $\tan \delta$), storage modulus (G') , and loss modulus (G'') are the properties of most interest and defined in Equation 2.1.^{75, 76}

$$G' = \frac{\sigma_o}{\gamma_o} \cos \delta$$

$$G'' = \frac{\sigma_o}{\gamma_o} \sin \delta$$

$$\tan \delta = G''/G'$$

$$\eta^* = \frac{\sigma_o}{j\gamma_o\omega} e^{j\delta}, \quad j = \sqrt{-1} \quad (\text{Equation 2.1})$$

The storage modulus represents the elastic or solid-like component of the shear response, while the loss modulus represent viscous or fluid-like component of the shear response. $\tan \delta$ measures of the degree to which a material behaves viscously versus elastically at a given oscillatory frequency. At frequencies where $\tan \delta < 1$, a material yields a primarily elastic response; where $\tan \delta > 1$ the material response is primarily viscous.^{75, 76}

2.3.2 Time-temperature superposition (TTS)

At a given temperature the stress relaxation spectrum of a polymer can span many orders of magnitude in time (commonly 7 or more). Unfortunately, techniques to measure stress relaxation such as oscillatory shear rheometry are typically only able to probe a time (or frequency) window of about 4 orders of magnitude. However, for homogeneous amorphous polymers, it was found with a change in temperature the relaxation curve shifts within the experimental time window but does not change shape. By raising or lowering the temperature of the experiment, different portions of the relaxation spectrum can be shifted into a time window that can be directly probed. Therefore, relaxation behavior equivalent to shorter time (higher frequency) relaxation at the reference temperature can be measured using a lower temperature. Likewise, longer time (lower frequency) relaxation can be probed at a higher temperature. This is

the basis behind the principle of time-temperature superposition (TTS) of linear viscoelasticity.⁷⁷⁻

79

In practice, TTS can be used to probe a broader stress relaxation spectrum of a material. This is done by measuring the viscoelastic response at multiple temperatures (with overlap in material response), and creating a master curve at a reference temperature by shifting all curves in time and stitching them together. For melt relaxation behavior near the glass transition temperature (T_g), this typically done using the Williams-Landel-Ferry (WLF) equation.^{78, 79} The WLF equation is shown in Equation 2.2 where a_T is the shift factor, T is the measurement temperature, T_o is the reference temperature, C_1 and C_2 are empirical constants specific to the material at the reference temperature, and η_T and η_{T_o} are the viscosity at temperature T and the reference temperature respectively.

$$\log a_T = -\frac{C_1(T-T_o)}{C_2+(T-T_o)} = \log \left(\frac{\eta_T}{\eta_{T_o}} \right) \quad (\text{Equation 2.2})$$

Examples of master curves from this work can be found in Appendix A-2.

2.4 Neutron Reflectometry

2.4.1 Background and overview

Neutron reflectometry (NR) is a non-destructive depth profiling technique used to probe the thickness, density, roughness, and compositional depth profile of thin films. In NR a highly collimated beam of neutrons illuminates an optically flat sample, at grazing incidence. Under these conditions, a portion of the incident neutrons undergo specular reflection at interfaces; i.e. the angle of reflection α_f is equal to the angle of incidence α_i . This is analogous to standard optical physics and is illustrated in Figure 2.2,⁸⁰ where k_i is the incident beam, k_f is the reflected beam, and Q_z the momentum transfer normal to the surface and given as $Q_z = 4\pi \sin(\alpha_i)/\lambda$.^{80, 81}

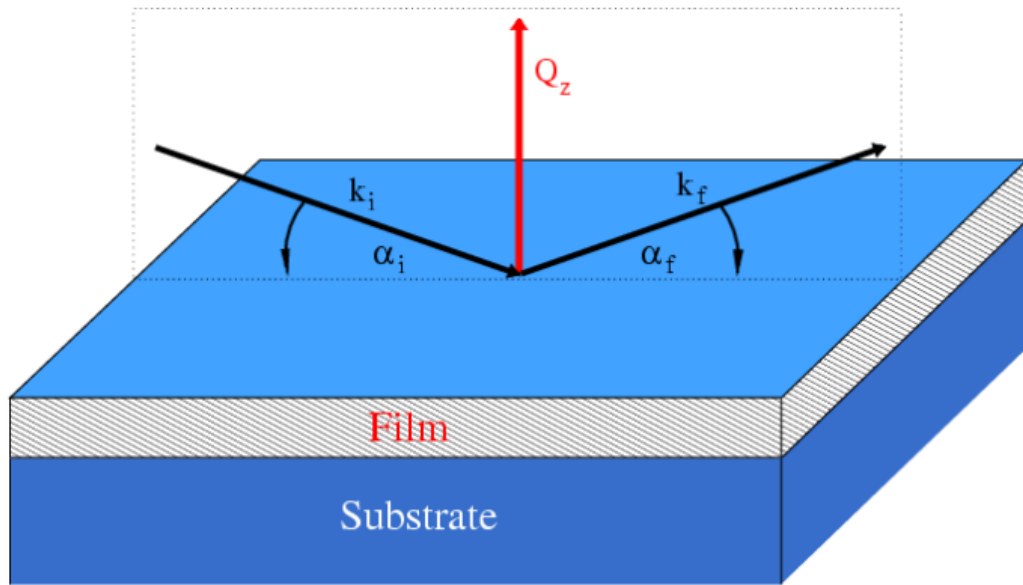


Figure 2.2 Diagram of specular scattering, $\alpha_f = \alpha_i$. The incident and reflected beams are defined as k_i and k_f respectively.

Just as in the complementary optical technique, ellipsometry, reflection will occur at any interfaces between which there is contrast between layers. However, unlike ellipsometry where contrast is defined by differences in refractive index, contrast in NR is defined by differences in the scattering length density (SLD) between materials. NR relies on the scattering of neutrons by the atomic nuclei within a material. As such, the SLD of a material is the sum of the scattering lengths of all nuclei present per unit volume.^{80, 81} Neutron scattering length is not a periodic property and varies between isotopes of an element. As such, it is possible to obtain good contrast for materials of similar density and chemical composition. This is particularly true if isotopic substitution is used (especially with hydrogen and deuterium). In the case of isotopic substitution, it is possible to obtain contrast between materials that are identical in all respects except their isotopic composition, for example polystyrene, $(C_8H_8)_n$, and its deuterated counterpart, $(C_8D_8)_n$. For such a system it would be impossible to achieve contrast using x-ray or optical techniques. This makes NR a very powerful technique for probing morphology and diffusion in polymer systems. Monitoring the inter-diffusion of like polymers in thin films⁸²⁻⁸⁴, as NR is used in this work, is one example of a common experiment that would be impossible using x-ray or optical reflectivity.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF FEW LAYER GRAPHENE

3.1 Background and Information

Despite the many favorable properties of graphene, large bulk scale production for use in composite materials has yet to be realized, owing to difficulty in efficiently producing high-quality stable material on a large scale. Large areas of pristine single and few layer graphene can be synthesized by chemical vapor deposition or epitaxial growth on surfaces. However, these methods are not practical for the production of isolated graphene for use in composites as total output is limited and production takes place on a substrate from which recovery can be difficult. As a consequence significant effort has focused on the production of few layer graphene (FLG) from either natural or synthetic graphite.

The most common methods used for producing FLG from graphite are direct exfoliation and dispersion by sonication, and the exfoliation and reduction of graphite oxide.^{30-33, 35-40, 42-44, 85-89} Exfoliation of graphite by sonication in organic solvent or aqueous surfactant solution is one of the simplest methods employed for the production of FLG.^{38, 43} Since, no chemical modification is necessary, direct exfoliation by sonication has the added benefit of maintaining the pure sp² structure of each layer. However, because of the strong Van der Waals forces and π - π interactions between layers, exfoliation is generally very inefficient, requiring dilute dispersions with only a fraction of the material being exfoliated. Additionally, the exfoliated material that is recovered is generally only lightly exfoliated (>8 layers), tends to aggregate, and retains properties that are closer to the parent graphite than graphene.^{38, 43}

One of the most promising methods for large scale production of FLG from graphite, has been by thermal or chemical conversion of graphene oxide (GO). This involves first oxidizing the starting graphite with strong oxidants, most commonly using a variation on the Hummers methods.⁹⁰ Oxidation introduces oxygenated functionalities and other sp³ defects that distort planarity of the formerly pure sp² layers. These distortions cause the interlayer distances to increase, decreasing the strength of the interactions between graphite layers, allowing for easier and more complete exfoliation, where single layers are commonly isolated. In addition, the oxygenated functionalities allow exfoliated GO to form stable dispersions at much higher concentrations than non-oxidized material.^{30-34, 36, 39-41, 44, 45, 85, 86} Heavily oxidized GO still has excellent mechanical properties and can be used as a material unto itself. However, oxidation introduces enough defects in the sp² structure to dramatically degrade the optical and electrical properties of graphene, and GO must be chemically or thermally reduced back to graphene (i.e. FLG) for many applications

Thermal reduction of GO to FLG is accomplished by the rapid, high temperature (>1000°C) heating of GO in an inert or partially reductive atmosphere. Under these conditions, the oxygenated moieties of GO rapidly decompose into CO₂ and H₂O, which may evolve explosively, exfoliating the layers and producing reduced FLG. Thermal reduction is capable of producing well exfoliated material, however, the explosive evolution of CO₂ may rip the layers apart and results in significant carbon loss; generally yielding material with small sp² domains and limited ballistic transport. Generally, It is possible to achieve well exfoliated material through thermal reduction, though the material tends to aggregate into multilayer stacks in solution.^{31, 33, 34, 45} The amount of oxygen left in thermally reduced GO is largely dependent on the conditions used.^{31-34, 39, 45}

Chemical reduction of GO typically involves the use of a strong reducing agent, most commonly aqueous hydrazine and hydrogen gas. Though both of these reductants are capable of near complete removal of oxygenated functionalities in one reduction step, they can be dangerous to handle on the large scale that are needed to produce bulk quantities of FLG. Additionally, the FLGs produced tend to aggregate and have low dispersibility and hydrazine reduced materials tend to have nitrogenated inclusions;^{33, 34, 36, 39, 40, 45} H_2 reduced material tends to have more sp^3 carbon defects.^{30, 45} It has been shown that more selective reducing agents, such as sodium borohydride ($NaBH_4$), can be used in a multistep reduction process to homogenize the functional groups, and allow for a more controlled reduction process.^{35, 41} The resulting FLGs tend to have fewer layers and sp^3 defects, where their dispersibility and remaining functionalities can be controlled by varying the subsequent reduction steps. Gao et al. showed that during the stepwise reduction, the composition and properties of the reduced GO can be well characterized between steps.⁴¹

Raman spectroscopy is a powerful tool to characterize graphitic particles. It can be used not only to quantify the amount of disorder in graphitic material but also the average optoelectric persistence width, or effective crystallite size, of the sp^2 domains.^{44, 45, 59, 61, 91-97} To a lesser extent it can also be used to qualitatively estimate the number and relative alignment of graphitic layers.

This chapter outlines the methods used to synthesize few-layer graphene (FLG) from graphite, as well as the characterization of the starting material, intermediate products, and final product. The FLG was generated via a slightly modified version of that outlined by Gao et al.⁴¹ Resulting products were characterized by elemental analysis, atomic-force microscopy, and Raman spectroscopy. The goal of this work was the production of high quality graphene fillers

for future use in nanocomposites. As a tangential outcome, a method of approximating the average chemical formula of the opto-electrically continuous domains has been developed.

3.2 Experimental

3.2.1 Materials

Graphite powder (GP), crystalline ~300 mesh, was produced by Alfa Aesar. As received graphite was found to contain significant amounts of oxidized impurities that could be easily filtered out. To best monitor the oxidative process the graphite powder was used in filtered form (fGP) for synthetic procedures. H_2SO_4 , HCl , and H_2O_2 (30% soln.) were purchased from Fisher Scientific, all ACS grade or higher, and used without further purification. NaBH_4 (98+%), KMnO_4 (99+%), and $\text{K}_2\text{S}_2\text{O}_8$ (99+%) were produced by Acros Organics and used as received. Na_2CO_3 (>99%) and P_2O_5 (>98%) were obtained from Sigma-Aldrich and used without further treatment. All water used was distilled (18 M Ω , Milli-Q).

3.2.2 Purification of Graphite

The as-received graphite powder (GP) contained a significant amount of oxygenated material. To ensure an accurate assessment of the efficiency of the oxidation reactions, steps were taken to purify the starting material. It was determined that oxygenated material could be filtered out easily. In this procedure, the GP was dispersed in deionized water at about 90 mg/ml by sonicating for 30 minutes in a bath sonicator (Branson Model 2510 Sonicator). The resulting slurry was then gravity filtered through fluted, medium porosity filter paper (Fisher Scientific P5), washed with several volumes of deionized water, and dried under vacuum at 150°C for 48 hours. The resulting filtered graphite powder (fGP) was 99.96% carbon by elemental analysis and was used as a reactant for all oxidative procedures.

3.2.3 Oxidation of Graphite

Oxidation of the filtered graphite was accomplished using a two-step variant of the Hummer's method outlined by Koutyukhova et al.,⁸⁵ the only significant addition being the isolation of GO in dried form. In this procedure, 10g of $K_2S_2O_8$ and 10g of P_2O_5 were added to 30mL of concentrated H_2SO_4 in a 500mL round bottom flask and the solution was heated to 80°C in a hot water bath. To this hot solution, 20g of fGP was added, resulting in a deep blue mixture. The reaction vessel was then removed from heat and wrapped in glass wool and aluminum foil to insulate, and allowed to cool to room temperature for 6 hours. The reaction mixture was then diluted with deionized water and gravity filtered (Fisher Scientific P5 filter paper). This pre-oxidized graphite (pGP) was washed with water until the rinse water tested pH neutral and dried on the filter overnight.

The pGP was then added to a 2L Erlenmeyer flask with 460mL of concentrated H_2SO_4 and chilled to 0°C in an ice bath. To the chilled mixture, 60 mg of $KMnO_4$ was added slowly and in small increments with continued cooling and stirring to keep the temperature below 20°C. Once fully mixed, the reaction mixture temperature was raised to 35°C in a water bath with stirring. After 2 hours the solution was diluted with 920mL of deionized water and stirred for 15 minutes. The reaction was then terminated by transferring it to a 4L beaker and diluting with approximately 2.5L of deionized water and 50mL of 30% H_2O_2 . The resulting clear-yellow solution was filtered through a hydrophilic, 0.22 micron polyvinylidene fluoride (PVDF) membrane (90mm GVWP, Millipore) and washed with 5L of dilute HCl solution (1 : 10 HCl : water). The resulting brown paste was suspended in water as a 2% dispersion and subjected to dialysis for 24 hours. After dialysis, the graphite oxide was exfoliated by brief bath sonication, flash-frozen in liquid nitrogen, and stored overnight at -20°C. Water was then removed by freeze drying (Labconco FreeZone 4.5L) to dissuade large scale aggregation. Freeze drying was carried

out for 48 hours with a collector temperature of -40°C . The freeze dried graphene oxide (GO) was further dried under vacuum at 70°C overnight and placed in a vacuum desiccator for storage. It is worth noting the volume of GO produced is much larger than the fGP used.

3.2.4 Reduction of Graphene Oxide

Chemical reduction and annealing of GO was carried out using methodology prescribed in the literature⁴¹ without notable deviations. Dried GO was dispersed in deionized water at a concentration of 1.0mg/mL with light bath sonication. The GO solution was then made basic by the addition of a 5wt% CaCO_3 solution until the pH reached ~ 9 . 8mg/mL of NaBH_4 was then added to the basic GO dispersion with stirring and the mixture was held at 80°C for 1 hour. After an hour, the reaction mixture was vacuum filtered (0.22 micron PVDF) and washed with several volumes of water. This first chemically converted graphene product (CCG1) was dried in a vacuum oven overnight at 150°C .

Dried CCG1 was further reduced by dispersing in concentrated H_2SO_4 and stirring for 12 hours at 120°C . The reaction mixture was then cooled, diluted with water, and vacuum filtered (0.22 micron PVDF). This second chemically converted graphene product (CCG2) was washed with water until filtrate tested neutral, and then dried under vacuum at 150°C and stored in a vacuum desiccator.

3.2.5 Annealing of Chemically Converted Graphene

Thermal annealing of CCG2 required significant deviation from the prescribed method⁴¹ to accommodate the use of equipment that was readily available. Deviations note are the lower temperature 1000°C vs. 1100°C , lower total gas flow of 100 cc/min vs 1300 cc/min, and the gradual furnace ramp vs fully preheated furnace. 5.0g of CCG2 powder were pressed into flakes at 5000psi using a hydraulic laboratory press (Carver Model C). The tube furnace was preheated

to 700°C. CCG2 flakes were loaded into a quartz tube in between quartz wool plugs to keep the flakes in the center of the tube while under gas flow. Gas flow was regulated by programmable and computer controlled mass flow controllers. Argon gas flow was set to 50cc/min and the sample tube was placed in the furnace and the temperature allowed to equilibrate. The temperature was then raised to 1000°C at 40°C/min while maintaining argon flow. Once 1000°C was reached, gas flow was changed to a mixed flow of 85cc/min argon and 15cc/min hydrogen for 15 minutes. During this time, the flakes exploded into powder and water vapor evolved forming condensation at the furnace exit. After the 15 minute annealing period, the gas flow was switched to 100cc/min argon, the furnace was turned off, and the lid was opened to allow the quartz tube to cool slowly to prevent shattering. The sample tube was allowed to cool to 200°C before removal from the furnace. Once cooled to room temperature, the annealed graphene (CCG3) was collected in a vial with any residual CCG3 powder being rinsed from the tube walls with acetone. The final CCG3 product was placed under vacuum at 60°C for 3 days to remove residual acetone.

3.2.6 Instrumental Analysis

Elemental micro-analysis (EA) was performed by *Atlantic Microlab, Inc*. The samples were analyzed for their carbon, hydrogen, and sulfur content by combustion analysis and oxygen content by pyrolysis using a LECO CHNS-932 with VTF-900 pyrolysis furnace.

Atomic force microscopy (AFM) images and height cross-sections were captured on a Veeco Metrology MultiMode AFM. All measurements were made in tapping mode. Samples for AFM analysis were prepared by dispersing GO in water and CCG2 in DMF and spin coating these dispersions on silicon then drying them on a 150°C hot plate.

Raman spectroscopy was carried out on a HORIBA Jobin-Yvon T64000 Raman spectrometer equipped with micro-stage using a 40x objective. Samples were analyzed in powder form on glass slides. An argon ion laser was used to provide 514.5nm sample excitation at laser powers not exceeding 1mW on sample. The spectrometer was used in single monochromator mode with an 1800 line/mm grating.

3.3 Results and Discussion

3.3.1 Elemental Analysis

EA results were returned as wt% of sample for each element analyzed for. The molar ratios of C/O and C/S, and the total percentage of the sample from the analyzed elements (Total Wt%) were calculated from these results, and are presented in Table 3.1. From the elemental analysis data, it is clear that dispersing and filtering the raw graphite powder (GP) increased the wt% carbon of the starting material by 4.74%. The increase in carbon content is most likely due to either the removal of absorbed oxides or the exfoliation of an oxidized surface layer. The manufacturer reports⁴¹ that the carbon content of the graphite powder is ~95%, however, they fail to account for the non-carbonaceous mass. Therefore, the filtered graphite powder (fGP) provides a much better starting material to allow the tracking of oxidative and reductive reactions, as the non-carbon content is reduced to a negligible level in this material.

Throughout the oxidation and reduction processes, the reported carbon, hydrogen, and sulfur contents closely match those reported in the literature for similar procedures⁴¹. The oxygen content, however, deviates by as much as 8.5 wt% from those reported in the literature for the CCG1. This may be explained by previous work that has shown that⁴⁴ the graphite source and type can impact the efficacy of oxidative processes and the quality of the reduced product. The source of the graphite in this work is Alfa Aesar, where the product is listed as crystalline and

Table 3.1 Results of elemental analysis

Sample	Carbon wt%	Oxygen wt%	Mole ratio C/O	Hydroge n wt%	Sulfur wt%	Mole ratio C/S	Total Wt%
GP	95.22	2.84	44.66	--	--	n/a	98.06
fGP	99.96	--	n/a	--	--	n/a	99.96
pGP	49.57	45.50	1.45	2.09	1.35	98.03	98.51
GO	47.46	47.13	1.34	2.32	1.12	113.13	98.03
CCG1	63.89	27.96	3.04	1.89	--	n/a	93.74
CCG2	82.65	15.41	7.14	0.48	0.72	306.46	99.26
CCG3	93.15	1.65	75.20	0.25	1.10	226.08	96.15

--indicates levels below detection

approximately 300 mesh which indicates particle sizes that are 43-53 microns. Though listed by the retailer (Fisher Scientific) as crystalline graphite, information obtained from the supplier (Alfa Aesar) revealed more specifically that the GP was produced synthetically from desulfurized petroleum coke. This type of synthetic graphite though typically very pure, have much thinner crystallites, lower densities, and larger interlayer distance than the natural flake graphite used in the literature procedure.⁹⁸ The lower density, larger interlayer distance, and crystals with fewer layers likely make the graphite used in this work more susceptible to oxidative attack and account for the higher oxygen content in GO, CCG1, and CCG2. Calculation of the molar ratio of oxygen and sulfur results in a value of 3.01 for CCG3, which corresponds directly to that expected for sulfonated aromatics. This indicates that the modified thermal annealing process carried out is sufficient to remove any remaining carbonyl or hydroxyl groups, but is not suitable for the elimination of sulfates. Noting that the C/S mole ratio decreases with thermal annealing, since there has been no further sulfur input, this decrease must be due to much higher relative carbon loss than sulfur loss during annealing. Taking this further and assuming all sulfur present in CCG2 is retained as sulfates in CCG3 (i.e. no sulfur loss) minimum levels of carbon, oxygen, and net hydrogen loss were calculated for the annealing process. This was done by first calculating the moles of each element (C, O, H, S) in 1kg CCG2 and 1kg CCG3 from their corresponding weight% and molar mass. Next, the [moles S]/[kg CCG2] was divided by the [mole S]/[kg CCG3] to give the mass of CCG3 yielded by annealing 1kg of CCG2 (0.654kg CCG3/1kg CCG2). This mass-to-mass conversion factor was then used to convert from [moles (C, O, H)]/[kg CCG3] to [moles (C, O, H) remaining]/[kg CCG2 annealed]. Subtracting these values from the [moles (C, O, H)]/[kg CCG2] yields a minimum carbon loss of 18.07mol/kg CCG2 annealed, oxygen loss of 8.96mol/kg CCG2 annealed, and net

hydrogen loss of 3.14mol/kg CCG2 annealed. These are considered minimum values because if sulfur loss is non-negligible the actual values would be higher. Hydrogen loss is classified as net loss because the annealing gas stream contains hydrogen.

3.3.2 Atomic Force Microscopy

AFM was used to characterize the average thickness of exfoliated few-layer graphene-oxide (GO) and few-layer chemically converted graphene (CCG2). Representative AFM images of GO and CCG2 are shown in Figure 3.1, and the cross-section analysis process is pictured in Figure 3.2. In the cross-section analysis of GO, a height profile along a straight line is generated. The flake heights were then determined from this profile by noting the height difference between the profile plateau and the height minima at the wafer surface. For this analysis, the flake heights were determined at 5 points on each sample and averaged. GO yielded 3 points with an average thickness of $1.53 \pm 0.05 \text{ nm}$ (1-2 layers) and 2 more points averaging $4.05 \pm 0.55 \text{ nm}$ (3-4 layers) and CCG2 averaged $2.9 \pm 0.4 \text{ nm}$ (7-9 layers).

3.3.3 Raman Spectroscopy

There are several Raman bands characteristic to graphitic materials, that vary in line shape, position, and intensity depending on the material tested. The primary bands of importance are the G-band ($\sim 1580 \text{ cm}^{-1}$), 2D-band (or G'-band, $\sim 2700 \text{ cm}^{-1}$), D-band ($\sim 1350 \text{ cm}^{-1}$), and D'-band ($\sim 1610 \text{ cm}^{-1}$). The G-band is a first-order Raman mode corresponding to the in-plane optical phonon modes, and the 2D-band is the second-order (two phonon) scattering mode; they are present in all graphitic materials including pristine graphite and graphene.⁵⁹ The D-band is an inter-valley transition that corresponds to the breathing of the hexagonal lattice, and the weaker D'-band is an intra-valley transition. Both the D and D'-bands only become Raman active in the presence of a layer boundary or other defect that breaks the translational symmetry.⁵⁹

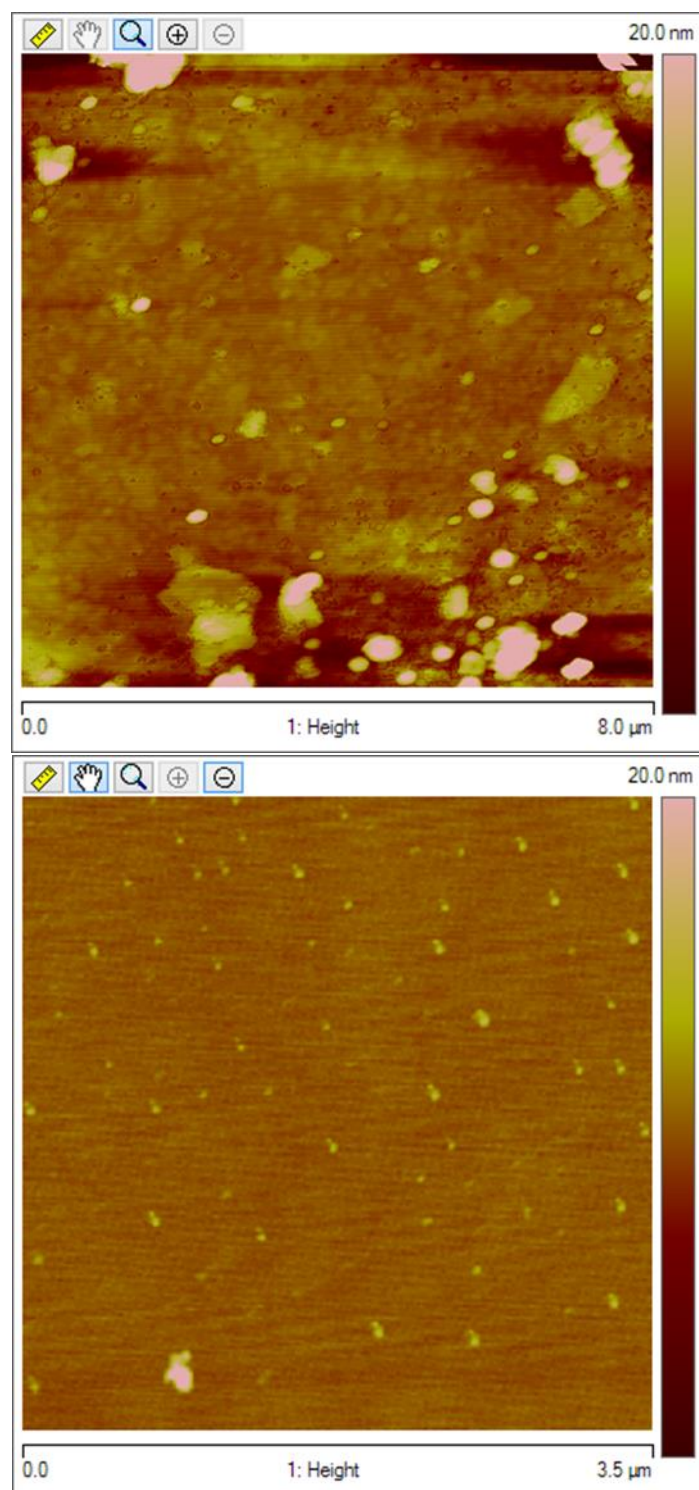


Figure 3.1 Atomic force microscopy images of GO (top) and CCG2 (bottom) on silicon.

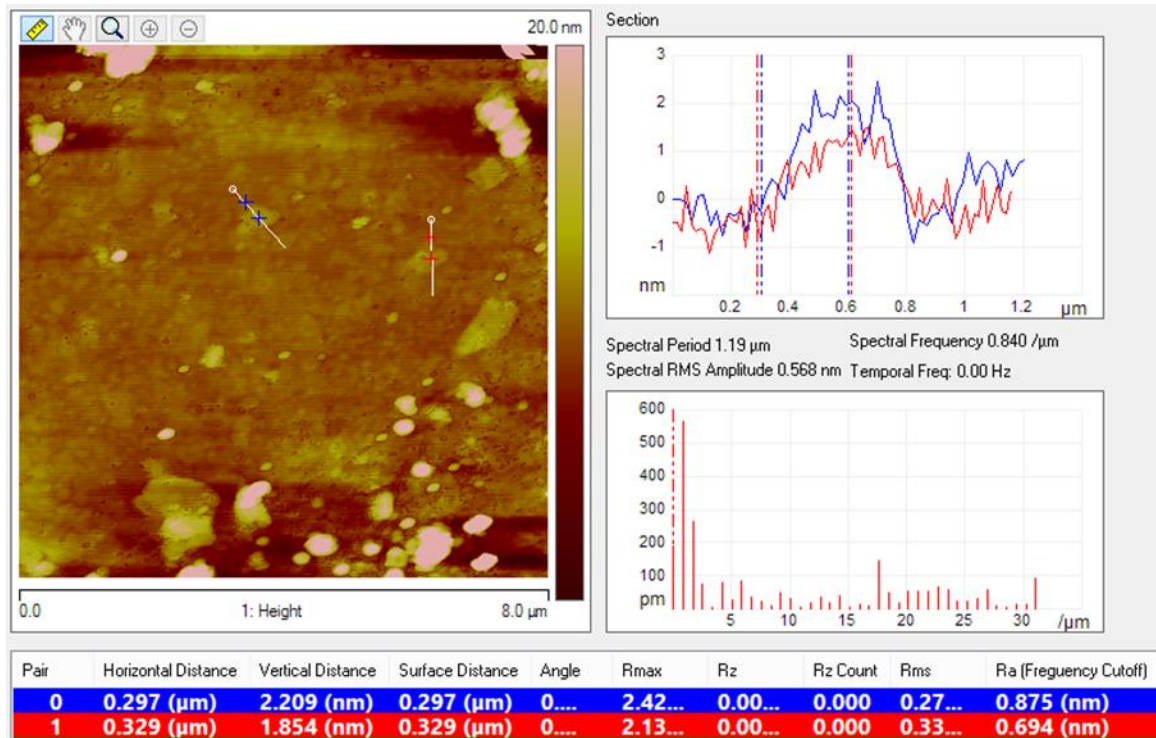


Figure 3.2 Example of cross-section height analysis on GO.

There are also other “secondary” defect activated bands that occur as combinations or overtones of the primary peaks already mentioned. The origins of most of these bands are less well defined^{45, 59}, and in this work only the D** ($\sim 1500\text{cm}^{-1}$), G* ($\sim 2450\text{cm}^{-1}$), D+D' ($\sim 2930\text{cm}^{-1}$), and 2D' ($\sim 3160\text{ cm}^{-1}$) are of concern and only because they overlap the peaks of interest and must be accounted for during fitting. Representative spectra for all samples are presented in Figure 3.3 and Figure 3.4. PeakFit fitting software was used to deconvolute the individual bands characteristic of each region of the Raman spectra.^{45, 61} As an example of the spectral deconvolution, Figure 3.5 shows the fitting results for CCG3 as well as relative positions for the graphitic and defect induced Raman bands. This fitting procedure was used to more accurately determine the positions of the bands of interest (the D, G, and 2D bands) as their position can falsely appear shifted, if they have become convoluted with other defect activated bands⁴⁵. This effect can be seen most strongly in the overlap of the G and D' bands in defect rich samples like GO. The effect of overlap of the G and D' bands and their approximate positions can be seen in Figure 3.4. Additionally, an increase in disorder within a graphitic structure increases the local density of states and therefore can significantly broaden the G-band. As measures of the level of disorder in the samples, the peak positions, as well as the intensity ratios of the $I(D)/I(G)$ and $I(D')/I(G)$ bands as well as the full-width at half maximum of the G band (Γ_G) were all recorded and are listed in Table 3.2.

Most of the opto-electric properties of FLGs are dependent on the effective crystallite size or average in-plane persistence width of the graphitic domains L_a . More specifically, it is the average width of the independent opto-electric domains within the graphitic layers, created by defects and out-of-plane distortions in the sp^2 structure. The crystallite size can be estimated from Raman spectra by using a few different empirically derived equations, each of which

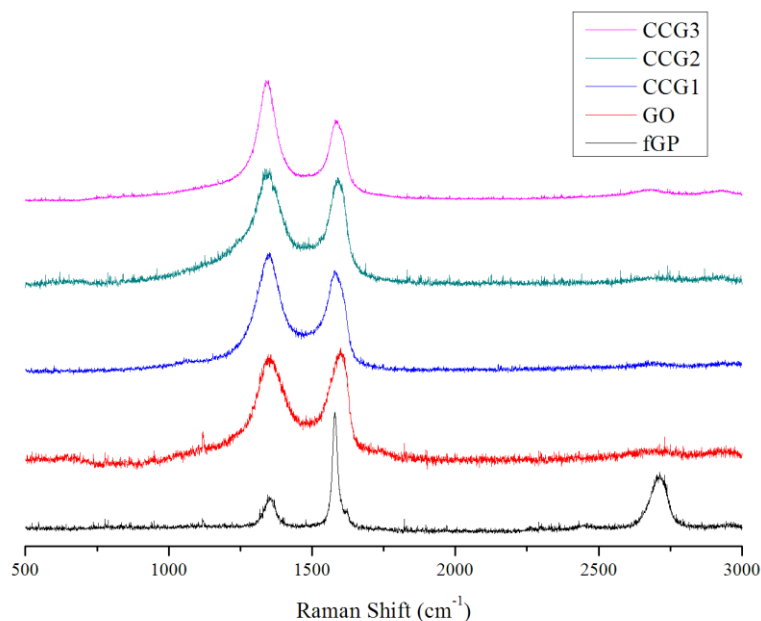


Figure 3.3 Raman spectra of filtered graphite (fGP), graphite oxide (GO), reduction products (CCG1 and CCG2), and final annealed product (CCG3).

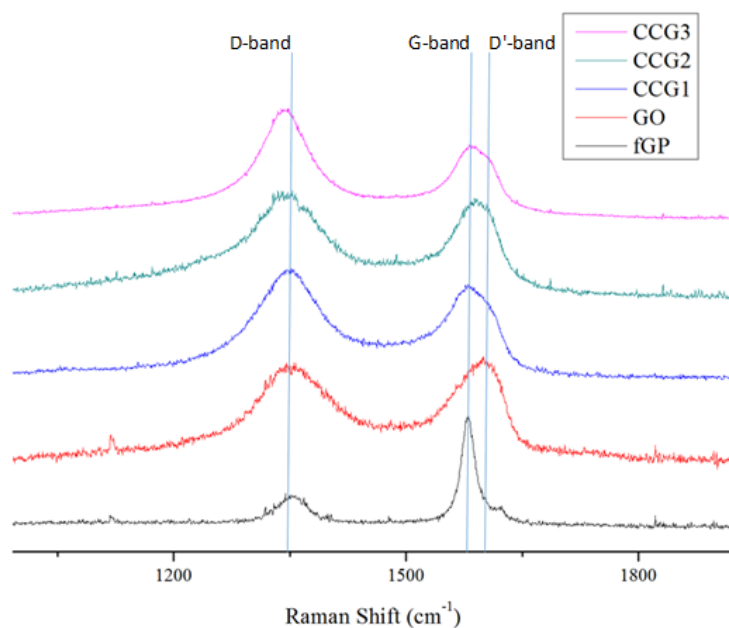


Figure 3.4 Blow-up of the D and G-band region of the Raman spectrum. The vertical lines approximately denote the locations of the D, G, and D' bands.

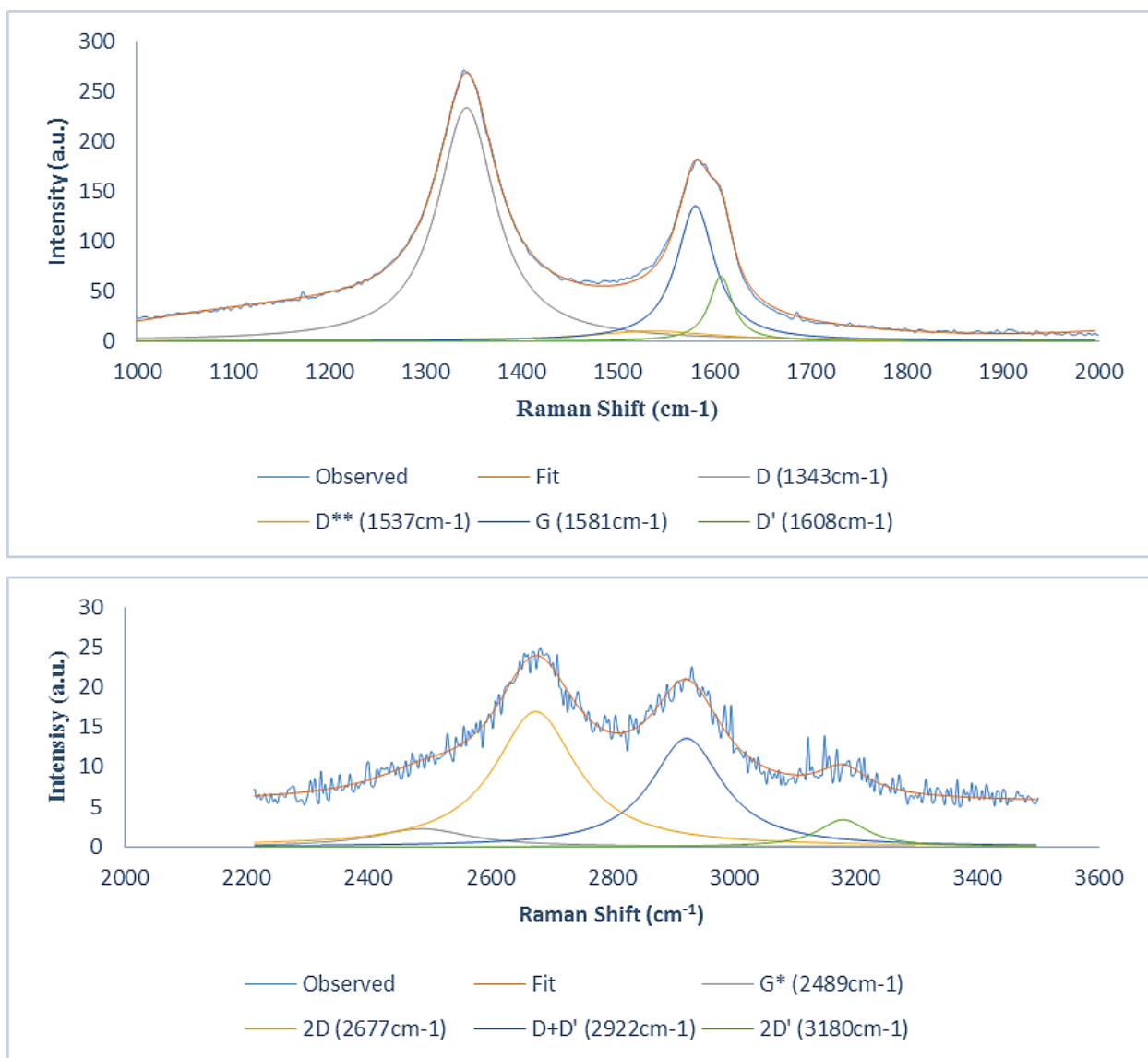


Figure 3.5 Fits of the characteristic Raman bands in the G (top) and 2D (bottom) regions for CCG3. Each of the constituent peaks is labeled by its conventional name and peak center.

Table 3.2 Raman peak positions, intensity ratios, and calculated L_a values.

Sample	D band/ cm⁻¹	G band/ cm⁻¹	2D band/ cm⁻¹	$I(D)/I(G)$	$I(D')/I(G)$	FWHM(G) / cm⁻¹
fGP	1353	1580	2699	0.26	0.09	21.05
GO	1353	1582	2694	1.48	0.87	62.07
CCG1	1348	1579	2688	1.43	0.55	49.38
CCG2	1348	1581	2695	1.37	0.65	54.03
CCG3	1343	1581	2677	1.59	0.26	57.34

correlates to the amount of defects/disorder in the graphitic structure. Here, L_a was calculated using four different equations. Two values for L_a were calculated from $I(D)/I(G)$ (Equation 3.1) and $I(D')/I(G)$ (Equation 3.2) using the empirically derived equations proposed by Cançado et al.^{91, 93, 94} where E_l is excitation laser energy and is 2.41eV (514nm) in this work.

$$L_a(nm) = \frac{560}{E_l^4} \left(\frac{I_D}{I_G} \right)^{-1} \quad (\text{Equation 3.1})$$

$$L_a(nm) = \frac{160}{E_l^4} \left(\frac{I_{D'}}{I_G} \right)^{-1} \quad (\text{Equation 3.2})$$

Additional L_a values were calculated from Γ_G using the following equation with empirically derived parameters A and B .

$$L_a = \frac{B}{\Gamma_G - A} \quad (\text{Equation 3.3})$$

L_a values were calculated with Equation 3.3 using the empirical parameters from Maslova et al. ($B=430\text{cm}^{-1}\text{nm}$, $A=14\text{cm}^{-1}$)⁹⁷ and Cançado et al. ($B=560\text{cm}^{-1}\text{nm}$, $A=11\text{cm}^{-1}$)⁹¹.

The L_a values that are calculated from these four analyses are tabulated in Table 3.3, along with the average and standard deviation. Multiple models were used to calculate an average L_a value as each method weights the effects of edge and point defects differently^{44, 59, 61, 91-97}, both of which should be taken into consideration to give a complete representation of the local structure and order within graphene oxide and reduced graphene oxide. It is important to emphasize that, L_a is not a measure of the full layer width in highly disordered graphitic species, but rather the average width of the continuous graphitic sp² network domains in a single graphene layer⁴⁴.

Further analysis of the Raman spectrum of fGP reveals a higher D/G ratio than that of the natural graphite starting material used in the literature⁴¹. This is typical of graphite composed of smaller crystallites, as there is a higher concentration of edge-defect sites within the sampling

Table 3.3 Calculated continuous sp² domain widths

Sample	$L_a(I_D/I_G)$ / nm	$L_a(I_D/I_G)$ / nm	$L_a(\Gamma_G)_M$ / nm[†]	$L_a(\Gamma_G)_C$ / nm[‡]	Avg L_a / nm	STDev
fGP	64.22	52.70	60.98	55.71	58.40	4.48
GO	11.24	5.47	8.94	10.96	9.15	2.30
CCG1	11.62	8.57	12.15	14.59	11.73	2.14
CCG2	12.15	7.31	10.74	13.01	10.80	2.17
CCG3	10.45	18.32	9.92	12.08	12.69	3.34

[†]calculated using empirical parameters of Maslova et al.

[‡]calculated using empirical parameters of Cançado et al.

area^{44, 45, 94}. Another noteworthy feature of the Raman spectrum of fGP is the location and shape of the 2D-band ($\sim 2700\text{cm}^{-1}$), which is featured in Figure 3.6. Graphite with well ordered and aligned basal planes such as natural flake graphite and HOPG, exhibit asymmetric 2D bands consisting of 2 components: a strong primary peak centered at $\sim 2710\text{cm}^{-1}$ and a prominent but much weaker shoulder at $\sim 2680\text{cm}^{-1}$.^{29, 45, 61, 96} However, as can be seen from Figure 3.6 and Table 3.2, the 2D band of fGP is centered at $\sim 2700\text{cm}^{-1}$ and consists of a single broad peak. This is typical of graphite having randomly aligned stacking of the basal planes (i.e. turbostratic)^{45, 59-61, 91}, which typically have larger interlayer spacing. It would be reasonable to attempt fitting the 2D-band of fGP to 2 closely overlapping peaks. However, both peaks would be centered above 2700cm^{-1} , and the spectrum would still lack the lower wavenumber shoulder characteristic of graphite with order stacking.

The efficiency of the oxidative process can be seen quite clearly by examining the Raman spectrum of the graphene oxide. This spectrum exhibits significant broadening of the D ($\sim 1350\text{cm}^{-1}$) and G ($\sim 1580\text{cm}^{-1}$) bands, along with the broadening and near disappearance of the 2D band. The broadening of the D and G bands is due the introduction of local variation in optoelectric sites, creating increased dispersity in the Raman active modes. Additionally, the G band appears shifted, however, deconvolution reveals that the apparent position is due to increased intensity of the D' ($\sim 1608\text{cm}^{-1}$) peak and its overlap with the G ($\sim 1580\text{cm}^{-1}$) peak and that neither peak has actually shifted. The redshift of the 2D band is typical of an increase in disorder. There are also roughly 5 fold, 10 fold, and 3 fold increases in $I(D)/I(G)$, $I(D')/I(G)$, and I_G respectively, which correspond to a ~ 6 fold decrease in L_a .

Reduction of GO to CCG1 with NaBH_4 results in a further redshift in the 2D band along with a 5cm^{-1} redshift in the D band and narrowing of the all Raman bands. More importantly,

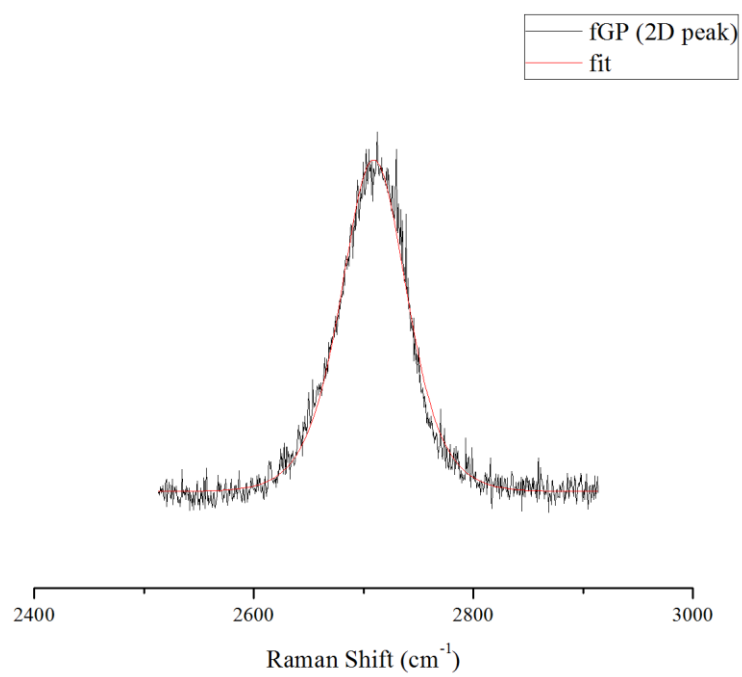


Figure 3.6 Blow-up of 2D-band region of Raman spectrum fGP sample including single peak fit.

there are significant reductions in $I(D')/I(G)$ and Γ_G , both of which are highly sensitive to point defects within graphene sheets^{95, 96}. The significant reduction in $I(D')/I(G)$ and Γ_G both while $I(D)/I(G)$ decreases only slightly, suggests that the number of point defects, or oxygenated functionalities, has been dramatically reduced by this reduction reaction, while the number of edge defects remains roughly the same. These observations are supported by elemental analysis and agree nicely with the reduction mechanism for GO with NaBH₄ that was outlined by Gao et al.⁴¹ In this mechanism NaBH₄ eliminates epoxides, ketones, lactols, and esters; reduces the number of hydroxyls; and significantly restores sp² structure.

Treatment of CCG1 with refluxing H₂SO₄ to produce CCG2 yields a material that produces a Raman spectrum with a 7cm⁻¹ blue shift in the 2D band and a slight broadening of all Raman bands. Additionally, there is a decrease in $I(D)/I(G)$ of 0.06 and increase in $I(D')/I(G)$ of 0.10. Together these two ratios suggest that acid treatment may have refined boundary type defects but the harsh conditions have introduced some point defects, in the form of mid-sheet sulfonation³⁵. This interpretation follows from $I(D)/I(G)$ being relatively insensitive to point defects compared the longer range disruptions in translational symmetry created by boundary defects. By comparison, though weaker, $I(D')/I(G)$ is sensitive to localized disorder without distinction between boundary and point defects.^{59, 60, 91, 95, 97} The blue shift of the 2D band is likely an effect of re-aggregation of acid refined layers, as the 2D-band of FLGs has been shown to be return to nearly the same position as the bulk graphite in as few as 5 layers.^{38, 45, 59, 61, 96}

Thermal annealing and exfoliation of CCG2 to produce CCG3 gives a material with a Raman spectrum that includes an increase in $I(D)/I(G)$ of 0.22 and decrease in $I(D')/I(G)$ of 0.39 and large redshift in the 2D band of 18cm⁻¹. A decrease in $I(D')/I(G)$ is expected because thermal annealing eliminates oxygenated organic functionalities, which is verified by elemental analysis,

and should restore some sp² structure in their place causing an overall decrease in disorder. The increase in $I(D)/I(G)$ is less expected, however this could be explained by an overall increase edge-type defects as the total crystallite surface area would likely be at least mildly contracted as 18.07 moles of carbon are burnt off per kg CCG2 annealed. $I(D)/I(G)$ would be more sensitive to this increase in the crystallite perimeter/surface area ratio than a decrease in mid-sheet defects.^{95, 96} The redshift of the 2D band may be due to thermal exfoliation of the CCG3 down to only 1-3 layers.^{38, 45, 59, 61, 96} Most research on N-layer and disorder effects on the 2D-band in few layer graphene is based on easily modeled, well aligned samples, rather than turbostratic graphite. However, it is clear though that CCG3 crystallites consist of fewer than 5 layers, as the 2D peak band shape and position have been shown to trend back to those of bulk graphite in samples that consist of 5 layers or more, even in highly disordered systems.^{59, 61, 96}

For any future batches of FLG produced, it may be best to use a higher quality source graphite (i.e. larger and more aligned sp² domains) so that the resulting end product has a larger opto-electric persistence width. Higher annealing temperature may aid in removal of residual sulfonate.

3.3.4 Calculation of average empirical formula of graphene layers

Using molar ratios of carbon/ and heteroatoms that are determined from elemental analysis, it is possible to derive an empirical formula for each of the oxidized and reduced graphene species, but not the starting graphite. Additionally, while a standard empirical formula provides some insight into disorder, it provides no information about the opto-electronic persistence width of the crystallite domains. To compensate for this, a method was developed to calculate an empirical formula based on the average crystallite persistence width obtained from Raman spectroscopy and a simple polycyclic aromatic hydrocarbon (PAH) growth model.

The derived PAH growth model assumes hexagonal growth generations from a central aromatic ring, such that any whole number, n , of growth generations results in a hexagonal bounded honeycomb and $n=0$ yields a benzene ring. Using this model, an equation for the total number of carbons, $c(n)$, as a function of growth generation was derived.

$$c(n) = 6(n + 1)^2 \quad (\text{Equation 3.4})$$

Then using the C—C bond length for graphene of 0.142nm, the diameter (as measured at opposing vertices), $D(n)$, in nm can be determined as a function of n .

$$D(n) = 0.246(2n + 1) \quad (\text{Equation 3.5})$$

Combining the Equations 2.4 and 2.5, and substituting the crystallite persistence width, L_a , for D , gives the following equation for number of carbons in a hexagonal crystallite layer.

$$c(L_a) = \frac{3}{2} \left(\frac{L_a}{0.246} + 1 \right)^2 \quad (\text{Equation 3.6})$$

The geometric derivation of these equations can be found in Appendix A-1.

By assuming that crystallites are continuous with no vacancies and all defects exist on the perimeter of the area described by L_a , the effective number of carbons in a crystallite layer can be approximated. These assumptions are reasonable as they are also assumptions that are included in calculating L_a . The molar ratio of carbon to each heteroatom can then be used to calculate the empirical formula for each sample. The carbon/heteroatom molar ratios, average crystallite persistence widths and scaled empirical formulas are listed in Table 3.4. Using the empirical formula allows for the efficient comparison of the structure of the graphene and graphite species throughout the oxidative and reductive processes by providing information on both composition and sp² domain size.

Table 3.4 Mole ratios, crystallite persistence widths, calculated number of carbon atoms per crystallite layer, and scaled empirical formulas for graphite and graphene samples.

Sample	Mole ratio C/O	Mole ratio C/S	Mole ratio C/H	Average L_a (nm)	Carbons/ sp² Domain	Scaled Empirical Formula
fGP	--	--	--	58.40	85254	C ₈₅₂₅₄
GO	1.34	113.13	1.72	9.15	2190	C ₂₁₉₀ O ₁₆₃₂ S _{19.4} H ₁₂₇₆
CCG1	3.04	--	2.84	11.73	3556	C ₃₅₅₆ O ₁₁₆₈ H ₁₂₅₃
CCG2	7.14	306.46	14.45	10.80	3027	C ₃₀₂₇ O ₄₂₄ S _{9.88} H ₂₀₉
CCG3	75.20	226.08	31.27	12.69	4150	C ₄₁₅₀ O _{55.2} S _{18.4} H ₁₃₃
-- indicates heteroatom levels below detection						

3.4 Conclusions

Production of graphite oxide and few-layer graphene was successful as more than 30g of materials were produced (GO, CCG2, and CCG3 combined) from 40g of fGP starting material. All materials are of suitable quality for future use in composites. However, if electrically conductive composites are desired, it is likely that higher loadings may be needed than with FLGs of larger graphitic domain size, owing to the smaller crystallite domains in CCG3 potentially limiting ballistic transport.

It was found that due to the limitations of the various empirical equations that have been used to calculate graphitic domain size using Raman spectroscopy, when probing materials with small domains, these limitations may be circumvented by averaging the results calculated from different spectral characteristics. By approximating crystallites with hexagonal growth generations, a series of equations was derived for providing an average empirical formula for the graphitic domains by combining elemental analysis and Raman spectroscopy data. The derived equations yield good estimates for the average empirical formula for the graphene crystallites, and provide a better overall representation of reduced GOs as it provides both compositional and opto-electrically relevant sample information.

CHAPTER 4

PROBING POLYMER CHAIN DYNAMICS IN NANOCOMPOSITES USING NMR RELAXOMETRY AND RHEOLOGY

4.1 Background and Introduction

Particulate and fibrous fillers have been used to form polymer composites with enhanced or otherwise modified properties, since the early days of polymer science. This has resulted in well-established theory for how the resulting composite's properties should compare to that of the parent materials. However, in recent years, composite research has largely shifted from macro and micro-scale fillers to composites containing nano-fillers to take advantage of the high surface area and unique properties of many nanoparticles (NPs). With this shift to nano-scale fillers, there have been many reports of the resulting polymer nanocomposites (PNCs) deviating from established theories of composite dynamics. Under traditional polymer composite theory, included hard particle fillers can be thought of stationary impediments to polymer diffusion, slowing the overall melt dynamics and increasing viscosity. This dynamic slowing down is one factor that can limit processing conditions and thus material applications of particle filled and fiber reinforced composites in an industrial setting. While a given filler loading may provide the desired level of mechanical reinforcement to a composite, the associated increase in melt viscosity may render the material unsuitable for common processing techniques such as extrusion and injection molding in an industrial setting. Therefore, it is important to have a more thorough understanding of the factors governing the dynamics of the components in a PNC, as depending on the application, the modified behavior could be either advantageous or detrimental.

Within the reports of anomalous melt dynamics, researchers working with nano-fillers of different geometries (spheres vs. rods) have reported distinctly different dynamic trends. Cosgove et al. observed a decrease in viscosity and faster chain dynamics in high molecular weight (MW) poly(dimethylsiloxane) PDMS filled with up to 30% spherical polysilicate nanoparticles.⁴⁸ Beyond 30% filler, reinforcement and an increase in shear viscosity was observed. However, in a simultaneous study⁴⁹ Cosgove et al. observed that low MW PDMS filled with the same NPs exhibited classical reinforcement at all filler loadings, and that the observed increase in polymer dynamics was molecular weight dependent. In follow up studies, the researchers showed that for this anomalous dynamic behavior to occur, the polymer matrix must be at least modestly entangled⁵⁴ and that a critical polymer/particle size ratio exists.⁵¹ If the matrix is not entangled or the NP is large enough relative to the matrix chains, classic reinforcement is seen at all loadings.

Winey et al. observed that composites of polystyrene (PS) and single-walled carbon nanotubes (SWNTs) exhibited a minimum in the matrix self-diffusion coefficient (at ~0.4%) as SWNT loading was increased from 0 to 4%.⁵² It was also observed that the depth of the minimum was dependent on MW (i.e. lower MW equaled a stronger minimum), but only present in PS of entangled MWs. A subsequent study showed a critical polymer/nanotube size ratio exists for anomalous dynamics in PS/nanotube composites as well.⁵³ The work of both of these groups demonstrates that chain entanglement and the relative size of the matrix chains and the nanofiller are critical factors driving anomalous dynamics observed in PNCs. However, they also show how particle geometry plays a key role in whether the dynamics anomalously speed up or slow down with nanoparticle addition. For this reason, it is the goal of this study to

systematically examine the melt dynamics of composites of similar NPs with varied dimensionalities in a common matrix.

One of the most common methods for studying the dynamic behavior of complex fluids is rheology. For polymers and polymer composites in the melt, oscillatory shear rheometry (OSR), is particularly useful for studying the melt dynamics of the material. In visco-elastic materials, OSR is useful at probing the solid-like (storage modulus, G') and liquid-like (loss modulus, G'') behavior of a material simultaneously, as well as extrapolating the viscosity to zero shear ($|\eta^*|$). This information can be very useful in determining suitability of use for different applications, and through the use of various known physical and theoretical relationships other useful properties can be determined, such as apparent molecular weight and molecular weight between entanglements. For most materials, time temperature superposition can be used to probe a broader dynamic range than can be acquired at a single temperature. This allows for the acquisition of a continuous stress-relaxation spectrum for the bulk material, as translated to a single temperature. Many instances of anomalous PNC melt dynamics have been observed with OSR.^{48, 50, 51, 54, 55, 99} However, because OSR can only probe the dynamics of the bulk PNCs and not segmental level dynamics, it falls short of describing why these anomalous dynamics occur, and the role that local chain dynamics may have.

In the past 25 years nuclear magnetic resonance spectroscopy (NMR) has gained increased utility in probing the dynamics of polymer melts. As technology has advanced, many different experiments, pulse sequences, and signal processing techniques have been utilized to glean more insight into chain mobility through NMR. Of particular interest is the study of transverse or spin-spin (T_2) ^1H NMR relaxation. Experiments based on the T_2 relaxation have been shown to be sensitive to chain diffusion, density fluctuations, molecular weight between

entanglements, and crosslink density^{48, 49, 65, 66, 71, 72, 100-105}. It has been shown from theory and early experiments with crosslinked elastomers, that because the T_2 relaxation is dependent on local density fluctuations, each local dynamic environment contributes separately to the overall T_2 relaxation^{65, 66, 71, 100, 101, 104, 105}. This means that any chain segments near crosslinks, or near entanglement points, and any freely mobile segments, will each have a unique contribution to the total signal relaxation, resulting in multiple exponential decays. Recently, it has been shown that by using fitting algorithms, such systems can accurately be fit to a multiple exponential decay containing a term for each local domain present.^{48, 49, 72} In a thorough series of studies, researchers filled low MW, high MW, and crosslinked PDMS with silicate NPs and were able to efficiently extract exponential decay terms for each local domain present. The studies showed good agreement between rheological and relaxometry data and suggest that the primary mechanism for the anomalous dynamics in PNC at low loadings is the disruption of polymer entanglements^{48, 49, 51, 54, 72}.

It is the goal of this study to examine the effect of NP geometry on bulk and local segmental dynamics in PNCs using chemically similar NP fillers in a common set of matrix polymers. Rheology and NMR T_2 relaxometry are used to probe the bulk and local dynamics, respectively. All NPs used in this study are graphitic, but with different geometries: hard spheres (C_{60} fullerenes), high-aspect ratio cylinders (SWNT), and sheets (few layer graphene). The common matrix set used is a series of poly(styrene-co-acrylonitrile) (SAN) random copolymers with acrylonitrile (AN) content from 0 mol% (i.e. polystyrene) to 56 mol%. SAN was chosen as the matrix to allow simultaneous study of how previously reported non-covalent NP-AN interactions²² affect the NP geometry dependency of PNC melt dynamics.

4.2 Experimental

4.2.1 Materials

The polymer matrices for these experiments were random copolymers of styrene and acrylonitrile (SAN) with acrylonitrile (AN) compositions of 0 mol% (PS), 29.5 mol% (SAN29), 36.8 mol% (SAN37), 45.0 mol% (SAN45), 48.8 mol% (SAN49), and 56.2 mol% (SAN56). The polymers were obtained from an industrial source with molecular weights averaging 50 kg/mol and polydispersity indices averaging 2.3. Exact post-processing specifications for each polymer are given in section 4.2.3. Single-walled carbon nanotubes (SWNTs, >95%) and C₆₀ fullerenes (C₆₀, >99.5%) were obtained from Nano-C and BuckyUSA respectively and used without further purification. Few-layer graphene (CCG3) was produced by the chemical conversion of graphite oxide as described in section 2.2 without further treatment. N,N-dimethyl formamide (DMF, HPLC grade, 99.5%) was obtained from Acros Organics and used as received.

4.2.2 Solution casting of sample stock

In this study, all composites were prepared at 1wt% NP w.r.t polymer and control samples were also examined, which consist of the pure polymer matrix. In an effort to vary only the nanoparticle filler, all composites and controls were prepared using identical casting procedures and solvent. NPs were dispersed in DMF at a concentration of 0.20 mg/mL by mild bath sonication for 1-3hrs until all visible aggregates were broken up and dispersed (control samples exclude this step). The desired matrix polymer was added at a concentration of 20mg/mL and dissolved with aid of a vortex mixer. Upon polymer dissolution, solutions were sonicated for an additional hour. Before casting, the solutions were thickened by heating on a hot plate with rapid stirring at a solution temperature of 155°C until solution volumes had decreased by ~60%. During this process, the airspace above each solution was continuously purged with

airflow to accelerate DMF evaporation and minimize NP aggregation during thickening. Rapid thickening dramatically increases solution viscosity, kinematically stabilizing the dispersions, and minimizes NP aggregation during casting when solutions can no longer be agitated. After thickening, the solutions were cast by transferring them to PTFE dishes and placing them in a preheated oven equipped with vacuum and gas purge (Lindburg Blue M). To rapidly drive off the remaining bulk DMF without inducing bubbling, the oven was held at 120°C with continuous dry air purge for 12hrs; redundant dry ice/ isopropanol traps were used to trap DMF vapors. The oven was then converted for dynamic vacuum and the temperature was raised to 165°C for 72hrs to pull off residual DMF. Cast samples were allowed to cool back to room temperature under vacuum before removal from the oven. Using optical microscopy and micro-Raman mapping, previous studies showed this casting method reliably yields 1wt% SWNT-SAN PNCs with good nanoparticle dispersion (using the same materials used in this study).²²

4.2.3 Characterization of samples

Cast control and composite samples were characterized for glass transition temperature (T_g) by differential scanning calorimetry (DSC). Weight-average molecular weight (M_w) and polydispersity index (PDI) of the processed matrix polymers were determined by gel-permeation chromatography (GPC) in THF. DSC experiments were performed on a TA Instruments Q-1000 DSC with multiple cycles (2-3) from 40 - 180°C until sample history was erased and consecutive cycles yielded overlapping heat flow vs. temperature curves. GPC experiments were run against polystyrene standards in THF on a Tosoh EcoSEC GPC equipped with 2 TSKgel SuperMultiporeHZ-M columns and refractive index detector. DSC and GPC results are summarized in Table 4.1 where samples are grouped by polymer matrix.

Table 4.1 Control and composite samples specifications grouped by polymer matrix

Sample	T _g (°C)	M _w (g/mol)	PDI
<u>Polystyrene (PS)</u>			
control	100.17	69663	3.488
1wt% C60	102.71		
1wt% SWNT	100.50		
1wt% Graphene	101.68		
<u>29% acrylonitrile (SAN29)</u>			
control	103.07	50422	1.749
1wt% C60	107.51		
1wt% SWNT	101.00		
1wt% Graphene	107.88		
<u>37% acrylonitrile (SAN37)</u>			
control	104.23	58258	2.142
1wt% C60	106.69		
1wt% SWNT	107.50		
1wt% Graphene	108.61		
<u>45% acrylonitrile (SAN45)</u>			
control	104.89	34209	1.863
1wt% C60	107.10		
1wt% SWNT	102.00		
1wt% Graphene	109.33		
<u>49% acrylonitrile (SAN49)</u>			
control	103.74	47364	2.037
1wt% C60	108.46		
1wt% SWNT	107.50		
1wt% Graphene	107.54		
<u>56% acrylonitrile (SAN56)</u>			
control	108.82	38465	2.285
1wt% C60	111.20		
1wt% SWNT	110.50		
1wt% Graphene	107.34		

4.2.4 Preparation of NMR relaxometry and rheology samples

Samples for NMR relaxometry experiments were prepared from solution cast stock by injection molding into a 5mm diameter cylindrical mold. Samples were released from the mold by freezing in liquid nitrogen (LN₂) and then inserted into macor solid state NMR rotors. Injection molding was done at 180°C and ~75rpm on a Laboratory Mixing Molder from Atlas Polymer Evaluation Products.

Rheology samples were melt pressed from stock at 180°C on a Carver Model-C laboratory press. Sample stock was pressed into a 25mm diameter, 1.2mm thick circular mold between 2 pieces of kapton film. Pressing was done twice for 5 min at 5,000 lbs. of pressure with excess folded back into the sample after each pressing, followed by a final 5 min pressing at 10,000 lbs. Samples were then cooled on the bench top and trimmed with a razor blade. This procedure was generally sufficient for avoiding bubbles in the control, SWNT, and C₆₀ samples. It should be noted that pressed CCG composites were opaque at that thickness and a clear assessment of the interior of the samples could not be made..

4.2.5 NMR relaxometry

Nuclear magnetic resonance relaxometry experiments were performed on a Varian INOVA 400 MHz spectrometer with solid-state probe and variable temperature stack. Samples were equilibrated and run 77°C above their T_g with sample spinning disabled and nitrogen as both heater and purge gas. Due to the high temperature of the experiments and variability of the nitrogen source (boil-off from a 120L high-pressure LN₂ Dewar), to protect the delicate electronics, the experiment time had to be limited to 3hrs before the spectrometer was cooled back down. For this study, the primary spin relaxation considered is the spin-spin or transverse relaxation time, T₂, which was probed using the Hahn Spin-Echo pulse sequence described in

Chapter 1 and depicted again in Figure 4.1. Before each T_2 experiment the proper 90° pulse width had to be calibrated and the spin-lattice (T_1) relaxation time had to be determined so a proper delay between scans ($5 \times T_1$) could be set. A typical spin-echo experiment consisted of acquiring 20 spectra with progressively longer values of τ ($T_2 = 2\tau$).

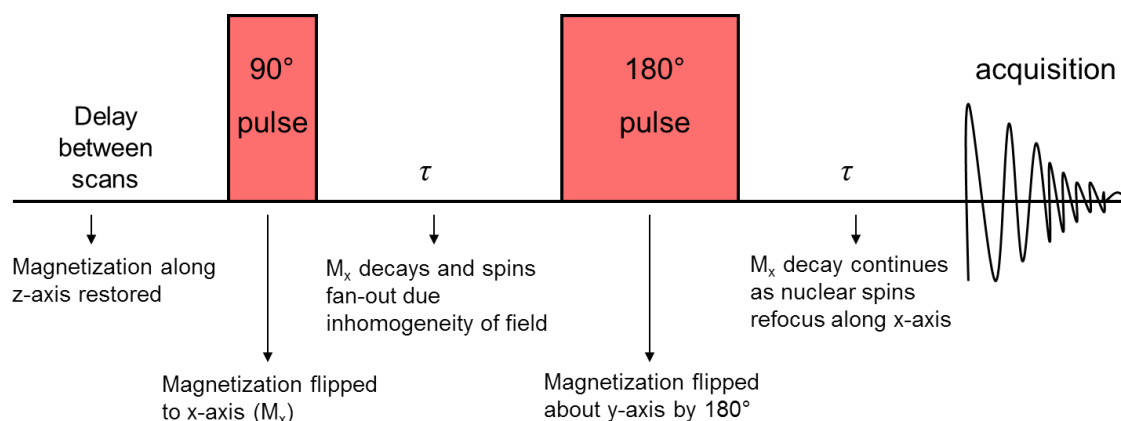


Figure 4.1 Hahn Spin-Echo pulse sequence

4.2.6 Rheology of polymer nanocomposites

Rheological measurements were acquired in oscillatory shear on an ARES 1500ex rheometer from TA Instruments equipped with the environmental testing chamber. Angular frequency was swept from 100 to 0.1 rad/s at a strain of 5% and temperature steps of 10°C from 200 to 130°C , with 4min of soak time and 10s of pre-shear after each temperature change. For the 130°C and 140°C steps the strain was reduced to 1% to prevent the required torque from loosening the drive shaft. Samples were loaded on the 25mm aluminum plate-plate geometries at 160°C and trimmed with the plate gap set at 1050 microns. The temperature was raised to 200°C and the gap set to 900 microns prior to the start of each sample run.

4.3 Results

4.3.1 NMR Relaxometry

Each T2 relaxometry experiment results in a data cube of decaying spectra vs. time. Solid-state ^1H NMR spectrum of PS and SAN at $\sim 180^\circ\text{C}$ consists of two broad overlapping peaks: a peak centered at $\sim 7\text{ppm}$ for the protons on styrene's phenyl ring and a peak centered at $\sim 2\text{ppm}$ for the aliphatic backbone protons. In order to concentrate on dynamics processes most directly related to full and segmental chain motion, attention was focused on the relaxation of the aliphatic signal. A 3-D plot of representative data is shown in Figure 4.2 with the region of interest highlighted in blue.

Each data cube was converted to a signal decay vs. relaxation time curve by integrating the spectrum at each τ value over the range of the aliphatic peak (0-4.5ppm) and normalizing by the maximum. As an example Figure 4.3 depicts the signal decay curves for the SWNT samples. It is clear from this log-log plot that the transverse magnetization decay cannot be described by a simple single exponential decay, as the curves do not have a constant concavity. This is to be expected for entangled polymers and any materials containing domains with locally perturbed dynamics, as each domain will contribute to the overall dynamics individually. Figure 4.4 illustrates some of the different local or segmental dynamics domains that might be expected to contribute to the dynamics in a SWNT composite. To accurately fit the data and extract in-depth information on system dynamics we need to account for the contribution to magnetization decay from each local dynamic process. This was done using a multiple-exponential decay equation, of the general form of Equation 4.1, where the total magnetization, $M(t)$, after the spins have been allowed to relax for some time, t , is the sum of the remaining magnetization for the nuclei in each local dynamic state.

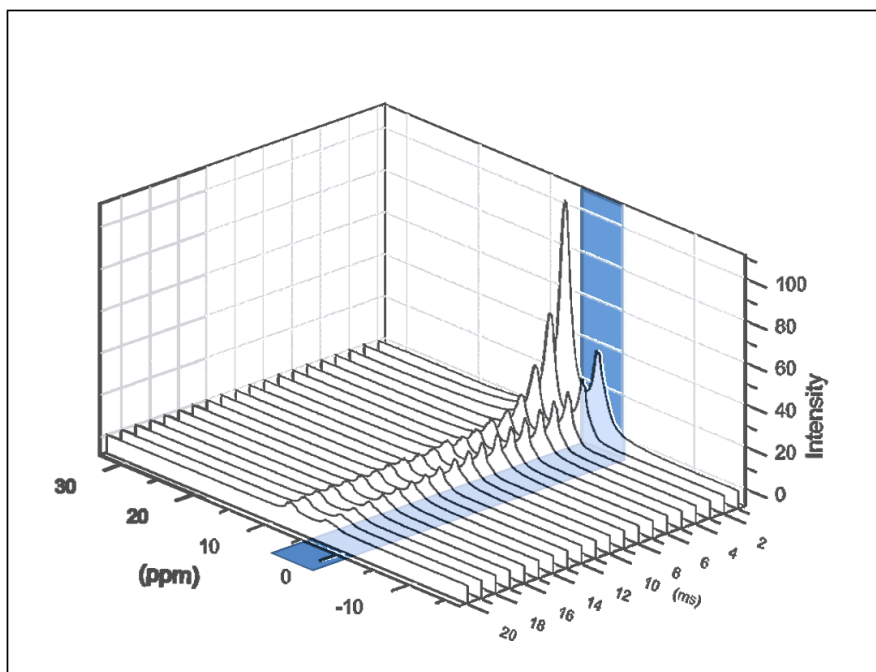


Figure 4.2 Representative spectral decay data cube from a standard Hahn spin-echo experiment. The aliphatic peak region (0-4.5ppm) is highlighted in blue.

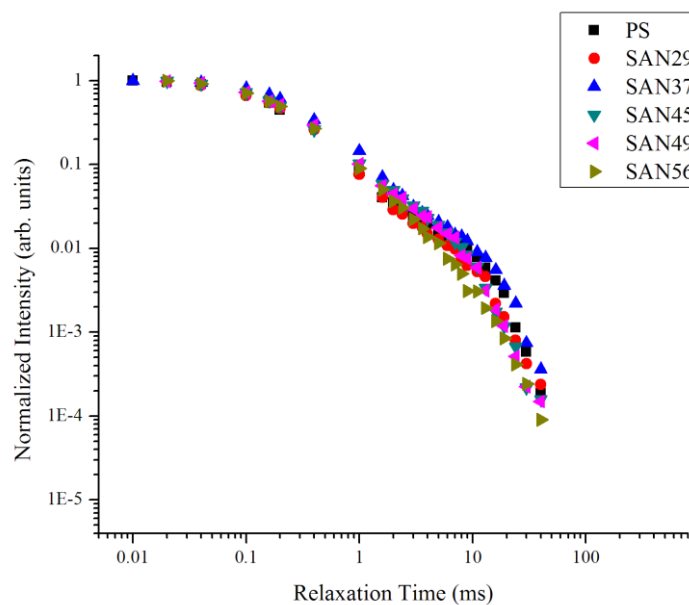


Figure 4.3 Normalized transverse magnetization decay curves for 1wt% SWNT composites. Legend lists corresponding matrix polymer.

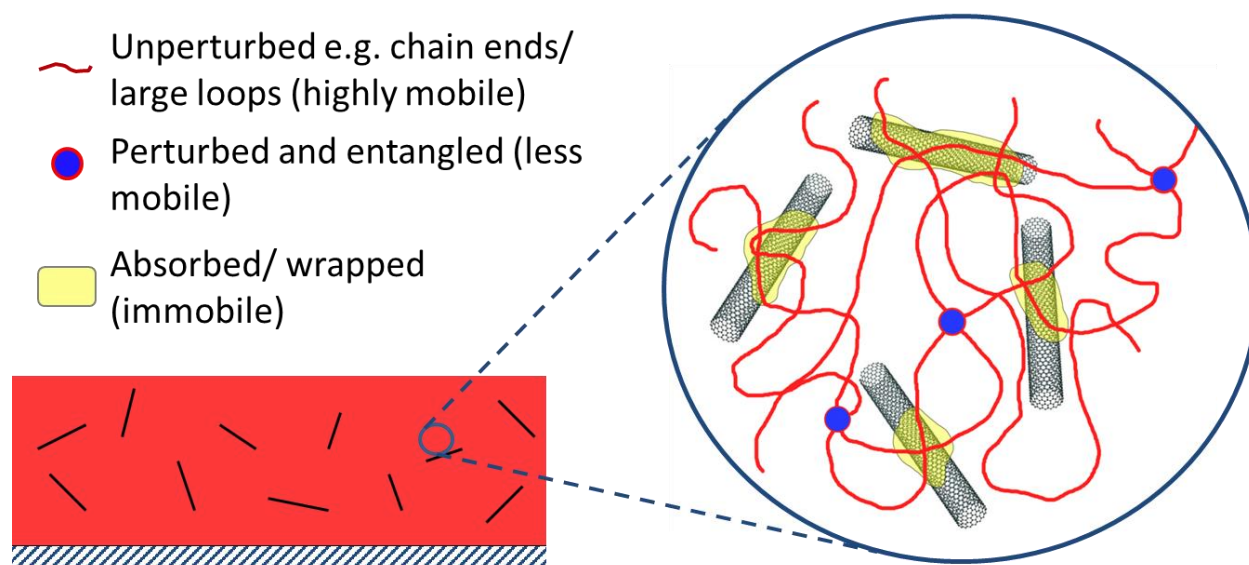


Figure 4.4 Illustration of some the possible local domains that could make individual segmental contributions to bulk SWNT composite dynamics.

$$M(t) = \sum_{i=1}^n A_i e^{\frac{-t}{\tau_i}} \quad (\text{Equation 4.1})$$

In Equation 4.1, A_i and τ_i are the scaling factor and decay time constant for each term. In this study, all samples required three exponential terms to achieve an adequate fit. A few samples could be fit using four exponential terms, however, convergence of those fits was largely dependent on initialization values and the fourth term did not improve fit quality. For reliability purposes and to avoid over-parameterization, fitting was limited to three exponential terms. As an example, the fitting of 1wt% SWNT in PS with both $n=2$ and $n=3$ can be found in Figure 4.5.

Once each decay is fit, a “bulk” T2 time can be calculated as the time it takes for the normalized total magnetization to decay to a value of $1/e$. A plot of the “bulk” T2 time vs. matrix composition and plots of scaling factors and time constants associated with each observed decay process vs. matrix composition, can be found in Figure 4.6 – Figure 4.9. These results will be examined further and compared with the rheological results in section 4.4.

4.3.2 Rheology

Oscillatory shear rheometry results were obtained as a temperature series with storage modulus (G'), loss modulus (G''), and complex viscosity ($|\eta^*|$) data as a function of angular frequency (ω) for each temperature step. Time-temperature superposition was then applied with good success using the Williams-Landel-Ferry (WLF) equation, generating $G', G'', |\eta^*|$ master curves at $T_g + 77^\circ\text{C}$ for each sample. As can be seen from the plot of $\text{Log}(a_i)$ vs. $1000/T$ for PS shown in Figure 4.10, for a given polymer matrix, 1wt% filler did not have an effect on the applicability of the WLF model, as the shift factors do not change. As a representative data set, Figure 4.11 shows the $T_g + 77^\circ\text{C}$ master curves for each PS sample. The full set of master curves

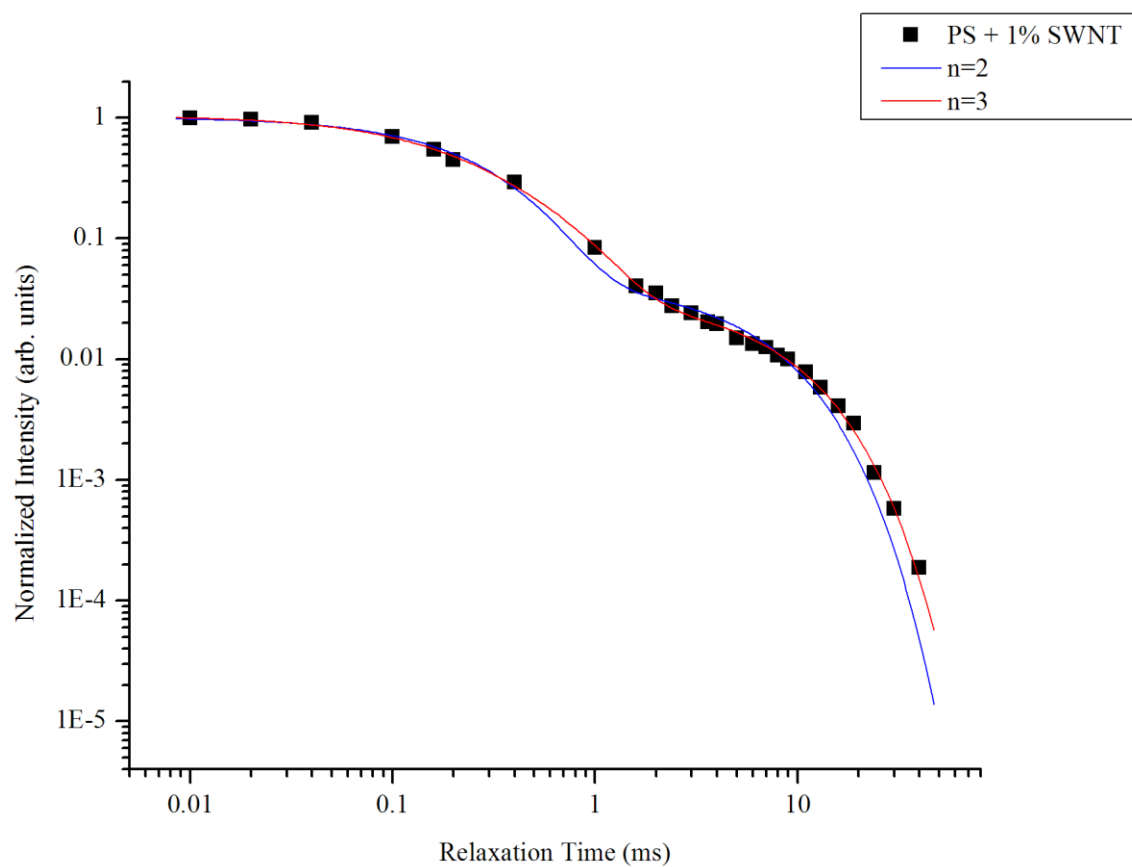


Figure 4.5 Plot of data and exponential fits of transverse magnetization decay for 1wt% SWNT in PS.

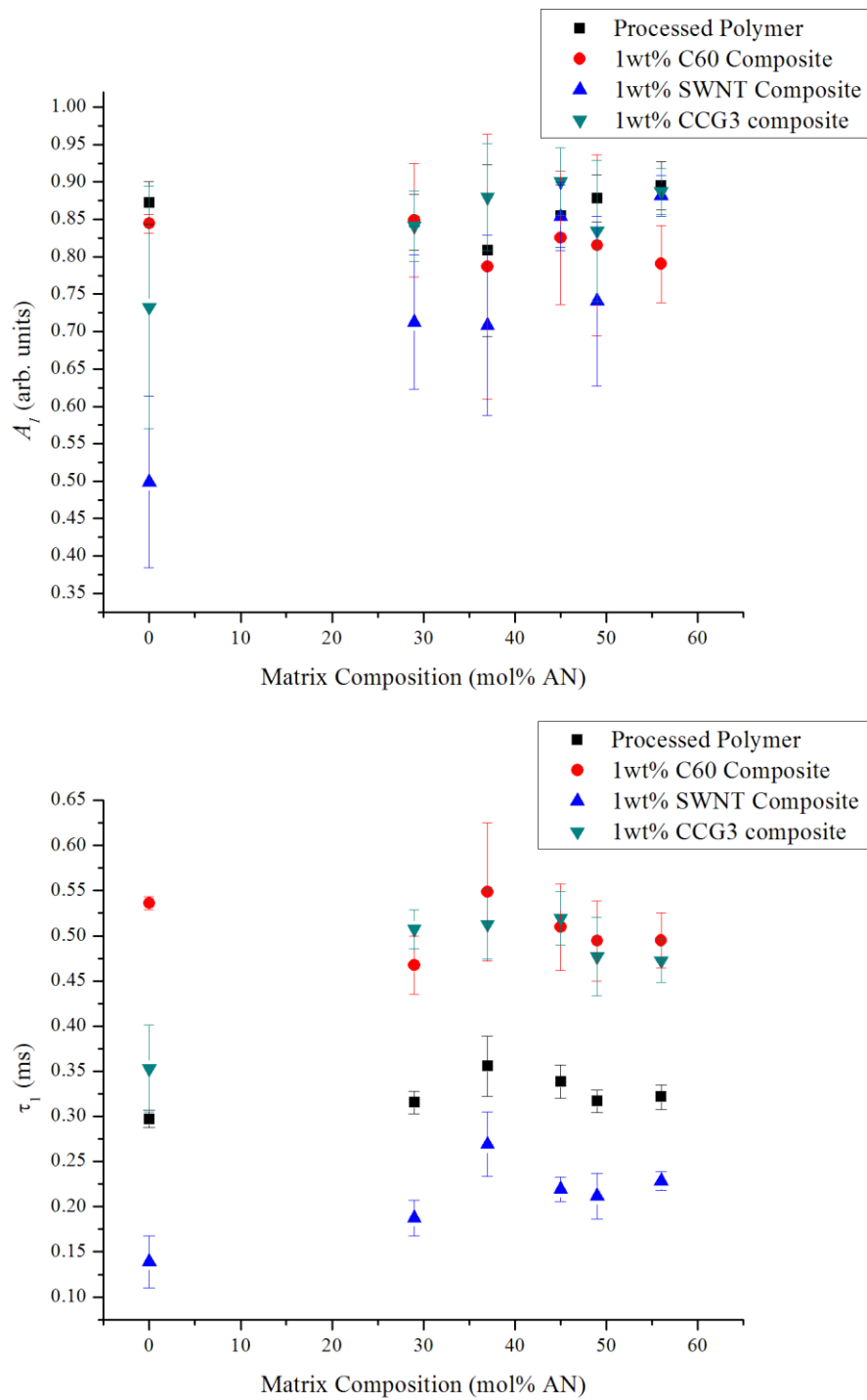


Figure 4.6 Scaling factor and decay constants for fastest magnetization decay process vs. matrix composition.

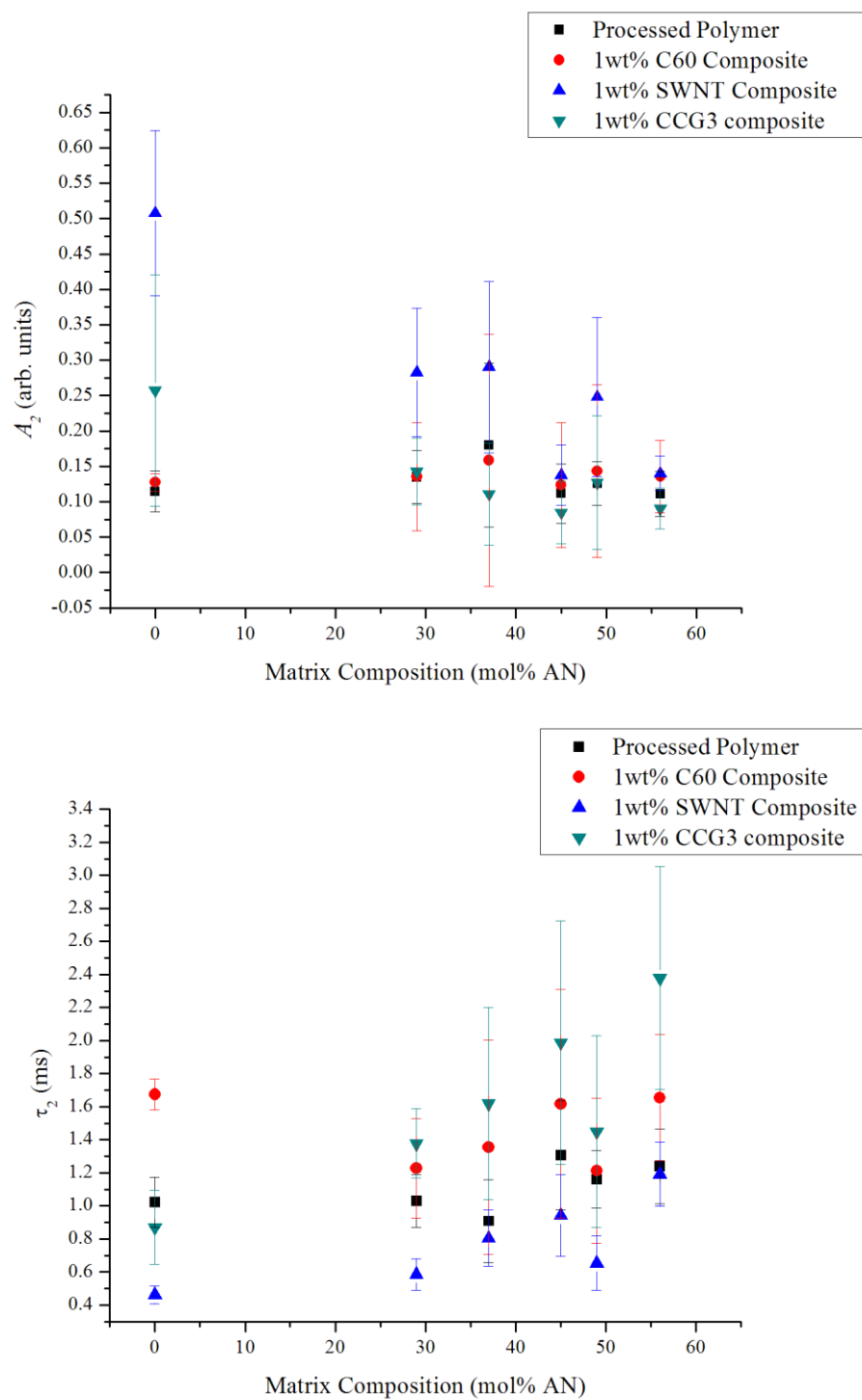


Figure 4.7 Scaling factor and decay constants for intermediate magnetization decay process vs. matrix composition.

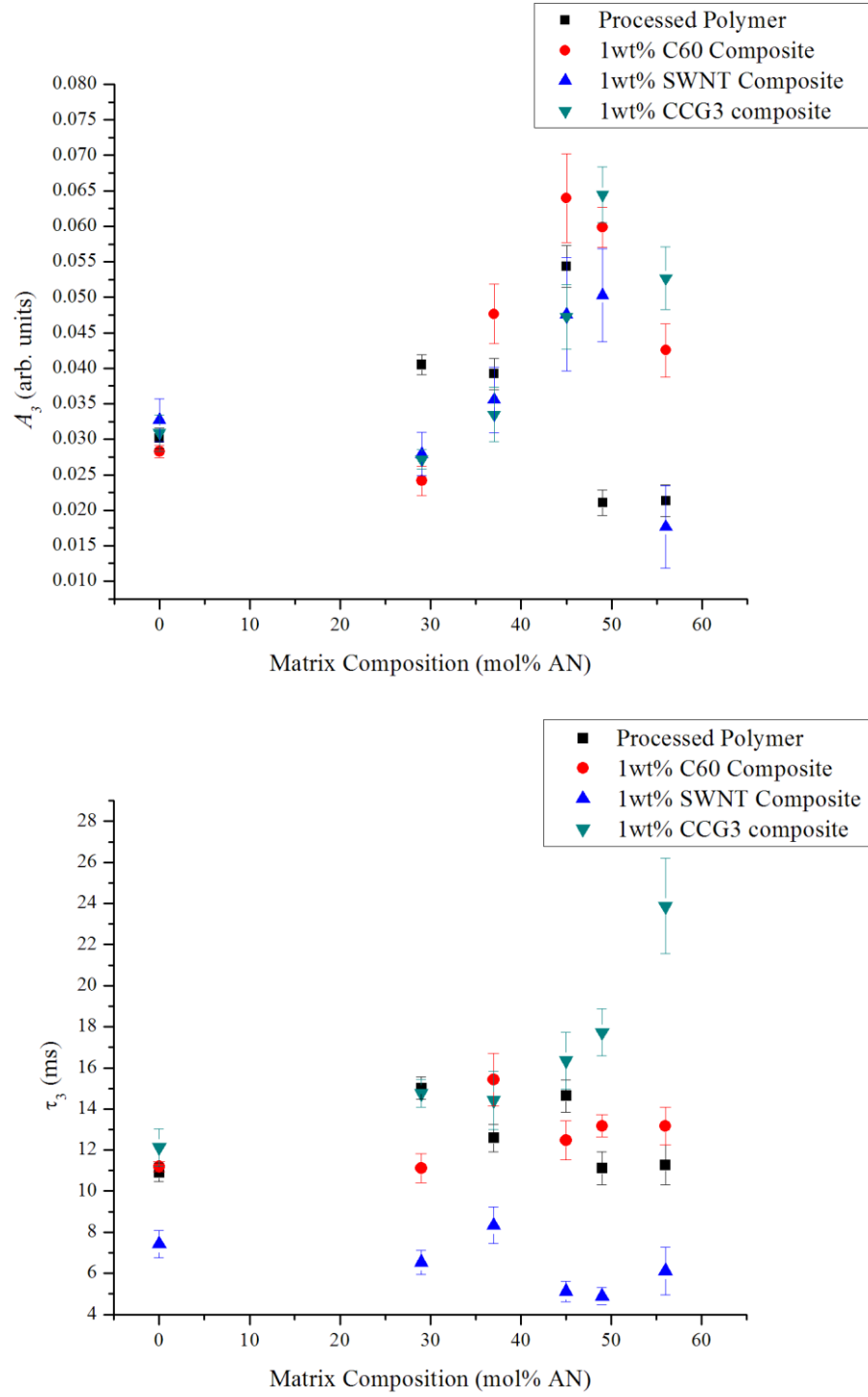


Figure 4.8 Scaling factor and decay constants for slowest magnetization decay process vs. matrix composition.

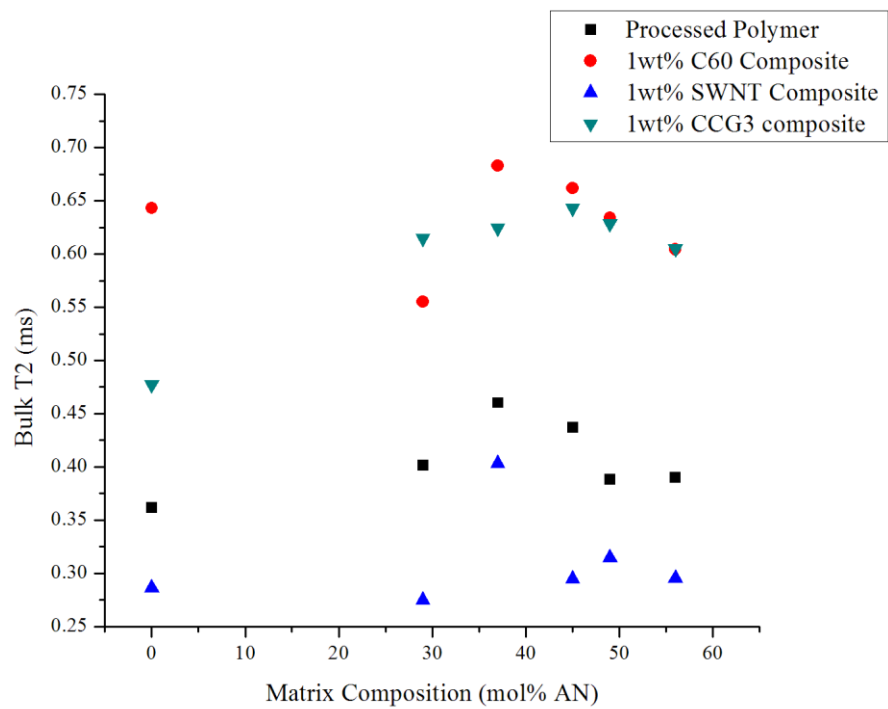


Figure 4.9 "Bulk" T2 relaxation time vs. matrix composition.

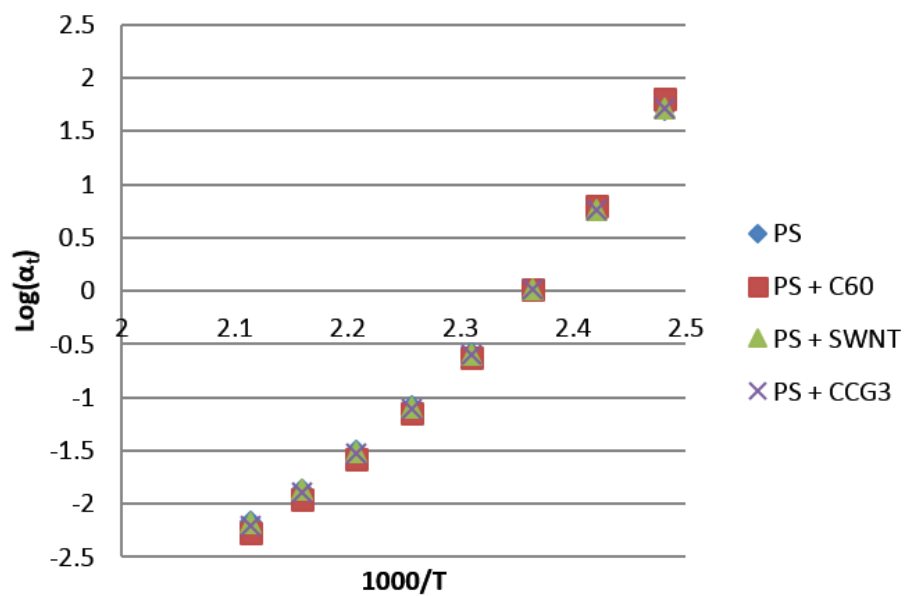


Figure 4.10 WLF shift factors vs. 1000/T for PS matrix samples

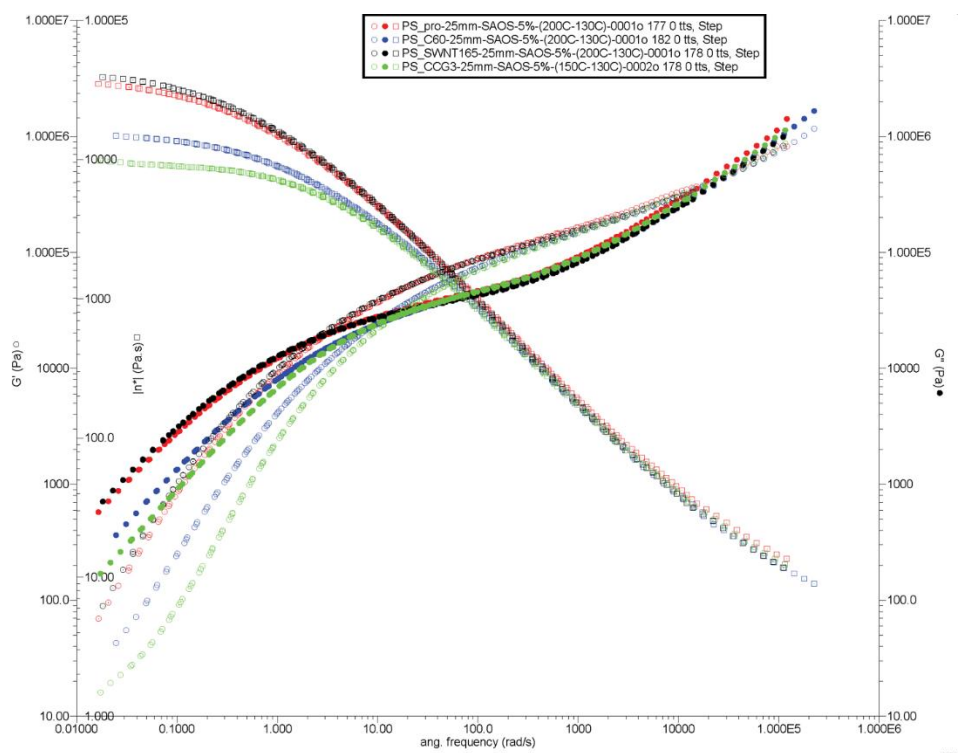


Figure 4.11 $T_g + 77^\circ\text{C}$ master curves for PS matrix samples

can be found in Appendix A-2. The rheological data will be examined further and compared with relaxometry results in the next section.

4.4 Discussion

4.4.1 Rheology

Figure 4.12 summarizes the complex viscosity data by plotting the ratio of the matrix zero-shear viscosity and the composites zero-shear viscosity as a function of the mole % AN (i.e. a value >1 indicates the pure polymer has a higher viscosity than the composite). On examining Figure 4.12 a few observations become obvious. First, it is clear inclusion of 1% CCG3 in all matrices up to 45% AN dramatically weakens the dynamic visco-elastic response of the parent polymer, resulting in a 3-4.3x decrease in the viscosity. Second, the only samples to show a definitive enhancement in visco-elastic response are the 1% SWNT composite in PS and SAN45. Lastly, the data also suggest that for C_{60} and SWNT samples there may be an optimal AN content at or around 45mol%, as it represents the minimal viscosity ratio for both fillers. The existence of an optimal AN content for dispersing SWNTs and C_{60} in SAN has been witnessed in previous work with SWNT-SAN, and C_{60} -SAN PNCs^{22, 106}. Also note worthy, is the agreement of PS sample results with recent simulations of rod, sheet, and icosahedra filled PNCs⁹⁹. In this report, rod filled and sheet filled PNCs had the highest and lowest viscosities respectively, and this ordering is attributed as a direct relation to the number of bridge chain (in contact with 2 or more NPs) present in each nanocomposite.

In intermediate to high MW polymers, average number of entanglements per chain (entanglement density) is generally the dominant factor effecting melt viscosity. The effect of NP inclusion on the entanglements in the matrix polymer can be characterized by the degree of polymerization between entanglements, DP_e , which can be calculated from the plateau modulus

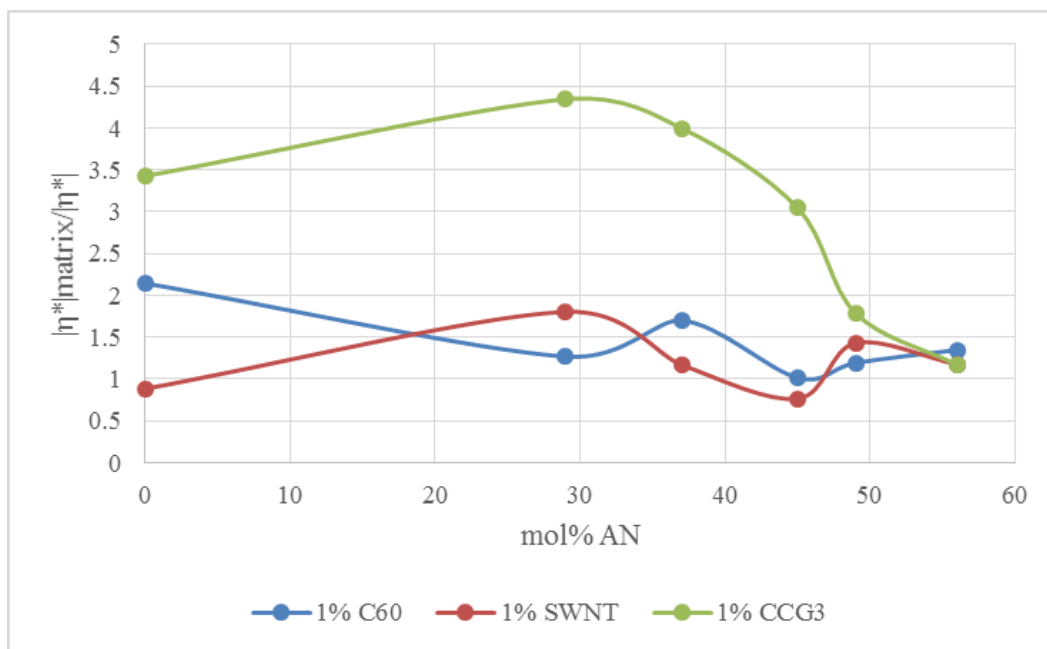


Figure 4.12 Ratio of the matrix zero-shear viscosity and the composite's zero-shear viscosity. The solid lines are a guide for the eye.

as outlined in Appendix A-2. The number of entanglements per chain equals the degree of polymerization (DP) of the polymer divided by the DP_e , therefore as DP_e increases the number of entanglements per chain decreases. As can be seen from the plot of DP_e vs. mol% AN in Figure 4.13, inclusion of C60 in SAN PNCs has almost no significant effect on the apparent number of entanglements per chain (the uncertainty in calculating DP_e is around 10%), whereas the SWNT-SAN29 PNC exhibits a decrease in entangled density (increase in DP_e) of greater than 50%. Most interestingly though, the dependence of DP_e on AN content in the CCG PNCs appears nearly linear (from 29 to 56% AN) and almost completely divorced from that of the base polymer. It is also worth noting that none of the NPs have an apparent effect on matrix entanglements in PS and SAN56 PNCs; similar observation were made by Winey et al. in SWNT-PS PNCs at varied NP loadings.⁵² The fact that an apparent decrease in the number of entanglements per chain does not occur in the PS PNCs suggests that NP-AN interactions significantly impact the entanglement behavior of the matrix in the presence of the NPs. In the case of 1% SWNT in PS, our results appear similar to those of others^{52, 53, 107}; showing mild reinforcement of the matrix without appreciably effecting DP_e . This is likely due to the high aspect ratio of nanotubes causing them to act as impediments to entanglements. Initially, as AN is incorporated into the matrix, it appears that NP-AN interactions may disrupt chain entanglements. However for SWNT PNCs, as AN content and the potential for SWNT-AN interactions increases, the apparent DP_e reverts toward that of the matrix and the viscosity increases until the previously observed optimum at 45% AN is reached. Beyond 45% AN, shear-flow reverts to a viscosity decrease, while DP_e largely continues to follow that of the base polymer.

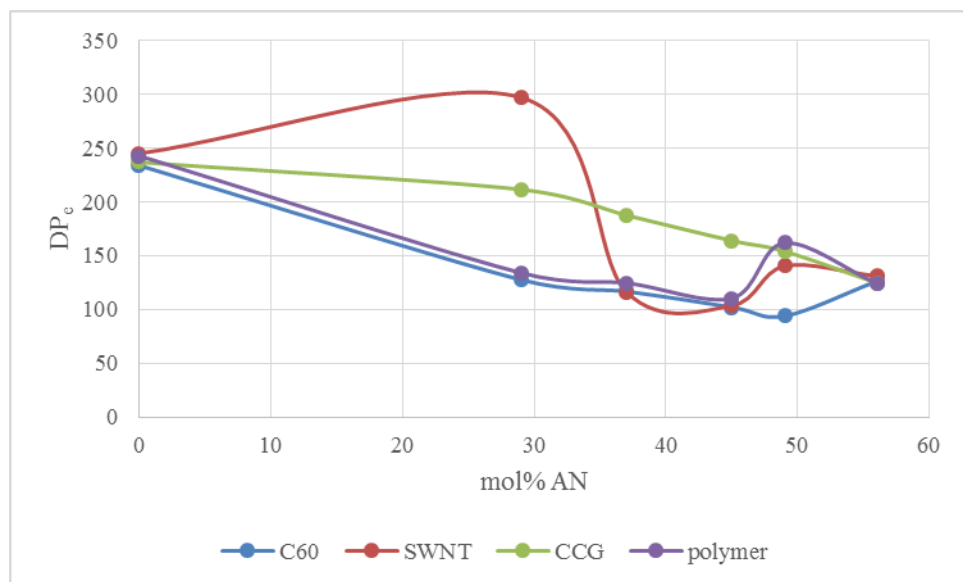


Figure 4.13 Degree of polymerization between entanglements vs. mol% acrylonitrile. Lower DP_e equals more entanglements. Lines are guides for the eye.

For the CCG PNC series, as is evident in Figure 4.12, an increase in shear-flow dynamics is observed at all matrix compositions. This is likely due to the CCG presenting as a large, flat, surface on the length scale of a polymer chain, disrupting polymer-polymer entanglements without introducing the possibility of NP-polymer entanglement. The result of this would be a layer of higher mobility at the NP-polymer interface. Polymer chains at this interface would be able to diffuse more rapidly parallel to the surface, resulting in increased NP-polymer slippage and a reduced viscosity. Increasing the number and strength of the NP-polymer interactions would serve to counter act this increased mobility. In examining the near-linear decrease in DP_e (Figure 4.13) for the CCG PNCs, it seems the apparent DP_e is dependent almost entirely on the mol% AN and is thus related to the formation of CCG-AN interactions. Given this, and the fact that the entanglements generally dominate shear-flow dynamics in the melt, if the flow behavior of the polymer is primarily dependent on CCG-AN interactions, the dependence of the viscosity on %AN should be inverse that of the dependence of DP_e on %AN. Stated physically, as the mol% AN increases, the number of interactions increases, and the monomers between interaction points (i.e. DP_e) decreases, thus increasing viscosity. To test this supposition, the normalized viscosity is plotted vs. mol% AN and DP_e in Figure 4.14 and Figure 4.15 respectively. The mirroring trends of Figure 4.14 and Figure 4.15 are therefore consistent with the CCG-AN interactions being the primary factor effecting DP_e and the shear flow dynamics in CCG-SAN PNCs.

There is also an initial increase in CCG PNC shear-flow dynamics as mol% AN increases from 0% to 29% of almost identical magnitude to that seen in the SWNT PNCs, as is evident in Figure 4.12. However, unlike the SWNT PNCs, beyond 29% AN the viscosity ratio decreases monotonically and never reaches a local minimum or state of melt reinforcement. For these high

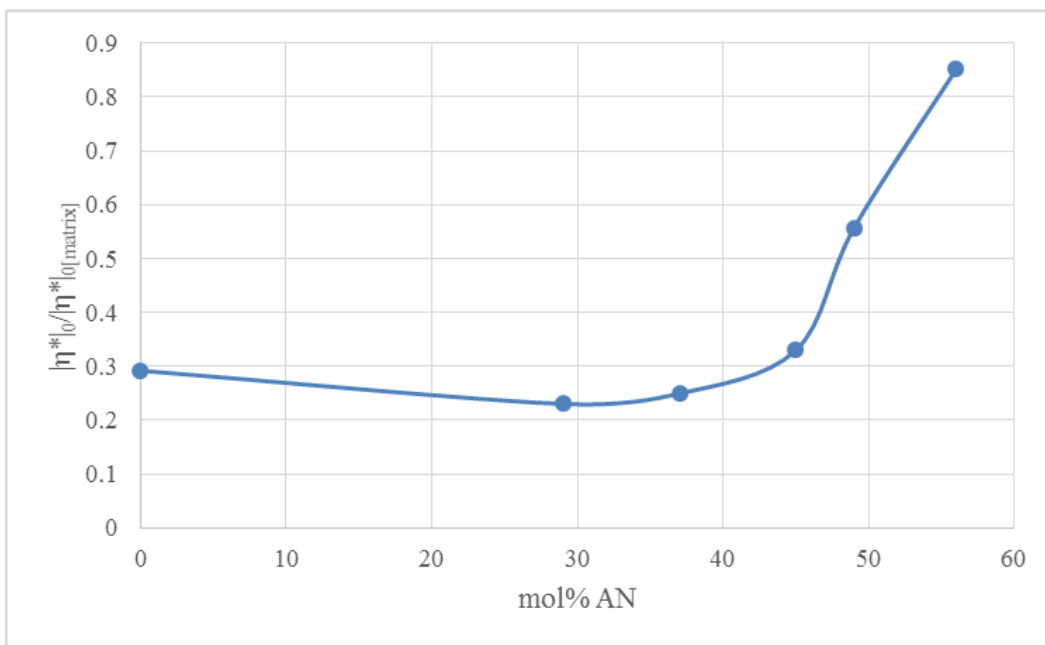


Figure 4.14 Matrix normalized viscosity vs. mol% AN for the CCG PNCs.

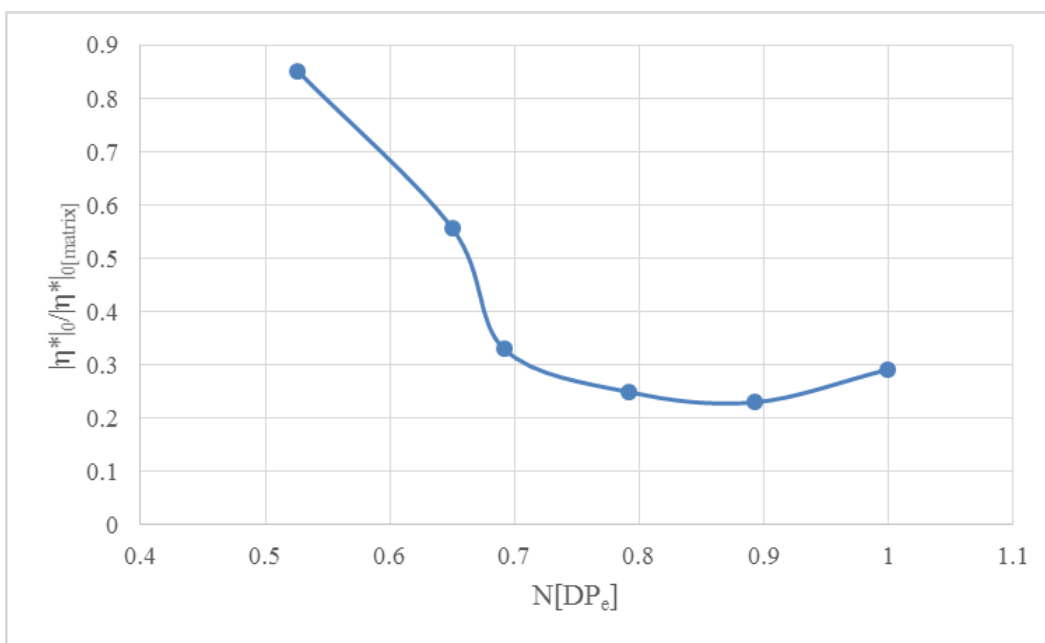


Figure 4.15 Matrix normalized viscosity vs. normalized (to 1) degree of polymerization between entanglements, N[DP_e], for the CCG PNCs. AN% in each sample decreases from left to right.

aspect ratio nanofillers, initial introduction of AN always increases dynamics. This suggests that for these largely immobile fillers, there is a mechanism by which the presence of AN at the NP-polymer interface sufficiently perturbs the entanglement behavior to reduce the bulk viscosity, even at 1% loading. One possible explanation is that the formation of NP-AN interactions creates a driving force for interfacial chains to associate more with the surface and further disentangle from the bulk. This scenario would create a layer with enhanced mobility near the NP surface, until AN content is sufficient that NP-AN interactions counter act the effect. The existence of a high-mobility layer near the NP surface is examined further based on segmental dynamics in the relaxometry discussion. The apparent convergence of the viscosity ratios above 45% AN suggests that this may represent a diminished ability of the matrix to effectively disperse the NPs. This is quite logical as the change in viscosity ratio with change in mol% AN is quite similar for SWNT and CCG PNCs until the convergence point. This would suggest that 45 mol% AN is likely the optimal matrix for achieving good CCG dispersion in SAN composites. Previous studies^{22, 106} evaluating SWNT and C60 dispersion in SAN PNCs are in agreement with the observed optimum at 45mol% AN.

Finally, the C60 PNCs exhibit an increase in dynamics for all but the SAN45 matrix. This is likely a result of the small size C60 (w.r.t. matrix R_g) and its ability to diffuse readily in polymer melts. This largely excludes C60 from behaving as an impediment to entanglements. Also, the small NP size and high curvature limit polymer-surface effects. As such, with the exception of SAN49, the addition of C60 has no effect on DP_e . Though the local maximum in viscosity ratio at 37 mol% AN may seem incongruent with logic, it and the overall trend of the viscosity ratios agrees very well with previous work examining C60 dispersion in SAN¹⁰⁶. That

is, the viscosity ratios follow the inverse trend of the miscibility limits; i.e. composites with better C60 dispersion yield slower dynamics.

4.4.2 NMR Relaxometry

Unlike rheology, NMR relaxometry measures dynamics on the segmental level so a response observed in these experiments at the local scale may not translate directly to the bulk level dynamic response of rheological measurements. The bulk level dynamics may be the result of the sum of the local dynamic processes or a particular local dynamic response may dominate the bulk dynamics, rendering contributions from the other processes largely moot. To monitor the impact of the presence of the nanoparticle on the local polymer dynamics, a plot of the ratio of the composite T_2 to that of the matrix T_2 as a function of mole % AN is shown in Figure 4.16. cursory examination of Figure 4.16 shows that even on the local level, SWNTs are the only NP that dynamically reinforce the matrix at 1% loading, and presents the same potential optimum AN content around 45%. Furthermore, inclusion of CCG3 and C60 clearly speed up matrix chain dynamics on the local level. Also, the near identical trend of $T_{2[C60]}/T_{2[matrix]}$ in the C60 composite to that of the C60 PNC viscosity ratio (Figure 4.12) suggests that the overall T_2 relaxation is characteristic of the bulk dynamic properties of the C60 PNCs. However, the T_2 ratio trends in the SWNT and CCG PNCs differ greatly from those of their viscosity ratios, indicating their local dynamics do not correlate directly to their shear-flow dynamics. In order to characterize how the local dynamics contribute to the overall bulk flow properties, each contribution to the total T_2 relaxation must be examined individually.

For a pure entangled matrix, basic theory predicts that the total transverse magnetization decay is the sum of two exponentials: one for chain segments near entanglement points that have restricted mobility, and one for highly mobile, largely unperturbed, loops and tails. However, for

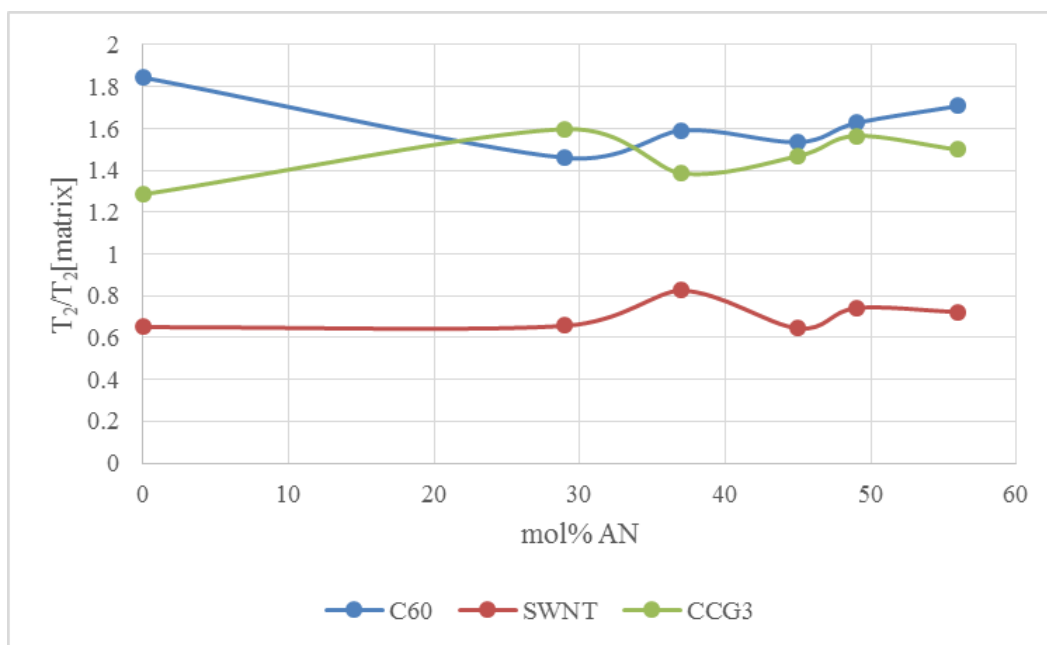


Figure 4.16 Ratio of the total relaxation time (T_2) for the composite to the matrix. Solid lines are guides for the eye.

the processed matrix samples, three exponentials were required to provide a good fit to the decay data. This is likely an effect of the high degree of polydispersity in both MW and AN composition could contribute to creating a dispersity of segmental relaxations. Unfortunately, the effect of the polydispersity is not confined to a single “corrective” decay process, but rather causes a signal of interest to be averaged across its temporal neighbors. As a result, for the matrix samples, correlation of a specific local process to a particular bulk flow property is not feasible. However, as can be discerned from the plots of normalized values of the inverse decay constants ($N[1/t_1]$, $N[1/t_2]$, $N[1/t_3]$) and degree of polymerization ($N[DP]$) vs. mol% AN in Figure 4.17, t_2 and t_3 carry a MW dependence, while t_1 does not. This suggests that a combination of t_2 and t_3 terms may be required to describe the bulk viscosity in terms of local segmental dynamics. Figure 4.18 is a plot of normalized viscosity, $1/t_2$, and $1/t_3$ as a function of mol% AN and further supports this, as both inverse decay constants trend similarly to the viscosity, but neither can adequately describe the viscosity behavior on its own.

As shown in Figure 4.16, there is clear reinforcement at the local level for all SWNT PNCs. However, the total relaxation does not appear to correlate directly to the rheological data, and the individual processes need to be examined separately. Moreover, no single process adequately describes the overall shear-flow behavior. However, it appears that $1/t_2$ correlates well to measured rheological data. Figure 4.19 is a plot of the normalized values of $1/t_2$ for the SWNT series and the DP_e of the SWNT PNCs and pure matrix as a function of mol% AN. The close correlation of $1/t_2$ to $N[DP_e]$ of the matrix and its mild correlation to $N[DP_e]$ of the PNCs, suggests that for the SWNT PNCs the intermediate decay process ($0.5\text{ms} \leq t_2 \leq 1.2\text{ms}$) is representative of entangled segments. More specifically, the close relationship between $1/t_2$ and the DP_e of the matrix suggests that $1/t_2$ corresponds to entangled chain dynamics that are largely

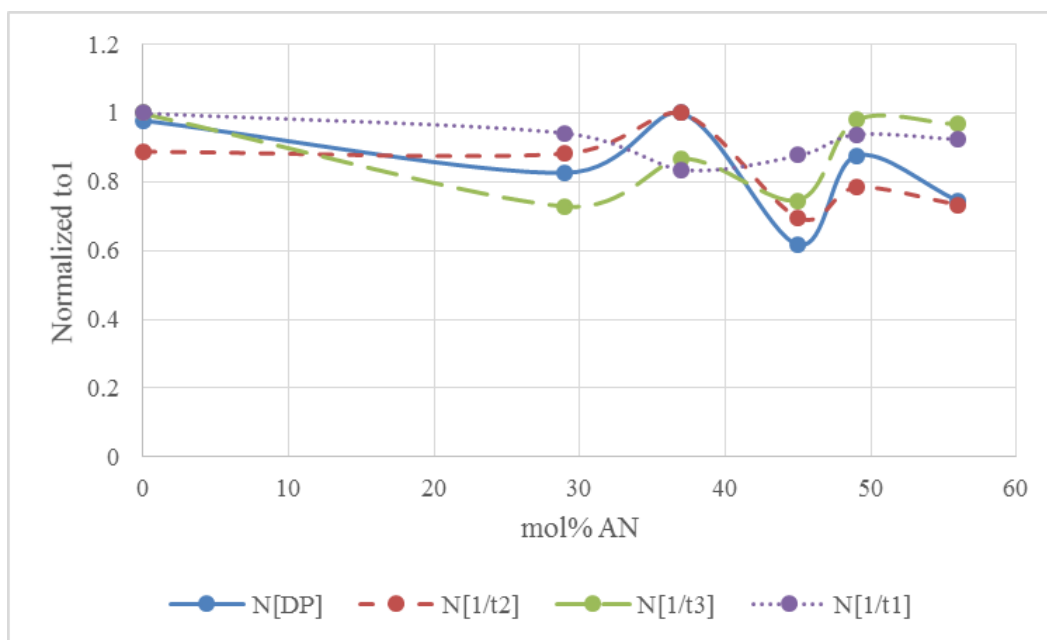


Figure 4.17 Normalized degree of polymerization (DP) and inverse decay constants ($1/t_1$, $1/t_2$, $1/t_3$) vs. mol% AN for the processed matrix samples.

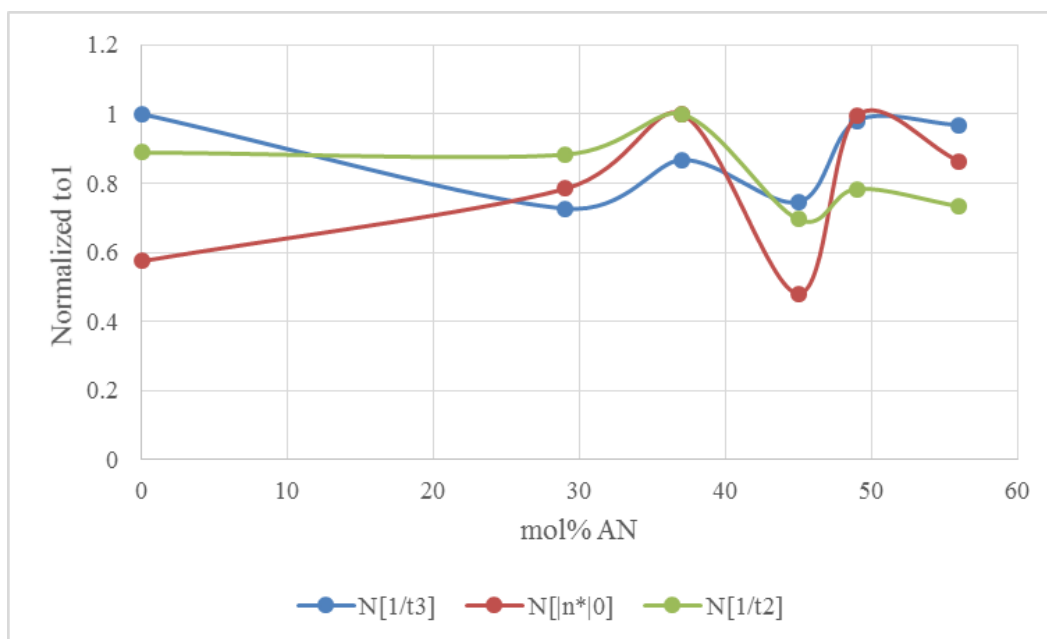


Figure 4.18 Normalized viscosity, and inverse decay constants $1/t_2$ and $1/t_3$ vs. mol% AN for the processed matrix samples.

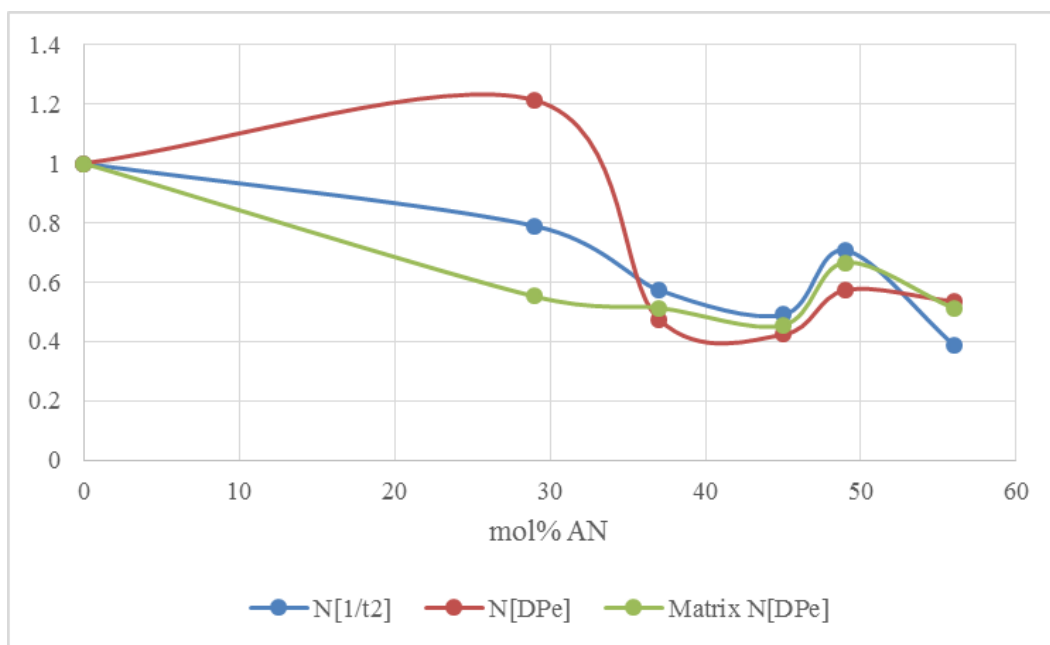


Figure 4.19 Normalized values of $1/t_2$ for the SWNT PNCs and DP_e for the SWNT PNCs and pure matrix vs. mol% AN.

unaffected by the NPs presence. The apparent lack of dependence of $1/t_2$ on the formation of NP-polymer interactions implies that $1/t_2$ represents the motion of PNC regions not in the vicinity of a NP. However, the precise physical picture surrounding the t_1 and t_3 decay processes is less clear. The normalized values of $1/t_1$ and $1/t_3$ are plotted as a function of mol% AN in Figure 4.20. From this plot, it appears that $1/t_1$ and $1/t_3$ have similar mol% AN dependencies, but with overriding opposing slopes. This suggests that the two processes are interconnected, as both are similarly dependent on the potential to form SWNT-AN interactions, and the opposing prevailing slopes suggests that the processes are inversely correlated.

Inspection of the CCG series indicates that it displays some unique behavior. As shown in Figure 4.21, $1/t_2$ of the CCG composites shows strong correlation to the DP_e of the matrix and little correlation to the DP_e of the CCG PNCs. This indicates that $1/t_2$ likely corresponds to polymer chain segments where the number of entanglements is largely unperturbed by the presence of the NP. However, unlike the other PNC samples, as shown in Figure 4.22 there appears to be a significant correlation between $1/t_3$ and DP_e in 1% CCG filled composites. Figure 4.23 shows that the viscosity of the CCG PNCs varies almost identically with DP_e and $1/t_3$. From this, it is clear that at 1% CCG loading, t_3 is representative of the local segment processes that are most responsible for the observed bulk shear-flow dynamics. Given that $1/t_3$ appears to be reflective of the PNC's effective DP_e and that both parameters decrease with an increased potential to form NP-AN interactions, it is logical to assign t_3 to the segmental motions near the CCG surface. This implies the existence of a high-mobility layer of polymer at the NP interface. This is in agreement with simulation and experimental results, reporting a reduction in the number of entanglements per chain in thin-films and at interfaces¹⁰⁸⁻¹¹¹, and recent results extending theory to PNCs^{112, 113}. Together, the rheological and relaxometry results suggest that

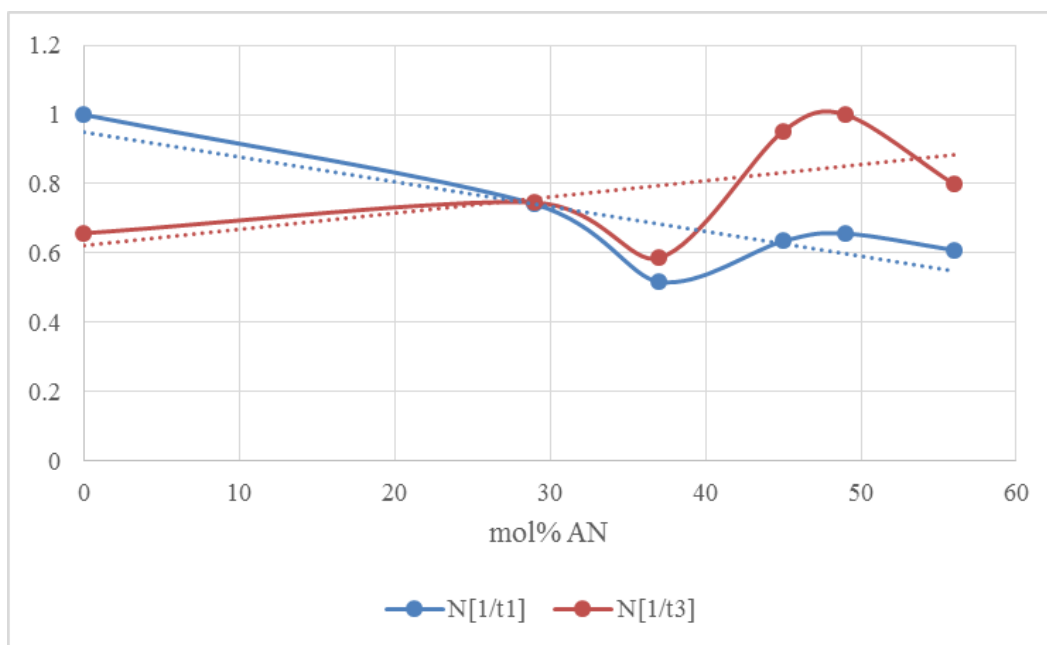


Figure 4.20 Normalized $1/t_1$ and $1/t_3$ values vs. mol% AN for SWNT PNC series. The dotted lines depict the prevailing downward and upward trends in $1/t_1$ and $1/t_3$ respectively.

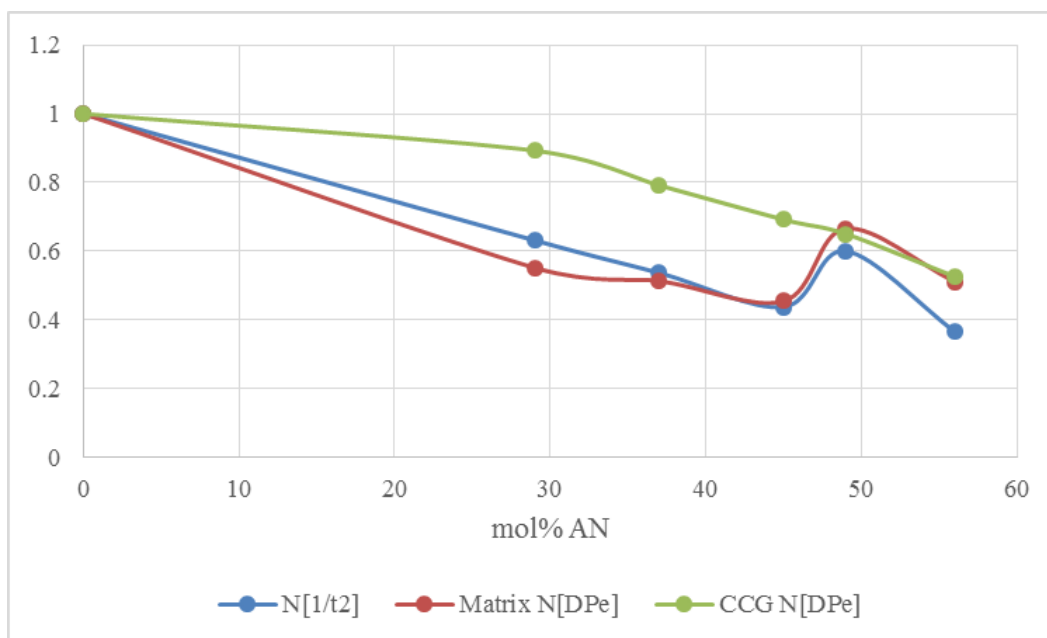


Figure 4.21 Normalized values of $1/t_2$ for the CCG PNCs and DP_e for the CCG PNCs and matrix vs. mol% AN

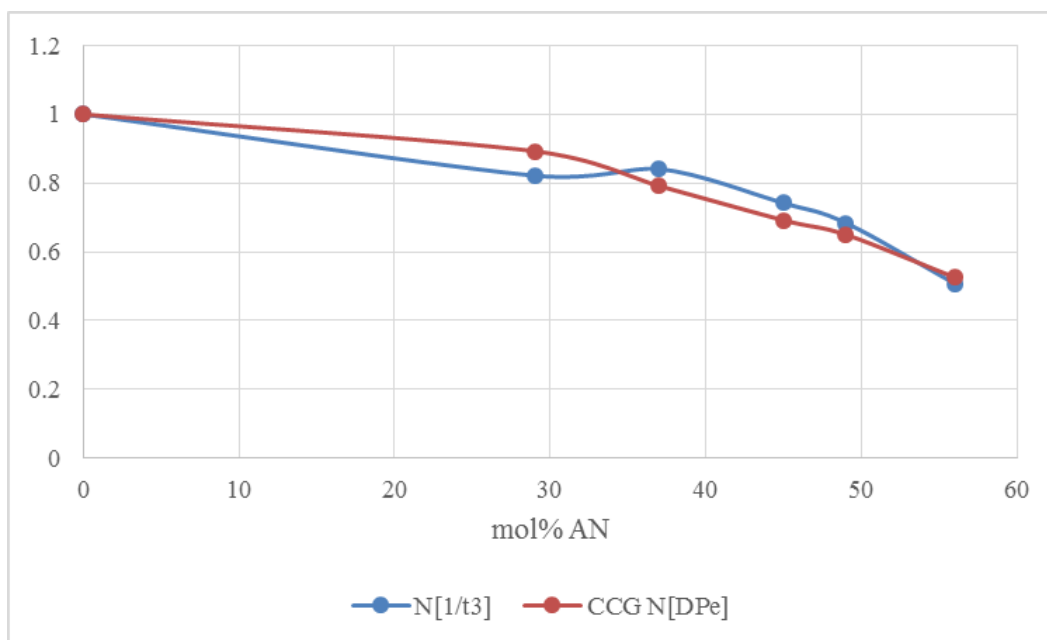


Figure 4.22 Normalized (to 1) values of $1/t_3$ and DP_e vs. mol% AN for the graphene PNCs.

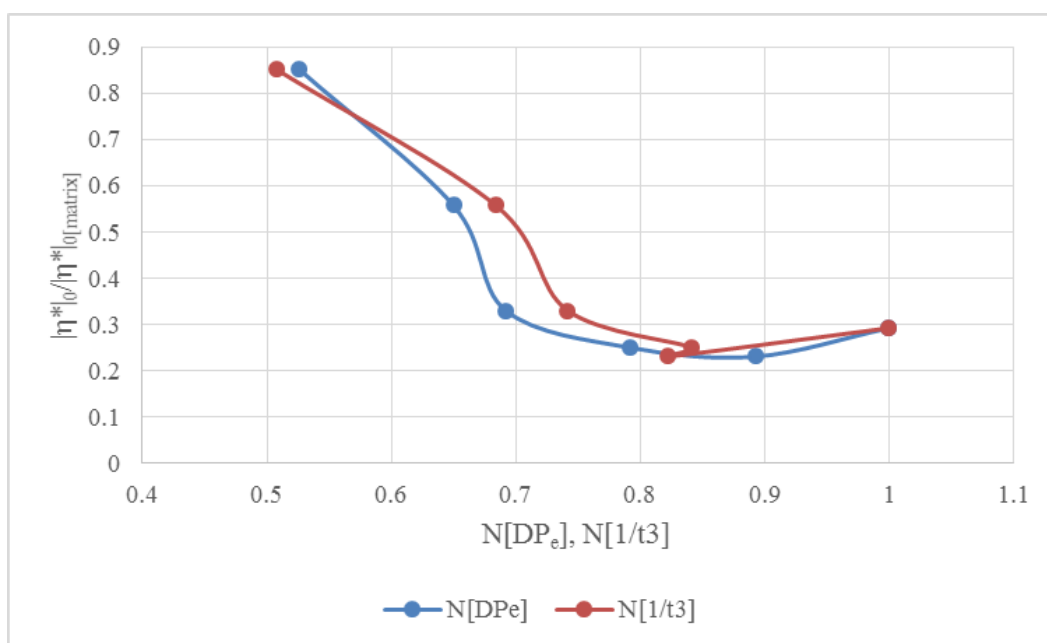


Figure 4.23 Zero-shear viscosity ratio vs. normalized values of DP_e and $1/t_3$ for CCG PNCs. The solid lines guide the eye through sequential matrix compositions. The mol% AN generally decreases from left to right.

the dramatically increased dynamics observed in CCG PNCs are due to chain disentanglement at the polymer-CCG interface creating a high-mobility, “lubricating” layer. The increase in viscosity and decrease in both $1/t_3$ and DP_e with increased AN content suggests that, increased formation of CCG-AN interactions creates a more tightly held layer with shorter loops between interactions points. The effect of this conformation is to temper the mobility of the interfacial layer, slowing down the dynamics of the PNC as a whole relative to PNCs with lower AN content. The t_1 decay process likely corresponds to less mobile chain segments closer to CCG-AN interaction points, but this cannot be said definitively without further study.

In the case of these high aspect ratio NPs (SWNT and CCG), the expected physical picture in Figure 4.4 does not appear to be a good representation of the actual local segmental domains. This inhibits a deeper correlation of the local diffusive dynamics to the bulk shear-flow dynamics. Adopting a single, NP level, physical interpretation of the relaxometry data allows the bulk dynamics to be related to local dynamics in a more straightforward manner. In this interpretation, a polymer chain segment at the surface of a NP can be affected dynamically in three ways: the formation of attractive NP-polymer interactions (which corresponds to a strong decrease in segment mobility), segmental wrapping of the NP (which corresponds to a mild to moderate decrease in segment mobility), and a reduction in the number of entanglements per chain due to surface effects^{110, 111} (which corresponds to a mild to moderated increase in segment mobility). If a wrapped or NP-interacting chain segment is considered a tethering point, and the contour length of this bound segment is less than DP_e , then these shorter segments would not be able to entangle to the same degree as free chains, reducing the number of entanglements per chain in this region. This would create a boundary layer of increased mobility, where the width of the layer, and the magnitude of the mobility change, are dependent on the effective MW of

these tethered segments. The observed bulk dynamics are then a combination of unmodified segmental dynamics, and the NP modified segmental dynamics. An illustrated representation of this model for the local dynamics of the SWNT PNCs is shown in Figure 4.24. In this depiction, areas of low mobility are blue, areas of high mobility are yellow, and red indicates areas of moderate mobility that are mostly unaffected by the NP. This scheme is designed so the total amount of a color (average color saturation times the area in which that color exists) should be an approximate representation of the corresponding normalized inverse relaxation constant. That is $1/t_1$ is represented by the amount of blue present, $1/t_2$ is represented by the amount of red present, and $1/t_3$ is represented by the amount of yellow present. A smooth, broad transition between colors indicates a high degree of interaction between the corresponding segmental domains, and a sharp-narrow transition represents little interaction between the domains.

For the SWNT series, the PS PNC represents a NP-polymer sample that has little interaction between the two components. This means that using the proposed physical interpretation; the only modified local contributions to the bulk dynamics are from NP wrapping and entanglement reduction. However, because of the high curvature of the SWNT surface, a polymer segment diffusing toward the NP surface could readily have its trajectory deflected around the SWNT rather than reflected back into the bulk of the polymer coil. This means that the effect of surface induced entanglement reduction is likely minimal compared to that of NP wrapping. This would suggest mild melt reinforcement without an appreciable effect on the effective DP_e of the bulk, which is in agreement with measured shear-flow dynamics. This is depicted in Figure 4.24 by a diffuse region of chain segments with mildly reduced mobility (dull blue), with long tails and loops that extend well into the bulk (red). Since there are no NP-polymer attractive interactions, these tails and loops can be relatively long, creating a broad

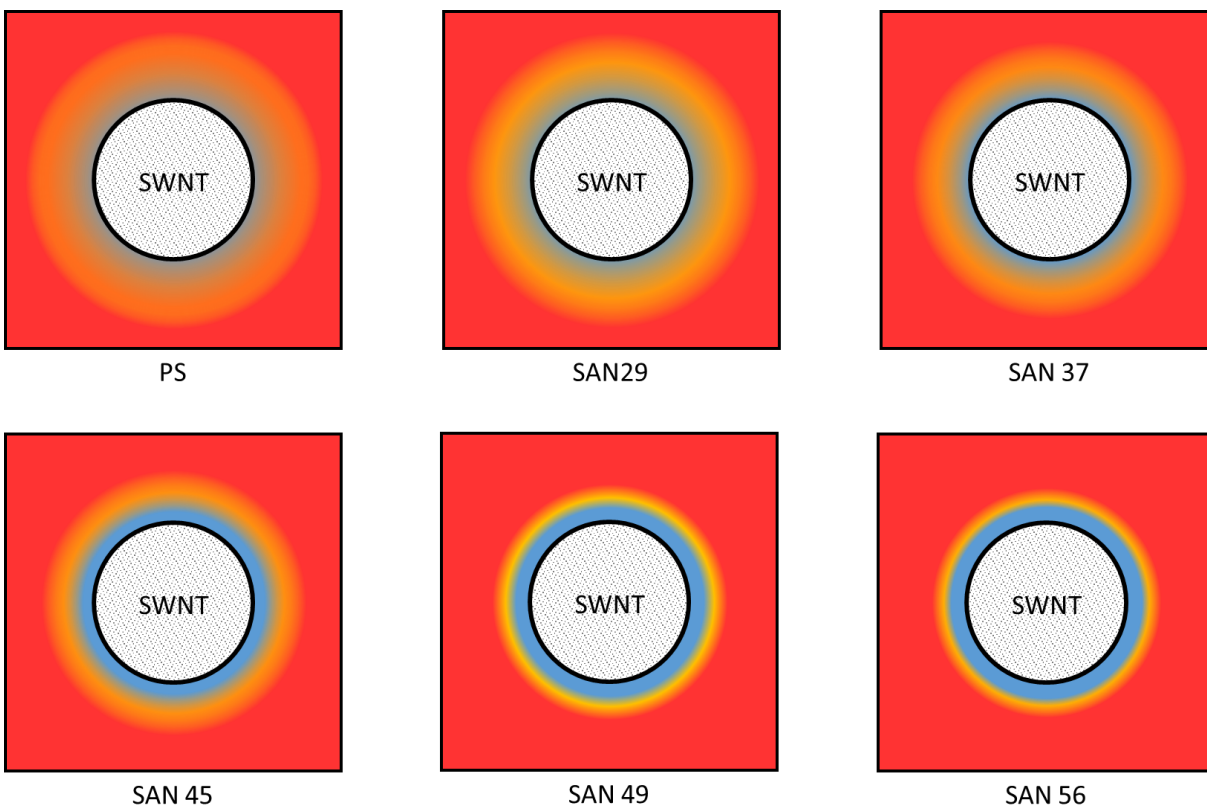


Figure 4.24 Radial cross-sections of single NP depiction of the local dynamic domains for the 1wt% SWNT series. Blue indicates low mobility, red indicates moderate mobility, and yellow indicates high mobility.

boundary layer (dull yellow) with a very mild increase in mobility but can still transfer the effects of NP wrapping to the bulk. Introducing a modest amount of NP-polymer interactions (SAN29) appears to decrease the mobility of surface chain segments only slightly while producing a significant increase in boundary layer mobility, and an overall increase in bulk dynamics. From the single NP perspective, this is quite logical. Introducing NP-polymer interactions creates more tethered segments, consequently shortening the length of loops and tails. If the effective MW of these loops and tails drops below a critical MW for entanglement with the bulk there would be a significant increase in the mobility of the boundary layer. If the boundary layer is mobile enough and broad enough it could function like a lubricating layer between the bulk and NP and cause the observed increase in bulk dynamics. However, as the AN content is increased further the surface segments become more immobile, the width of the boundary layer decreases with only a small increase in boundary layer mobility. The balancing of the surface segment mobility with tail and loop length likely controls how much the surface segment mobility vs. boundary layer mobility affects the bulk dynamics. In such a scenario the SAN45 PNC likely represents the critical point beyond which tails and loops are too short and the boundary too sharp to effectively transfer the effects of surface chain immobility to the dynamics of the bulk. These likely gives rise to the minimum in the viscosity ratio observed in the SAN45 PNC.

The proposed low-mobility surface layer/mobile boundary layer structure aligns with results from colleagues that suggest a low mobility layer at the silica NP surfaces outside of the anomalous regime¹¹⁴, and recent results suggesting that a low density layer may exist within the anomalous regime. This dual mobility structure would also agree with the phenomenological “trap” model proposed by Winey et al. to describe anomalous polymer diffusion near SWNTs.⁵²

In this model, polymer chain dynamics near the SWNT are defined by a boundary layer of restricted mobility at the SWNT surface. Such slow diffusing boundary layers have been witnessed by collaborators in spherical silica NP PNCs.¹¹⁴ However, in the trap model, chain diffusion in this boundary layer is anisotropic; having a faster diffusive mode parallel to the SWNT and a slower diffusive mode perpendicular to the SWNT. Such a model might be useful in developing a clearer physical picture behind the t_1 and t_3 processes. This also suggests the possibility of an extra, highly mobile domain represented by long loops and tails from unperturbed chains, which is not being accounted for. However, if such a domain does present itself as a unique local process, its contribution to the overall transverse magnetization decay is likely too weak to be reliably detected within the parameters of this study. It is important to note that, while the trap model has been able to describe anomalous diffusion in SWNT PNCs to a high- degree, the separate diffusive modes it proposes have not been observed experimentally.

Applying a similar physical picture as used in the SWNT PNC analysis above describes the CCG PNC results very well. However, the primary difference that must be taken into account is that the CCG is effectively a large flat surface on the length scale of a polymer chain. This means that polymer chain wrapping cannot contribute to the dynamics, and mobility reducing NP-polymer interactions and mobility increasing surface effects dominate the local segmental dynamics. Based on this model, a non-interacting matrix (PS) should show a significant increase in bulk dynamics, as there are no local interactions to counteract the chain slippage at the NP surface caused by surface induced disentanglement. Similarly to the SWNT PNCs at 29 mol% AN, modest NP-polymer interaction may cause surface loops and chains to recede from the bulk increasing the mobility of the boundary zone. Further increases in AN content begin to counteract the increased mobility of the surface chain segments, causing a slow decrease in bulk

dynamics with increasing mol% AN. In the model, this effect tapers off as surface tails and loops become too short to effectively transfer the effect of surface interactions into the bulk. This exact trend is observed in the viscosity ratio data, strongly suggesting that the proposed physical model of the local dynamics describes the local segmental dynamics that guide the shear-flow dynamics of the bulk materials.

Looking closer at the C₆₀ results on a molecular level reveals that C₆₀ is very small compared to the matrix chain and can readily diffuse in the melt. The isotropic nature of the nanoparticle means that any entanglement disruption or formation of NP-polymer interactions only alter the dynamics on a very local length scale. The result of this perspective is that the C₆₀ bulk dynamics do not deviate significantly from those of the pure matrix and examination of the individual local dynamic segmental motions does not provide additional insight into the bulk dynamic behavior. In fact the C₆₀ PNCs are the one set of PNCs that shows good agreement between the viscosity ratio data (Figure 4.12) and the total relaxation time ratios (Figure 4.16). Overall, at 1% loading, the dynamics of the C₆₀ PNC appear to largely reflect those of the parent polymer, only slightly faster. C₆₀ is far smaller than the polymer R_g and the other NPs and is known to readily diffuse in PNCs melts. The implication is that C₆₀ does not alter the entanglements in the polymer matrix and when attractive interactions are formed, can still diffuse readily at 1wt% regardless of the presence of non-covalent interactions. From this perspective, C₆₀ PNCs are likely to behave as classical hard sphere nanocomposites, which are known to exhibit faster dynamics at low particle loading (within the $R_g/R_{NP} \geq \sim 3$ regime). Knowing this, it is likely this technique is not sensitive enough to probe the low concentration of the PNC specific segmental domains present at 1wt% C₆₀.

4.5 Conclusions

NMR relaxometry was successfully used to probe local chain dynamics and combined with oscillatory shear rheometry to monitor the impact of nanoparticle shape on the local and global dynamics of 1% polymer nanocomposites. A physical description of the correlation between the local dynamic processes and the bulk dynamics was developed.

For all NPs studied, 1wt% loading is sufficient to significantly alter the dynamics of the polymer in the PNC. However, NP shape plays a major role in defining how the presence of the NPs alters the polymer dynamics. At 1wt% NPs, the ability to form NP-polymer entanglements is a crucial factor in determining whether an NP will slow down or speed up the melt dynamics of the polymer chains. The overall effect of NP-AN interactions is also important, but not as straightforward. At low AN content, the non-covalent interactions tend to speed up dynamics while at higher AN content, up to an optimum, their presence tends to slow down chain dynamics.

Interpretation of the results suggest that the observed changes in chain dynamics are due to the formation of a high-mobility boundary layer between the bulk and chain segments that interact with the NP surface. The mobility of this layer and its effect on the bulk dynamics are determined by NP shape and AN content. NP shape is the primary factor effecting the formation of this layer, and NP-AN interactions serve to counter-act or reinforce the effects of NP shape. SWNT can reinforce the melt because of its ability to entangle with the matrix. Likewise, CCG and C60 cannot entangle with the matrix and therefore their presence speeds-up melt dynamics. For the anisotropic CCG and SWNT NPs, as NP-AN interactions are introduced the highly-mobile boundary layer results in an effective disentanglement, which translates to faster dynamics. However, as AN content further increases the mobility of this layer decreases, resulting in less bulk disentanglement, and slower bulk dynamics (w.r.t PNCs of lower AN

content). However, C60 is sufficiently small that surface effects do not cause apparent disentanglement, while bridging chains and NP diffusion are likely the primary factors effecting bulk dynamics. There is an optimum matrix content of 45mol% AN, above which increased NP-AN interaction may be detrimental to NP dispersion. This is in agreement with previous work studying C60 and SWNT dispersion in SAN.

CHAPTER 5

DETERMINING THE EFFECT OF NANOPARTICLE FILLERS ON POLYMER MATRIX DIFFUSION USING NEUTRON REFLECTIVITY

5.1 Background and Introduction

In the constant pursuit of newer and better engineering materials, researchers are ever more frequently turning to nanotechnology and nanocomposites for solutions. Polymer nanocomposites are of particular interest because of their potential to translate many of the desirable properties of nano-scale fillers into processable bulk materials. However, frequently this is not a straightforward task. In many instances, fillers will aggregate, or the nanocomposite otherwise fails to achieve the predicted enhancement in mechanical, electrical, optical, or thermal properties desired for the bulk material. In such cases, a higher than anticipated loading of the nanoparticle may be required, or the desired properties may be unattainable. Recent reports of anomalous melt dynamics in nanoparticle filled polymer matrices^{47-49, 52-54, 107, 115-117} have sparked a lot of curiosity in the effects of nano-scale fillers on the diffusive behavior of polymer chains. If a greater understanding can be obtained of how inclusion of a nanoparticle (NP) filler affects the chain dynamics of a polymer composite in the melt, than that information can aid in designing matrix/NP systems and processing conditions that translate NP properties into bulk material properties more efficiently.

Much of this anomalous melt behavior has been reported at low nanoparticle loading. Low NP loading composites are of particular interest because the NP filler typically constitutes much of the expense associated with nanocomposites, and using less filler lowers costs. Additionally, low-loading composites have the potential for better retention of favorable matrix

properties such as optical transparency or ease of processing, in tandem with NP enhanced bulk material properties.

Previous studies have noted anomalous composite dynamics from numerous materials and varied methods. Winey et al. used elastic recoil detection to monitor the diffusion of thin deuterated polystyrene (dPS) tracer films into thick polystyrene (PS)/carbon nanotube (CNT) composites.^{52, 53, 107} The researchers reported that as the CNT concentration increased, dPS tracer diffusion coefficient decreases until a minimum at ~0.4 vol%. Beyond the minimum (up to 4 vol%) the PS diffusion coefficient increased towards the original value at 0 vol%.^{52, 107} A follow up study using CNTs of various diameters showed that the presence and depth of the minimum was strongly dependent on the ratio of the radius of gyration ($R_{g,dPS}$) of the dPS to the radius of the CNT (R_{CNT}).^{53, 107} More specifically it was found that if $R_{g,dPS} > R_{CNT}$ then a minimum in the PS diffusion was observed with concentration, but if $R_{g,dPS} < R_{CNT}$ no minimum was observed. These observations led these researchers to propose a new diffusive model to describe the diffusive behavior polymer chains near CNTs.^{52, 107, 115} The model is able to depict the dependence of the diffusive minimum on $R_{g,dPS}:R_{CNT}$ by splitting dPS diffusion into separate modes: diffusion perpendicular to the CNT and parallel to the CNT. The result of this anisotropic diffusion is that for $R_{g,dPS} > R_{CNT}$, the diffusion mechanism for dPS along the CNT resembles that motion along a surface (parallel), and is faster than diffusion away from the CNT (perpendicular). In this model, entanglement of the PS with CNTs restricts perpendicular diffusion, while confinement of the PS by the surface induces disentanglement, forming a diffusive “trap” at the CNT surface. Once $R_{g,dPS} \leq R_{CNT}$, no minima is observed as polymer chains do not entangle with CNTs. At a given $R_{g,dPS}:R_{CNT}$, the model predicts that a minimum occurs because the slower perpendicular diffusion lowers the diffusion coefficient until a

threshold CNT concentration. At this threshold, diffusive percolation is reached, and chains diffuse along the percolated “trap network” and tracer diffusion is recovered.⁵³ These results suggest that the size of a nano-filler relative to the polymer chains may be one of the primary driving forces behind anomalous diffusion events in low-loading nanocomposites.

Anisotropic diffusion of polymers near CNTs is possible due to their high aspect ratio and their ability to entangle with polymer chains. However, for composites containing spherical NPs, NP entanglement may not be possible, therefore anomalous melt dynamics in spherical NP composites should be considered separately. Cosgrove et al. observed that hard, spherical, polysilicate nanoparticles in PDMS cause an apparent reduction in polymer entanglement and speed up chain dynamics below a critical filler concentration (~30 vol%) for high molecular weight polymer⁴⁸. Beyond this critical filler content, an abrupt shift to reinforcement is seen. This behavior was absent at low molecular weights⁴⁹, and reinforcement is observed at all filler concentrations. Combined with a rigorous follow up study⁵⁴, these researchers showed that an observed maximum in diffusion was only observed when the matrix was sufficiently far above its entanglement molecular weight. The observed diffusive maximum is distinctly different from the minimum seen by Winey et al.^{52, 53, 107} in CNT composites, and highlights how NP geometry must be considered heavily when interpreting composite melt dynamics. Cosgrove et al. also show the dependency of anomalous melt behavior in composites on the level of entanglement in the base polymer, as well as on $R_{g, \text{matrix}}:R_{\text{NP}}$.

Numerous techniques have been used to study polymer dynamics and diffusion in the melt. Some of the most common techniques used are rheology¹¹⁸⁻¹²¹, nuclear magnetic resonance (NMR) relaxation^{48, 49, 54, 84, 122}, numerous ablative ion-beam profiling techniques^{52, 53, 84, 116, 123-125}, and light, x-ray, or neutron scattering^{82, 83, 126-131}. Of these, ion-beam techniques, and x-ray

and neutron scattering are most appropriate for the study of diffusion in polymer thin films. Neutron reflectivity is particularly attractive for the examination of thin films due to its excellent spatial resolution (<1 nm in depth) compared to ion-beam techniques (~ 10 - 100 nm in depth). Moreover, neutron techniques can incorporate contrast by isotopic substitution, while large differences in electron density are required to achieve good contrast in x-ray scattering.

From the body of research currently available, reasonable qualitative predictions can be made for how a hard non-interacting NPs will affect polymer dynamics taking into account $R_{g,matrix}:R_{NP}$,^{51, 53, 54} polymer MW^{48, 49, 115}, and NP aspect ratio.^{48, 52} However, it is still unclear what effect particle softness has on the matrix dynamics in composites containing soft NPs. To this end, it is the goal of this study to examine the dynamics of polystyrene in composites that contain a recently reported^{46, 47, 117} new class of soft, polystyrene-based nanoparticles to examine the effect of the NP softness (or rigidity) on matrix diffusion. These nanoparticles are unique in their inherently high miscibility with their linear analogs and the ability to tailor the stiffness of the particles synthetically. This study uses neutron reflectivity to probe matrix diffusion in thin film composites containing soft NPs of equivalent size and varying stiffness. For comparison, diffusion of neat PS and in samples containing C₆₀ fullerenes were also studied.

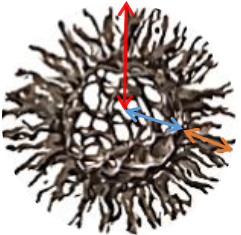
5.2 Experimental

5.2.1 Materials

Deuterated polystyrene (dPS, $M_n = 525K$, PDI = 1.09) and protonated polystyrene (PS, $M_n = 535K$, PDI = 1.2) were obtained from Polymer Source and used as received. Polystyrene soft nanoparticles (nanoparticle 1 (NP1) and nanoparticle 2 (NP2)) were synthesized by emulsion polymerization of styrene and p-divinylbenzene (DVB) as reported by collaborators.⁴⁶ As determined by small angle neutron scattering (SANS) in solution and atomic force microscopy

(AFM) on mica, the PS nanoparticles can best be described as fuzzy gel particles with a homogeneously cross-linked core and a corona of free chain-ends and loops. Details of the particle synthesis and characterization can be found elsewhere.⁴⁶ Table 5.1 lists selected properties for NP1 and NP2, and illustrates the fuzzy-gel particle structure characterized by Holley et al.⁴⁶ The listed DVB content (x) is that of the emulsion feed and related to the crosslink density of the nanoparticle; the glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC); and the apparent molecular weight (M_w), mean particle radius ($\langle R_p \rangle_n$), mean core radius ($\langle R_c \rangle_n$), fuzzy surface half-width (τ_{surf}), and network correlation length (ξ) were determined from solution SANS. The C₆₀ fullerenes were purchased from Bucky USA and used as received. The toluene used was HPLC grade and obtained from Fisher Scientific. Silicon wafers used for the reflectivity experiments were undoped, varied from 3-6 mm thick, and were from multiple sources. Concentrated sulfuric acid and 30% hydrogen peroxide solution were purchased from Fisher Scientific and used as received.

Table 5.1 Molecular properties and illustration of soft PS nanoparticles.

Sample	$x^{(a)}$ (mol %)	$M_w^{(b)}$ (10 ⁶ g/mol)	T_g (°C)	$\langle R_c \rangle_n$ (nm)	$\langle R_p \rangle_n$ (nm)	$\tau_{surf}^{(c)}$ (nm)	$\xi^{(d)}$ (nm)
NP1	0.81	0.78	108	3.80	9.34	2.77±0.1	3.96±0.8
NP2	1.91	0.81	111	5.49	9.75	2.13±0.1	3.99±1.5
 Fuzzy Gel $\langle R_p \rangle_n$ = mean particle radius $\langle R_c \rangle_n$ = mean core radius $2 * \tau_{surf}$ = corona width $\tau_{surf} = (\langle R_p \rangle_n - \langle R_c \rangle_n) / 2$				(a) composition of cross-linker (DVB) in emulsion feed, (b) apparent molecular weight determined by SANS, (c) half-width of fuzzy surface layer, (d) network correlation length or mesh size between cross-links. *Illustration and data used with permission.			

5.2.2 Wafer Preparation

Silicon wafers were cleaned by soaking in a piranha solution (3:1 sulfuric acid to 30% hydrogen peroxide) for 2hrs and then rinsed with ultra-pure water (resistivity greater than 18M Ω) and dried with a stream of nitrogen gas. To ensure a uniform SiO_x layer, wafers were then subjected to 15min of ozonolysis in a Jelight Model 144AX UVO cleaner.

5.2.3 Preparation of Bilayers

Bilayer samples were prepared by spin casting a PS matrix layer directly onto the cleaned silicon, and float coating a dPS matrix layer on top. Films were spin cast from toluene solutions containing 2.6 wt% polymer with respect to (w.r.t.) solvent and (excepting the control sample) 1 wt% nanoparticles w.r.t. polymer. First, test samples of each solution were spin cast at 2500 rpm for 30s onto small test wafers to verify film thicknesses by ellipsometry, and if necessary small concentration adjustments were made prior to casting the actual films examined by reflectivity. Once all sample solutions were verified to form films of 80-120nm, solutions containing protonated polystyrene (pPS) (with nanoparticles when applicable) were cast onto the cleaned silicon wafers, and film thicknesses were again measured by ellipsometry. Next, the deuterated polystyrene (dPS) solutions (also containing nanoparticles when applicable) were spun cast on to polished, monolithic, sodium chloride salt plates. The salt plates were used to facilitate the float coating process; however, ellipsometric measurements were not possible on the NaCl substrates.

The float coating process, depicted in Figure 5.1, involves scraping the edge of the coated salt plates with a razor blade to remove any excess polymer. The scraped salt plate was then slowly lowered, at an angle, into a trough of ultra-pure water. The water dissolves a thin layer of the salt plate as it is lowered, releasing the dPS film which floats on the surface of the water due to surface tension. After the film releases, the salt plate is immediately removed from the water

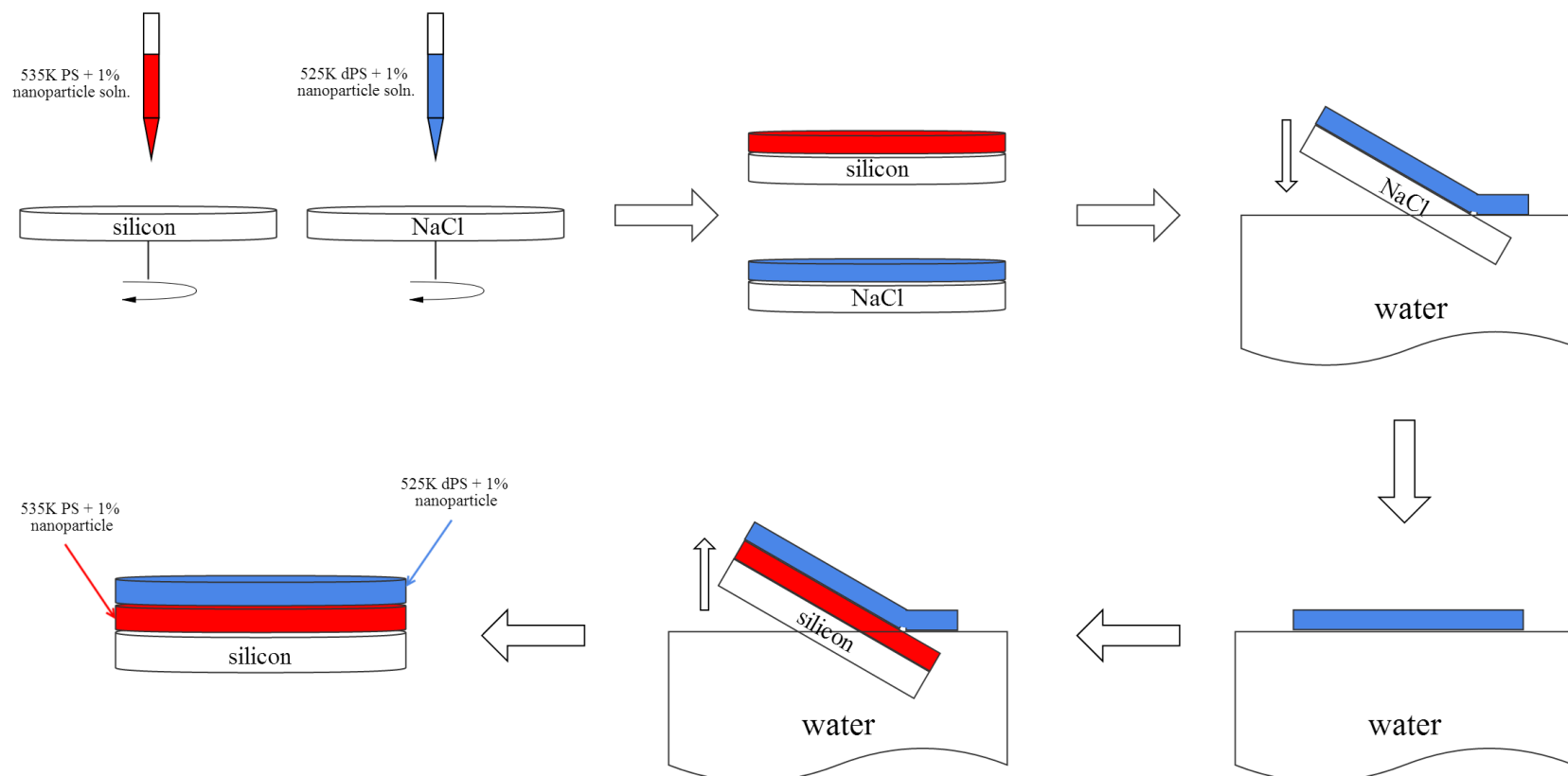


Figure 5.1 Illustration depicting bilayer assembly by spin coating and subsequent float transfer

and dried so it can be re-polished and reused. The silicon wafer coated with the corresponding PS film is lowered beneath the surface of the water, and slowly raised up at an angle below the floating dPS layer, capturing it on top of the PS layer. A kimwipe is used to dry the uncoated side of the wafer and gently wick away water trapped in between the layers. The freshly prepared bilayers were dried under vacuum overnight at room temperature.

5.2.4 Ellipsometry

Ellipsometric measurements were performed on a DRE GmbH model ELX-02C ellipsometer equipped with a 632nm laser and set at a 70° angle of incidence. The model used to calculate the thickness of cast films is summarized in Table 5.2.

Table 5.2 Summary of ellipsometric model for PS on surface oxidized silicon

Material	Refractive Index		Thickness (nm)
	real part (n)	imaginary part	
air	1.0000	+j 0.0000	--
PS	1.5800	-j 0.0035	variable
SiO _x	1.4571	+j 0.0000	2.4
Si	3.8816	-j 0.0190	--

5.2.5 Neutron Reflectivity

Neutron Reflectivity (NR) experiments were performed on the Liquids Reflectometer at Oak Ridge National Laboratory's Spallation Neutron Source (SNS). Measurements were taken at 7 angles for an effective q -range of 0.009 – 0.2 Å⁻¹. For specular reflection, q is defined as the scattering vector normal to the sample surface, and is given by $q = 4\pi \sin(\alpha_i)/\lambda$, where α_i is the incident angle and λ is the radiation wavelength. Interlayer diffusion was monitored by acquiring NR profiles of samples that are as-cast and after annealing at 150°C for 5, 10, 15, 23, 30, and 60

minutes. Annealing was completed under vacuum in a preheated Lindberg Blue M oven with thermal mass added for temperature stability during sample exchange. Upon removal from the annealing oven, samples were immediately quenched on a chilled metal block.

The data for multiple incident angles was reduced and combined into a single reflected intensity (R) vs. q ($\text{\AA}^{-1}$) curve for each sample run, using software provided at the SNS facility. A scattering length density (SLD) profile was extracted by fitting the specular reflectivity data to a substrate supported bilayer model using the Microsoft Excel based fitting module *Layers*, which was provided by the Liquids Reflectometer instrument team. The fitting process was iterative, starting with a model of the as-cast sample based on the thickness obtained from ellipsometry, and the SLDs estimated using the SLD calculator built into *Layers*. The model was refined by systematically and incrementally varying the SLD, thickness, and interfacial roughness of each layer until the best, physically realistic, fit was achieved. This process was continued for subsequent annealing times using the final fit from the previous annealing time as the starting point, and keeping the layer thicknesses constant between subsequent annealings whenever possible. All fitting was completed with data plotted as Rq^4 vs q to increase emphasis on any structural detail present. As an example data fit, a plot of the reduced data set for the control sample after 10min of annealing and its corresponding fit can be found in Figure 5.2.

Once the SLD depth profiles were generated for all annealing times of a given sample, the facility provided Excel module *Tiles* was used to reproduce the SLD depth profiles without air or substrate interfaces. The air and substrate-free profiles were then used to verify the mass-balance for all annealings of a given sample. In a thermally equilibrated material there is no net change in mass with annealing, which yields a constant integration of the SLD depth profile. As such, the area under the SLD-depth profile of a bilayer should be constant at all annealing times.

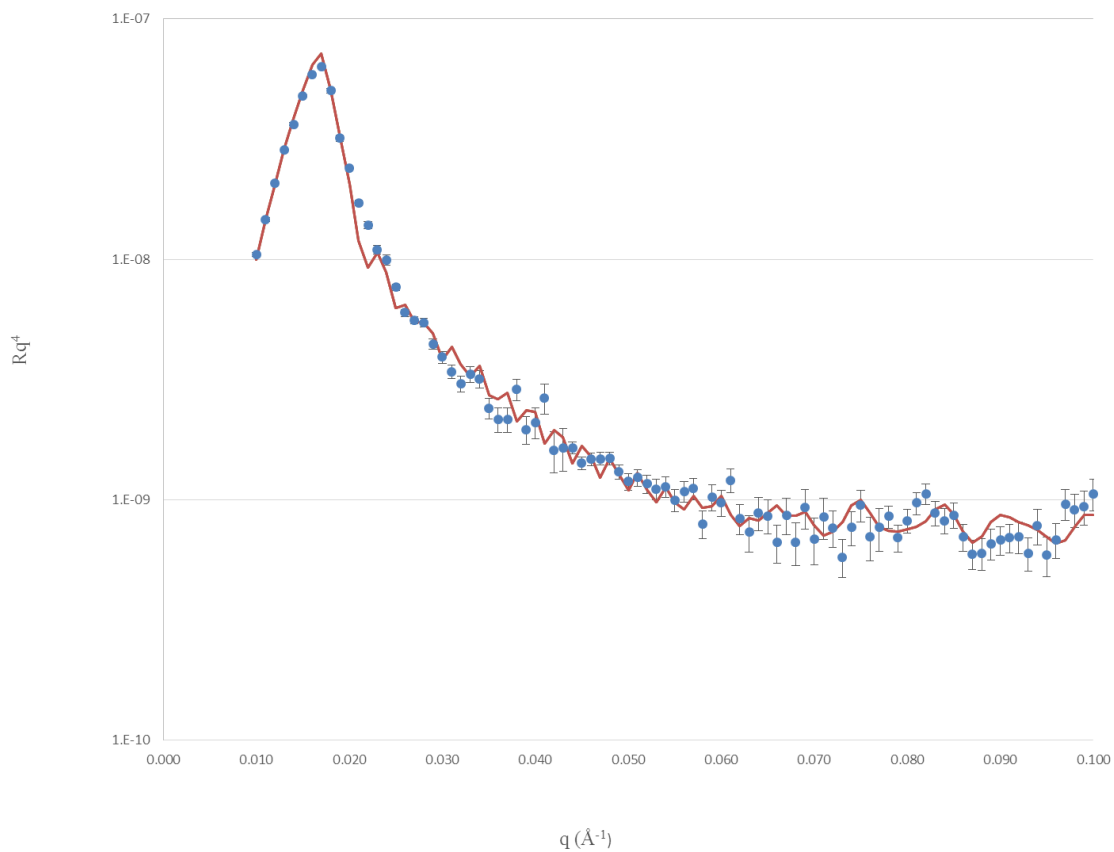


Figure 5.2 Reduced Rq^4 vs q data and *Layers* fit for the control sample after 10 minutes.

Therefore, the mass-balance for all annealing times of a sample was verified by integrating the area under each SLD-depth profile and checking that this value deviated by less than $\pm 1\%$ from the mean for that sample. If a deviation of greater than $\pm 1\%$ was found, the fit that generated the offending SLD profile was re-examined along with the fits for any subsequent annealings. This process was repeated until mass-balance had been achieved within $\pm 1\%$ for all samples, while maintaining a physically realistic model.

5.3 Results

5.3.1 Ellipsometry

Appropriate spin coating conditions for each sample were verified by measuring film thickness using ellipsometry. All films thicknesses were measured at five different points laid out in a cross pattern and showed good sample uniformity, as there was very little variation between measurements. The average thicknesses for each film were used as first estimates in fitting the NR profiles and are listed in Table 5.3; the thicknesses from NR fits are included for comparison. For dPS films, the average thicknesses are those of test films that are cast on silicon wafers under conditions identical to those used to spin cast films on salt plates. All samples were in excellent agreement with the optical model used to calculate thickness as can be seen in Figure 5.3, and no adjustment of the refractive index was necessary at 1% nanoparticle loading.

5.3.2 Neutron Reflectivity

All reflectivity data were fit as described in section 5.2.5. However, due to exceptionally high off-specular scattering, some data for the 1% C₆₀ bilayer (as-cast, 5 min, and 60 min) and the 1% NP2 bilayer (60 min) could not be adequately reduced and consequently could not be fit.

Table 5.3 Average film thickness as measured by ellipsometry; NR fit bilayer thicknesses also included.

Sample	Average Thickness (nm)	$\pm$ StdDev (nm)	NR fit (nm)
PS control	98.11	0.04	98.5
dPS control	85.34 ^a	0.01	107.5
PS + 1wt% NP1	107.36	0.01	118.5
dPS + 1wt% NP1	114.21 ^a	0.01	120.0
PS + 1wt% NP2	108.27	0.01	120.1
dPS + 1wt% NP2	104.89 ^a	0.01	117.5
PS + 1wt% C ₆₀	111.56	0.01	120.0
dPS + 1wt% C ₆₀	111.45 ^a	0.02	122.6

^a values obtained from test films spun cast on silicon wafers.

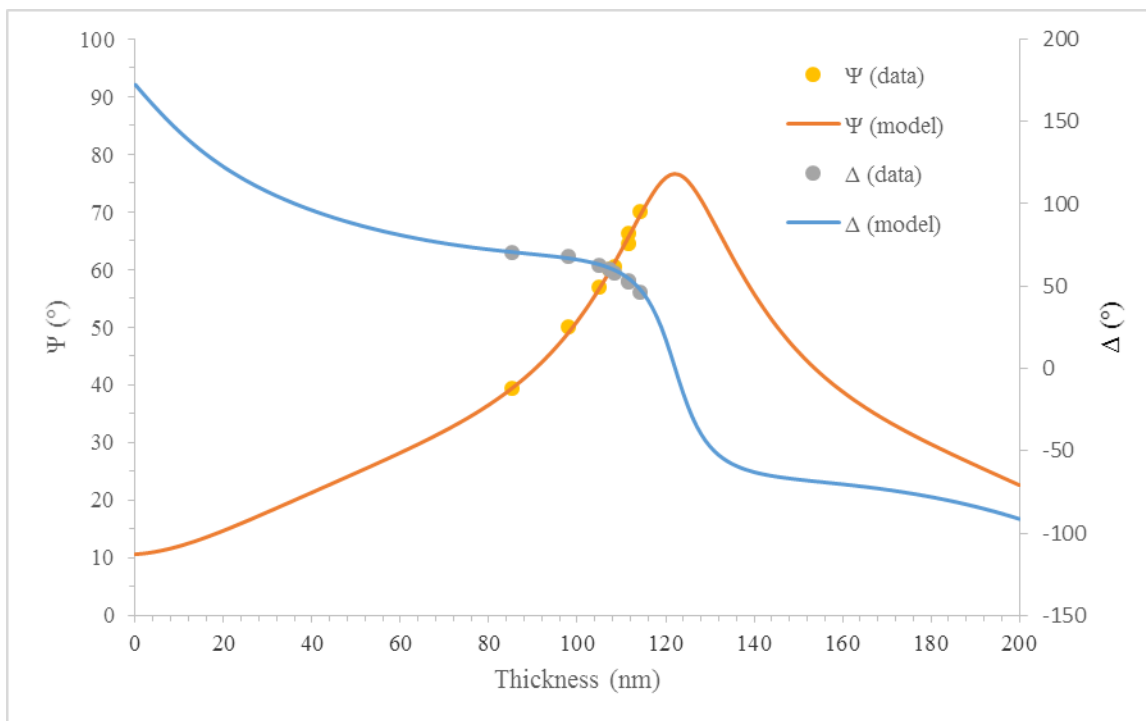


Figure 5.3 Δ and Ψ vs film thickness for cast layers and the optical model. PS/dPS ($n = 1.5800 - j 0.0035$), SiO_x ($n = 1.4571 + j 0.0000$, 2.4nm) and Si ($n = 3.8816 - j 0.0190$).

A summary of the SLD and layer thickness obtained for each as-cast bilayer can be found in Table 5.4. The SLD depth profiles obtained from the fitting process were shifted so the air-dPS interface is bisected by the y-axis, then converted to depth profiles of the volume fraction of dPS (ϕ_d) by normalizing each profile using the SLDs obtained from the as-cast bilayers. The evolution of the depth profile with annealing for each bilayer can be seen in Figure 5.4–Figure 5.7.

Table 5.4 Bilayer thicknesses and SLDs for as-cast samples obtain from *Layers* fitting model

	control bilayer	1% NP1 bilayer	1% NP2 bilayer	1% C₆₀ bilayer^a
dPS thickness (Å)	1075.0	1200.0	1175.0	1226.0
dPS SLD (Å ⁻²)	6.000E-6	6.000E-6	6.000E-6	6.000E-6
PS thickness (Å)	985.0	1185.0	1201.0	1200.0
PS SLD (Å ⁻²)	1.420E-6	1.410E-6	1.331E-6	1.350E-6

^a layer thicknesses and SLDs are from sample after 10 minutes of annealing

Since the dPS and PS used in these experiments are of equivalent molecular weight, they will interdiffuse symmetrically. Given this fact, the time dependence of the SLD, β , at depth, x , and time, t , can be expressed in accordance with Fick's Second Law as:

$$\beta(x, t) = \frac{\beta_d(t)}{2} \operatorname{erf}\left(\frac{x \, cE}{\sigma_a}\right) + \frac{\beta_h(t) - \beta_d(t)}{2} \operatorname{erf}\left(\frac{x - h_d}{\sqrt{4 \, D \, t}}\right) + \frac{\beta_h(t)}{2} \operatorname{erf}\left(\frac{(h_d + h_h - x) \, cE}{\sigma_s}\right)$$

$$\beta_d(t) = \beta_{d0} - \frac{(\beta_{d0} - \beta_{h0})h_h}{h_d + h_h} \exp\left(\frac{-h_h}{\sqrt{4 \, D \, t}}\right)$$

$$\beta_h(t) = \beta_{h0} + \frac{(\beta_{d0} - \beta_{h0})h_d}{h_d + h_h} \exp\left(\frac{-h_d}{\sqrt{4 \, D \, t}}\right) \quad (\text{Equation 5.1})$$

where $\beta_d(t)$, h_d , $\beta_h(t)$, and h_h are the SLD at time, t , and layer thickness for dPS and PS respectively. cE is a fitting constant used in generating the SLD profile in *Layers*, and σ_a , and σ_s are the roughness at the air-dPS interface and PS-substrate interface.

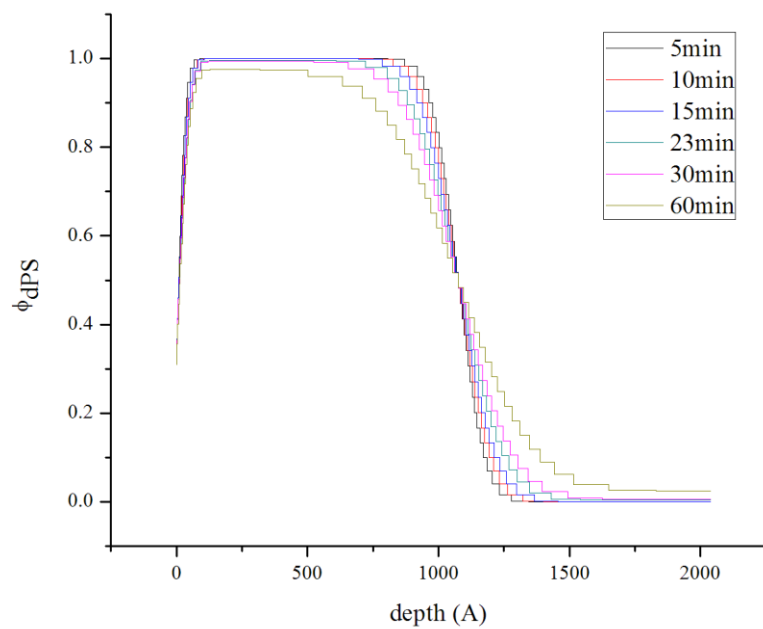


Figure 5.4 dPS composition depth profiles for control sample.

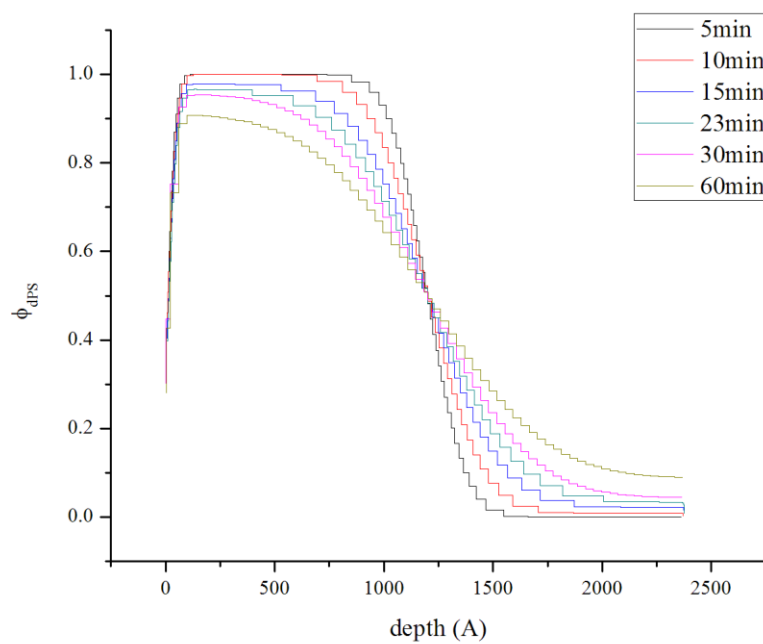


Figure 5.5 dPS composition depth profiles for NP1 sample.

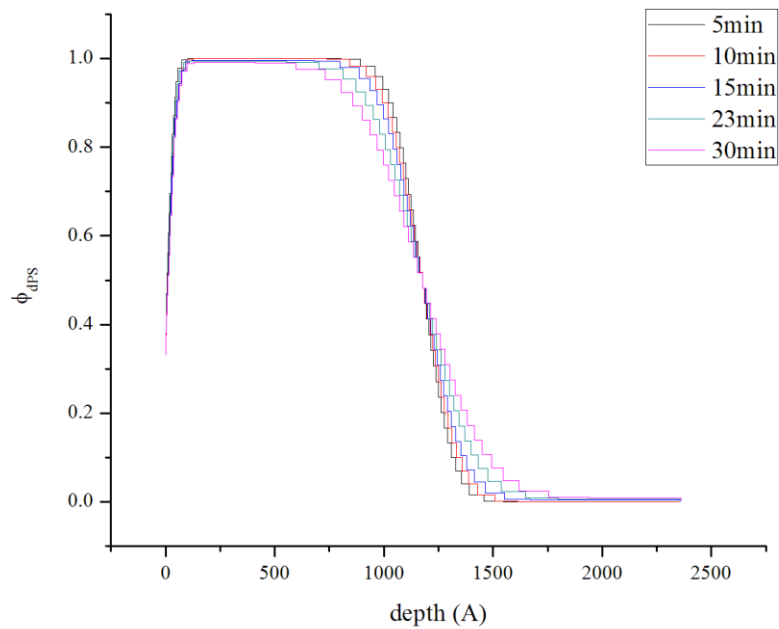


Figure 5.6 dPS composition depth profiles for NP2 sample.

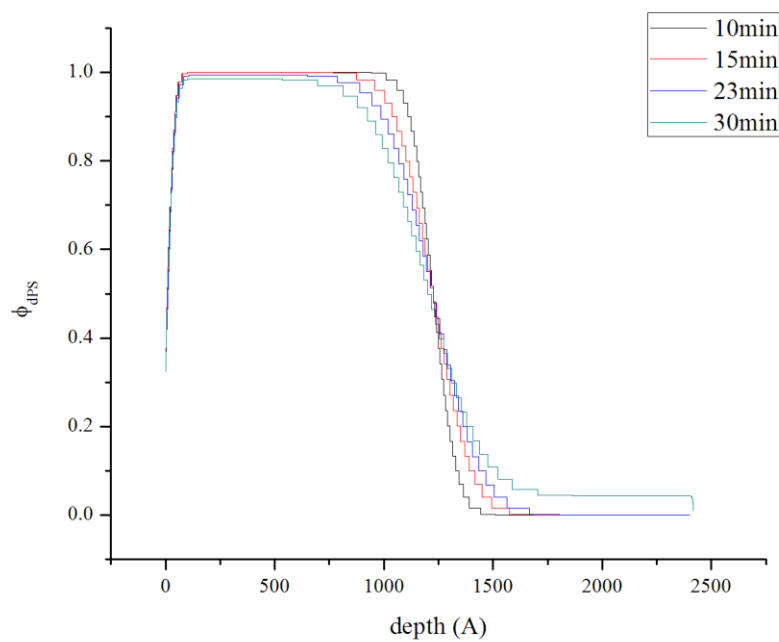


Figure 5.7 dPS composition depth profiles for C₆₀ sample.

The SLDs of the as-cast layers are represented as β_{d0} and β_{h0} and D , as written, is the mutual diffusion coefficient, but is equivalent to the self-diffusion coefficient under the conditions of this study ($MW_{dPS} = MW_{PS} \therefore D_{dPS} = D_{PS} = D$). The terms $\beta_d(t)$ and $\beta_h(t)$ in Equation 5.1 are designed to ensure proper mass balance convergence as $t \rightarrow \infty$ based on the thickness of each layer. Additionally, they account for the scaling of the SLD of each layer with time as the model transitions from pure layers above and below a narrow dPS-PS interface, to slowly converging dPS-PS mixtures on either side of a broad interface. It should be noted that this scaling relationship assumes mixing is athermal, the bilayers are the only dynamic structures probed by the beam, and that there is no net lateral mass flux during annealing. These expressions can be converted to the volume fraction of dPS using the relationship:

$$\phi_d(x, t) = \frac{\beta(x, t) - \beta_{h0}}{\beta_{d0} - \beta_{h0}} \quad (\text{Equation 5.2})$$

The diffusion coefficient after time, t , of annealing can then be found from either the SLD or ϕ_d depth profiles using Equation 5.1 or Equation 5.2 respectively, and fitting for D . Figure 5.8 shows two representative SLD depth profiles and their corresponding fits. A summary of the diffusion coefficient for each bilayer as a function of annealing time can be found in Figure 5.9.

5.4 Discussion

5.4.1 Impact of Soft Nanoparticles on PS Diffusion

As can clearly be seen in Figure 5.9, inclusion of 1wt% NP1 causes the diffusion rate to increase by a factor of 4, while the presence of NP2 causes an increase in D of a factor of 2. The increase in polymer diffusion may be explained by the relative size of the nanoparticles and the matrix polymer chains. Using Equation 5.3 the radius of gyration (R_g) of the matrix can be estimated based on its molecular weight.¹³²

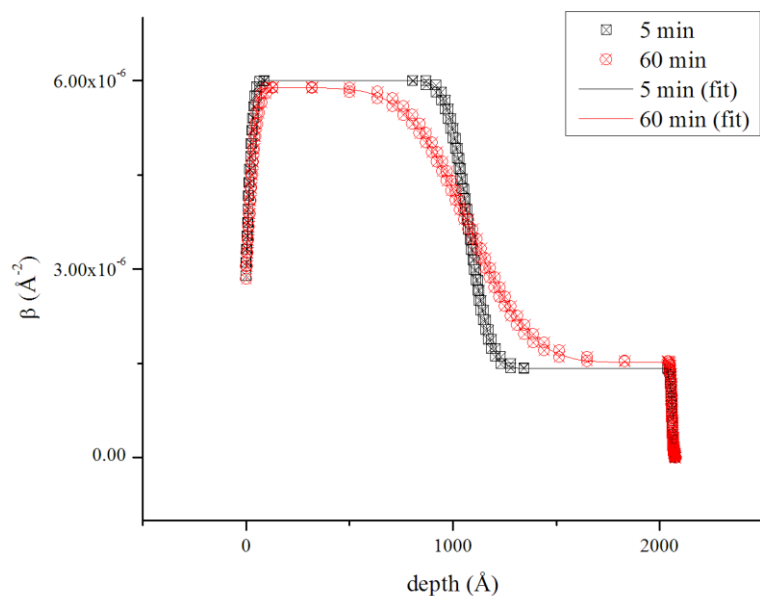


Figure 5.8 SLD depth profiles of control bilayer after 5 and 60 minutes. Solid lines are the fits of $\beta(x,t)$ at $t=300\text{s}$ ($D = 1.077 \pm 0.034 \text{E-}15 \text{ cm}^2\text{s}^{-1}$) and $t=3600\text{s}$ ($D=0.764 \pm 0.019 \text{E-}15 \text{ cm}^2\text{s}^{-1}$).

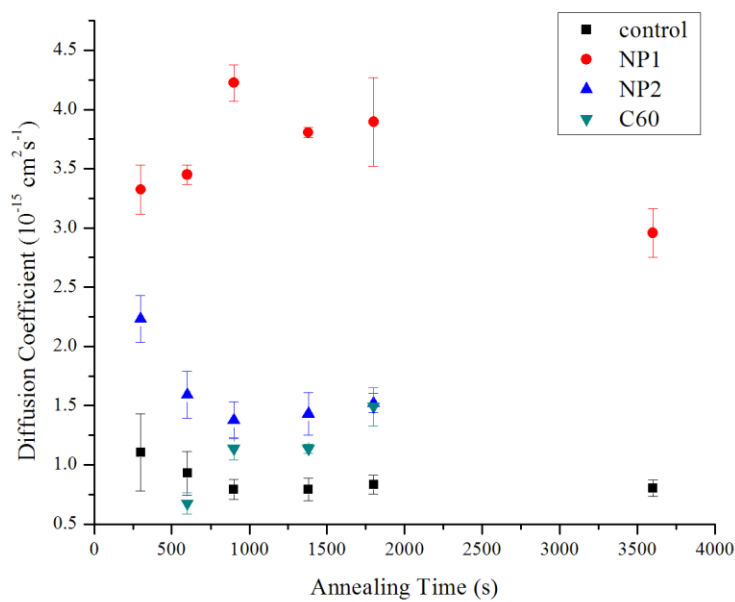


Figure 5.9 Plot of instantaneous diffusion coefficient, D , vs annealing time for all samples.

$$R_g = \frac{a\sqrt{M_w/M_0}}{\sqrt{6}} \quad (\text{Equation 5.3})$$

M_w is the weight average molecular weight, M_0 is the molar mass of the monomer unit, and a is the monomer length. Using Equation 5.3, the R_g for 535 KDa PS is ~20 nm, while the average particle radii of NP1 and NP2 are 9.34 nm and 9.75 nm, respectively. The radii of the NPs are roughly the same as the R_g of a 130KDa linear PS chain. Therefore, one way to envision this process is that as the crosslink density of the soft nanoparticle approaches zero, the addition of the NP become equivalent to PS molecules that have an R_g of 9.6nm, if the NP radius is maintained. Given this assumption, it would be expected that zero crosslink density (i.e. $x=0$) represents an upper limit of the diffusion coefficient, D , of the polystyrene in the presence of a soft NP. Using the standard reptation model for diffusion coefficient scaling with molecular weight (M)⁵², $D = D_0 M^{-2}$, the self-diffusion coefficient for 130K PS at 150 °C can estimated. D_0 is estimated from the pure matrix control sample. Then using the established theory^{83, 123}, the individual self-diffusion coefficients of the mixture can be used to estimate the mutual-diffusion coefficient of a blend that consists of 1% 130K PS and 99% 535K PS, which gives a value of $1.33\text{E-}14 \text{ cm}^2\text{s}^{-1}$ for the diffusion coefficient of PS in the $x=0$ limiting case.

Using this upper limit to the PS diffusion coefficient and the experimental data, the self-diffusion coefficient was plotted versus mol% DVB in Figure 5.10. From this plot, matrix self-diffusion appears to decrease exponentially as the mol% cross-linker increases and the NPs become stiffer and more dense, decreasing the effective plasticization. However, as a true exponential dependency of the diffusion coefficient on soft nanoparticle cross-link density precludes reinforcement, it is likely that a more complex relationship may emerge as composites with NPs of higher crosslink density are studied. The existence of critical crosslink density for the onset of matrix reinforcement will be examined in future experiments. Due to the nature of

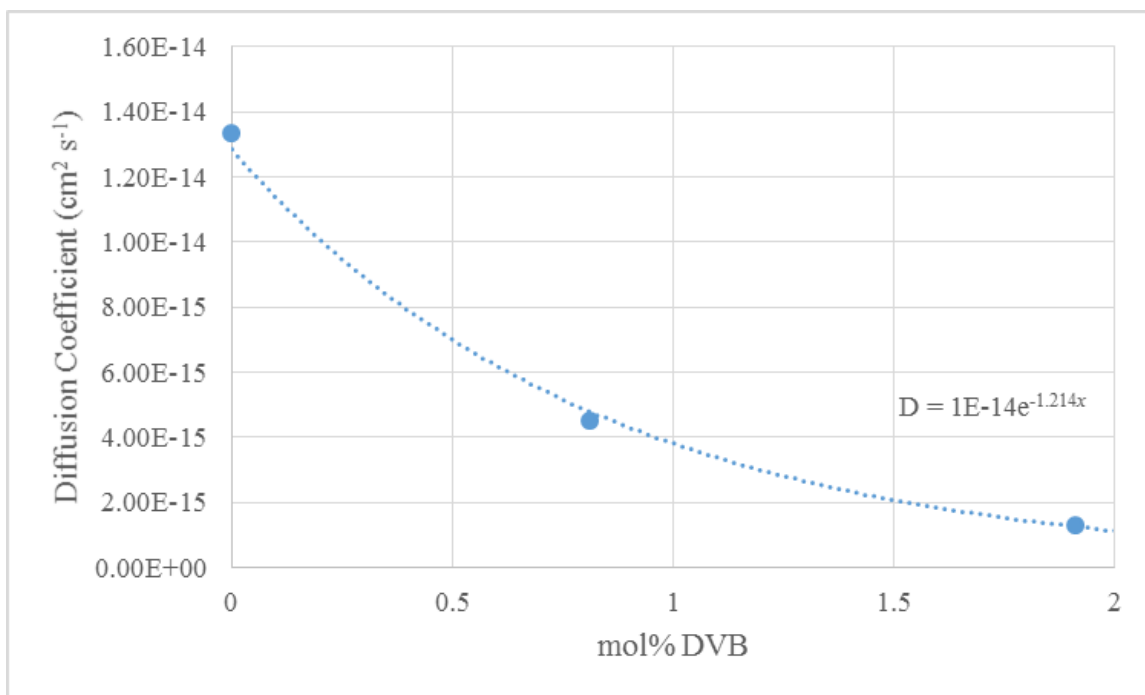


Figure 5.10 Plot of diffusion coefficient vs. mol% crosslinker. The dotted line illustrates the possible exponential trend.

the particles, increasing crosslink density will not only stiffen the NPs, but may also cause the NPs to transition from a penetrable, deformable, fuzzy particle to an impenetrable rigid particle, which may significantly alter the dynamics of the surrounding polymer matrix. Therefore, it will be important to study composites of soft NPs with a wide range of crosslinker content to fully detail the impact of soft nanoparticle crosslink density on polymer matrix diffusion. The examined systems contain soft nanoparticles where the amount of cross-linker in the nanoparticle is roughly doubled – creating a stiffer, less deformable NP with a larger core and thinner corona. This variation in nanoparticle softness results in a decrease in the diffusion coefficient of the PS matrix from $\sim 4 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ (NP1) to $\sim 1.5 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ (NP2) as can be seen from Figure 5.9 and Table 5.1.

It should be noted that due to samples being relatively thick and being overly rough as cast, there were not clear Kiessig fringes present in the reflectivity profiles, as can be seen from Figure 5.2. This increases the difficulty and uncertainty associated with the fitting process. As a result, the uncertainty in the diffusion coefficient values becomes dominated by how much the interfacial roughness can be varied without appreciably changing the quality of the data fit. Therefore, as a best approximation to the overall uncertainty, the diffusion coefficients were calculated at the upper and lower limits of the accepted roughness range, and reported as the mean ± 1 standard deviation.

Examination of Figure 5.9 demonstrates that inclusion of 1wt% NP1 in PS causes a significant increase (roughly 4x) in the diffusion coefficient of the PS matrix. It is also clear that the presence of 1wt% NP2 induces only a mild increase in the matrix diffusion coefficient (roughly 1.5x). Though these two soft nanoparticles are approximately the same size, the dramatic difference the presence of each has on the diffusion of the matrix can be related to the

structure of the NPs. As can be found in Table 5.1, while NP1 and NP2 have nearly identical network correlation lengths ($3.96 \pm 0.8 \text{ nm}$ and $3.99 \pm 1.5 \text{ nm}$ respectively), the average core radius of NP2 is much larger (3.80 nm and 5.49 nm respectively). This means that, while the NP cores have similar structure, NP2 is less “fuzzy” and the stiffer core material (as compared to coronal PS) composes a larger percentage of the NP, making NP2 stiffer and less deformable overall. However, the crosslinking that is present does not sufficiently stiffen NP2 to counteract the alteration of PS diffusion due to its small size w.r.t. the matrix. From the data presented, it is clear that the presence of soft NPs has a significant effect on composite melt dynamics at low loading. However, further study is needed to precisely quantify the effect of varying NP stiffness and varying the matrix/particle size ratio to provide a more thorough fundamental understanding of this effect.

The inclusion of hard C_{60} nanoparticles results in a, roughly 2x monotonic increase in the diffusion coefficient over the annealing time range available. Though the data set is limited, this short-range trend appears significantly different from both the diffusion of neat PS and soft NP bilayers. This deviation in diffusive behavior is likely due to the small size of C_{60} ($R_{NP} < 0.5 \text{ nm}$) allowing it to diffuse very readily through the matrix during casting and annealing. It is possible the increase observed could be from either equilibration of surface C_{60} enrichment from solvent evaporation during casting, or the result of diffusive C_{60} aggregation during annealing. Though more data is needed to form longer range trends and draw firm conclusions, an overall increase in diffusive dynamics at low C_{60} loading is in alignment with recent literature observations that at low loading a high R_g/R_{NP} size ratio will result in faster chain dynamics in high molecular weight PNCs.^{47, 48, 52-54, 117}

5.4.2 Self Consistent Analysis of Interfacial Width

The time dependence of the interfacial width between the PS and dPS layers with thermal annealing can also be analyzed to extract information about the molecular level dynamics that occur to broaden the interface. Fickian diffusion predicts that the interfacial width (w) will change with time as $w = \sqrt{4 D t}$, which is observed in the log-log plots of w vs t that are shown in Figure 5.11 -Figure 5.13 for the neat PS bilayers, and the samples that contain NP1 and NP2. Inspection of these plots shows that at early annealing times, $w \sim t^{0.25}$, which is consistent with Rouse-like motions of the polymer chain. For the control, the $t^{1/4}$ time dependence of w occurs in the $t < 900$ s regime, with a transition to a $t^{1/2}$ dependence for $t > 900$ s. Such a transition is in agreement with theory and has been reported in simulation¹³³⁻¹³⁶ and time-resolved neutron reflectivity experiments^{82, 83} and serves to validate the analysis. Calculating the value of $\Delta(w^2)/4(\Delta t)$ in the $t^{1/2}$ regime of the pure dPS/PS sample gives a diffusion rate ($D(t^{1/2})$) of $8.90 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, which is consistent with the values reported in Figure 5.9 above. Moreover, this diffusion coefficient can be used to estimate the time that the chains transition from Rouse to reptative dynamics using Equation 5.4:

$$\tau_r = \frac{N b^2}{3 \pi^2 D} \quad (\text{Equation 5.4})$$

where N is the degree of polymerization and b is the segment length ($b=0.67\text{nm}$). This calculation yields a reptation time (τ_r) of 876s, which corresponds nicely with the transition from $t^{1/4}$ to $t^{1/2}$ time dependence observed in Figure 5.10.

Similarly, analysis of the time dependence of the interfacial width between the PS and dPS layers of the 1wt% NP2 composite yields an average diffusion coefficient and reptation time of $1.44 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ and 541s respectively. This diffusion coefficient value is in good agreement with Figure 5.9 and the reptation time roughly aligns with the $t^{1/4}$ to $t^{1/2}$ crossover in Figure 5.12.

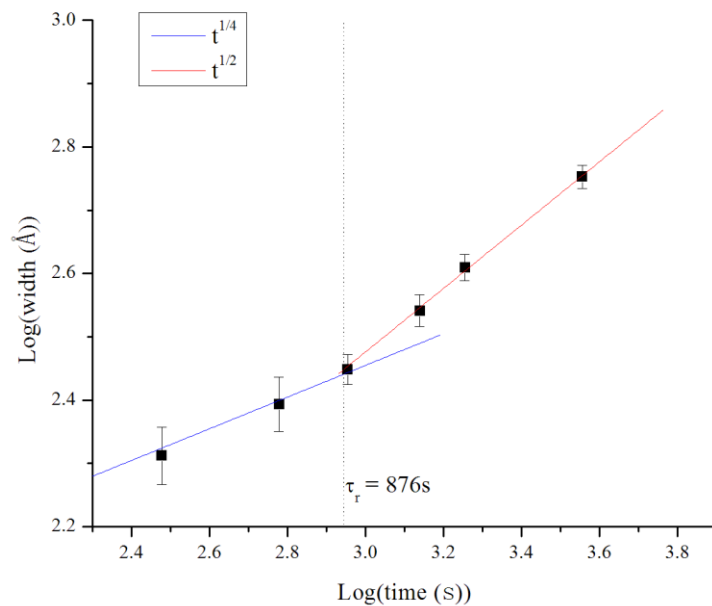


Figure 5.11 Log (interfacial width) vs Log(time) for control bilayer. Solid lines illustrate $t^{1/4}$ and $t^{1/2}$ power-law dependencies.

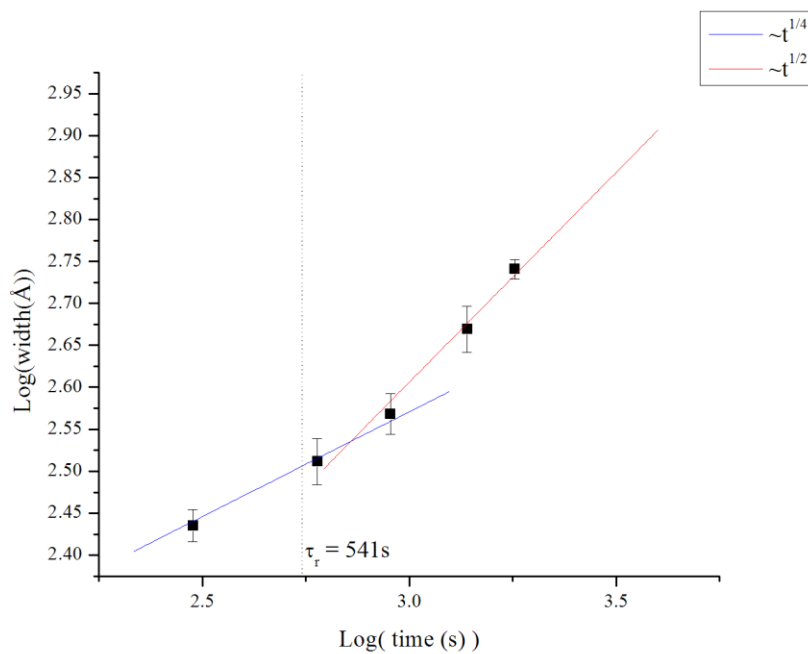


Figure 5.12 Log (interfacial width) vs Log(time) for NP2 bilayer. Solid lines illustrate $t^{1/4}$ and $t^{1/2}$ power-law dependencies.

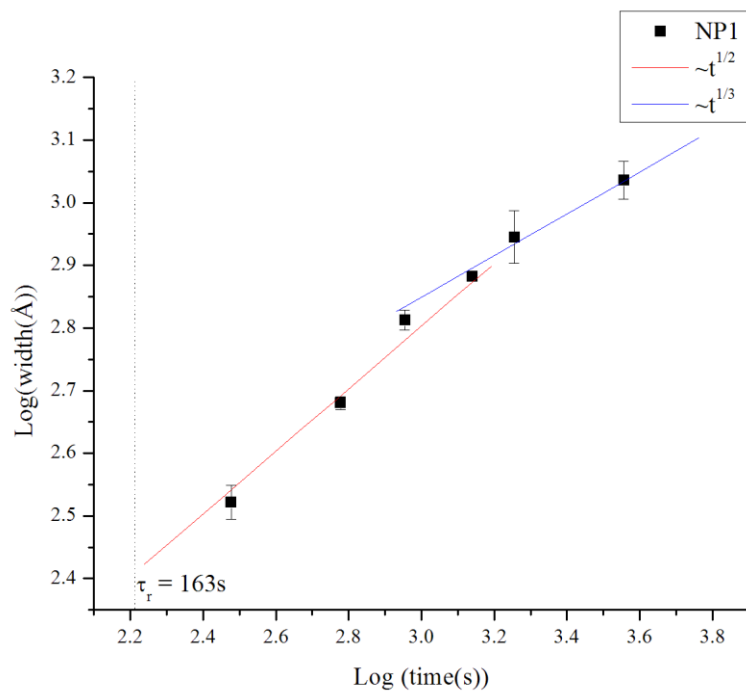


Figure 5.13 Log (interfacial width) vs Log(time) for 1wt% NP1 bilayer. Solid lines illustrate $\sim t^{1/2}$ and $\sim t^{1/3}$ power-law dependencies.

Shown in Figure 5.13 is the $\text{Log}(w)$ vs $\text{Log}(t)$ plot for the NP1 bilayer. Inspection of this plot shows that the width increases as the square root of time from the beginning of the data set, implying that the onset of reptative diffusion occurs at a shorter time scale than was measured in these experiments. The diffusion coefficient that is estimated from the slope of this plot provides $D(t^{1/2}) = 4.68 \times 10^{-15} \text{ cm}^2\text{s}^{-1}$, which is consistent with the values reported in Figure 5.9. The absence of an observed Rouse regime is confirmed by estimating the reptation time from the diffusion coefficient and Equation 5.4, giving a value of $\tau_r = 163\text{s}$, which is before the first annealed time.

Interestingly, Figure 5.13 also indicates a change of the time dependence of the width to a $\sim t^{1/3}$ dependence as the dPS-PS interfacial roughness, σ , approaches the thickness of the thinnest layer and the Parratt-Formalism fails. Beyond this point, obtaining an accurate value for the interfacial roughness value becomes increasingly difficult. Fortunately, at long times Equations 5.1 and 5.2 become less dependent on interfacial width in determining D , and more dependent on mass-balance. Since the mass balance is more dependent on the effective SLD and thickness of each layer, the Fickian analysis described by Equations 5.1 and 5.2 may help extend the time during which polymer diffusion in symmetric bilayers can be effectively probed by neutron reflectivity. Based on these analyses, it is clear that the time dependent scaling terms incorporated into Equations 5.1 and 5.2 provide excellent fits to the depth profiles and provides excellent agreement to both theory and literature within the Rouse and reptative regimes.

5.5 Conclusions

The results of this study qualitatively show that there is an inherent acceleration of diffusion of polystyrene matrix chains by the inclusion of small ($R_g/R_{NP} \approx 2$) soft NPs in the polymer matrix at 1% loading. This study also clearly shows that the extent of the increase

depends directly the degree of NP softness as defined by crosslinker content. It is also clear that these soft NPs are ideal for examining the effect of filler softness on matrix dynamics as the softness can be tuned during synthesis. The potential high miscibility of these NPs in the matrix and the more than 3x decrease in the diffusion coefficient with a doubling of the DVB content suggest very high levels of tunability in the dynamics of composites containing these PS nanoparticles. It is also clear that these soft NP have a distinctly different effect on chain diffusion and dynamics than a more traditional hard-sphere particle like silica nanoparticles and C₆₀.

CHAPTER 6

CLOSING REMARKS AND FUTURE WORK

6.1 Closing remarks

As the demand for stronger, faster, lighter and more efficient products ever increases, so do the challenges faced by material scientist and engineers who must find suitable materials to address these demands in a cost effective way. Increasingly, the versatility of polymer composites is being leveraged to satisfy ever more demanding use conditions and criteria. The versatility of polymer composites stems largely from the increased ability to tailor the resulting material to the desired use. This type of bespoke materials engineering can be achieved through the careful selection of polymer matrix, filler, and filler loading to yield the desired balance of properties. Nanoparticle (NP) fillers are being turned to more and more, as scientist strive to meet ever-increasing performance standards, and produce new materials with novel properties. This is because the resulting polymer nanocomposites (PNCs) have the potential to translate many of the unique optical, thermal, electrical, and mechanical properties that exist on the nanoscale, to enhanced or unique bulk scale material properties. However, compounding of PNCs is not without difficulties, as the shift to nanoscale fillers presents new challenges that must be addressed to reliably and economically produce high quality materials. Paramount among these challenges is, in many cases PNCs do not behave dynamically in accordance with the well-established theory used in the predictable compounding of composites containing micro and macro scale fillers.

Anomalous dynamic behavior in PNCs can manifest from multiple factors. However, it is generally becoming accepted that the size relation between the matrix chains and the NP is one

of the primary predictors for classical vs anomalous dynamics. Though the mechanism for this behavior may still be under debate; in most systems studied, it has been found that if $R_g/R_{NP} \geq \sim 3$, a PNC will exhibit anomalous behavior—provided the matrix is at least mildly entangled. As such, the primary goal of this thesis was to study the effects of NP shape and softness (deformability) on PNC dynamics within this regime. Additionally, this work probed the role of NP induced disruptions to matrix entanglement network—and any NP shape and/or attractive interaction dependence of these disruptions—in the observed dynamics.

In chapter 4, rheometry and NMR relaxometry were used to probe shear-flow and diffusive melt dynamics for PNCs containing graphitic NPs of varied shape (spheres, rods, and sheets). It was found that, at 1% loading, all three NP geometries induce some degree anomalous melt dynamics. This implies that the empirical expression, $R_g/R_{NP} \geq \sim 3$, of the threshold for non-classical dynamics may be more appropriately written as:

$$2R_g/d_{NP}^o \geq \sim 3 \quad (\text{Equation 6.1})$$

where d_{NP}^o is the nanoparticles smallest dimension—in terms of diameter, width, or thickness. However, to verify this, thorough molecular weight dependent studies of PNCs of all three NPs need to be undertaken. Also, while the polymer to NP size ratio may be indicative of whether anomalous dynamics should be expected, the nature (faster or slower) and magnitude of the deviation from classical predictions is dependent on NP geometry—more specifically, aspect ratio.

A revised physical model based on a single particle dispersed in the matrix, was developed for describing the local segmental domains present in the PNCs. In addition to providing a logical depiction of origin of the different local domains and how they interact, the model provides good agreement with bulk shear-flow dynamics. The proposed model provides

logical and useful description of how the local dynamic processes contribute to the bulk dynamics.

Based on this model A dimensionally isotropic NP that is very small compared to the matrix chains (C_{60}), can only disrupt matrix entanglement and form attractive interactions on a very small length scale, and cannot appreciably entangle with the matrix. This prevents the NP from forming the long-range physical and/or attractive interactions needed to yield an increased elastic response. Therefore, local disentanglement and NP diffusion (which would dampen the effect of both local attractive interactions and disentanglement) yield a moderate to mild net increase in viscous flow (i.e. faster dynamics) at low loading.

Using the model to describe a highly anisotropic rigid-rod NP (SWNT) PNC, the NP can interact with matrix over a very long length scale. This includes NP induced matrix disentanglement, NP-matrix entanglement, and attractive NP-matrix interactions. The long length scale over which the NP interacts with the matrix, renders the NP immobile creating a long-range impediment to chain diffusion radially, and a comparatively mild potential for net (NP surface induced) disentanglement axially. The net result of this interpretation is that a rigid-rod PNC will exhibit melt reinforcement when there is a balance between the reduced mobility of the surface chains and the width and mobility of the boundary zone. As a result melt reinforcement is only seen in the non-interacting regime (SWNT-PS) and the moderately interacting regime (SWNT-SAN45).

The case of an extensive sheet NP (CCG), the proposed PNC model suggests a scenario largely similar to that of a rigid-rod PNC. The primary exception being that NP-polymer “entanglement” can only occur at the sheet edges, and is therefore negligible compared to the massive NP surface area. This means that for the non-attractive case (CCG in PS),

disentanglement at the surface due to surface effects dominates. This disentanglement effect creates a “lubricating” surface layer and yields greatly increased viscous response in the bulk while having little effect on the overall elastic response provided by the bulk of the matrix not in the vicinity of NPs. The model also suggests that much like in rigid-rod PNCs, introduction of a modest number of attractive NP-polymer interactions, creates a tighter association of surface-chains with the NP surface, further disentangling surface-chains from the bulk. Similarly, further increase in the mol% AN increases the elastic nature of the surface layer. However, for sheet PNCs, it appears the mobility of the surface layer by itself is responsible for the bulk viscoelastic response—not competitive combination with a surface-chain to bulk boundary layer.

In chapter 5, the impact of PS soft-nanoparticles on the self-diffusion of PS was studied by neutron reflectivity. Much like the C₆₀ PNCs studied in chapter 4, low-loadings of these soft-NP nanocomposites also yield accelerated dynamics compared to the pure matrix. However, for soft-NP composites, it is likely NP deformation and diffusion that contributes to accelerated PNC dynamics. NP stiffness—and possibly core radius—serve to dampen the accelerated chain diffusion. It is worth noting that while the size ratio of the matrix chains to the NP for these PNCs is ~ 2 , the ratio relative to the core radius is higher. In fact, for NP2 which exhibits a very mild increase in the diffusion coefficient, the ratio relative the core is just above 3. This means the empirical factor of 3 for the size-ratio may apply for these NPs as well. This may be worth further study as the factor of 3 size-ratio could serve as a convenient design rule when formulating low loading composites.

6.2 Future Work

The very good correlation of diffusive segmental dynamics to bulk shear-flow dynamics, presented in chapter 4 paints a strong physical picture of the dynamic processes responsible for

anomalous dynamics in graphitic NP composite. However, external verification of physical model would be ideal. If the described physical model can be verified experimentally, it would support the trap model proposed by Winey et al. and greatly facilitate the further development of robust models for the design of low loading PNCs. Given the density differences implied by the stratified structure of the proposed model, and the inherent nuclear contrast between graphitic and protonated material, wide and small angle neutron scattering may be ideal for this task. Additionally, neutron scattering with in-situ rheometry, as is available on the SNS Liquids Refractometer, may be useful for probing this model under dynamic conditions. Additionally, it could be interesting to test if the minimum in viscous flow for the SWNT-SAN45 PNC is molecular weight dependent. At constant mol% AN, would varying MW change the extensibility of the surface chains into bulk resulting in a shift of the minimum? Would it simply lower the surface-layer chain concentration with changing effecting the minimum? If the later, this would certainly seem to be verification of polymer chain wrapping of the SWNT in the melt.

Soft-nanoparticle PNCs being a rather young field, there a certainly a wide range of parameter that could be studied. This includes the obvious MW and NP concentration series studies, as well as studying diffusion of the NPs themselves, and the matrix NP miscibility limit. However, a less obvious and more subtle experiment would be testing the limiting, factor of 3 matrix/NP size relationship for anomalous dynamic behavior. Is it simply coincidental or is there a physical relationship behind it? Does it hold true for all soft-NP PNC when related to core radius? Is there a more complex relationship at play, such as relation to an equivalent hard-particle radius? If a relationship such as the latter were at play, it could be exploited to probe physical properties such as NP modulus in-situ. A less obvious implication of relation to an equivalent hard particle radius would be simplification of dynamic simulations for otherwise

complex PNC systems. A MW dependent diffusion study would be the first step in examining this relationship. Beyond that would be, the complicated prospect of a constant core radius and stiffness study with varied corona width, and the equally complicated study of constant core and particle size with varied core stiffness.

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APPENDIX

A-1

Derivation of equations for polycyclic aromatic hydrocarbon growth

A-1.1 Defining the model

The equations derived here in are based on the idea of representing graphene as a series of, n number of concentric hexagonal growth generations, where the diameter increases by a constant value from one generation to the next. In this model $n=0$ represents no growth and can be thought of as a simple benzene ring. Coronene is the result of after $n=1$, with one complete layer of aromatic rings (6 in this case) built off the previous layer. The process continues similarly from subsequent generations. One important note is that the vertices of the concentric hexagons are actually located at the midpoint of the C—C bonds rather than at carbon centers. This is a consequence of the growth process, but also allows for simpler and lower energy zig-zag edges. An illustration of this model can be seen in Figure A-1.1

This model is used as the basis to derive equations for the total number of carbons after n growth generations, the diameter after n generations, and ultimately the number of carbons included within a given diameter. The diameter here is defined as the distance between two 180° opposed vertices such that bifurcation through them would form two trapezoids (tbd). When counting carbons, carbons involved in bonds that are intersected by a particular growth generation are designated as belonging to that generation.

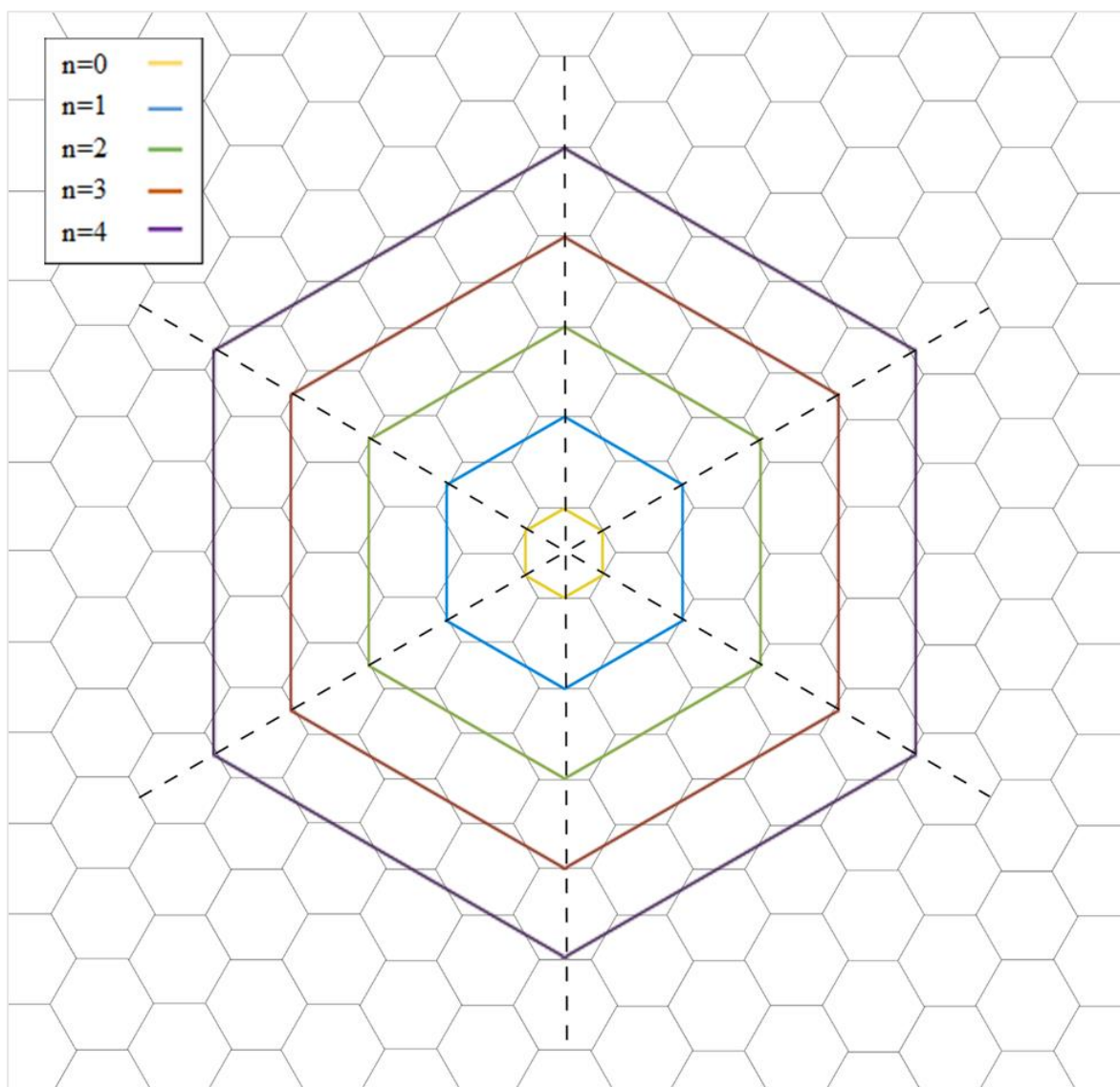


Figure A-1.1 Illustration of PAH growth model aligned overtop of a graphene lattice. Dashed lines indicate primary growth axis. Note that subsequent growth generations have a radius increase of exactly the bond-to-bond bisectonal width of one lattice unit.

A-1.2 Equation derivations

It can be seen by counting aromatic rings between growth generations in Figure A1.1, that each generation completes “6 times the generation index” number rings. This can be expressed as:

$$H_i = 6i \quad (\text{Equation A-1.1})$$

where H_i is the number of rings per generation, i .

Since each generation is adding onto an already established core, only the perimeter carbons are unique to a given generation. Each generation adds two carbons for each aromatic ring it completes, plus one additional carbon for each ring located on a primary growth axis. $\therefore$ the number of carbons per generation, c_i can be represented as follows.

$$c_i = 6(2i + 1) \quad (\text{Equation A-1.2})$$

As such, the total number of carbons, $c(n)$ after $i=n$ generations is derived as follows.

$$c(n) = \sum_{i=0}^n 6(2i + 1) = \sum_{i=0}^n 6 + \sum_{i=0}^n 12i \quad (\text{Equation A-1.3})$$

which are standard discrete sums whose solutions are known to be of the form:

$$c(n) = 6(n + 1) + \frac{12n(n+1)}{2} = 6(n + 1)(1 + n) \quad (\text{Equation A-1.4})$$

commutation and simplifications leaves:

$$c(n) = 6(n + 1)^2 \quad (\text{Equation A-1.5})$$

The derived PAH growth model assumes hexagonal growth generations from a central ring, such that any whole number, n , of growth generations results in a hexagonal bounded honeycomb and $n=0$ yields a benzene ring. Using this model, an equation for the total number of carbons, $c(n)$, as a function of growth generation was derived.

$$c(n) = 6(n + 1)^2 \quad (\text{Equation A-1.5})$$

Given that one complete growth generation adds one aromatic ring to each exposed edge, the total diameter must increase by two aromatic rings. With a bond length of 0.142nm for graphene,

the bond-to-bond bisectonal width of one ring is 0.246nm and the total tbd, $D(n)$ after n generations is given by:

$$D(n) = 0.246(2n + 1) \quad (\text{Equation A-1.6})$$

Solving $c(n)$ for n , and substituting this into $D(n)$, yields tbd as function of the total number of carbons.

$$n = \sqrt{\frac{c}{6}} - 1$$

$$D(c) = 0.246 \left(2 \left(\sqrt{\frac{c}{6}} - 1 \right) + 1 \right)$$

$$D(c) = 0.246 \left(\sqrt{\frac{2c}{3}} - 1 \right) \quad (\text{Equation A-1.7})$$

Finally, solving $D(c)$ for c and replacing the model parameter D with the experimental parameter L_a yields $c(L_a)$ which provides an estimate of the number of carbons within a graphitic domain of given persistence width.

$$c(L_a) = \frac{3}{2} \left(\frac{L_a}{0.246} + 1 \right)^2 \quad (\text{Equation A-1.8})$$

A-2

Rheometry Supplement

A-2.3 Master curves grouped by common matrix

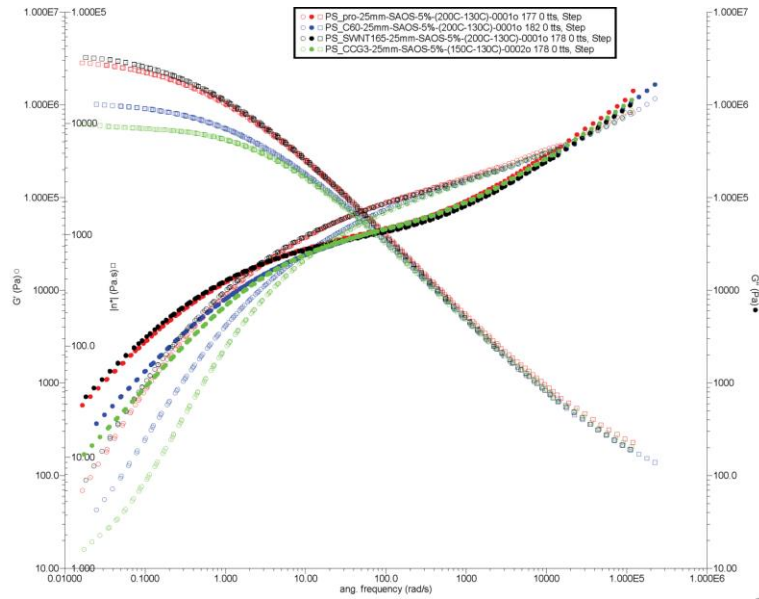


Figure A-2.1 $T_g + 77^\circ\text{C}$ master curves for PS matrix samples.

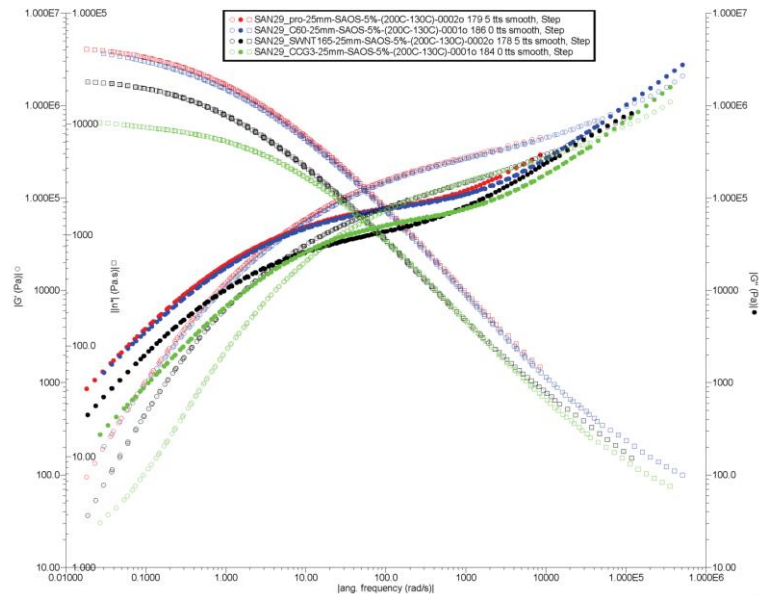


Figure A-2.2 $T_g + 77^\circ\text{C}$ master curves for SAN29 matrix samples.

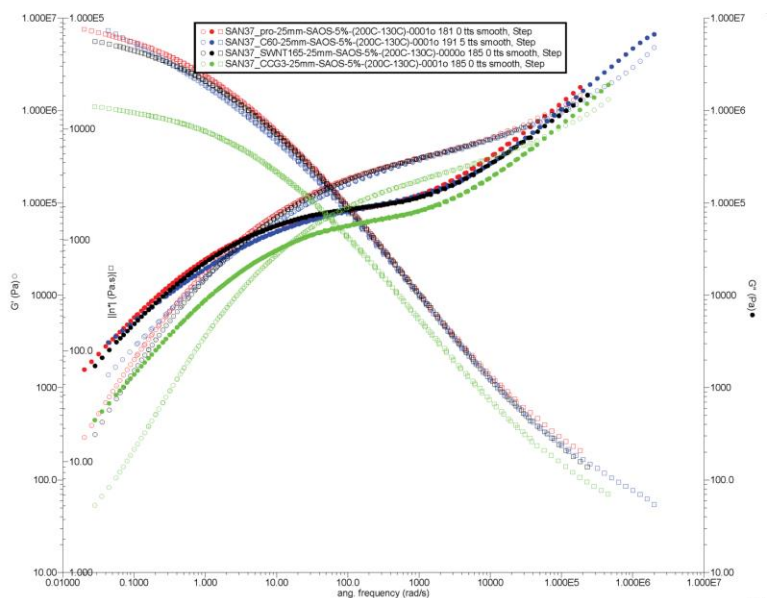


Figure A-2.3 $T_g + 77^\circ\text{C}$ master curves for SAN37 matrix samples.

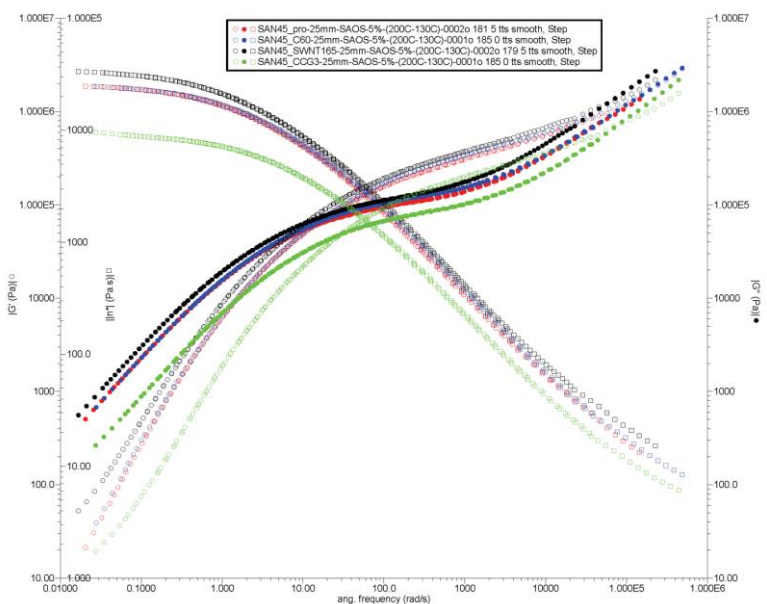


Figure A-2.1 $T_g + 77^\circ\text{C}$ master curves for SAN45 matrix samples.

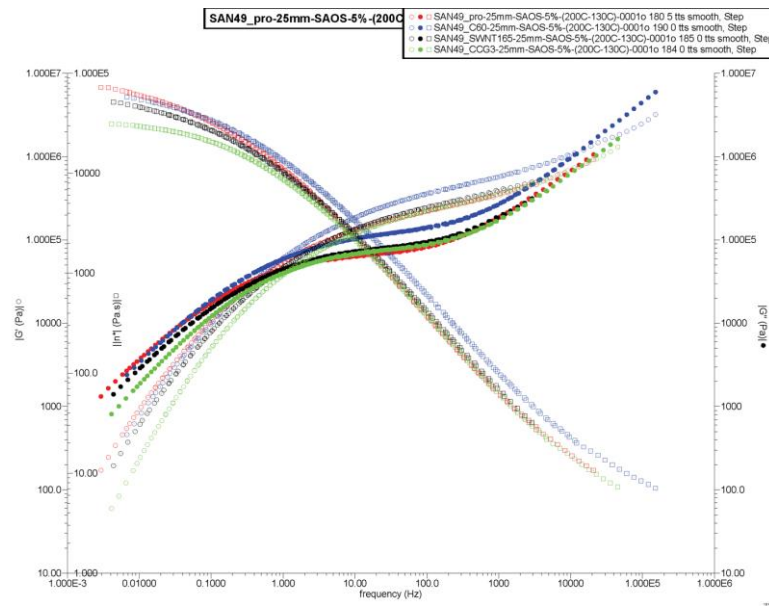


Figure A-2.2 $T_g + 77^\circ\text{C}$ master curves for SAN49 matrix samples.

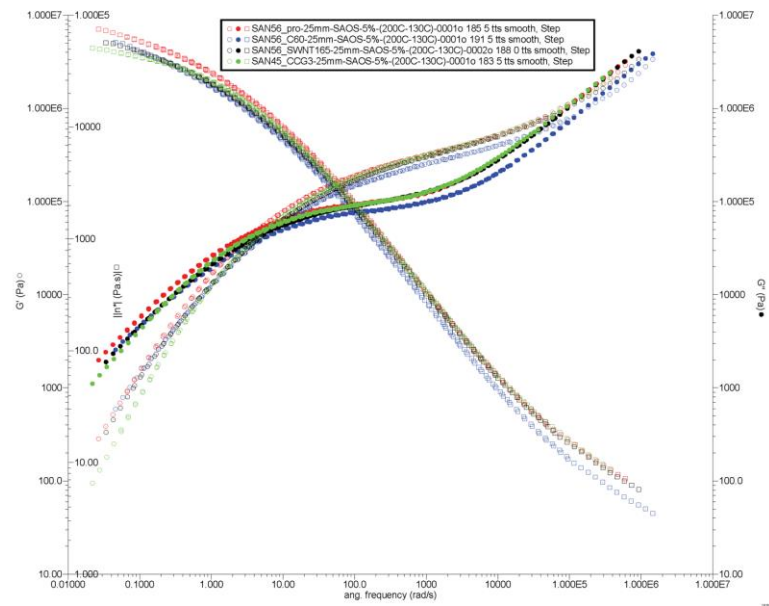


Figure A-2.1 $T_g + 77^\circ\text{C}$ master curves for SAN56 matrix samples.

A-2.4 Calculation of entanglement molecular weight

Entanglement molecular weight, M_e was calculated from the plateau modulus, G_N^o , according to Equation A-2.1

$$M_e = \frac{4}{5} \frac{\rho RT}{G_N^o} \quad (\text{Equation A-2.1})$$

where ρ is the polymer density, R is the universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature in Kelvin.^{137, 138} However, first G_N^o must be known. The plateau modulus was determined using the empirical tan-delta-minimum approach.¹³⁸ In this approach the plateau modulus is taken to be the value of the storage modulus, G' , associated with frequency (ω) at which the loss tangent, $\tan \delta$, is at a minimum. Algebraically this is expressed as shown in (Equation A-2.2).

$$, G_N^o = G'(\omega)_{\tan \delta_{min}} \quad (\text{Equation A-2.2})$$

The loss tangent expresses the ratio to which a material behaves viscously versus elastically; therefore, the minimum in the loss tangent represents the frequency at which the material is most elastic.

Since matrices are random copolymers, values of M_e from Equation A-2.1 were then converted to a more meaning full degree of polymerization between entanglements, DP_e . This was done by divide each M_e value by the molar composition weighted, average repeat unit molar mass. The results are tabulated in Table A-2.1.

Table A-2.1 Plateau modulus and DP_e for all samples.

Matrix	G_N^o (Pa)				DP_e			
Identity	polymer	C60	SWNT	CCG	polymer	C60	SWNT	CCG
PS	1.14E+05	1.20E+05	1.13E+05	1.17E+05	242.7908	233.779	244.8364	236.8776
SAN29	2.42E+05	2.58E+05	1.09E+05	1.55E+05	133.9504	127.5902	297.0371	211.45
SAN37	2.73E+05	2.99E+05	2.96E+05	1.83E+05	124.6487	116.6442	116.2574	187.5222
SAN45	3.25E+05	3.54E+05	3.44E+05	2.20E+05	110.3473	102.0171	103.5137	163.9411
SAN49	2.27E+05	3.99E+05	2.64E+05	2.40E+05	161.6736	93.75892	140.2618	153.9569
SAN56	3.13E+05	3.12E+05	2.98E+05	3.10E+05	124.1095	126.218	130.9858	124.6444

Vita

Bradley C. Miller was born on December 17, 1984 in Westfield, NY to Gary Miller and Dr. Holly Forester-Miller. He grew up Charleston, WV and Durham, NC. In May of 2002 he graduated from Jordan High School in Durham. The following August, Brad started his undergraduate career at Appalachian State University in Boone, NC, where received his ACS-certified B.S. in Chemistry, with minors in Physics, and Mathematics in May of 2006. While attending Appalachian State, Brad met his wonderful, loving, and supportive wife, Lesley. In August 2006, he started he pursuit of his doctorate in Polymer Chemistry at the University of Tennessee under the direction of Dr. Mark Dadmun. On June 14, 2008, Brad and Lesley were married, and on September 1, 2014 they welcomed their firstborn child, Anderson. On July 30, 2015 Brad's graduate career culminated with the successful defense of his Ph.D. dissertation.