

Role of Polymer and Nanoparticle Properties on the Dynamics and Local Structure of Polymer Nanocomposites

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Abstract

Polymer nanocomposite (PNC) research is a burgeoning field of study in material science owing to the interesting material properties afforded to nanoscale interaction between polymer and nanoparticle. Despite the wealth of different applications being pursued for study, the fundamental parameters that control these emergent properties are not well understood. These knowledge gaps include what controls the interfacial polymer layer 1-5 nm away from the nanoparticle surface as well as what role nanoparticle characteristics play in affecting the macroscopic properties of PNCs. This dissertation combines different static and dynamic experimental techniques to probe both polymer- and nanoparticle-specific parameters with the goal of understanding how they control dynamics and local structure in PNCs. For the polymer perspective, a conceptually more accurate heterogeneous model analysis of the dielectric spectra of PNCs is shown to reveal two important features: that the interfacial polymer layer grows significantly with cooling and that the chains in the interface have less freedom of motion because of chain stretching. This analysis is further used to demonstrate that polymer chain rigidity increases the extent of the interfacial layer above a critical rigidity. The conformational state of polymers is further explored with dielectric spectroscopy where stretched or flattened chains are shown to have a reduced dielectric amplitude from the neat polymer. From the nanoparticle perspective, unique macroscopic properties are shown to be achievable with small, attractive 2 nm nanoparticles (NPs) that are on the order of a polymer segment size. These PNCs with 2 nm NPs differ from PNCs with conventionally sized NPs studied previously by having large changes in mechanical properties while simultaneously having small changes in viscoelastic properties at high temperatures. These effects are attributed to enhanced NP

mobility, which is controlled by the temperature-sensitive polymer-NP desorption time. The diffusion of nanoparticles in a polymer melt is studied systematically with polymer molecular weight. The diffusion results are explained with a simple model which argues that NPs transition from a NP-dominant core-shell mechanism to a polymer-dominant vehicle mechanism as the chain length increases, a transition which depends on NP size and the polymer-NP desorption time.

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1. Introduction

A brief overview of the scientific motivation for the dissertation followed by an outline of the thesis itself.

1.1. Motivation

Polymers are macromolecules with many repeating units (monomers), which have unique viscoelastic properties [1] that are advantageous for a variety of applications. However, they typically lack sufficient mechanical strength to be useable for practical applications on their own [2, 3]. To overcome this problem, researchers have studied ways to reinforce polymers with fillers to increase mechanical strength while still maintaining their useful properties. Ubiquitous in material science are polymer composites that use micron-scale fillers for reinforcement, with some prominent examples including carbon fiber [4] and carbon black reinforced rubber [5, 6]. More recently, polymer *nanocomposites* have been developed where nanometer-sized fillers are dispersed in a polymer melt. The nanoscale size of the particles allows for a greater interaction area between polymers and nanoparticles, and this interaction causes many interesting emergent properties, including enhanced mechanical, electrical, optical, and transport properties [7, 8]. Despite the excitement stemming from their potential utility, the fundamental physics of these materials is not well understood.

The goal of PNC research is to understand what are the nanoscopic parameters that control these enhanced macroscopic properties, so that the nanocomposites can be rationally designed for desired applications. Research into PNCs typically involves understanding the structure and dynamics of PNC components, both for the polymer chains and the nanoparticles

themselves. Of particular interest is the 1-5 nm polymer layer adsorbed to the surface of nanoparticles, termed the interfacial layer, which controls many of these macroscopic properties [9]. This interfacial layer has structure and dynamics distinct from the bulk polymer chains in the composite. The difficulty in investigating the interfacial layer and polymer composites in general comes from trying to isolate coupled effects that often occur on the nanoscale, which requires either careful experimental design or accurate analysis methods. To this end, this dissertation attempts to better understand the parameters controlling polymer nanocomposites by a holistic examination of both polymer and nanoparticle components. This investigation involves measuring the structure and dynamics of polymers in the interfacial layer as well as observing how nanoparticle structure and dynamics can affect these polymer properties. This dissertation attempts to answer the following: how do polymer and nanoparticle features affect the dynamics and local structure of polymer nanocomposites?

1.2. Thesis Outline

Chapter 2 gives a thorough literature review starting with essential definitions of polymer parameters used throughout the thesis. The current understanding of polymer dynamics is outlined with special emphasis on the segmental dynamics associated with the dynamic glass transition. Nanoparticle dynamics in a polymer melt and sample preparation are next topics discussed followed by a significant discussion of the different experimental techniques used to measure properties of polymer nanocomposites. Finally, a summary of the relevant parameters already studied in polymer nanocomposites is provided.

Chapter 3 outlines the main experimental techniques used in this dissertation (broadband dielectric spectroscopy (BDS), dynamic light scattering (DLS), and temperature-modulated

differential scanning calorimetry (TMDSC)). Additional techniques not central to the thesis but used in some chapters are also discussed.

Chapter 4 investigates the different broadband dielectric analysis methods used in the literature to study the polymer interfacial layer of PNCs. The case is put forth that a heterogeneous model analysis with an explicit interfacial layer contribution is the best analysis method, and the results of this conclusion are explored in some detail. The most important findings are that the interfacial layer has a distinct dielectric amplitude from the bulk polymer owing to chain stretching, and that the interfacial layer thickness increases with decreasing temperature.

Chapter 5 uses the previous chapter's dielectric analysis methods in conjunction with structural and thermodynamic measurements to study the effect of chain rigidity on the interfacial layer for different polymer systems based on the polymer's characteristic ratio, C_{∞} . All three techniques (small-angle X-ray scattering (SAXS), BDS, TMDSC) demonstrate that the interfacial layer thickness increases with increasing chain rigidity above a critical characteristic ratio. The existence of this critical C_{∞} is argued to be related to the dynamic heterogeneity length scale.

Chapter 6 explores in more detail the effect of dielectric amplitude in polymer systems, comparing neat, PNC, and polymer adsorbed NPs (PNCs with free polymer removed) dielectric spectra for different molecular weights. These measurements showed that the temperature dependence of the dielectric amplitude of the neat polymer (which increases with decreasing temperature following the Curie-Weiss law) differs from the temperature dependence of the polymer composite systems, where the polymer chains have modified chain conformations.

Chapter 7 shifts towards more nanoparticle specific parameters that control PNC dynamics by doing a comparative study of PNCs with conventionally sized 25 nm NPs and PNCs with 2 nm NPs that are of size on the order of a polymer segment. The addition of these 2 nm NPs to the polymer melt result in large changes in T_g and fragility, while simultaneously having small changes in viscoelastic properties; these effects are not present in conventionally sized NPs. These results are explained by the high mobility of the 2 nm NPs caused by their finite desorption time from the polymer chains.

Chapter 8 explores this effect of nanoparticle mobility more closely, where the diffusion of 10 nm and 2 nm NPs are measured in a polymer melt. A simple model is proposed to describe nanoparticle diffusion as a crossover from a NP-dominant core-shell regime to a polymer-dominant vehicle regime, where the polymer-NP desorption time plays a critical role.

Chapter 9 summarizes the five experimental chapters and provides an outlook for future study of PNCs based on the exciting findings of this dissertation.

2. Historical Background

This chapter provides a literature summary of polymer nanocomposites from a theoretical and experimental point of view. A brief introduction on the structure and dynamics of polymers is given along with a discussion on the glass transition. Next, the topic of polymer nanocomposites is introduced with a discussion of the various properties and applications. Emphasis is given to the interfacial polymer layer surrounding the nanoparticle surface. The polymer nanocomposite literature review is divided into sections: first addressing polymer nanocomposite sample preparation, followed by nanoparticle properties and dynamics in polymer nanocomposites, followed by a discussion of the measurement techniques used to probe the interfacial polymer layer, and finally some different parameters that have already been shown to affect the interface.

2.1. Polymer Structure

Polymers are macromolecules consisting of many repeating units called monomers connected together in one molecule. Naturally occurring polymers such as natural rubber, wool, or silk have been used by humans for hundreds of years. The first synthetic polymers were inadvertently created in the 19th century, originally thought to be colloidal structures. It was not until the early 20th century that chemists realized they were synthesizing large macromolecular chains by covalently bonding individual monomer units, in a process now called polymerization [1]. The size of a polymer chain is typically given in terms of its molecular weight, which is simply the mass of an individual monomer times the number of monomers. What is called the molecular weight is more precisely the molar mass, but “molecular weight” is the commonly used term in the literature (units are kg/mol). For polymer *melts* consisting of many polymer

chains, the average molecular weight can be determined from various experimental methods, and this value gives a general description related to the average chain length.

The simplest model used to describe the motion of a single, linear polymer chain is the 3-dimensional random walk, where a sufficiently long chain of N units and unit length l undergo Brownian motion with volume effects ignored. Any real polymer chain has excluded volume resulting from bond angles θ caused by covalent bonds and van der Waals interactions in the individual monomers. To account for these restrictions, polymer models make modifications to Brownian motion to describe the structure and motion of polymer chains in the melt state. From these polymer models, we extract a few parameters that are used frequently in polymer physics. The first of which is the Kuhn length, which attempts to average over the complicated bond structure of individual monomers and instead treat real polymer chains as freely jointed chains of N polymer segments with Kuhn segment length b [1]. The language of “polymer segments” is helpful when describing the macromolecular structure and dynamics of a chain. The Kuhn segment can be used for all flexible, linear polymer chains, where the chemically specific characteristics are contained in the Kuhn length b . Additionally, when describing the physical length of a polymer chain in a melt state, it is more helpful to describe the average distance of a polymer chain relative to its center of mass, a quantity called the radius of gyration R_g [10]. The radius of gyration accounts for the fact that the polymer chains will have various conformations in the melt state based on the number of bonds n , the length of a monomer l , and the bond angle θ . The formal definition of the radius of gyration is as follows:

$$R_g^2 = \frac{1}{n+1} \sum_{i=0}^n (R_i - R_{CM})^2; R_{CM} = \frac{1}{n+1} \sum_{i=0}^n R_i \quad (2.1)$$

Here, n refers to the number of bond vectors in the polymer chain, where $n + 1$ is the number of backbone atoms. The practical definition of the radius of gyration is defined in terms of its root mean square value:

$$\sqrt{\langle R_g^2 \rangle} = \sqrt{\frac{Nb^2}{6}} = \sqrt{C_\infty \frac{nMl^2}{6m_0}} \quad (2.2)$$

The first definition contains the number of Kuhn segments N and the Kuhn length b . These quantities are not known so the second definition gives a more working description of R_g . These known quantities are as follows: M is the molecular weight, l is the bond length, m_0 is the molar mass of an individual monomer, n is the number of bonds per monomer, and C_∞ is the characteristic ratio. The characteristic ratio is a dimensionless quantity which is defined as the ratio between the mean square unperturbed end-to-end distance of a polymer chain and the distance expected for a freely jointed chain of the same number of bonds with the same length[10]. More concretely, the quantity can give a qualitative description of the rigidity of a given polymer; for real polymers $C_\infty > 1$, usually with values ~ 4 -10.

When discussing characteristics of the polymer melt, there are a few other helpful definitions. One such definition is the tube diameter (d_t), the diameter of a confining tube that surrounds a given polymer chain where the individual monomers are allowed to move perpendicularly to the tube axis [1]. The confining tube is meant to account for the constraints imposed by surrounding chains that prevent the chain from moving freely and instead force it to reptate (move in a snake-like motion). Closely related to the tube diameter is the number of entanglements (N/N_E), a measurement of the number of topological constraints polymers cause on each other preventing them from crossing. The N_E is the number of monomers in the

entanglement strand, which for a given monomer molar mass m_0 gives the molecular weight between entanglements $M_E = N_E m_0$. Crudely, the number of entanglements can be imagined as the average number of polymer chains that hook around a given chain, and this quantity scales with molecular weight. A N/N_E sufficiently greater than 1 is said to be in the entangled regime, otherwise the system is in the unentangled regime. Going from the unentangled to the entangled regime creates a sizeable transition in scaling behavior for viscosity and other dynamic properties, where this viscosity transition is shown in Figure 2.1 [11].

2.2. Polymer Dynamics

The macromolecular structure of polymers gives them complex dynamic processes that span over different time and length scales [12]. When a dynamic process is probed, there is a time associated with that system returning to equilibrium. This time scale is called the *relaxation time*, and the process of a perturbed system returning to its equilibrium state is referred to as *relaxation* [1]. In a typical measurement of a dynamic process, the response to a small

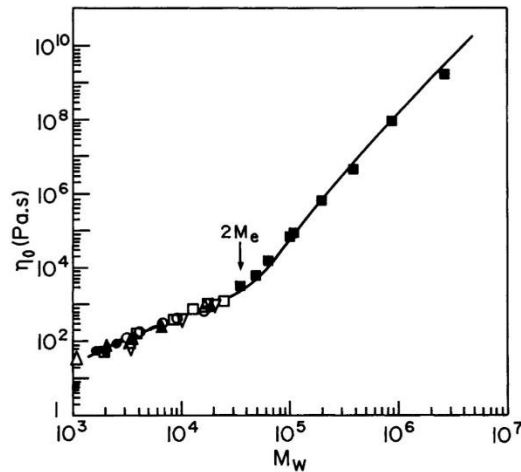


Figure 2.1: Viscosity as a function of molecular weight. There is a transition in scaling behavior of viscosity as you increase the molecular weight from unentangled to entangled regime. Taken from [11].

perturbation of the system is equated with the relaxation response of a spontaneous fluctuation in equilibrium. This equivalency is called the Fluctuation-Dissipation theorem, and it allows the linear response from a perturbation (which puts the system in a non-equilibrium state) to describe the statistical fluctuation of the system (the relaxation that occurs in an equilibrium state) [13]. For each of these systems, the response can be described with some form of an exponential decay, where the characteristic timescale is the relaxation time. For each dynamic process of polymers outlined, the mechanism as well as the general properties of the relaxation will be discussed.

2.2.1. Segmental Dynamics

The main structural relaxation of polymers is the segmental relaxation, also called the α -relaxation. The segmental relaxation is generally agreed to be the time scale of conformational changes of a few polymer segments that occur because of the cooperative motion of other polymer segments. Segmental dynamics can be probed with a variety of experimental techniques, including mechanical, dielectric, and light scattering spectroscopies [12], where the segmental dynamics evolve with temperature. This evolution is most readily apparent in broadband dielectric spectroscopy (BDS), described in detail in Chapter 3. Figure 2.2 shows the BDS loss spectra of a neat poly(vinyl acetate) polymer for a range of temperatures. The peak position corresponds to the frequency of the average relaxation time for the segmental motion at a given temperature. As expected, the segmental dynamics slow down with decreasing temperature. The slowing down of segmental dynamics with temperature is an important reason why they are associated with the glass transition of polymers. The glass transition occurs for amorphous solids, such as glasses and polymers, which do not have the long-range ordering that

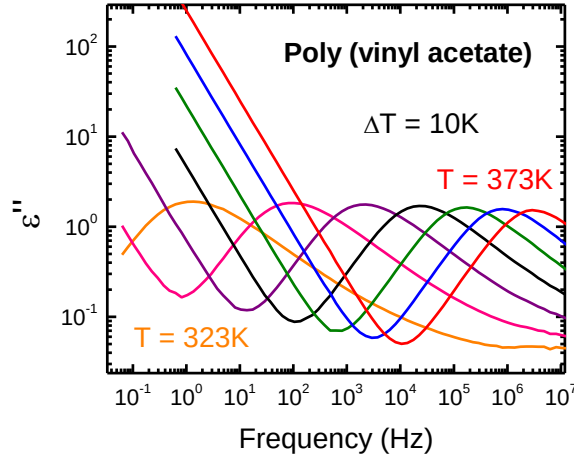


Figure 2.2: Dielectric loss spectra of a poly(vinyl acetate) (PVAc) polymer which shows the temperature evolution of the segmental relaxation peak.

crystalline solids have. Qualitatively, the glass transition of a polymer is the smooth and gradual change from a molten, rubbery state to a glassy brittle state with decreasing temperature. The internal degrees of freedom in the system go from an equilibrium state to a metastable non-equilibrium state upon cooling to below the glass transition [14, 15]. This metastable non-equilibrium state is the result of the segmental dynamics becoming essentially frozen at low enough temperature where they are not able to relax quickly. If the polymer is kept at a given temperature in its frozen state, segmental motion will eventually relax and return the system to an equilibrium state, in a process known as ageing. Figure 2.3 shows a demonstration of ageing for an amorphous solid, where the glass at temperature T_A evolves towards an equilibrium state. The temperature at which the relaxation time of segmental motion reaches $\tau = 100\text{-}1000\text{s}$ is defined as the dynamic glass transition temperature, labeled T_g in Figure 2.3 [16]. The glass transition is reversible upon heating and cooling.

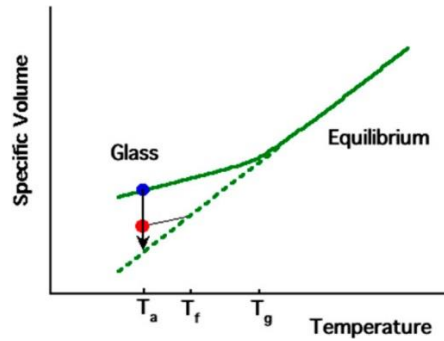


Figure 2.3: Plot of specific volume for an amorphous material as a function of temperature. The glass is in a non-equilibrium state when cooled below the glass transition temperature but evolves towards equilibrium in a process called ageing. Taken from [16].

The glass transition is manifested by significant changes to the temperature dependence of a material's properties, including density, specific heat, and thermal expansion coefficient [17]. Perhaps most striking is the significant (up to 14 orders) increase in viscosity as the sample is cooled over a relatively small temperature window. The glass transition temperature is cooling/heating rate dependent, where a slower cooling rate allows the segments to relax easier and the transition occurs at a slightly lower temperature. This cooling rate dependence is shown in the differential scanning calorimetry (DSC) data in Figure 2.4 for polystyrene [16]. The midpoint of the heat capacity step from DSC is taken to be the calorimetric glass transition temperature, and for a cooling rate of 10-20K/min, this temperature roughly corresponds to the temperature where the segmental dynamics' relaxation time is $\tau \sim 100$ s. The smooth continuous decrease in heat capacity indicates that the glass transition of amorphous solids is not a phase transition, where there would be a discontinuous change in mechanical or dynamic properties.

The temperature dependence of the structural relaxation is an important feature of amorphous solids because it describes dynamics of polymer segments as the polymer is cooled towards the glass transition.

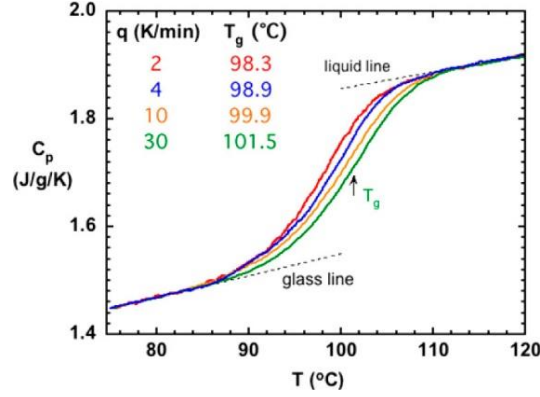


Figure 2.4: Differential scanning calorimetry data for polystyrene measured at different cooling rates. The shift in the midpoint of the continuous heat capacity step indicates that the glass transition temperature is cooling rate dependent for polymers. Taken from [16].

For molecular conformational changes that have a constant activation energy with temperature, the relaxation times τ_α can be described by the Arrhenius equation:

$$\tau_\alpha = \tau_0 \exp(E_A/k_B T) \quad (2.3)$$

In this equation E_A represents the activation energy necessary to jump over the free energy barrier separating two conformational states. The τ_0 is the relaxation time for a process extrapolated to very high temperature. The Arrhenius temperature dependence produces a straight line when plotted on as $\log(\tau)$ vs $1/T$, which is shown in Figure 2.5 [18] where the $1/T$ is scaled by T_g in what is called an Angell plot [19]. The Arrhenius equation can be used to fit the temperature dependence of the relaxation time spectra for certain viscous glasses such as silica [14]. However, it cannot be applied to the segmental motion of polymers as the activation energy increases upon cooling toward T_g , manifesting in rapidly increasing viscosity and relaxation time. Understanding the origin of this rapid slowing down of segmental relaxation is the main challenge of the physics of amorphous materials. To describe the temperature

dependence of segmental relaxation times, the empirical Vogel-Fulcher-Tammann [20] equation is used, given by:

$$\tau_{\alpha} = \tau_0 \exp\left(\frac{B}{T-T_0}\right) \quad (2.4)$$

Here B and T_0 are free parameters. This equation can fit the T-dependence of the relaxation time spectra over many decades; however, it is conceptually flawed because the T_0 parameter implies there is a finite temperature where the relaxation time of the polymer is infinite. It has been suggested that the T_0 temperature could roughly correspond to the temperature of the Kauzmann paradox, the temperature at which the extrapolated entropy of the supercooled liquid is lower than that of the corresponding crystal [21]. The exact nature of the VFT equation is not perfectly understood but it is a helpful description of the energy landscape controlling polymer segmental relaxation near T_g . An important value taken from the VFT curve is its slope at T_g , a quantity called the fragility m [14, 19], defined as:

$$m = \left. \frac{\partial \log_{10} \tau_{\alpha}}{\partial T_g/T} \right|_{T=T_g} \quad (2.5)$$

Amorphous materials with strongly non-Arrhenius behavior are called “fragile”; ones that more closely follow an Arrhenius dependence are called “strong” [14]. Strong liquids usually have very small fragilities, $m \approx 20$ -30; polymers, on the other hand, have a very wide range of fragilities, $m \approx 20$ -190 [22]. The physical origin of fragility is a topic of debate; there are several phenomenological theories to explain its origin, including Adam-Gibbs theory [23], Random First Order Transition (RFOT) theory [24], and Mode-Coupling theory [25]. Common to Adam-Gibbs and RFOT theory is a description of a dynamic heterogeneity length scale, defined as the characteristic length scale at which the local dynamics can be described as distinct; in other

words, the length scale at which heterogeneities in the dynamics can be observed. Adam-Gibbs theory speculates that this length scale corresponds to the size of a cooperatively rearranging region (CRR) that facilitates the relaxation of polymer segments [23]. According to the theory, as the material is cooled down, this CRR increases in size and requires more energy to facilitate cooperative motion, hence the increase in activation energy upon cooling to T_g . A complete description of the dynamic heterogeneity length scale, fragility, and activation energy remains an open theoretical problem for the physics of glasses.

2.2.2. Secondary Dynamics

Secondary relaxation dynamics typically occur at times faster than segmental dynamics. The sources of these secondary processes vary, and typically there are given labels of β , γ , etc. The most common type of secondary process for polymers comes from internal conformational changes, such as the rotation of side groups on the main chain [12]. However, secondary relaxations can also be observed in low molecular weight liquids, so it is not a uniquely polymer conformation phenomenon [26]. The secondary relaxation of polymers is manifest as a broad, symmetric peak in dielectric spectra that occurs at lower temperatures, as seen in blue in Figure 2.6a. The relaxation time of the secondary β -relaxation follows an Arrhenius temperature dependence (Fig 2.6b), in contrast to the segmental α -relaxation.

The segmental and secondary relaxations of polymers are generally believed to be deconvoluted [27, 28]; from an analysis standpoint, this deconvolution means the spectra can be analyzed separately. For some polymers, such as poly(methyl methacrylate), the secondary β -relaxation has a much greater amplitude in the dielectric spectra than the segmental α -relaxation. The secondary β -relaxations are sensitive to local packing around the polymer chain, so faster secondary dynamics are associated with a reduced local density and increased free volume [29].

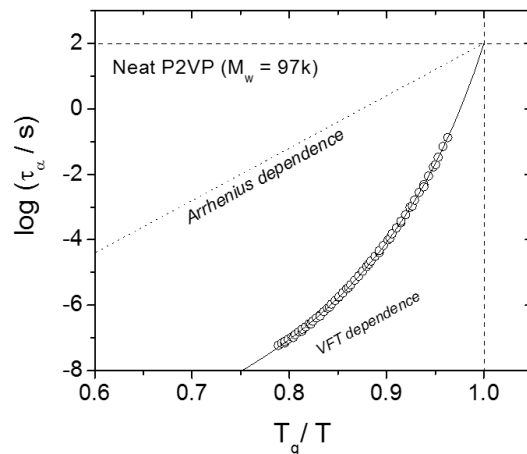


Figure 2.5: Angell plot for poly(2-vinyl pyridine) where the inverse temperature axis is normalized to the glass transition temperature, T_g . Taken from [18].

Free volume is difficult to quantify, but the general concept of pockets of free space in a polymer melt is widely accepted to be important for understanding the glass transition and for different polymer applications [30-33].

2.2.3. Fast Dynamics

The fast dynamics occur at higher frequencies than the secondary relaxation, but below the vibrational excitations of individual molecules at very high frequency. These fast dynamics are the result of “cage-rattling”, the rattling motions that occur as a molecule attempts to escape the “cage” of its surrounding molecules [34]. Similar to the secondary relaxation process, an increased amplitude in fast dynamic response indicates a higher free volume in the polymer. The fast dynamics are most readily accessible from Brillouin light scattering and quasi-elastic neutron scattering. However, the fast dynamics are not investigated in this dissertation, and will not be discussed further.

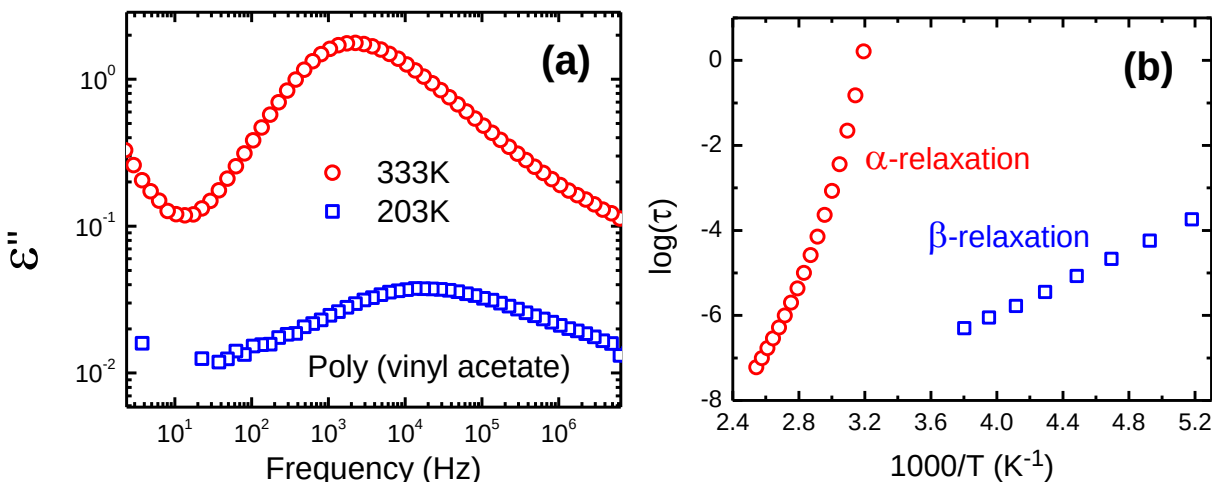


Figure 2.6: (a) Secondary relaxation spectra (blue) from dielectric spectroscopy at 203K, in comparison to segmental relaxation (red) at 333K for poly(vinyl acetate) (PVAc). (b) The α -relaxation time spectra (red) and β -relaxation time spectra (blue) for neat PVAc. The α -relaxation follows a Vogel-Fulcher-Tammann temperature dependence, while the β -relaxation follows an Arrhenius temperature dependence.

2.2.4. Chain Dynamics

Polymers also exhibit full chain dynamics at times longer than segmental relaxation, where this chain relaxation involves the motion of the entire chain. Certain polymers, such as poly(propylene glycol) (PPG), have their dipoles moments aligned along the backbone of the polymer. This uncommon dipole orientation allows measurement of the full chain dynamics using dielectric spectroscopy. This process is shown in Figure 2.7, and the amplitude of the normal mode process grows with molecular weight for PPG [35]. The chain dynamics of PPG are briefly discussed with regards to their contribution to the dynamic light scattering spectra of Chapter 8.

2.3. Polymer Nanocomposites

Polymers are advantageous from a material science perspective owing to their elasticity, light weight, and processability [7, 10]; however, they typically lack sufficient mechanical

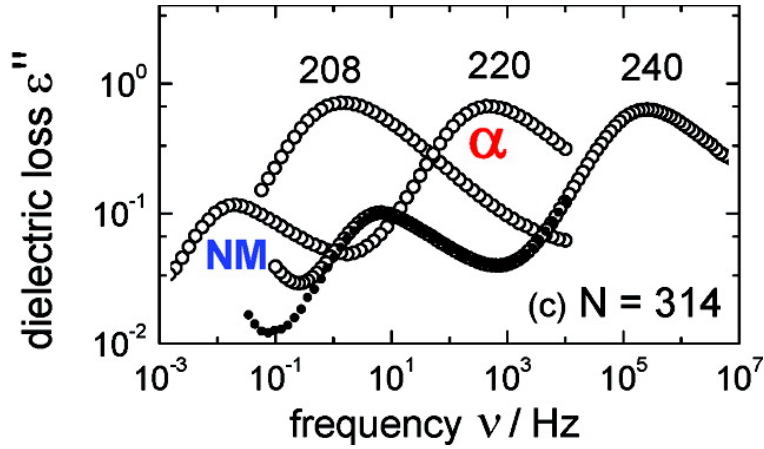


Figure 2.7: Plot of dielectric loss spectra of polypropylene glycol (PPG) with a molecular weight of 314kDa. The peak labeled NM for normal modes corresponds to the relaxation of dipole vectors aligned along the chain. Taken from [35].

strength for many applications [2, 3]. To combat this problem, extensive research has been done on reinforcing polymers with fillers to increase mechanical strength while simultaneously taking advantage of the useful properties of polymers [8]. Polymer composites with micron-scale fillers are ubiquitous in materials applications, with prominent examples including carbon fiber [4] and carbon black reinforced rubber [5, 6]. Recently, extensive research has been made on polymer composites with nanoscale fillers, called polymer nanocomposites (PNCs) [2, 3, 7, 8, 36-42]. From a topological point of view, nanoscale fillers have a much larger interaction area than micron-size fillers, and subsequently less unused weight inside nanoparticle cores. Aside from mechanical reinforcement [2, 38, 43], polymer nanocomposites have been shown to have other unique properties, including enhanced electrical [44-47], optical [48-50], thermal [51, 52], and transport properties [31, 53, 54].

Despite the large demand for polymer nanocomposites, the underlying physics of these materials is still poorly understood [3, 7]. Rational design of PNCs necessitates a “bottom-up”

understanding of the nanoscopic parameters that control the desired macroscopic properties. To this end, PNC research has focused on studying ways that the structure and dynamics of PNC components can be tuned to create interesting macroscopic properties. Much of polymer nanocomposite research has focused on the complex structure and dynamics of polymers in PNCs, especially with respect to the polymer chains directly impacted by the nanoparticle surface [55-59]. This interfacial polymer layer that extends a few nanometers away from the nanoparticle surface has been shown to influence many of the macroscopic properties of PNCs, and thus much attention has been dedicated to understanding it [7, 9, 58]. Studies have also investigated the nanoparticle structure and dynamics in PNCs, as the nanoparticle geometry [60-62], loading [57, 63], and polymer-nanoparticle interaction [41, 58, 64, 65] can have a major impact for certain applications. This literature review will focus on both nanoparticle and polymer aspects of PNCs, as both components are important for how dynamics and local structure are modified in polymer nanocomposites. It is difficult to disentangle the effects of one without addressing the other. So, while the sections will separate nanoparticle and polymer properties, both will be discussed throughout. This literature review will first cover sample preparation, followed by a discussion of intrinsic nanoparticle properties and dynamics. An extensive outline of the ways of measuring the interfacial layer will be given, followed by discussion of several PNC parameters already shown to affect the interface. This review will provide the backdrop to the experimental sections of this dissertation, which will emphasize the importance of both polymer and nanoparticle components to rational PNC design.

2.3.1. Sample Preparation

The goal of polymer composite mixing is to achieve good dispersion of the fillers in the polymer matrix to maximize the interaction between the two. Mixing polymer composites with

micron-sized fillers is usually done with physical mixing [66, 67]. For nanocomposite samples, understanding the chemical interactions between filler and polymer is necessary for good dispersion. Fillers that are not chemically attracted to the polymer will aggregate into microscale conglomerates even at low concentrations [68]. Different approaches have been reported in the literature to achieve mixing of organic polymers with bare, inorganic fillers, including ball milling [69], in-situ polymerization [70], melt mixing [71], and solvent mixing [72]. Solvent mixing is generally the most successful and commonly used in the literature because it significantly reduces viscosity and allows better dispersion of fillers. The procedure is essentially as follows: the polymer and nanoparticle are dissolved in solvent and mixed under stirring before the solvent is evaporated, either in ambient conditions or by vacuum. The type of solvents used are chemically specific and determine how well the final PNC is mixed.

Prior to measurements, polymer nanocomposites are typically dried in vacuum at elevated temperatures. This drying removes residual solvent and other moisture from the polymer and nanoparticles, which are typically hydrophilic and trap atmospheric moisture [73]. Drying at temperatures well above T_g is also important for removing effects of sample preparation by annealing the polymer chains towards thermodynamic equilibrium.

2.3.2. Nanoparticle Properties in PNCs

Nanofillers in PNCs can be many different geometries, including spheres [42], sheets [62], rods [44], and tubes [74]. One of the great challenges of polymer nanocomposite design is finding nanoparticles that can be dispersed evenly throughout the polymer matrix at a high concentration [68, 75-77]. Generally, nanoparticles with attractive interactions with polymer chains will disperse well in the matrix while non-attractive or repulsive interactions cause the nanoparticles to conglomerate into micron-size aggregates [9, 68]. A higher nanofiller

concentration has been shown to increase the T_g of PNCs with attractive polymer-nanoparticle interactions, and higher concentrations generally increase the interaction area between nanoparticle and polymer [57, 58]. There is some controversy over the extent of the T_g shift in PNCs with increased loading. For example, one study on poly(2-vinyl pyridine)/silica showed a 15 K shift in T_g with a loading of only 0.5 vol% [39]; another study on the same P2VP/silica system showed that for loading up to 30 vol% there was only a small 2 K shift in T_g [57]. The shift in T_g has remained a quoted quantity for many PNC studies, although its usefulness as a metric to describe changes in segmental dynamics in PNCs is somewhat suspect given the methods used to probe the T_g are not uniform [9].

Spherical nanofillers are used exclusively in this dissertation and will be simply referred to as “nanoparticles”. Spherical nanoparticles have the advantage of isotropy that other filler types do not have; there is no need to orient the nanoparticles once dispersed, making mixing simpler. In principle, smaller nanoparticles are more desirable for PNCs because they have larger interaction area at the same volume fraction of nanoparticles.

2.3.3. Nanoparticle Dynamics in PNCs

Nanoparticles diffuse through the polymer environment in PNCs and these dynamics can be important to properties relating to processing and mixing [78]. The classical description for a spherical penetrant diffusing in a Newtonian liquid is the Stokes-Einstein (SE) equation:

$$D_{SE} = \frac{k_B T}{6\pi\eta R_{NP}} \quad (2.6)$$

where η is the macroscopic viscosity of the fluid and R_{NP} is the radius of the nanoparticle. For polymer systems, the macroscopic viscosity η scales with molecular weight following the power law dependences shown in Figure 2.1 [1]. This simple Stokes-Einstein relation describes the

diffusion of sufficiently large, non-interacting particles in a polymer melt with low to moderate number of entanglements (where “sufficiently large” means the R_{NP} is larger than the tube diameter d_t and the R_g of the polymer) [79, 80]. However, for most systems related to polymer nanocomposite research, the measured experimental diffusion fails to match this classical description [79, 81-84]. The measured diffusion is conventionally described in relation to the Stokes-Einstein expression, using the ratio D/D_{SE} [80]. A D/D_{SE} value greater than 1 is said to have “enhanced” diffusion, while a value less than 1 is “slowed” diffusion relative to the SE relation. The D/D_{SE} is also called the Stokes-Einstein violation if it deviates from 1 significantly.

Sufficiently large, attractive nanoparticles have been shown to have slowed diffusion relative to SE [79], where the deviation from SE increases with increasing polymer molecular weight. This discrepancy is explained in that study by using the SE relation with a modified NP radius, one that includes a bound polymer layer with a thickness proportional to R_g , giving a total effective radius of $R_{eff} \sim R_{NP} + R_g$. This simple model asserts that the bound layer increases the effective size of the nanoparticle, growing proportionally with the polymer chain length. When R_{eff} is substituted into the SE equation, the slowed diffusion is properly accounted for.

For small nanoparticles with diameters around or below the tube diameter, there exist only a handful publications describing their diffusion in a polymer melt [81-83]. The non-attracting nanoparticles in these studies exhibit large SE violations (up to $D/D_{SE} \sim 200$), especially at higher molecular weight. These SE violations are caused by the discrepancy between local viscosity and macroscopic viscosity: at large molecular weight, the small

nanoparticle does not notice or feel the effects of the increasing chain length as much. The local viscosity remains essentially constant while the macroscopic viscosity continues to increase with molecular weight. A force-level theory [80, 85] has quantified the SE violations of small non-attractive NPs by parameters such as nanoparticle size, tube diameter, and number of entanglements. The SE violations are described as a combination of a hydrodynamic Stokes-Einstein contribution and non-hydrodynamic friction-like contribution that grows with increasing polymer entanglement. A later extension of that theory accounted for polymer-nanoparticle interactions and predicted that the SE violations level off at sufficient degree of entanglement [85]. Until now, there have been no studies on the nanoparticle diffusion of small attractive nanoparticles in a polymer melt.

2.3.4. Measuring the Polymer Interfacial Layer

The polymer interfacial layer is a 1-5 nm polymer layer extending out from the nanoparticle surface. The interfacial layer includes all polymer chains that are affected by the presence of the nanoparticle surface, including free chains that are not physically attached to the nanoparticle [86]. The non-interfacial polymer is referred to as the “bulk” polymer, and it is often assumed to have similar behavior to the neat polymer (i.e., the regular polymer melt with no nanofillers). The interfacial layer is often confused/used interchangeably with the bound layer, which is the layer of adsorbed polymer chains whose average thickness scales with the R_g of the polymer [87]. The bound polymer layer is typically made up of adsorbed polymer chains in different conformations, approximately described as trains, loops, and tails [88]. The interfacial layer is composed of not only the adsorbed polymer, but all chains whose structure and dynamics are modified by the presence of the nanoparticle. The confusion is likely the result of the bound layer described in polymer thin films, where the definition is conflated for PNCs.

Figure 2.8 shows the difference between the two for polymer nanocomposites. The bound layer (black dashed line) average thickness grows in proportion to R_g , meaning the bound layer is expected to continuously grow as MW is increased. The interfacial layer (orange dashed line), however, does not necessarily grow with MW because the way polymer chains organize at high MW is different than at low MW. Chain organization near the nanoparticle surface is interpreted by how the interfacial layer differs from the neat polymer. The properties of the interfacial layer can be probed with different experimental techniques that measure different aspects of PNCs.

Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) are two techniques that determine the static structure of the composite [89, 90]. When X-rays or neutrons are scattered off the materials, components with different structural properties have distinct scattering length densities (SLD). These differences produced distinct scattering cross sections, and the intensity spectra of PNCs can be fit to provide estimates of the interfacial polymer fraction and its mass density [57, 91]. Figure 2.9 shows normalized (a)SAXS and (b)SANS spectra for a PMMA-silica composite [91], where the differences related to the presence of the nanoparticle are quite noticeable at low q . A polymer nanocomposite with no or minimal interfacial layer can be fit with a two phase (polymer and nanoparticle) model [92, 93]. If the interface has a sufficiently distinct density, the composite is fit with a polydisperse core-shell model which gives quantitative estimates of the interfacial polymer layer thickness and density [57, 91, 92]. Surprisingly, the interfacial layer polymer is often found to have a reduced mass density in comparison to the bulk [93]. The fitting parameters can be used to estimate the thickness of the static interface, which has been shown to have a length $l_{int} \sim 2\text{-}5\text{ nm}$ [57, 86, 91].

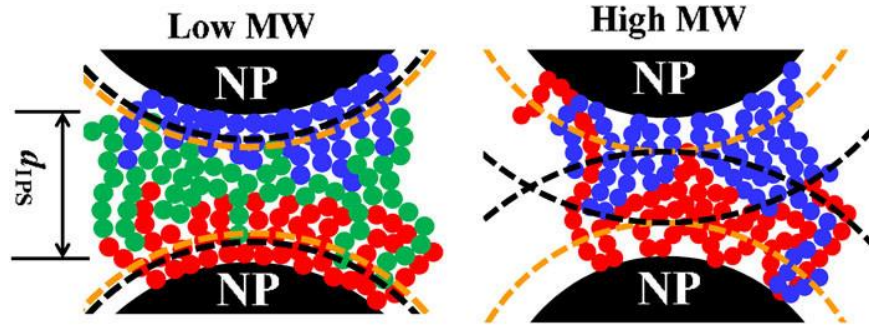


Figure 2.8: Schematic of the differences between the bound layer and the interfacial layer for different molecular weights. The bound layer (black dashed lines) has an average thickness proportional to the R_g of the polymer which scales with molecular weight. However, the interfacial layer (orange) only covers the polymer chains that have modified structure and dynamics from the bulk, meaning it does not necessarily scale with R_g . Taken from [86].

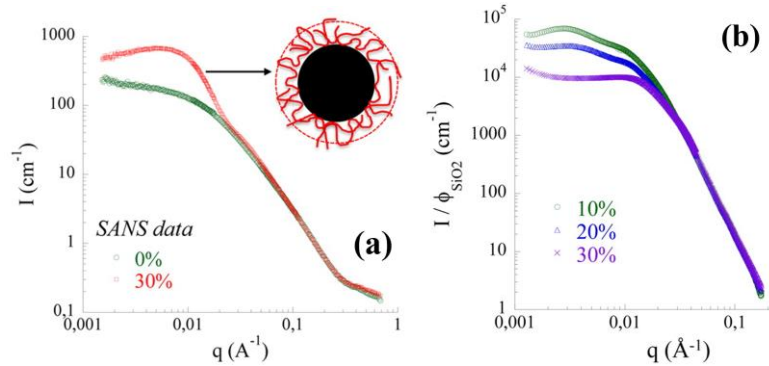


Figure 2.9: (a) Small-angle neutron scattering (SANS) and (b) small angle X-ray scattering spectra for a PMMA-silica PNC at different loadings. There are clear distinctions between the neat polymer and the polymer nanocomposite that are related to the presence of the nanoparticles. This effect is seen for different loadings in (b), where the intensity has been normalized to the silica fraction to more easily compare the low- q (local) scattering. SANS and SAXS spectra can be fit in order to determine the static interfacial layer thickness. Taken from [94].

Nuclear magnetic resonance (NMR) [95-97], broadband dielectric spectroscopy (BDS) [42, 57, 98-101], and quasi-elastic neutron scattering (QENS) [102, 103] measure the polymer dynamics of polymer nanocomposites at various timescales. NMR measurements have determined that the interfacial polymer has distinct dynamics from the bulk, where some studies have gone as far as to say the polymer chains are immobilized near the nanoparticle surface [76, 97]. Though there are some studies [104, 105] measuring segmental dynamics using QENS, the technique can only be used at very high frequencies in a limited frequency range. Broadband dielectric spectroscopy, however, offers a much broader frequency range to study segmental dynamics with a high experimental accuracy. Measurements from BDS have shown that the interface is not an immobilized glassy layer but instead is dynamically alive [57, 86, 100, 106]. Figure 2.10 shows the dielectric loss and derivative spectra of a neat PVAc (red) and PVAc-silica (blue), where the PNC clearly has distinct features from the neat polymer. These differences are seen clearly in the α -peak, where the intensity, broadening, and peak frequency are all altered by the presence of the nanoparticle and interface. Most important is the interfacial layer contribution, which is responsible for the broad shoulder on the α -peak at lower frequencies. The analysis of the interfacial layer contribution is the subject of chapter 4 of this thesis, but it should be emphasized that the quantitative results from BDS are very analysis dependent. Estimates of the interfacial layer thickness from BDS usually fall in the range of $l_{int} \sim 2-5$ nm.

Dynamic mechanical analysis (DMA) [107, 108] and Brillouin light scattering (BLS) [109] measure macroscopic mechanical properties of PNCs. Dynamic mechanical analysis has been done on a variety of PNCs [107, 110] where the presence of an adsorbed layer with a much higher T_g has been observed. Brillouin light scattering can give an estimation of the shear and

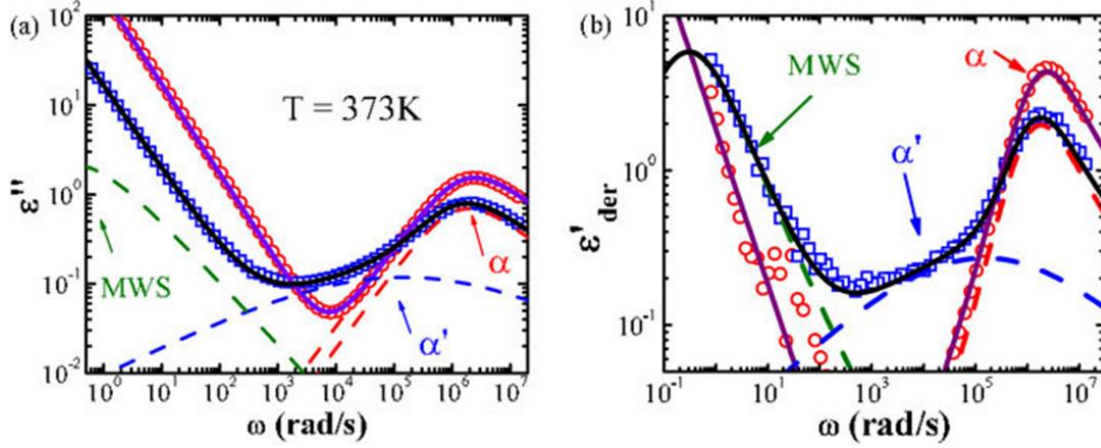


Figure 2.10: (a) Dielectric loss and (b) derivative spectra for neat PVAc (red) and PVAc-silica (blue). The presence of the nanoparticle and interface reduces the α -peak intensity, broadens the peak, and shifts it to lower frequency. The interfacial layer creates the broad shoulder at lower frequency and is expressed as its own separate peak, α' . Analysis of dielectric spectra can give information on interfacial dynamics and thickness. Taken from [86].

bulk modulus and has shown that PNCs have enhanced mechanical moduli [109, 111, 112]. As seen in Figure 2.11, this enhancement grows with loading (red symbols) and exceeds the two-phase model prediction (blue line) that simply accounts for the NP and polymer contributions [93]. This discrepancy demonstrates the presence of an interfacial layer that has enhanced mechanical moduli from the neat polymer. Using an interfacial layer model for BLS, the thickness of the interface is estimated to be $l_{\text{int}} = 3\text{ nm}$.

Atomic force microscopy (AFM) is another mechanical technique that can probe the local mechanical properties of the interface with high precision. Like previous mechanical methods, an enhanced interfacial modulus has also been measured using AFM [55, 113]. Figure 2.12 shows the mapping of a slice of a polymer nanocomposite, where the interfacial layer can be distinguished from the bulk polymer (blue) and the nanoparticle (red and yellow) using an AFM technique called resonance frequency shift [93]. The frequency shifts for these different regions can give estimations of each region's size, determined from the center of the nanoparticle. The

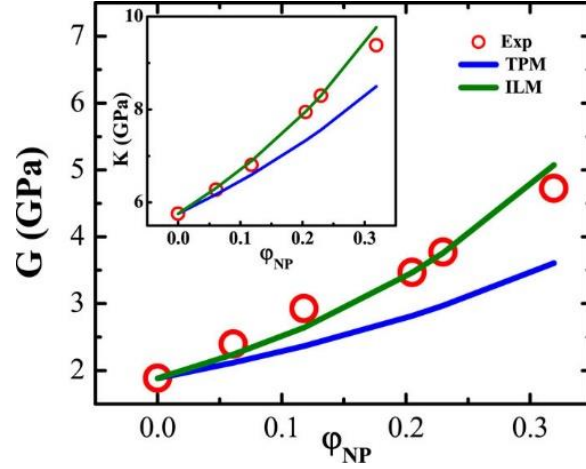


Figure 2.11: Shear modulus G and bulk modulus K (inset) for PVAc-silica composites of different loadings measured from Brillouin light scattering. The blue line represents the prediction from the two-phase model which the measured data exceeds. This discrepancy indicates that the interfacial layer has a greatly enhanced moduli from the neat. Using an interfacial layer model, this interface is expected to extend $l_{int} = 3$ nm away from the nanoparticle surface. Taken from [93].

frequency shifts in figure 2.12b represent the paths 1 and 2 in figure 2.12a, from which the interface was estimated to be $l_{int} \sim 3$ nm.

Temperature-modulated differential scanning calorimetry (TM-DSC) [57, 63, 114] measures the thermodynamic properties of PNCs, as seen in Figure 2.13 for a P2VP-silica PNC of different loading fraction [57]. The raw heat capacity of the neat, PNC, and bare silica is shown in the inset, where the silica does not have a thermodynamic transition in this temperature range. This silica contribution can be subtracted out, leaving the normalized polymer spectra in the main figure. The shoulder that appears above T_g is the result of the interfacial layer having modified thermodynamic properties from the neat polymer. This shoulder demonstrates that the interfacial layer is thermally active, counter to what some previous DSC studies on interfaces have argued [63]. Using the breadth of the heat capacity step, ΔC_p , and the shoulder step, δC_p , shown in Figure 2.13b, the interfacial volume fraction can be estimated as $\varphi_{int} =$

$$(1 - \varphi_{NP}) \delta C_p / \Delta C_p.$$

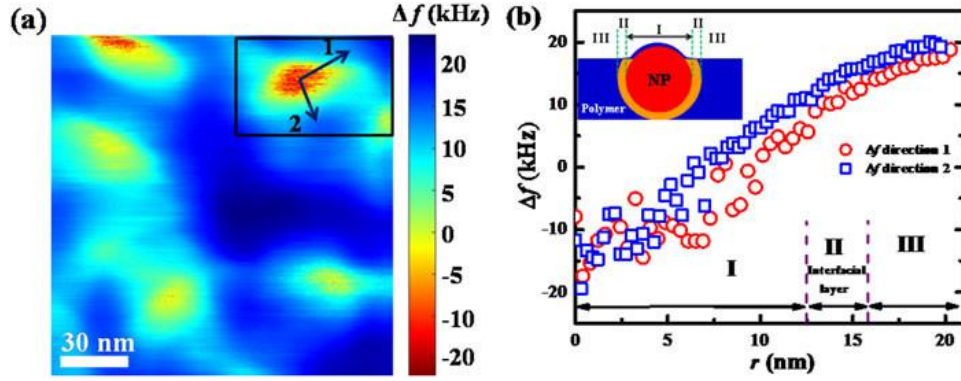


Figure 2.12: (a) Resonance frequency shift map of the surface of a PVAc-silica PNC measured using atomic force microscopy. The red and yellow regions are the nanoparticles and the blue regions are the bulk polymer. The remaining colors represent the interfacial polymer which has a distinct modulus from the bulk. (b) The frequency shift Δf as a function of distance from the nanoparticle center. The red and blue points represent the frequency shifts for the lines marked 1 and 2 in (a), and from this analysis an estimation of the interfacial thickness can be achieved, where $l_{int} \sim 3$ nm. Taken from [93].

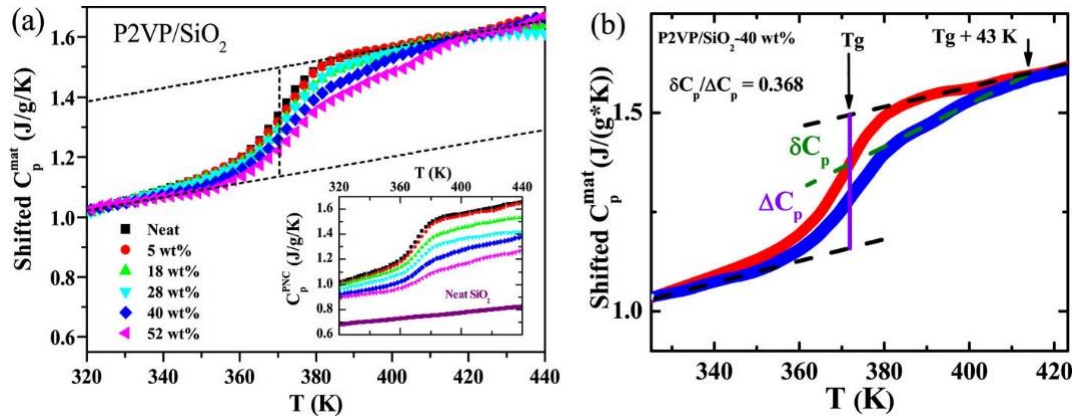


Figure 2.13: (a) Temperature-modulated differential scanning calorimetry data for a P2VP-silica composite of different loadings. The raw TM-DSC data is contained in the inset, including the silica heat capacity. The main figure shows the polymer fraction of each sample with the silica fraction normalized out. The broad shoulder above the T_g midpoint is the result of the interfacial polymer that has modified thermodynamic properties. (b) Same dataset with an emphasis on the heat capacity step ΔC_p and shoulder step δC_p , from which can be estimated the interfacial volume fraction, $\phi_{int} = (1 - \phi_{NP}) \delta C_p / \Delta C_p$. Taken from [57].

The difficulty in measuring the effects of the interfacial layer is in quantifying the structure and dynamics of interfacial polymers in a systematic way that does not vary from study to study. This lack of uniformity has led to confusion over even the basic question of whether the interface is mobile or not. Studies using NMR [97] and DSC [63] have led people to argue that the interfacial layer is dynamically arrested and can essentially be treated as a “dead” layer. This DSC study, however, does not account for the silica contribution, and later DSC studies have shown that the interface is thermodynamically active [57]. The most convincing demonstration of the interfacial layer’s dynamic nature is from broadband dielectric spectroscopy, where the interface is treated as having its own dynamic process distinct from the bulk polymer [100, 101, 106]. Coupled with this controversy over the dynamic nature of the interface is the use of T_g shifts to determine differences in dynamics at the interface. Different techniques use different approaches to measuring T_g , some of which are more direct and accurate than others. Using a single value to describe the interface is prone to errors and does not give a full picture of its dynamic state. The reason T_g is used as a measure of interfacial changes in PNCs is because T_g shift is a common method of describing the interface of polymer thin films.

A companion field to polymer nanocomposites, the study of thin polymer films involves nanoscale polymer films interacting with a substrate. This simple system also has an interfacial layer and is often approximated as a composite with a sufficiently large nanoparticle size [39]. Polymer thin films are extremely useful in discussions of polymers under nanoconfinement, as the interfacial polymers can be directly probed by ellipsometry and dilatometry [115]. The studies of thin polymer films have illustrated two important concepts of polymers at the interface: they have modified dynamics as a result of the surface interaction [116, 117], and they have a gradient of mobility away from the surface [118]. An analogy has been drawn between

the film thickness in thin polymer films and the interparticle spacing of PNCs [119], defined as $d_{IPS} = R_{NP}\{[3\varphi_{NP}/4\pi]^{-1/3} - 2\}$, where R_{NP} is the nanoparticle radius and φ_{NP} is the nanoparticle volume fraction. A master plot of two PS-silica systems, thin films (green circles) and PNCs, is shown in Figure 2.14, where the change in T_g of the two systems is very similar with interparticle spacing or film thickness [119]. Polymer thin films are useful for certain coating and membrane technologies; however, they contain only a limited amount of polymer which requires very sensitive techniques to probe. Further, thin films are troublesome to equilibrate to the same extent as PNCs [120]. Despite the advantages of easier sample preparation and measurement, polymer nanocomposites are a much more complicated system to probe the interface. This complication stems from the fact that the interfacial layers are dispersed throughout the material, and because chains can bridge between NPs and complicate the interfacial description.

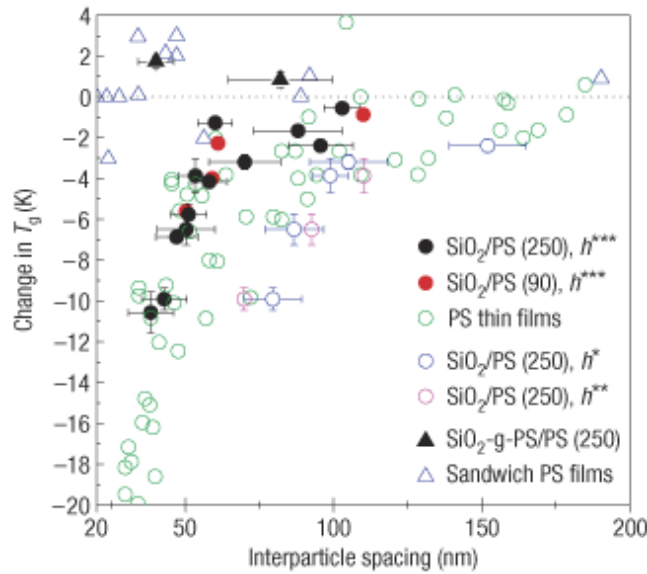


Figure 2.14: Measured change in T_g from the neat PS for two systems: PS-silica thin films and PS-silica polymer nanocomposites, where the x-axis is the film thickness for polymer thin films and the interparticle spacing for PNCs. The resemblance between the two systems' behavior with interfacial distance shows why polymer thin films are often used in comparison to PNCs. Taken from [119].

2.3.5. Parameters Controlling the Interfacial Layer of PNCs

There are certain PNC parameters that have already been demonstrated to affect interfacial properties; one parameter that is more nanoparticle-oriented is the surface chemistry, which determines the polymer-nanoparticle interaction. Many of the polymer-nanoparticle interactions in PNCs occur with hydrogen bonding, where polymers can bond with the OH groups on titania or silica nanoparticles, for example [73]. This hydrogen bonding is categorized as physical adsorption, and the bond has a finite lifetime [65]. Polymers can be covalently bonded to nanoparticles in a process called grafting [121, 122], where this bonding is much stronger than physical adsorption. Grafting is a useful technique for improving nanoparticle dispersion that otherwise would not mix with a polymer [123]. The difficulty with experimental studies of polymer-nanoparticle interaction is being able to systematically study the interaction strength [95]. Chemically altering the nanoparticle surface can change dispersion [121, 124] and chemically altering the polymer changes many other parameters, making isolating the chemical interaction difficult [95]. For this reason, much of the work on polymer-nanoparticle interactions has come from simulations studies. These studies have shown that stronger interaction strength leads to a denser interface and a significant slowing down in the interfacial polymer dynamics compared to the neat [125, 126]. In contrast, repulsive nanoparticle interactions should cause the interface to have faster polymer dynamics than in the bulk [64, 127].

Another factor that can affect the interfacial layer is the nanoparticle size. Smaller NPs have a greater curvature and this will affect the efficiency of chain packing at the interface [128, 129]. One study showed that even though interfacial polymer fraction decreases with increasing size, this decrease is smaller than expected from the reduced surface area [42]. Using the following expression for interfacial layer thickness:

$$l_{int} = R_{NP} \left(\left(\frac{\varphi_{int} + \varphi_{NP}}{\varphi_{NP}} \right)^{1/3} - 1 \right) \quad (2.7)$$

they found the thickness of the interface grows with increasing nanoparticle size, as seen in Figure 2.15. The authors attribute this growth to the decreased curvature of the nanoparticle, which for large nanoparticles confines more segments per unit area than a small, more curved nanoparticle. The interfacial thicknesses of different sized nanoparticles might have a different temperature dependence, but this effect has not been studied.

The polymer chain length is another critical parameter that affects the properties of the interface. For polymer thin film studies, it was found that increasing chain length increased the size of the bound layer, which they argue correlates with the size of the interfacial layer [130, 131]. These thin film studies also showed that increased chain length slowed down the interfacial dynamics. These results confirmed theoretical studies that also showed the bound layer should scale with R_g [88] and that the interfacial dynamics slow with chain length [132]. For polymer nanocomposites, however, a recent study on poly(2-vinyl pyridine)/silica and poly(vinyl acetate)/silica showed an unexpected non-monotonic dependence of molecular weight on both interfacial thickness and interfacial dynamics [86]. Shorter chains were found to have slower dynamics and a larger interfacial layer from both BDS and DSC while the long chains had a smaller interfacial layer and faster dynamics. These dynamics results are coupled with SAXS data that showed that the longer chains have a reduced density in the interfacial layer. The explanation given for this counter-intuitive result is chain packing at the interface: shorter chains pack more efficiently and as a result affect the polymer dynamics to a greater extent away from the nanoparticle surface. This packing is illustrated schematically in Figure 2.16. Interparticle spacing d_{IPS} also plays a role in creating packing frustration in the interface; when $d_{IPS} < 2R_g$,

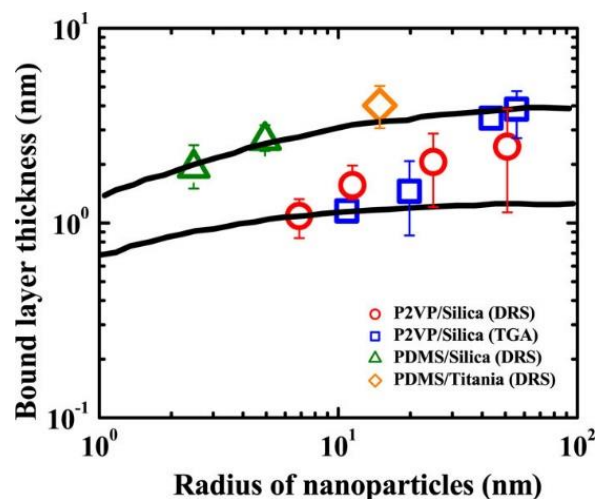


Figure 2.15: Thickness of the interfacial layer (authors call it bound layer) for different polymer nanocomposite systems of increasing nanoparticle size. The interfacial layer thickness grows modestly with NP radius owing to the more efficient packing that occurs for larger NPs with less curvature than small NPs. Taken from [42].

the polymer chain becomes confined from the presence of neighboring nanoparticles. The authors argue there are two competing effects that control the interfacial dynamics: an enthalpic effect from chain adsorption, which slows down dynamics at the interface, and an entropic effect from the inefficient chain packing which creates more free volume and faster dynamics. The chain packing near the interface will be a point of emphasis in this dissertation.

2.4 Summary

Polymer's complex macromolecular structure and dynamics give them interesting properties that are valuable to material science research. The addition of nanoparticles to polymer melts allow for enhanced mechanical, electrical, transport, and optical properties of polymer nanocomposites. The goal of PNC research is to find the nanoscopic parameters that control these interesting macroscopic properties so that composites can be rationally designed for different applications. Polymer nanocomposite research involves investigation of the structure and dynamics of both polymers and nanoparticles since their interaction is what facilitates these

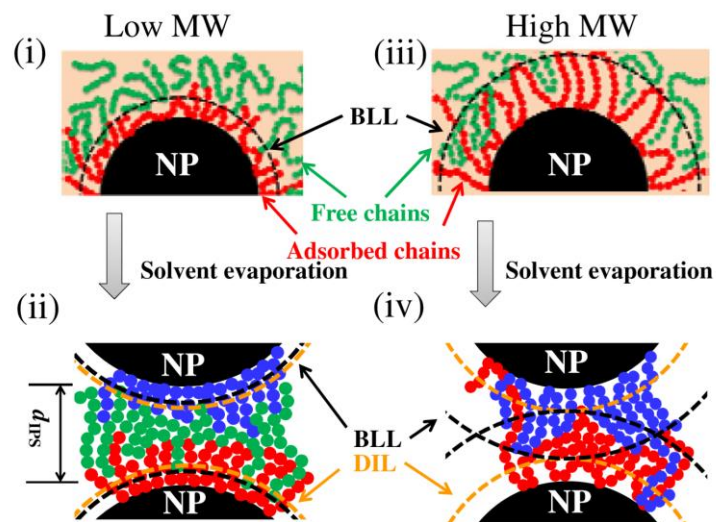


Figure 2.16: Schematic showing the effect of molecular weight on chain packing in the interfacial layer. The lower molecular weight systems (i,ii) exhibit more efficient chain packing, while the high molecular weight systems (iii, iv) have more frustrated chain packing which results in higher free volume. This increased free volume at higher molecular weight is the reason for the potentially counter intuitive (compared to the bound layer dependence) decrease of the interfacial layer thickness. Taken from [86].

enhanced properties. Of particular importance is the polymer interfacial layer between the polymer chains and the nanoparticle surface, which has been shown to have modified properties from the bulk polymer. Other important experimental factors controlling PNC properties include nanoparticle loading, nanoparticle diffusion, polymer-nanoparticle interaction, nanoparticle size, and polymer molecular weight. These studies motivate the essential problem of this dissertation: what ways do polymer and nanoparticle properties control the dynamics in polymer nanocomposites that control their macroscopic properties?

3. Experimental Methods

This chapter gives an overview of the different experimental methods used in this dissertation. This dissertation covers both polymer-specific and nanoparticle-specific parameters of polymer nanocomposites (PNCs). We are interested in measuring the different aspects of polymers related to its glassy, amorphous nature, especially how the interfacial polymer differs from the bulk polymer. We use small-angle X-ray scattering (SAXS) to measure the static interfacial polymer layer, which has distinct density properties from bulk. The thermodynamic properties of PNCs are measured with temperature-modulated differential scanning calorimetry (TM-DSC), where analysis can demonstrate distinct thermodynamic behavior in the interface. The dynamic properties of the polymers are measured with broadband dielectric spectroscopy (BDS), where the interfacial polymer is shown to have distinct dipole relaxation responses from the bulk. As for nanoparticle-specific studies, these techniques are used in addition to dynamic light scattering (DLS), which allows measurement of the diffusion properties of nanoparticles in the polymer melt. Other techniques described are used for viscosity measurements (rheology) and nanoparticle loading determination (thermogravimetric analysis). A subsection is given for each technique, where the physics of the method itself will be described as well as how this information is useful for this dissertation.

3.1. Broadband Dielectric Spectroscopy (BDS)

Polymer structures, from chain ends to individual monomers to side groups, often have a permanent dipole moment due to asymmetrical structure or charge distributions. When an

external electric field is applied to these dipoles, they will orient in an energetically favorable position during polarization. Upon the release of the applied electric field, called depolarization, the dipoles are able to reorient to the original alignment. The timescale and degree of this reorientation depends on the electrical susceptibility of the material. Materials which are polarizable by an electric field are called *dielectric*, and the study of the depolarization response of a material from an applied electric field is call dielectric spectroscopy. Since the applied electric field can be done over a very broad frequency range, the technique is called broadband dielectric spectroscopy (BDS). This technique will be used in chapters 4, 5, 6, and 7 of this dissertation to study the various relaxation processes in polymer nanocomposite systems.

3.1.1. Principles of Broadband Dielectric Spectroscopy

Electromagnetic fields' interaction with matter is described by Maxwell's equations:

$$\nabla \times \mathbf{E} = -\frac{\partial}{\partial t} \mathbf{B} \quad (3.1)$$

$$\nabla \times \mathbf{H} = \mathbf{j} + \frac{\partial}{\partial t} \mathbf{D} \quad (3.2)$$

$$\nabla \cdot \mathbf{D} = \rho_f \quad (3.3)$$

$$\nabla \cdot \mathbf{B} = 0 , \quad (3.4)$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields, $\mathbf{D}$ is the displacement field, $\mathbf{H}$ is the magnetic induction, $\mathbf{j}$ is the current density, and ρ_f is the density of free charges. For small electric fields, $\mathbf{D}$ can be described by

$$\mathbf{D} = \varepsilon^* \varepsilon_0 \mathbf{E} , \quad (3.5)$$

where ε_0 is the dielectric permittivity of vacuum ($\varepsilon_0 = 8.854 \times 10^{-12} \text{AsV}^{-1}\text{m}^{-1}$). The ε^* is the dielectric permittivity function, which for a system with a periodic electric field $E(t) = E_0 \exp(-i\omega t)$ is defined by

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega), \quad (3.6)$$

where $\varepsilon'(\omega)$ is the real part and $\varepsilon''(\omega)$ is the imaginary part of the dielectric permittivity. An external electric field applied to a dielectric medium will induce a polarization $\mathbf{P}$, which is defined as

$$\mathbf{P} = \mathbf{D} - \varepsilon_0 \mathbf{E} = (\varepsilon^* - 1)\varepsilon_0 \mathbf{E}. \quad (3.7)$$

The polarization $\mathbf{P}$ is the relevant macroscopic quantity measured from dielectric spectroscopy; for linear, homogeneous, and isotropic dielectric materials, it is related to the applied electric field in a first-order linear manner.

The macroscopic polarization $\mathbf{P}$ can be directly related to the permanent microscopic dipole moments $\boldsymbol{\mu}$ in a material by

$$\mathbf{P} = \frac{1}{V} \sum_i \boldsymbol{\mu}_i + \mathbf{P}_\infty = \frac{N}{V} \langle \boldsymbol{\mu} \rangle + \mathbf{P}_\infty, \quad (3.8)$$

where $\frac{N}{V}$ denotes the number of dipoles for a given volume in the system, $\langle \boldsymbol{\mu} \rangle$ represents the mean dipole moment, and $\mathbf{P}_\infty = \lim_{\omega \rightarrow \infty} \mathbf{P}(\omega)$, is the sum of the induced polarizations not caused by dipole orientational polarization, such as the electronic and atomic polarization that occur at high frequency. In general, evaluation of these terms is not possible from experimental measurements, so approximations must be made. Based on the assumption that dipole-dipole interactions and local electric field differences do not strongly affect the macroscopic polarization $\mathbf{P}$, we can express the average dipole moment using Boltzmann statistics as

$$\langle \boldsymbol{\mu} \rangle = \frac{\int_{4\pi} \boldsymbol{\mu} \exp\left(\frac{\boldsymbol{\mu} \cdot \mathbf{E}}{k_B T}\right) d\Omega}{\int_{4\pi} \exp\left(\frac{\boldsymbol{\mu} \cdot \mathbf{E}}{k_B T}\right) d\Omega} . \quad (3.9)$$

Since only dipole moments oriented parallel to the applied electric field will contribute to polarization, $\boldsymbol{\mu} \cdot \mathbf{E} = \mu E \cos(\theta)$, and for small values of dipole interaction energy, equation 3.9 reduces to

$$\langle \boldsymbol{\mu} \rangle = \frac{\mu^2}{3k_B T} \mathbf{E} . \quad (3.10)$$

Substituting equation 3.10 into equation 3.8 yields

$$\mathbf{P} = \frac{\mu^2}{3k_B T} \frac{N}{V} \mathbf{E} + \mathbf{P}_\infty . \quad (3.11)$$

Using equation 3.7, one can write an expression for the relationship between the dipole moment and the dielectric function as

$$\Delta \varepsilon = \varepsilon_S - \varepsilon_\infty = \frac{1}{3\varepsilon_0} \frac{\mu^2}{k_B T} \frac{N}{V} , \quad (3.12)$$

where $\varepsilon_S = \lim_{\omega \rightarrow 0} \varepsilon'(\omega)$. The $\varepsilon_\infty = \lim_{\omega \rightarrow \infty} \varepsilon'(\omega)$ term covers the electronic and atomic polarization contributions to the dielectric signal in the limit of infinite frequency. Equation 3.12 gives what is called the dielectric strength of the dipolar reorientation process that results from an applied electric field. In its current form it gives a direct comparison between the microscopic magnetic dipoles and the macroscopic electric field. However, one must keep in mind this relation is only valid in systems where the dipoles do not interact (only true for very diluted systems) and where the local electric field is roughly equal to the applied electric field (not true since the dipoles are surrounded by other dipoles which shield the applied electric field). A more working definition of the dielectric strength was derived by Kirkwood and Fröhlich[133], who treated N' molecules

explicitly and treated the remaining $N - N'$ molecules as an infinite continuum whose dielectric behavior is characterized by the static permittivity ϵ_s . From these assumptions a more general but less precise definition for dielectric strength gives

$$\Delta\epsilon = \epsilon_s - \epsilon_\infty = \frac{1}{3\epsilon_0} F g \frac{\mu^2}{k_B T} \frac{N}{V}, \quad (3.13)$$

where F is the Onsager factor[134] related to the infinite background continuum and g is the Kirkwood-Frohlich factor, which models the interaction between dipoles relative to their ideal, non-interacting case. These terms will be referred to in a qualitative sense in this dissertation, but the formal definitions of F and g are not relevant to the scope of this research.

In a polymer system, the polarization response to a small applied electric field is a special case of linear response theory, where the time-dependent polarization response can be expressed as:

$$\mathbf{P}(t) = \mathbf{P}_\infty + \epsilon_0 \int_{-\infty}^t \epsilon(t - t') \frac{dE(t')}{dt'} dt', \quad (3.14)$$

where $\epsilon(t)$ is the time dependent dielectric function and $\mathbf{P}_\infty$ is the induced polarization. The $\epsilon(t)$ can be measured directly as the time dependent response of a step-like electric field, where $\epsilon(t) = (P(t) - P_\infty)/\Delta E \epsilon_0$. This relationship is shown schematically in Figure 3.1.

This time-dependent polarization response of equation 3.14, for a sufficiently small electric field, can be described in the context of the Fluctuation-Dissipation theorem, where the polarization response is described as an autocorrelation function of polarization fluctuations:

$$\Phi(t) = \frac{\langle \Delta P(0) \Delta P(t) \rangle}{\langle \Delta P(0)^2 \rangle}. \quad (3.15)$$

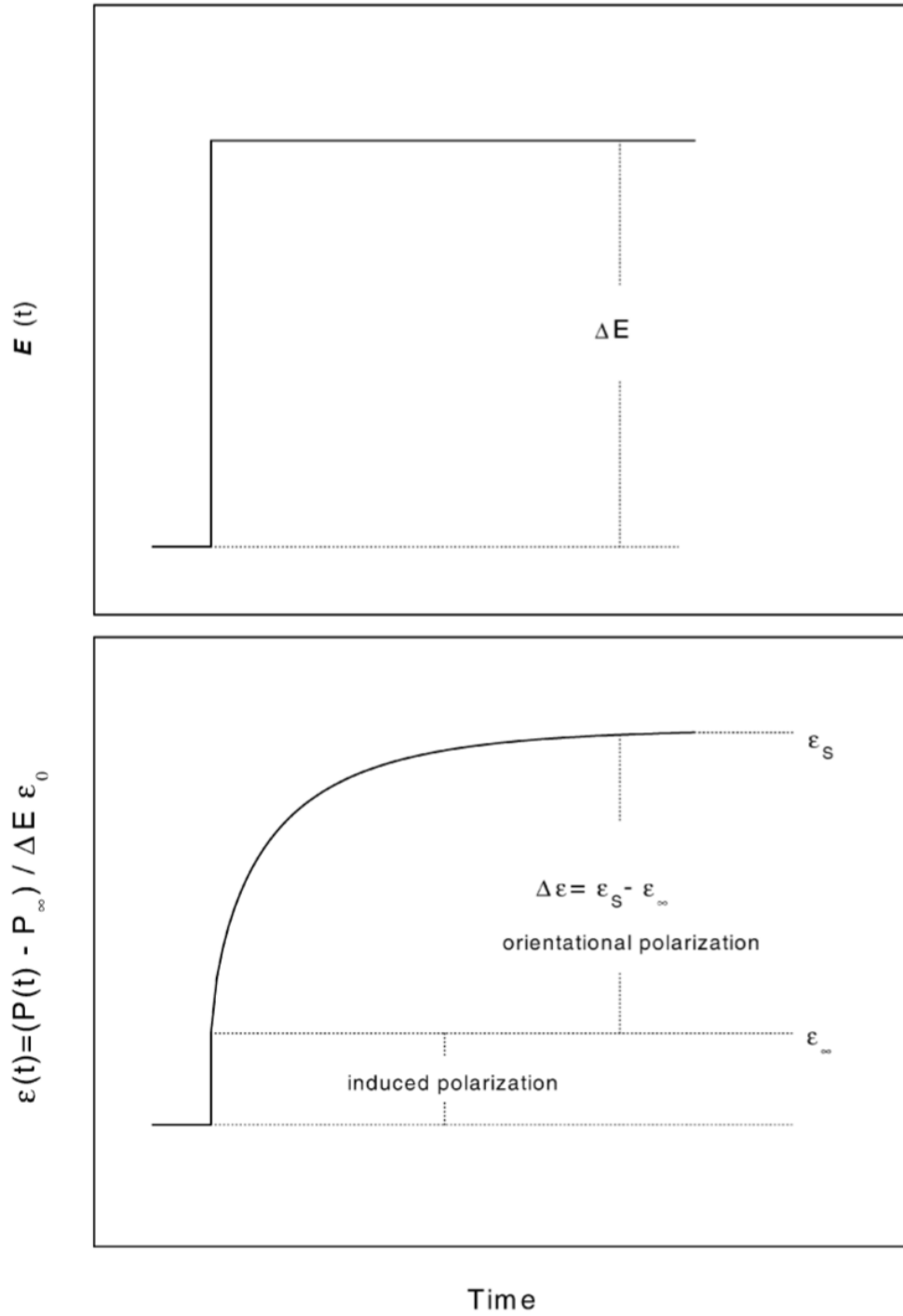


Figure 3.1: Relationship between time dependent electric field E , the polarization P , and the dielectric response function ϵ [12]. When the electric field E is applied in a step-like manner, the polarization P and dielectric response function ϵ responds more slowly over time.

$\Delta P(0)$ is the $t = 0$ polarization fluctuations and $\Delta P(t)$ is the polarization of spontaneous fluctuations about the average value over a time t . This autocorrelation function $\Phi(t)$ accounts for the stochastic fluctuations of the polarization about the mean value over time. It is related to the complex permittivity function by the following relation:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty - \int_0^\infty \Delta\varepsilon \exp(-i\omega t) \frac{d\Phi(t)}{dt} dt . \quad (3.16)$$

This relationship between $\Phi(t)$ and $\varepsilon^*(\omega)$ allows us to relate the response from a small perturbation directly to the equilibrium fluctuations in the same system. The real part of the dielectric permittivity $\varepsilon'(\omega)$ is related to the energy reversibly stored in the system per cycle and the imaginary $\varepsilon''(\omega)$ is related to the energy dissipated per cycle.

Dielectric relaxation is difficult to evaluate explicitly because the polarization of a system, except in rare cases, cannot be described for all coordinates and momenta. The simplest model used to describe dipole reorientation assumes that the polarization function $\mathbf{P}(t)$ is proportional to its actual value by a first order differential equation and a characteristic decay time τ_D :

$$\frac{d\mathbf{P}(t)}{dt} = -\frac{1}{\tau_D} \mathbf{P}(t) . \quad (3.17)$$

The solution of this equation is an exponential decay for the correlation function:

$$\Phi(t) = \exp\left[-\frac{t}{\tau_D}\right] . \quad (3.18)$$

From (16) we get the following expression for the complex dielectric function:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+i\omega\tau_D} . \quad (3.19)$$

This model for an isolated dipole with a single decay time is called the Debye model, and it rarely works for real dielectric systems since there is generally a heterogeneity of decay times for different dipoles in a system. This situation is also true for polymeric systems, where the connectivity of polymer chains leads to greater heterogeneity in dipole motion. For polymer systems, the correlation function can be empirically described by

$$\Phi(t) = \exp \left[- \left(\frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \right], \quad (3.20)$$

where β_{KWW} is the Kohlrausch-Williams-Watts stretching parameter which broadens the decay function. In the frequency domain, the most general dielectric response function is given by the empirical Havriliak-Negami function:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1 + (i\omega\tau_{HN})^{\alpha})^{\gamma}}, \quad (3.21)$$

where α and γ are the symmetric and asymmetric stretching parameters, respectively. While some qualitative insights into the relaxation time distribution function can be gleaned, there is no direct relationship between non-Debye relaxation and a heterogeneous distribution of relaxation times. The dielectric relaxations of polymer nanocomposites are more involved forms of the Havriliak-Negami function, which will be discussed in detail in chapter 4.

3.1.2. Broadband Dielectric Spectroscopy Instrumentation Details

All broadband dielectric spectroscopy measurements were carried out on a Novocontrol Concept 80 system with an Alpha impedance analyzer. A schematic of the setup is shown in Figure 3.2, where the sample setup is a polymer film pressed between a parallel plate capacitor configuration.

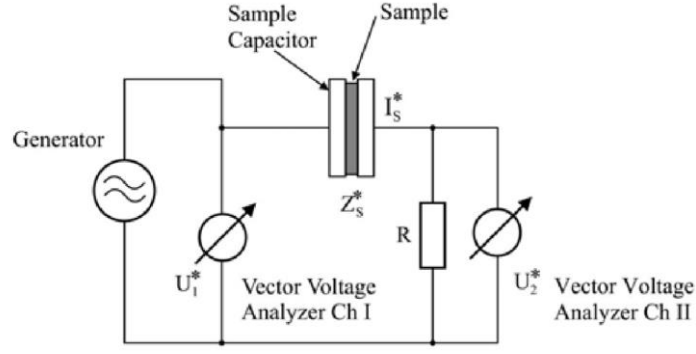


Figure 3.2: Schematic of dielectric spectroscopy setup for a Novocontrol Concept 80 system [12]. The sample is sandwiched between two parallel plate capacitors in series.

The frequency window used in this dissertation is 10^{-2} to 10^7 Hz, which is accessible with Fourier correlation analysis. A generator applies a sinusoidal voltage $U_1(t)$ to the sample capacitor for the entire frequency range of 10^{-2} to 10^7 Hz. A known resistor R converts the sample current $I_S(t)$ into a voltage $U_2(t)$. Two sine wave correlators analyze $U_1(t)$ and $U_2(t)$ with respect to the phases and amplitudes of their Fourier transforms $U_1^*(\omega)$ and $U_2^*(\omega)$. The complex sample impedance is taken from these Fourier transforms:

$$Z_S^*(\omega) = \frac{U_S^*(\omega)}{I_S^*(\omega)} = R \left(\frac{U_1^*(\omega)}{U_2^*(\omega)} - 1 \right). \quad (3.22)$$

The complex dielectric permittivity of the sample can be expressed in terms of this measured complex impedance (22) by

$$\varepsilon^*(\omega) = \frac{1}{i\omega Z_S^*(\omega) C_0}, \quad (3.23)$$

where C_0 is the empty cell capacitance. All measurements were performed with gold-coated electrodes of 20 mm and a sample film thickness of 0.1-0.3 mm. The polymer nanocomposite samples were hot pressed into a film between Kapton paper before being placed between the

electrodes. The sample sandwiched between electrodes was then placed into a cryostat under dry nitrogen atmosphere while remaining in the circuit shown in Figure 3.2. The sample temperature was controlled by a Novocontrol Quatro system, where the heating and cooling was performed using nitrogen gas with a temperature stability of ± 0.1 K. The sample was first annealed for a 5 min test run at the highest measurement temperature to ensure good contact between polymer film and electrode. The samples were typically measured on cooling in steps of 5 K for measurements above T_g , and in steps of 10-20 K below T_g . At each temperature step the samples were equilibrated for 20 minutes before measurement to ensure the sample was in thermal equilibrium.

3.2. Dynamic Light Scattering

When a laser source is applied to a heterogeneous liquid, local changes in the dielectric constant can be detected by the light emitted by the optically polarized molecules. An ensemble of those fluctuations can be measured to determine the diffusion properties of those molecules throughout the liquid. This technique is called dynamic light scattering, because it measures the intensity of the scattered light as a function of time. Conceptually it is very similar to dielectric spectroscopy in that it measures the response of polarized electromagnetic waves and follows the Fluctuation-Dissipation theorem. For polymer nanocomposites, this technique can be used to determine the size of nanoparticles in solution as well as to measure the diffusion properties of nanoparticles in a polymer melt.

3.2.1. Principles of Quasi-elastic Light Scattering (QELS)

When a monochromatic electric field given by

$$\mathbf{E}_i(\mathbf{r}, t) = \mathbf{n}_i E_0 e^{i(\mathbf{k}_i \cdot \mathbf{r} - \omega_i t)}, \quad (3.24)$$

where $\mathbf{n}_i$ is the polarization vector, E_0 is the electric field amplitude, $\mathbf{k}_i$ is the incident wave vector, and ω_i is the angular frequency. When light enters a medium, the field exerts a force on the molecule's electrons. The electric force induces the dipole moments of the molecule to oscillate at the same frequency as the incident field. This oscillation causes light to be radiated, in a process called scattering. If there are no local heterogeneities in the dielectric constant, the light scattered from one region will destructively interfere with the scattered light of a different region. The net result is that no scattered light will emerge over a macroscopic scale. However, most mediums are not homogeneous and do have local changes in dielectric constant that can be expressed as in terms of the dielectric tensor $\vec{\epsilon}(\mathbf{r}, t) = \epsilon_0 \vec{\mathbf{I}} + \vec{\delta\epsilon}(\mathbf{r}, t)$, where the scattered light in different regions will have altered amplitude, frequency, and wave vector corresponding to changes in the orientation, position, and motion of the molecules in the medium. The scattered electric field is given by

$$E_s(\mathbf{q}, R, t) = \frac{-k_f^2 E_0}{4\pi R \epsilon_0} e^{i(k_f R - \omega_i t)} \delta\epsilon_{if}(\mathbf{q}, t), \quad (3.25)$$

where $k_f = \frac{2\pi n}{\lambda_f}$ is the wave vector of the scattered light and $\delta\epsilon_{if}(\mathbf{q}, t) = \hat{\mathbf{n}}_f \cdot \vec{\delta\epsilon}(\mathbf{q}, t) \cdot \hat{\mathbf{n}}_i$ is the dielectric constant fluctuation tensor component that is along the initial and final polarization directions. For quasi-elastic light scattering (QELS), the magnitude of $\mathbf{k}_i$ and $\mathbf{k}_f$ are generally approximately equal, meaning that $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ can be expressed as $q = \frac{4\pi n}{\lambda_i} \sin(\frac{\theta}{2})$, where θ is the angle between incident and final wave vectors, which for our setup is 90 degrees. For the quasi-elastic regime, it is the dielectric constant fluctuations changing with q that cause the scattered electric fields. A schematic of the general setup for QELS is shown in Figure 3.3.

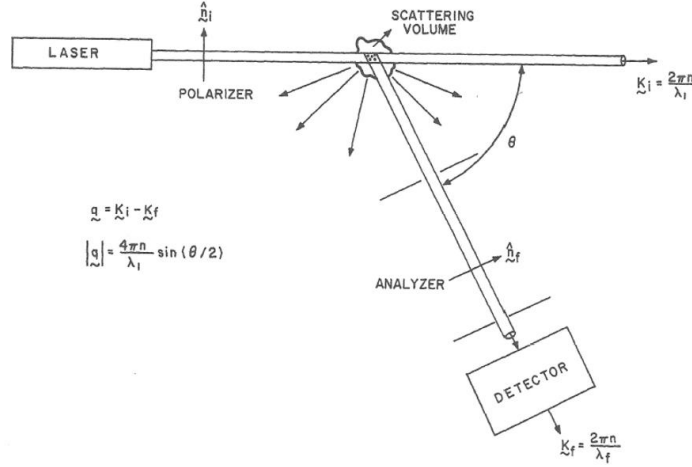


Figure 3.3: Schematic of quasi-elastic light scattering setup. Taken from [135]. The monochromatic laser source is scattered off the sample and the response is captured on a detector at an angle away from incidence.

Translational and rotational motion of molecules will alter the scattered electric field as a function of time, and the rate at which the detector captures these motions can be obtained from the intensity:

$$I(q, t) = \langle E_S^*(q, R, 0) E_S(q, R, t) \rangle = \frac{k_f^4 |E_0|^2}{16\pi^2 R^2 \epsilon_0^2} \langle \delta\epsilon_{if}(q, 0) \delta\epsilon_{if}(q, t) \rangle. \quad (3.26)$$

The type of QELS used for this dissertation, dynamic light scattering, directly measures the intensity of scattered light as a function of time. Taking these intensity measurements at different times and converting them into an intensity correlation function, $\langle I(q, 0) I(q, t) \rangle$, one can estimate the diffusive motion of the molecules. Equation 3.26 indicates the local fluctuations of the dielectric constant can be directly related to the measured light spectrum; this relationship is the same mechanism (Fluctuation-Dissipation) that dielectric spectroscopy uses to relate macroscopic measurements to local heterogeneities. Having established this relationship, we must distinguish the two types of scattering that occur for this system, *polarized* and *depolarized*.

Polarized scattering occurs for isotropic fluctuations in density and concentration, which in turn alter the optical polarizability and therefore the dielectric permittivity of the molecules. These fluctuations can be used to describe the molecules' translational motion. Depolarized scattering occurs for anisotropic fluctuations in the optical polarizability of molecules and can be used to describe their rotational motion. For this dissertation we are only concerned with the translational motion of a spherical nanoparticle in the polymer medium, captured in polarized scattering.

In dynamic light scattering experiments, we are interested in the normalized intensity correlation function $g^{(2)}(q, t)$, which is defined as

$$g^2(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle}{\langle I(q)^2 \rangle} . \quad (3.27)$$

The denominator of equation 3.27 is the static structure factor correlation function. From the Siegert relation taken in the limit of a large number of scattered particles [136], this normalized intensity correlation function can be re-written as $g^2(q, t) = 1 + \beta |g^1(q, t)|^2$, where β is the coherence factor which depends on the size and shape of the nanoparticles as well as the surface area of the photodetector, and $g^1(q, t)$ is the self-intermediate scattering function. Assuming Brownian motion of the scattered molecules, $g^1(q, t)$ can be calculated as $g^1(q, t) = \exp(-q^2 D t) = \exp(-t/\tau_D)$, where D is the translational self-diffusion coefficient. For the purposes of the nanoparticle mobility study in Chapter 8, we use this translational self-diffusion coefficient to study the diffusion of spherical nanoparticles in a polymer melt.

3.2.2. Analysis of Dynamic Light Scattering for Nanoparticle Diffusion

The exponential decay function of the self-intermediate correlation function is similar to the correlation function for the Debye Model outlined in the dielectric spectroscopy section. This

single exponential function works for describing NP diffusion when the system has a homogeneous nanoparticle size distribution; it fails when there is polydispersity in NP size. The distribution of NP sizes can be described by a stretched exponential function, $g^1(q, t) = \exp\left(\left(\frac{-t}{\tau}\right)^\beta\right)$, similar to the KWW function used for dielectric spectroscopy.

Since it is known that the nanoparticles studied have favorable attractions with each other, we can justifiably describe $g^1(q, t)$ as the sum of two or more exponentials, where each exponential corresponds to a different nanoparticle size. The general expression for $g^1(q, t)$ is given as follows:

$$g^1(q, t) = \left(A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + \dots\right)^2 + \text{const } t. \quad (3.28)$$

The experimental diffusion for a given decay function (corresponding to one NP size) is simply

$$D_{exp} = \frac{1}{q^2 \tau}. \quad (3.29)$$

This value can give an estimate of the nanoparticle size using the Stokes-Einstein relation, assuming the fluid the NP is suspended in is Newtonian and the local viscosity does not differ much from the macroscopic viscosity η :

$$R_{NP} = \frac{k_B T}{6\pi\eta D_{exp}}. \quad (3.30)$$

3.2.3. Dynamic Light Scattering Experimental Technique

The quasi-elastic light scattering method used for this dissertation is called dynamic light scattering, which measures light scattering at times from 10^{-6} to 10^3 seconds. A rough schematic of the laser setup is shown in Figure 3.3. A monochromatic laser (HeNe, $\lambda = 633$ nm) is first passed through a polarizer so that vertically or horizontally polarized light is selected. This light

is focused on a sample in a cylindrical glass vial. The 90° scattered light is passed through another polarizer which filters for either polarized or depolarized light. This scattered light is focused onto a photodiode via a fiber optic coupling device. The translational motion of the nanoparticles will modulate the scattered intensity, and how these fluctuations change with time will be directly reflected in the timescales of nanoparticle motion. The signal from the photodiode is passed to an autocorrelation device (ALV-7004 fast digital correlator) which computes the intensity autocorrelation function (ICF) $g^2(q, t) = \frac{\langle I(q,0)I(q,t) \rangle}{\langle I(q,0)^2 \rangle}$, where $I(t)$ is the measured intensity with time.

3.3. Temperature-Modulated Differential Scanning Calorimetry

The glass transition is an important property for understanding the structure and dynamics of amorphous materials such as polymers. The calorimetric glass transition determines the temperature at which a polymer goes from a molten, rubbery state to a glassy, brittle state upon cooling. Differential scanning calorimetry (DSC) is an experimental technique that probes the thermodynamic properties of a material by measuring the heat flow through the material at a constant heating or cooling ramp. For temperature-modulated DSC, a sinusoidal modulation is added to the constant heating ramp to help separate reversible and non-reversible thermodynamic processes. TM-DSC is used in Chapters 4, 5, and 7 of this dissertation to both determine the calorimetric glass transition of the PNCs studied, and to study the thermodynamic properties of the interfacial layer.

3.3.1. Principles of Temperature-Modulated Differential Scanning Calorimetry (TM-DSC)

Differential scanning calorimetry (DSC) measures how the thermodynamic properties of a material change with temperature and time. For amorphous materials such as polymers, it is

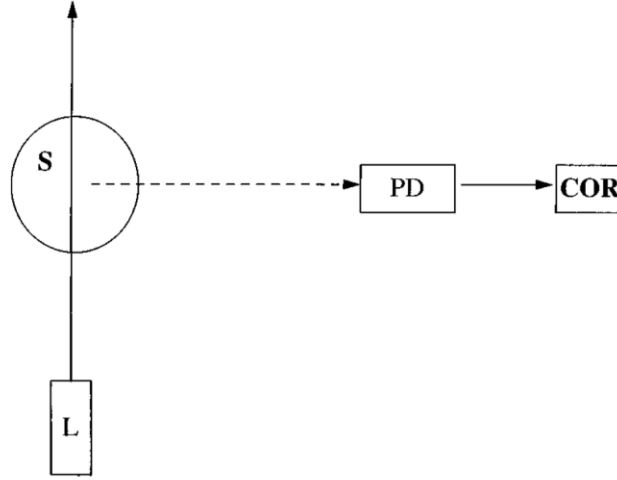


Figure 3.4: Schematic of a photon correlation spectroscopy setup. The laser (L) passes through the sample (S), and the scattered light at 90 degrees strikes a photodiode (PD). The spectral pattern recorded on the photodiode is analyzed with a correlator which converts the measured intensity into the electric field correlation function. Taken from [137].

useful for measuring the calorimetric glass transition temperature. A typical DSC, using a known heating or cooling rate, measures the temperature difference between two thermally conductive pans: one with the measured material inside and the other empty used as a reference. This temperature difference is converted to the heat flow rate by:

$$\dot{q} = E(T)\Delta T , \quad (3.31)$$

where the proportionality factor $E(T)$ depends on the individual DSC setup. To determine the relationship between the measured temperature differences and the heat flow, a model where the DSC heat flow (q) measurement is treated as a circuit of thermal resistances (R) and heat capacities (C) is typically used. Figure 3.5 shows an example of this, where the subscripts s and r refer to the sample and reference, respectively. The T_0 refers to the temperature of the DSC enclosure.

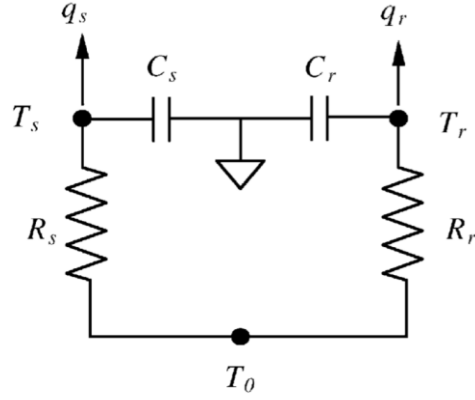


Figure 3.5: DSC heat flow (q) measurement modeled as a circuit consisting of thermal resistances (R) and heat capacities (C). The subscripts s and r refer to the sample and reference, respectively. T_0 is the temperature of the sample enclosure. Taken from [138].

From this a heat balance can be performed where the heat flow rates of the sample and reference are given by:

$$\dot{q}_s = \frac{T_0 - T_s}{R_s} - C_s \frac{dT_s}{dt}, \quad (3.32)$$

$$\dot{q}_r = \frac{T_0 - T_r}{R_r} - C_r \frac{dT_r}{dt}. \quad (3.33)$$

The heat flow rate of the sample material, $\dot{q}$, is given by the difference between the sample and the reference, which when rearranged is expressed by the following equation:

$$\dot{q} = -\frac{T_s - T_r}{R_r} + (T_0 - T_s) \left(\frac{1}{R_s} - \frac{1}{R_r} \right) + (C_r - C_s) \frac{dT_s}{dt} - C_r \frac{dT_r}{dt}. \quad (3.34)$$

The first term corresponds to the conventional DSC heat flow, while the second and third terms reflect differences in heat capacity and thermal conductivities in the sample and reference calorimeters. The fourth term is the heat flow from differences in heating rate between sample and reference calorimeters, although this term is ignored when measuring with temperature-modulated DSC. However, differences in heat flow rate in the pans themselves can also be

accounted for by modifying the original circuit model of Figure 3.5. Figure 3.6 shows the updated circuit where the subscript p represents the properties of the pans themselves. The component we are interested in is the $\dot{q}_{sam}$ in the diagram, the heat flow of the sample itself. The measured sample heat flow (which includes both the sample and the sample pan) as well as measured reference heat flow are expressed by:

$$\dot{q}_s = \dot{q}_{sam} + m_{ps}c_{pan} \frac{dT_{ps}}{dt}, \quad (3.35)$$

$$\dot{q}_r = m_{pr}c_{pan} \frac{dT_{pr}}{dt}, \quad (3.36)$$

where m_{ps} , m_{pr} are the mass of the sample and reference pan, respectively, and c_{pan} is the specific heat capacity of the pan material. Rearranging these two equations we get the following expression for the sample heat flow:

$$\dot{q}_{sam} = \dot{q}_s - \dot{q}_r \left(\frac{m_{ps}(dT_{ps}/dt)}{m_{pr}(dT_{pr}/dt)} \right). \quad (3.37)$$

For determining the temperature of glass transition alone, this conventional DSC is sufficient for looking at reversible dynamical processes. However, analysis used for this dissertation looks at the absolute values of changes in specific heat capacity, for which temperature-modulated DSC is necessary.

Temperature-modulated differential scanning calorimetry (TM-DSC) divides the heat flow response of a material into reversible and non-reversible components. The reversing component is related to reversible processes like the calorimetric glass transition temperature. The non-reversing component relates to time-dependent non-reversible processes, such as evaporation, crystallization, enthalpic recovery, curing, and decomposition. The distinction

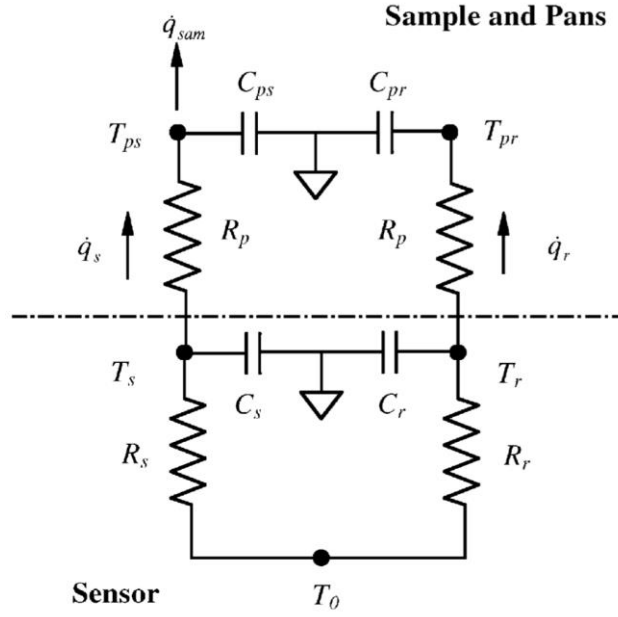


Figure 3.6: Updated circuit for differential scanning calorimetry heat flow measurements where the effect of differences in pan heat flow is accounted for. The *s* subscript refers to the sample and pan together while the *sam* subscript refers to the sample itself. Taken from [138].

between reversible and non-reversible heat flow allows for better interpretation of the thermodynamic properties of the different components in polymer nanocomposites.

3.3.2. TM-DSC Experimental Setup

The experimental setup for TM-DSC is the same as for conventional DSC, but the heating/cooling profile is changed: a sinusoidal modulation is applied over the linear temperature ramp. Now instead of simply altering the heating rate, different modulation amplitudes and frequencies are accessible for DSC. The effect this modulation has can be expressed in the following equation:

$$\dot{q}_s = -\frac{dT}{dt} [C_p + f''(t, T)] + f(t, T), \quad (3.38)$$

where $\dot{q}_s$ is the heat flow rate through the sample and pan, $\frac{dT}{dt}$ is the heating rate, C_p is the heat capacity of the sample itself, $f''(t, T)$ is the thermodynamic heat flow component, and $f(t, T)$ is the kinetically-limited heat flow. What this equation shows is one contribution (the reversible) is heating rate dependent, while the second (non-reversible) is only dependent on absolute temperature. The measured heat flow is deconvoluted via a discrete Fourier transform analysis which separates the reversing and non-reversing heat flow. This measured heat flow can then be converted into heat capacity. The reversible heat capacity is the component we are interested in studying for polymer nanocomposites, because it allows us to accurately track the magnitude of the glass transition step, the glass transition temperature, and the absolute values of specific heat capacity. These quantities will be used to analyze the thermodynamic behavior of the interfacial layer in PNCs and will complement the dynamic measurements of the interface.

3.4. Other Experimental Techniques

3.4.1. Rheology

Rheology measures the deformation and flow of materials. While rheology makes no fundamental distinction between a solid and a liquid, materials are generally described as existing on a continuum from viscous behavior (obeying Newtonian mechanics) to elastic behavior (obeying Hooke's Law). A material that exhibits both properties, such as a polymer melt, is described as viscoelastic. When a stress σ is applied to a fluid between two plates as shown in Fig 3.7, the response can be described in terms of the general Kelvin-Meyer-Voight (KMV) equation:

$$\sigma = G\gamma + \eta \frac{d\gamma}{dt}, \quad (3.39)$$

where G is the elastic modulus, γ is the shear strain, and η is the viscosity. For this dissertation, we use two types of rheological tests, one using a continuous shear rate to measure the viscosity of a Newtonian polymer melt, and the other using a small-angle oscillatory shear amplitude to measure the complex modulus of a viscoelastic PNC. All measurements were performed on a AR-2000ex rheometer (TA Instruments).

For the continuous shear rate measurements, the polymer melt in question is polypropylene glycol (PPG), which is assumed to have Newtonian-like properties. We assume the elastic modulus G is sufficiently small that we can approximate the KMV equation to represent viscosity as $\eta = \sigma/\dot{\gamma}$, where $\dot{\gamma}$ is the applied continuous shear rate of 10 s^{-1} and σ is the measured stress. The average viscosity value is measured over a length of time (in this case, 2 min) to determine the macroscopic viscosity of the sample. The viscosity measurements of PPG are done in Chapter 8.

The small angle oscillatory shear amplitude measurements are done to determine the rheological behavior of the elastic modulus and complex viscosity for poly(2-vinyl pyridine) (P2VP) polymers mixed with octaaminophenyl polyhedral oligomeric silsesquioxane (OAPS) nanoparticles. The top plate of the parallel plate setup of Figure 3.7 is displaced sinusoidally by $\delta \sin(\omega t)$, where $\delta \ll h$. This produces a top plate velocity of $U(t) = \delta \omega \cos(\omega t)$, which gives a shear rate of:

$$\dot{\gamma}(t) = \frac{\delta}{h} \omega \cos(\omega t) . \quad (3.40)$$

Using Boltzmann's tensor equation for stress in three dimensions, we can re-express equation 3.39 in a more general form that accounts for the “memory” of previous strains applied to viscoelastic materials:

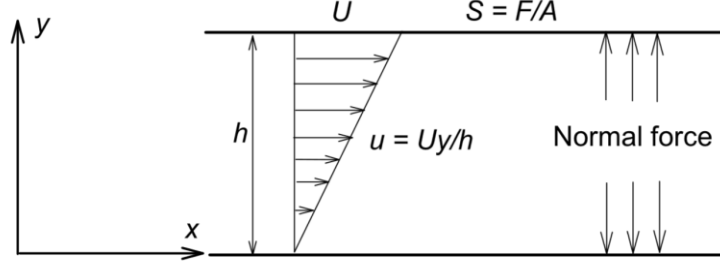


Figure 3.7: Diagram of the basic properties of rheology for a fluid between two parallel plates. The symbol h is the height of the material, U is the velocity of the top plate, and S is the stress. Taken from [139].

$$\mathbf{S}(t) = 2 \int_{-\infty}^t G(t - t') \mathbf{D}(t') dt' , \quad (3.41)$$

where $\mathbf{S}(t)$ and $\mathbf{D}(t')$ are the stress tensor and strain rate tensor, respectively. For the small angle oscillatory shear amplitude measurements, the only non-zero component is the shear stress:

$$S_{12} = \int_{-\infty}^t G(t - t') \frac{\omega \delta}{h} \cos(\omega t') dt' . \quad (3.42)$$

This equation can be evaluated to return to a similar form as equation 3.39

$$S_{12} = G'(\omega) \gamma_0 \sin(\omega t) + \eta'(\omega) \dot{\gamma}_0 \cos(\omega t) , \quad (3.43)$$

where $G'(\omega)$ is the storage modulus, $\gamma_0 = \frac{\delta}{h}$ and $\dot{\gamma}_0 = \frac{\omega \delta}{h}$ are the strain and strain rate amplitudes, respectively, and $\eta'(\omega)$ is the dynamic viscosity. $G'(\omega)$ and $\eta'(\omega)$ are defined by the following integrals:

$$G'(\omega) = \int_0^{\infty} \omega G(s) \sin(\omega s) ds , \quad (3.44)$$

$$\eta'(\omega) = \int_0^{\infty} G(s) \cos(\omega s) ds , \quad (3.45)$$

where the substitution $s = t - t'$ is made. Directly related to these quantities is the loss modulus

$G''(\omega)$ and the storage viscosity $\eta''(\omega)$ expressed by

$$G''(\omega) = \omega\eta'(\omega) , \quad (3.46)$$

$$\eta''(\omega) = \frac{G'(\omega)}{\omega} , \quad (3.47)$$

These physical quantities can be expressed as complex variables, where the complex modulus is $G^*(\omega) = G'(\omega) + iG''(\omega)$ and the complex viscosity is $\eta^*(\omega) = \eta'(\omega) - i\eta''(\omega)$. The time-temperature superposition of these complex moduli is analyzed to determine the flow behavior of the P2VP-OAPS composites in Chapter 7.

3.4.2 Small Angle X-ray Scattering (SAXS)

Small angle x-ray scattering (SAXS) is performed to study the static structure of polymer nanocomposites as well as determine the dispersion properties of the nanoparticles in the polymer melt. The q dependence of the scattering intensities $I(q)$ is given by:

$$I(q) = \int_0^\infty n(r)[P(q)]^2 S(q) dr , \quad (3.48)$$

where $n(r)$ is the particle size distribution, $P(q)$ is the form factor of single particle scattering, and $S(q)$ is the structure factor of the interparticle interference [92]. The $S(q)$ determines the dispersion state of the nanoparticles in the matrix, and the $P(q)$ is used for describing the nanoparticle itself (and whether it has an interfacial layer). By fitting the scattering intensity data with models based on known scattering responses for certain geometries, it is possible to get estimations of the length and density of the interfacial polymer layer in polymer nanocomposites. The form factor will vary based on the aspect ratio of the scattering object (in this case the nanoparticle), while the structure factor will be a correlation factor for inter-particle scattering. For 25 nm silica nanoparticles in a polymer melt, the form factor is modeled assuming a hard sphere (where there is no interfacial structure) given by [92]:

$$P(q)^2 = \frac{A}{V_c} \left[3V_c(\rho_c - \rho_{solv}) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} \right]^2 + C_0, \quad (3.49)$$

or they are expressed in terms of a core-shell model (where the interfacial layer has a separate structure (density) from the bulk polymer), given by:

$$P(q)^2 = \frac{A}{V_s} \left[\begin{array}{c} 3V_c(\rho_c - \rho_s) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} + \\ 3V_s(\rho_s - \rho_{solv}) \frac{\sin(qr_s) - qr_s \cos(qr_s)}{(qr_s)^3} \end{array} \right]^2 + C_0. \quad (3.50)$$

The subscripts mean the following: *c* is the core, representing the nanoparticle, *s* is the shell, representing the interfacial polymer, and *solv* is for solvent, which represents the bulk polymer. For these equations, *V* is the volume of the spherical nanoparticle core or shell with radius *r*, ρ is the scattering length density, *A* is the scale factor, and C_0 is the background. For the 25 nm silica nanoparticles, the $S(q)$ is a hard-sphere structure factor. This scattering analysis for 25 nm silica NPs is used in Chapter 5.

The OAPS nanoparticles were also measured with SAXS in Chapter 7 to determine their size and dispersion state. The form factor used for the OAPS nanoparticles is the fuzzy sphere model given by:

$$P(q) = \frac{3[\sin(qR) - qR \cos(qR)]}{(qR)^3} \exp\left(-\frac{(\sigma_{fuzzy} q)^2}{2}\right), \quad (3.51)$$

where *R* is the radius of the sphere and σ_{fuzzy} is the width of the smeared particle surface. All scattering experiments were performed at room temperature in a transmission geometry.

3.4.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed on a Q50 analyzer (TA Instruments) to characterize the mass fraction of nanoparticles in the composites. A temperature ramp of 20

°C/min from room temperature up to 800 °C was performed for all samples. All polymer material, bulk and interfacial, is burned off well below this temperature, so the remaining mass fraction can be reliably assigned to the inorganic nanoparticles, which burn at significantly higher temperatures. The mass fraction m_{NP} is usually converted to volume fraction of nanoparticles, φ_{NP} , by the following expression:

$$\varphi_{NP} = \frac{m_{NP}/\rho_{NP}}{m_{NP}/\rho_{NP} + (1-m_{NP})/\rho_m}, \quad (3.52)$$

where the ρ_{NP} and ρ_m are the mass densities of the nanoparticles and polymer matrix, respectively.

4. Analysis of Interfacial Layer Properties Using Broadband Dielectric Spectroscopy

The segmental and secondary dynamics are examined with broadband dielectric spectroscopy (BDS) on a model poly (vinyl-acetate)-silica nanocomposite system. Three different analysis methods present in the literature are outlined and their quantitative results are compared to each other. With the heterogeneous model analysis (HMA), the interfacial layer volume fraction is more carefully probed when using an interfacial layer model (ILM). Additionally, important features of PNCs can be distinguished that are not present from other analyses.

4.1. Introduction

Broadband dielectric spectroscopy (BDS) measures polymer dynamics over a very broad frequency range with a high degree of accuracy [12, 140, 141]. Polymer nanocomposite research uses BDS extensively, with particular emphasis on illuminating properties of the interfacial layer dispersed throughout the composite [7, 9, 57, 58, 106]. It is generally accepted that there is a dynamic interfacial layer of 1-5 nm in PNCs that has modified dynamics relative to the bulk polymer [9, 57, 142]. However, a strong Maxwell-Wagner-Sillars (MWS) polarization and a high dc-conductivity in polymer nanocomposite systems will often overlap the interfacial layer contribution to the dielectric spectra [42, 57]. As a result, analysis of the interfacial layer is complicated and typically model-dependent. There are three prevailing methods in the literature: the single Havriliak–Negami (HN) function approach [42, 114], the two HN functions approach [57, 100, 106, 132], and the heterogeneous model analysis (HMA) approach [65, 86, 99].

Depending on the initial assumptions of each model, the final quantitative details can be very different.

In this chapter, the three analysis methods will be applied to a model poly(vinyl acetate)-silica (PVAc-silica) nanocomposite system with increasing nanoparticle volume fraction. Comparing the quantitative results of the interface, the following conclusions will be drawn: (1) the single Havriliak-Negami (HN) function fails to properly fit the spectra over a broad frequency range; (2) the two HN functions fit the spectra well but underestimate the interfacial layer thickness and its temperature dependence; and (3) the heterogeneous model analysis (HMA) with an interfacial layer model (ILM) not only fits the spectra well but also most accurately describes the thickness and dynamics of the interfacial layer, as well as their temperature dependence. We use these results as justification for employing the HMA approach for Chapter 5 of this thesis.

4.2. Materials and Methods

Poly(vinyl acetate) (PVAc) with molecular weight of 40 kg/mol and polydispersity of 1.76 was purchased from Spectrum Chemical MFG Corp. and used as received. Methanol, ethanol, acetone, and methyl ethyl ketone (MEK) were purchased from Sigma-Aldrich and used as received. The silica nanoparticles of radius of $R_{NP} = 12.5$ nm were synthesized in ethanol at a concentration of 15 mg/mL using the modified Stöber method [143].

PVAc-silica nanocomposites of different loadings have been prepared in the following procedures: Parent PVAc/MEK solution with a concentration of 0.01 g/mL was first prepared and filtered by a 20 μ m PTFE filter to remove any impurities and dust. For each loading, 30 mL of the parent solution was transferred into a 100 mL round-bottom flask. Then, different amounts

of silica/ethanol suspension were added into the PVAc/MEK solution in a dropwise manner under stirring. After 2 h of mixing, the nanocomposite solution was quickly dried under a rotary bath at a bath temperature of 313K. The precipitate was redissolved into 10 mL of acetone and transferred into a Teflon dish to first dry under hood (10 h) and then in a vacuum oven (10^{-5} bar) at 353K for 7 days and at 393K for another 2 days. The above procedure ensures good dispersion of nanoparticles, which was confirmed by transmission electron microscopy and by small-angle X-ray scattering data published earlier [86, 93].

The samples of PNCs without free polymers were prepared by following the procedure through a solvent extraction. Specifically, the same PVAc-silica composites were redissolved in acetone for 3 hours under stirring. The adsorbed nanoparticles were then allowed to precipitate to the bottom of the vial while the free polymer remained in the solvent. The clear solvent was then removed via a syringe. This procedure was repeated a total of five times to ensure most of the free polymers were removed as demonstrated before [87].

Thermogravimetric analysis (TA Instruments, Discover Q50) was performed from 313K to 1073K under air at a heating rate of 20 K/min to determine the weight fractions of nanoparticles. The mass densities of the PNC samples, neat silica (2.4057 ± 0.0019 g/cm³), and neat PVAc (1.2058 ± 0.0018 g/cm³) are taken from an earlier publication [93]. The volume fraction of the nanoparticles, ϕ_{NP} , was calculated from the weight fraction and the density of each component accordingly. The average interparticle surface-to-surface distance is estimated assuming random packing of nanoparticles [144]:

$$d_{IPS} = R_{NP} \{ [3\phi_{NP}/4\pi]^{-1/3} - 2 \} \quad (4.1)$$

Temperature-modulated differential scanning calorimetry (TMDSC) measurements were carried out on a Q2000 (TA Instruments) from 433K to 233K at a cooling rate of 2 K/min with a modulation of ± 0.5 K/min. The measurements were done after a base line calibration by indium and sapphire standards. The T_g (DSC) is determined from the inflection point of the initial specific heat capacity jump of the DSC curve, and the accuracy is ± 2 °C. Table 4.1 summarizes the sample characterization for the PNCs of different loadings.

Broadband dielectric spectroscopy measurements were carried out by a Novocontrol Concept-80 system with an Alpha-A impedance analyzer and a Quatro Cryosystem temperature controller. The measurements were done in a frequency range of 10^7 – 10^{-2} Hz on a polymer film with a thickness of 0.1 mm and a diameter of 14 mm at temperatures from 393K to 173K upon cooling down and from 173K to 393K upon heating up at the same temperature intervals to ensure reproducibility of the measurements. A 20 min thermal stabilization was performed at each temperature before the measurement to ensure thermal equilibrium.

Table 4.1: Characterization of the PVAc-silica composites. Density was taken from a previous paper [142]. The T_g (DSC) was taken as the inflection point in the reversible heat capacity step. The T_g (BDS) was estimated using a fit of the dielectric relaxation time distribution to the Vogel-Fulcher-Tammann (VFT) equation [12] extrapolated to $\tau = 100$ s.

Sample	Weight %	Volume %	T_g (DSC) (K)	T_g (BDS) (K)	d_{IPS} (nm)	Density (g/cm ³)
PVAc Neat	0	0	313.6	304.7	-	1.2058 ± 0.0018
PVAc-6%	13.8	6.11	314.4	307.2	29.60	1.2702 ± 0.0018
PVAc-12%	24.1	11.8	314.6	309.5	18.85	1.3384 ± 0.002
PVAc-20%	36.33	20.5	314.7	309.8	11.47	1.4379 ± 0.0024
PVAc-23%	38.27	23	314.6	309.9	10.1	1.4573 ± 0.0012
PVAc-32%	48.8	31.9	314.8	309.7	6.475	1.5315 ± 0.0015
Silica	100	100	-	-	-	2.4057 ± 0.0019

4.3. Results

4.3.1. Temperature-Modulated Differential Scanning Calorimetry (TM-DSC)

Initial sample characterization is done with temperature-modulated differential scanning calorimetry (DSC), traditionally applied to study the thermodynamic characteristics of PNCs [57]. Figure 4.1a shows the TMDSC measurements of the neat PVAc, the neat silica nanoparticles, and the PVAc nanocomposites with different loadings. The neat polymer and PNCs contain a clear thermodynamic process whose step size decreases with increasing nanoparticle loading; the bare nanoparticles themselves have no thermal event in this temperature range. To directly compare the thermodynamic features of the polymer matrix in PNCs, we follow a previously proposed analysis [57, 141] to normalize the specific heat capacity to the mass fraction of the polymer matrix, $C_p^{mat} = \frac{C_p^{PNC} - C_p^{NP} m_{NP}}{1 - m_{NP}}$, where C_p^{mat} , C_p^{PNC} , and C_p^{NP} are the specific heat capacity of the polymer matrix, the polymer nanocomposites, and the nanoparticles, respectively, and m_{NP} is the mass fraction of the nanoparticles. Figure 4.1b shows this normalized specific heat capacity. The inflection point of the glass transition step indicates no significant shift in T_g . However, the extent of the glass transition step in the PNCs broadens and their thermodynamic step is completed at a temperature much higher than in the neat polymer. This effect is most obvious at 32 vol% where the specific heat jump ends at $T = 350\text{--}355\text{K}$, compared to the neat polymer which ends around $T = 315\text{K}$. This change suggests that the presence of nanoparticles causes a broad distribution of T_g s in the PNCs. The vertical location of the inflection point decreases with loading; however, the normalized specific heat capacities of the neat PVAc and the PNCs are almost identical at temperatures well below (273 K), and well above (423 K) T_g . This convergence of the normalized C_p^{mat} values suggests that all

degrees of freedom of the polymer matrix are restored at sufficiently high temperature. This convergence also clearly indicates the absence of any significant “glassy” or “dead” layer in these PNCs [57]. Further, the extended step in the specific heat capacity of PNCs (Figure 4.1b) indicates the presence of an interfacial layer with slower segmental dynamics [99]. These DSC results help justify the study of the interfacial layer dynamics with broadband dielectric spectroscopy.

4.3.2. Segmental Dynamics

The dielectric spectra of the segmental dynamics are shown in Figure 4.2 for the neat poly (vinyl acetate) (PVAc) and the PVAc-silica nanocomposites of loading fractions of 6%, 12%, 20%, 23%, and 32vol%. At temperatures above the glass transition temperature, the segmental relaxation process typically dominates the dielectric spectra of neat polymers and appears as a peak in the dielectric loss spectra, $\varepsilon''(\omega)$. The segmental relaxation processes can also be seen in the derivative spectra of $\varepsilon'(\omega)$, given by $\varepsilon'_{der}(\omega) = -\pi/2 \times \partial\varepsilon'(\omega)/\partial\ln(\omega)$. The derivative spectra can be helpful for discerning different relaxation peaks normally covered by dc conductivity, which does not contribute directly to $\varepsilon'(\omega)$; however, these relaxation peaks of the derivative spectra are narrower than the actual relaxation process in $\varepsilon''(\omega)$. As is typical for most polymers, the segmental relaxation peak of the neat PVAc can be fit by one Havriliak–Negami (HN) function, where the fitted characteristic relaxation time corresponds to the segmental relaxation time, τ_α . Adding nanoparticles to neat polymers leads to several changes to the dielectric spectra, as seen in our model system (Figure 4.2): (1) a decrease in the α -relaxation peak intensity with increased loading of nanoparticles (Figure 4.2a); (2) a significant broadening of the α -relaxation peak combined with the emergence of a shoulder on the lower frequency side of this α -relaxation peak, especially obvious in the derivative analysis (Figure

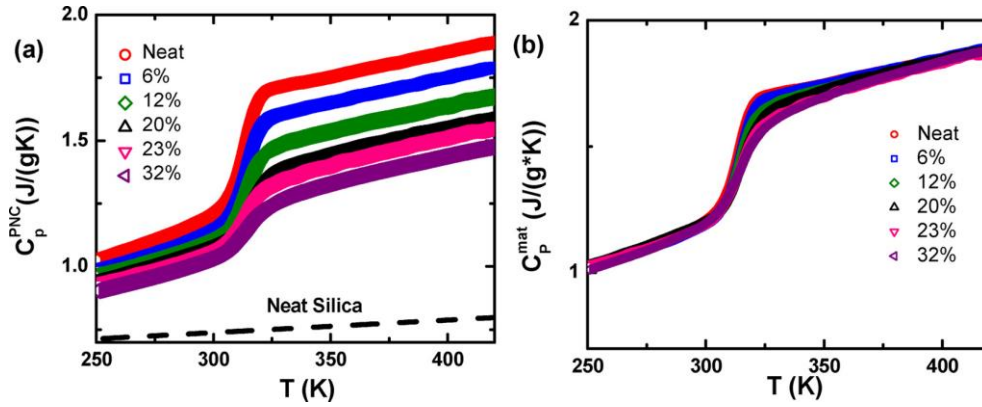


Figure 4.1: (a) Specific heat capacity for poly(vinyl acetate)-silica (PVAc-silica) nanocomposites of different loadings measured with differential scanning calorimetry (DSC). The neat silica specific heat capacity (dashed black line) is shown to have no thermal event in this temperature window. (b) Specific heat capacity for the polymer matrix, where the PNC specific heat capacities are corrected for the silica contribution, which normalizes the polymer matrix response for PNCs with different silica concentrations.

4.2b); (3) a slight shift of the peak position to lower frequencies; (4) appearance of a strong peak from Maxwell-Wagner-Sillars polarization (Figure 4.2b); (5) a change in the dc conductivity resulting from the competing effects of nanoparticle inclusion and an increased impurities during sample preparation. The MWS process typically has the spectral shape of a Cole–Cole process which appears at a frequency when the conductivity contribution to $\varepsilon''(\omega)$ is equal to $\varepsilon'(\omega)$. These dielectric features are typical of PNCs and are consistent with previous studies [42, 57, 99, 106, 141].

In many earlier BDS studies on PNCs, the dielectric spectra had a high dc conductivity that hides features of the interfacial layer process [57, 141, 145]. However, the dc conductivity of the PVAc-silica system is significantly decreased (~ 10 – 100 times) in comparison to the neat polymer (Figure 4.2). Additionally, the MWS processes in all studied PVAc-silica PNCs are sufficiently removed (~ 6 orders) from the α -process, leaving a large frequency window for analysis of the interfacial layer dynamics. This reduced conductivity makes the PVAc-silica

system a great model PNC to test the previously proposed approaches for dielectric analysis of PNCs as well as get quantitative estimates of interfacial layer parameters.

4.3.3. Secondary Dynamics

The dynamics of the secondary process are shown in Figure 4.3 for the neat PVAc and the PVAc-silica PNCs. These local relaxation processes occur at a much smaller length scale, which can be measured with BDS at temperatures well below T_g . The spectra in Figure 4.3 is at $T = 203\text{K}$, which is 110K below their T_g . The secondary relaxation peaks of the nanocomposites change dramatically in terms of both the peak shape and peak position, indicating that the nanoparticles can create a major difference in the local dynamics. Surprisingly, the secondary relaxation peak has a non-monotonic dependence on nanoparticle loading: the peak shifts to lower frequencies at low loadings but then shifts to higher frequencies at high loadings (Figure 4.3a). These are unusual results because in other studies the secondary relaxation has little to no changes in dynamics with loading [57, 146]. Taking advantage of the time-temperature superposition principle, these features can also be clearly visualized in the temperature dependence of the loss intensity at a fixed frequency $f = 10^5 \text{ Hz}$ (Figure 4.3b), where the α -peak positions of all samples sit at around $T = 353\text{K}$.

4.4. Discussion

The simplest approach to study segmental dynamics of PNCs is the use of a slightly modified single Havriliak-Negami (HN) function. The second approach most widely used in the literature is the two HN function approach, where a second HN function is added to the neat response to explicitly account for the interfacial contribution. This approach assumes an additive

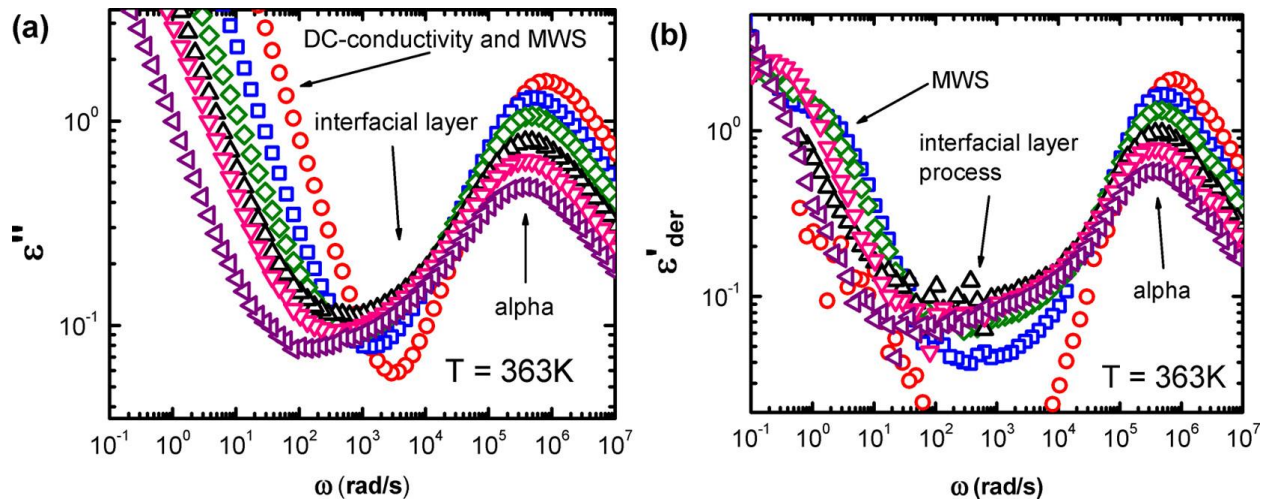


Figure 4.2: Broadband dielectric spectra of poly(vinyl acetate)-silica (PVAc-silica) nanocomposites of different nanoparticle loading from neat to 32 vol%. (a) The segmental dynamics as shown at 363K in the dielectric loss spectra (ϵ''). The interfacial layer is manifested as a broad shoulder to the left of the alpha peak, which is suppressed with increased loading. (b) The segmental dynamics of the PVAc-silica as shown in the derivative spectra of the dielectric storage, (ϵ'_{der}). The derivative spectra are useful because the ϵ' data does not contain any contribution from dc-conductivity and the MWS process is clearly visible.

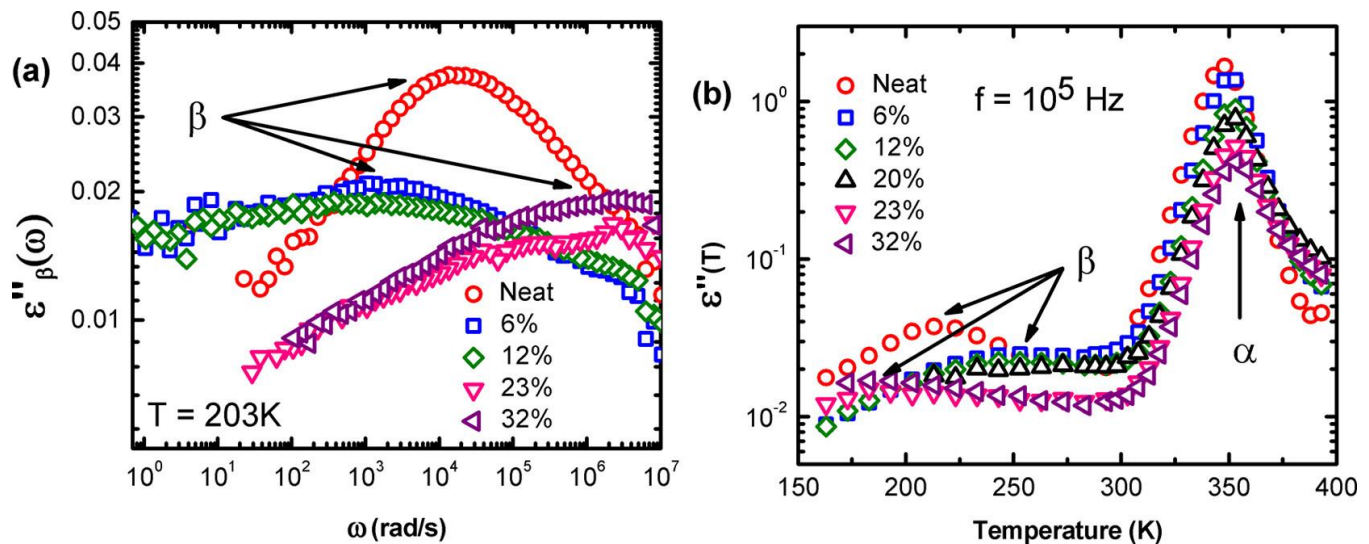


Figure 4.3: Secondary dynamics of the PVAc-silica nanocomposites as a function of (a) frequency and (b) temperature. The secondary relaxation dynamics are unusual for PNC systems, which typically have little changes in secondary dynamics with loading.

contribution of different phases to the dielectric spectra. A third approach, the heterogeneous model analysis, uses a more complicated function that accounts for the interference that arises from boundaries in a heterogeneous dielectric medium. In this approach the neat, nanoparticle, and interface all have separate HN functions that are combined into one function for the PNC dielectric response. In the following discussion, we will analyze the BDS spectra of the PVAc-silica composites using all three approaches and will discuss their advantages and drawbacks.

4.4.1. Three Methods for Dielectric Analysis of PNCs

Single Havriliak-Negami function

The single HN function approach assumes that the interfacial layer does not directly contribute to the dielectric spectra; instead, the nanoparticle presence will cause the segmental relaxation peak of the bulk-like polymer to broaden and potentially change the averaged relaxation time. The dielectric relaxation spectra are fit with a single Havriliak-Negami (HN) function:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1+(i\omega\tau_{HN})^{\alpha}]^{\gamma}} - i \frac{\sigma}{\varepsilon_0\omega} \quad (4.2)$$

where ε_{∞} is the dielectric permittivity at infinite frequency, $\Delta\varepsilon$ is the dielectric amplitude of the relaxation process, τ_{HN} is the HN characteristic relaxation time of the relaxation process, ε_0 is the vacuum permittivity, σ is the dc conductivity, and α and γ are the shape parameters of the HN function that represent the symmetric and asymmetric stretching of the relaxation process, respectively. The advantage of this approach is it has a small number of free parameters, which can be further reduced by taking the two HN exponents to merge into the Kolrausch–Williams–Watts (KWW) stretching exponent β [42], given by the relation $\gamma = 1 - 0.812(1 - \alpha)^{0.387}$ and $\beta = (\alpha\gamma)^{1/1.23}$. From the fit, the volume fraction of the bulk-like polymer

in the PNC is estimated as $\varphi_{bulk} = \Delta\varepsilon_{PNC}/\Delta\varepsilon_{neat}$, where $\Delta\varepsilon_{PNC}$ and $\Delta\varepsilon_{neat}$ are the dielectric amplitude of the PNC and the neat P2VP from the fit. This relation can provide an estimate of the interfacial layer volume fraction, $\varphi_{int} = 1 - \varphi_{bulk} - \varphi_{NP}$ (here φ_{NP} is the volume fraction of the nanoparticles from TGA), which with a simple geometric relation gives the interfacial layer thickness l_{int} :

$$l_{int} = R_{NP} \left(\left(\frac{\varphi_{int} + \varphi_{NP}}{\varphi_{NP}} \right)^{1/3} - 1 \right) \quad (4.3)$$

This approach is applied to the dielectric spectra of the PVAc-silica PNCs in Figure 4.4, where the ε' and ε'' spectra are fit directly, and the fit of the derivative spectra is calculated from the derivative of the fit of the ε' spectra (this procedure for calculating the derivative spectra is used for all three analysis methods). The single HN function can fit the neat PVAc (gray) nicely over the entire frequency range. However, it clearly falls short for the lower frequency part of the PNC (red) (Figure 4.4). Since the dc conductivity and the MWS process are sufficiently far away from the alpha process, the discrepancies between the fits and the experimental data are quite large in all three representations (ε' , ε'' , and the derivative analysis of ε'). These deviations increase with increasing nanoparticle loading (Figure 4.4d), implying the existence of an additional relaxation process due to the influence of nanoparticles. This simple approach does not provide details about this extra relaxation process, it only absorbs it into the broadening of the bulk alpha relaxation.

Two Havriliak-Negami functions

A straightforward improvement to fitting the PNC spectra is to add an additional HN function for the interfacial layer contribution. This two HN approach assumes additive contributions to the dielectric spectra coming from the bulk-like and interfacial polymer:

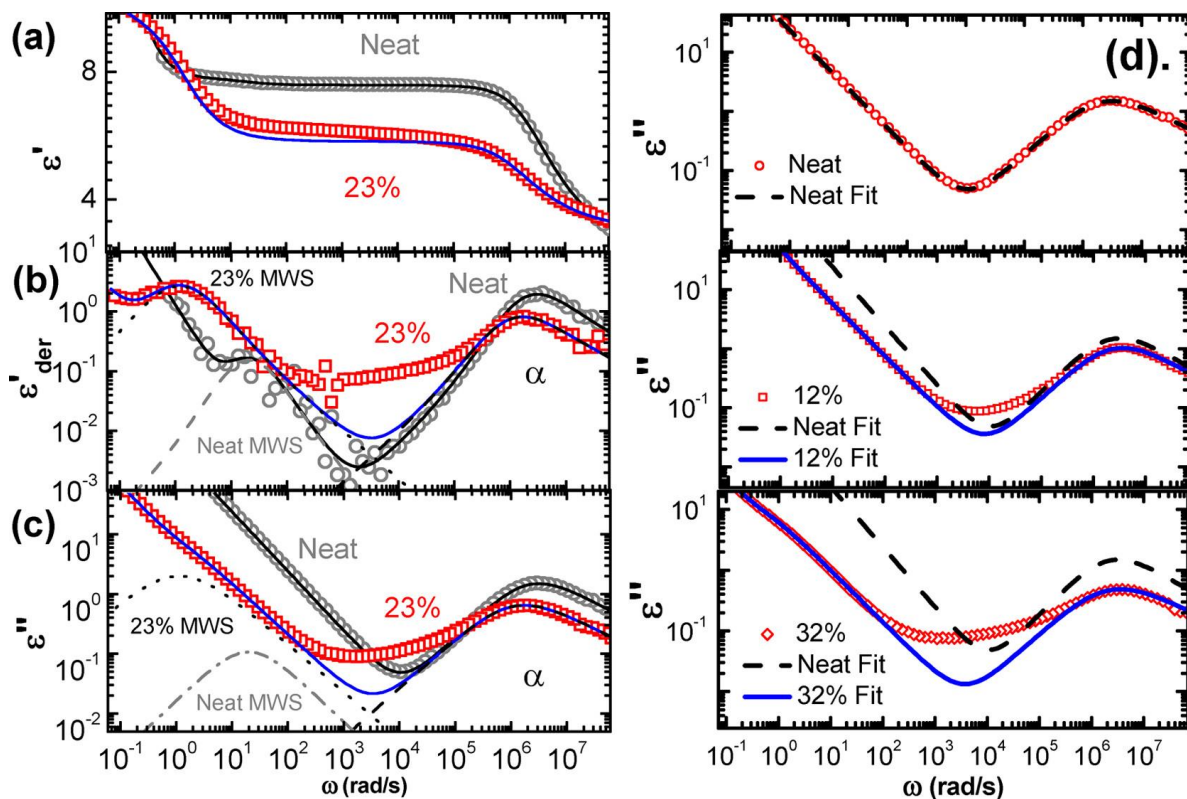


Figure 4.4: The dielectric storage (a), derivative (b), and loss (c) spectra of neat PVAc and PVAc-23% samples (symbols) and their fit (lines) using the single Havriliak–Negami (HN) function approach. The single HN fit (blue lines) clearly fails to describe the spectra over the entire frequency range. (d) The neat, PVAc-12%, and PVAc-32% samples spectra (symbols) and their best fit using the single HN approach (lines). The neat spectra fit (black dashed line) is shown in each plot to compare. Clearly the fitting gets worse at higher loading.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_{bulk}}{[1+(i\omega\tau_{bulk})^{\alpha_1}]^{\gamma_1}} + \frac{\Delta\varepsilon_{int}}{[1+(i\omega\tau_{int})^{\alpha_2}]^{\gamma_2}} - i \frac{\sigma}{\varepsilon_0\omega} \quad (4.4)$$

where the $\Delta\varepsilon_{bulk}$ and $\Delta\varepsilon_{int}$ are the dielectric amplitude associated with the bulk polymer and the interfacial layer, respectively, and the τ_{bulk} and τ_{int} are the respective relaxation times. To limit the amount of the free fit parameters, the spectral shape (stretching exponents) of the bulk polymer process is typically assumed to be identical to that of the neat polymer. The amplitude and relaxation time of the bulk polymer are set free, although this assumption is not required for the two HN functions approach. The interfacial layer contribution has its own distinct dynamic process with free stretching parameters and typically a slower relaxation time. By assuming the dielectric amplitude per volume is the same in the bulk and interfacial polymer, the two HN functions approach provides an estimate of the interfacial layer volume fraction as $\varphi_{int} = (1 - \varphi_{NP}) \times \frac{\Delta\varepsilon_{int}}{\Delta\varepsilon_{int} + \Delta\varepsilon_{bulk}}$. This volume fraction can be used to calculate the thickness of the interfacial layer using equation 4.3.

This approach can fit the dielectric spectra of PNCs very well for the entire frequency range, as seen in Figure 4.5. Moreover, it provides quantitative information on the segmental dynamics of the interfacial layer. Because of its straightforward procedure, the two HN functions approach is widely used by different groups [57, 106, 132, 147]. However, to obtain an estimate of the interfacial layer thickness, the two HN functions approach makes two strong assumptions: (1) the interfacial layer and bulk polymer relaxation contributions to the PNC dielectric spectra are additive, and (2) the dielectric amplitude per unit volume is the same for the interfacial layer and for the bulk polymer. The first assumption is known to be incorrect in heterogeneous dielectric systems, where the boundary between dielectric media does not have complete

transmission of electromagnetic waves, resulting in signal interference [12]. The second assumption would require that the interfacial and bulk polymer share an identical Kirkwood–Fröhlich factor since the dielectric amplitude $\Delta\epsilon \sim g \times N/V$, where the g is the Kirkwood–Fröhlich factor and N/V is the number density of relaxing dipoles for a given process. This assumption is questionable if the molecular arrangements and chain stretching are different in these two polymer regions (see the discussion below).

Heterogeneous Model Analysis

The heterogeneous model analysis (HMA) takes the nonadditive nature of the dielectric response of heterogeneous materials explicitly into account, and computes the response based on either a two-phase model (TPM) [99, 148] (Figure 4.6a) or an interfacial layer model (ILM) (Figure 4.6b) [86, 148]. The HMA is based on the Maxwell–Wagner equation, where PNCs are taken to have an effective boundary condition between different dielectric media. The TPM predicts the dielectric function of the nanocomposites as [99, 148]:

$$\begin{aligned} \epsilon_{PNC}^*(\omega) &= \epsilon_{bulk}^*(\omega) \frac{(1+2\varphi_{NP})\epsilon_{NP}^*(\omega) + (2-2\varphi_{NP})\epsilon_{bulk}^*(\omega)}{(1-\varphi_{NP})\epsilon_{NP}^*(\omega) + (2+\varphi_{NP})\epsilon_{bulk}^*(\omega)} \\ &= (1 - \varphi_{NP})\epsilon_{bulk}^*(\omega) + \varphi_{NP}\epsilon_{NP}^*(\omega) - (1 - \varphi_{NP})\varphi_{NP}\epsilon_{cross}^*(\omega) \text{ where} \end{aligned} \quad (4.5)$$

$$\epsilon_{cross}^*(\omega) = \frac{(\epsilon_{bulk}^*(\omega) - \epsilon_{NP}^*(\omega))^2}{(1-\varphi_{NP})\epsilon_{NP}^*(\omega) + (2+\varphi_{NP})\epsilon_{bulk}^*(\omega)}.$$

$\epsilon_{PNC}^*(\omega)$, $\epsilon_{bulk}^*(\omega)$, and $\epsilon_{NP}^*(\omega)$ are the complex dielectric functions of the composites, the matrix, and the nanoparticles, respectively. Here, $\epsilon_{bulk}^*(\omega)$ and $\epsilon_{NP}^*(\omega)$ are the measured spectra of the neat polymer and nanoparticles measured independently. This means the two-phase model contains no free parameters and provides a first-order approximation of the dielectric spectra of PNCs. The first two terms of eq. 4.5 correspond to the additive dielectric contribution of the two

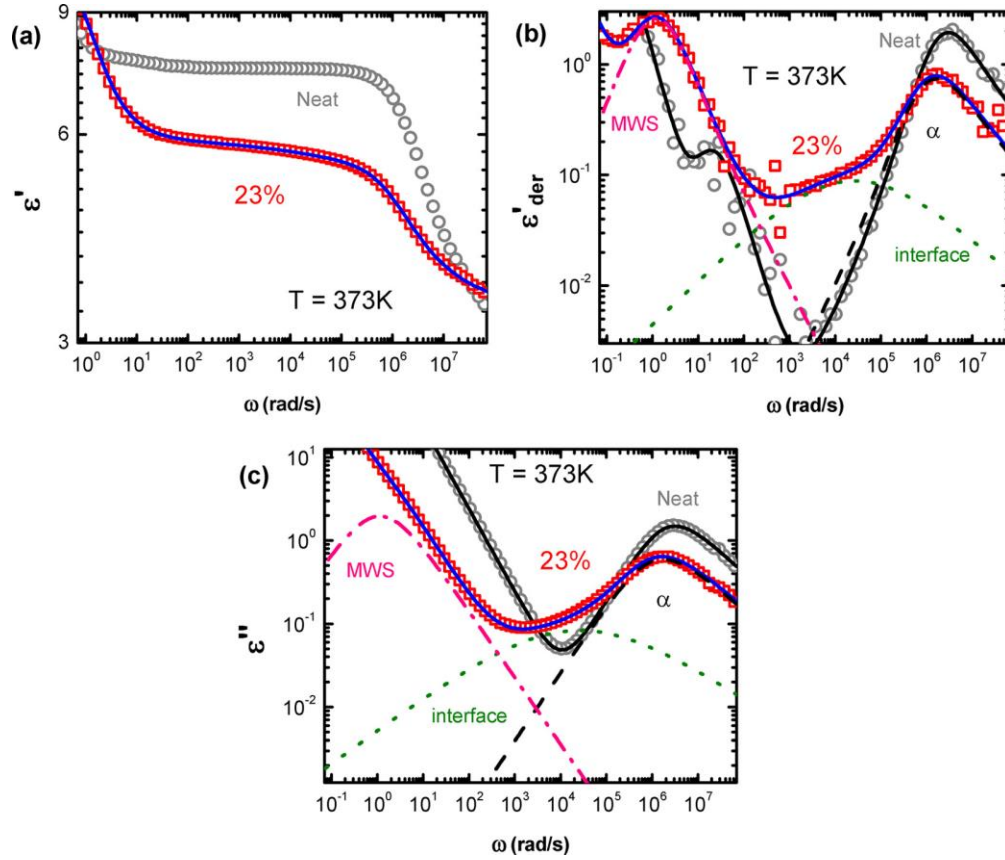


Figure 4.5: The dielectric storage (a), derivative (b), and loss (c) spectra of neat and PVAc-23% samples (symbols) and their fit (solid lines) using the two HN functions approach for the PNCs. The interfacial layer is expressed as a separate relaxation process (green dotted lines) that is added to the bulk contribution (black dashed lines)

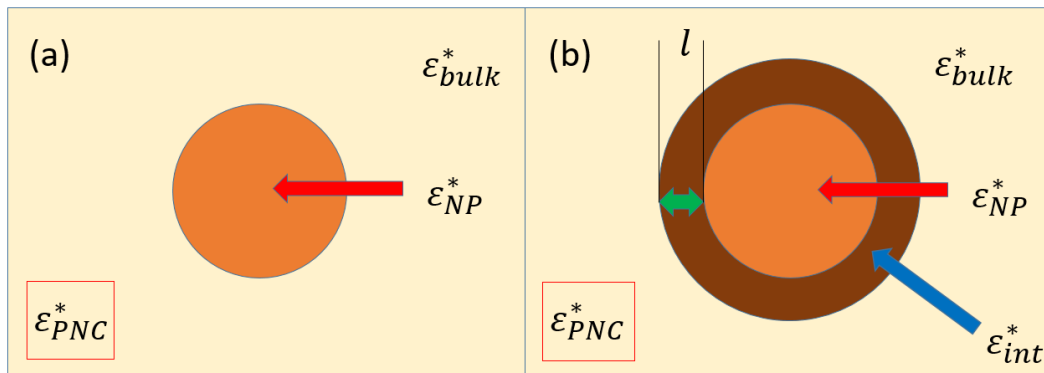


Figure 4.6: Schematic of (a) the two-phase model (TPM) and (b) the interfacial layer model (ILM) used for the heterogeneous model analysis (HMA). The $\varepsilon_{bulk}^*(\omega)$, $\varepsilon_{NP}^*(\omega)$, and $\varepsilon_{int}^*(\omega)$ are the dielectric response functions of the bulk polymer matrix, nanoparticle, and interfacial layer, respectively. The l is the thickness of the interfacial layer, which is determined from the volume fraction, φ_{int} .

components in the PNC, the polymer and nanoparticles. The third term containing $\varepsilon_{cross}^*(\omega)$ represents the interference between the polymer and the nanoparticles; note the interference term itself is always positive, meaning the subtracted interference term always reduces the dielectric permittivity.

Figure 4.7 shows the analysis of the PNC dielectric spectra using the TPM (equation 4.5) with no adjustable parameters. The TPM spectra shows the expected reduction in the α -peak intensity. We would also expect a slight broadening of the α -peak due to the interference term, but it is relatively small for this system. Attributing broadening and a decrease in peak amplitude to interference is a departure from the two previous outlined methods, where these features would be assigned to increased dynamic heterogeneity and decreased bulk polymer fraction, respectively. However, the TPM fails to describe the dielectric relaxation spectra of PNCs over the entire frequency range (Figure 4.7), indicating there are more explicit changes in the segmental dynamics of PNCs.

To take these dynamical changes into account, the ILM adds an interfacial layer with dielectric response $\varepsilon_{int}^*(\omega)$ to the two-phase model, as seen in Figure 4.6b. This modification gives the following more complicated dielectric function [148]:

$$\varepsilon_{PNC}^*(\omega) = \frac{\varepsilon_{NP}^*(\omega)\varphi_{NP} + \varepsilon_{int}^*(\omega)\varphi_{int}R^* + \varepsilon_{bulk}^*(\omega)\varphi_{bulk}S^*}{\varphi_{NP} + \varphi_{int}R^* + \varphi_{bulk}S^*} \quad (4.6)$$

where $R^* = \frac{2\varepsilon_{int}^* + \varepsilon_{NP}^*}{3\varepsilon_{int}^*}$, $d = \frac{\varphi_{NP}}{\varphi_{NP} + \varphi_{int}}$, $\varphi_{NP} + \varphi_{int} + \varphi_{bulk} = 1$, and

$$S^* = [(\varepsilon_{int}^*(\omega) + 2\varepsilon_{bulk}^*(\omega))(\varepsilon_{NP}^*(\omega) + 2\varepsilon_{int}^*(\omega)) + 2d(\varepsilon_{int}^*(\omega) - \varepsilon_{bulk}^*(\omega))(\varepsilon_{NP}^*(\omega) - \varepsilon_{int}^*(\omega))]/[9\varepsilon_{int}^*(\omega)\varepsilon_{bulk}^*(\omega)].$$

The $\varepsilon_{bulk}^*(\omega)$ is the dielectric function of the bulk polymer that is identical to the dielectric function of the neat polymer. In comparison to the TPM, the ILM introduces an interfacial layer volume fraction φ_{int} , and an interfacial dielectric function, $\varepsilon_{int}^*(\omega)$, that can be approximated by an additional HN function. The φ_{int} and $\varepsilon_{int}^*(\omega)$ are the new free parameters in this model. The HMA with ILM (henceforth “ILM approach”) is valid absent strong overlapping in the interfacial layers. Judging from the characteristic surface-to-surface distance between nanoparticles, d_{IPS} , in Table 4.1, the ILM is applicable to the highest loading in this study. Most importantly, as can be seen in Figure 4.7 in blue, this ILM approach can fit the dielectric spectra over the entire frequency range.

The additional free parameters used in the ILM approach require a standard fitting procedure to minimize the possibility of nonunique fits to the spectra. The parameters of $\varepsilon_{NP}^*(\omega)$ and φ_{NP} are known; $\varepsilon_{bulk}^*(\omega)$ is approximated by an HN function with the spectral shape of the neat polymer; $\varepsilon_{int}^*(\omega)$ is approximated by an HN function with free stretching parameters; and φ_{bulk} is itself a free parameter. The τ_{bulk} is usually initialized by the peak position of the PNC α -relaxation process. The τ_{int} can be initialized using a generalized regularization procedure on the relaxation time distribution function calculated from the dielectric spectra [99, 149]. However, this method only provides a range of values, so initializing the τ_{int} from the two HN method is equally as useful and much simpler. This procedure goes as follows: first fit the PNC with two Havriliak-Negami functions, where the bulk HN contribution fixes the τ_{neat} and spectral shape (both stretching parameters) of the neat polymer fit. This process leaves the interfacial HN function parameters free and the dielectric amplitude of the bulk contribution free. Next, fit the PNC spectra with the ILM function, using the τ_{int} from the two HN fitting just performed and again keeping the bulk spectral shape and relaxation time the same as the neat.

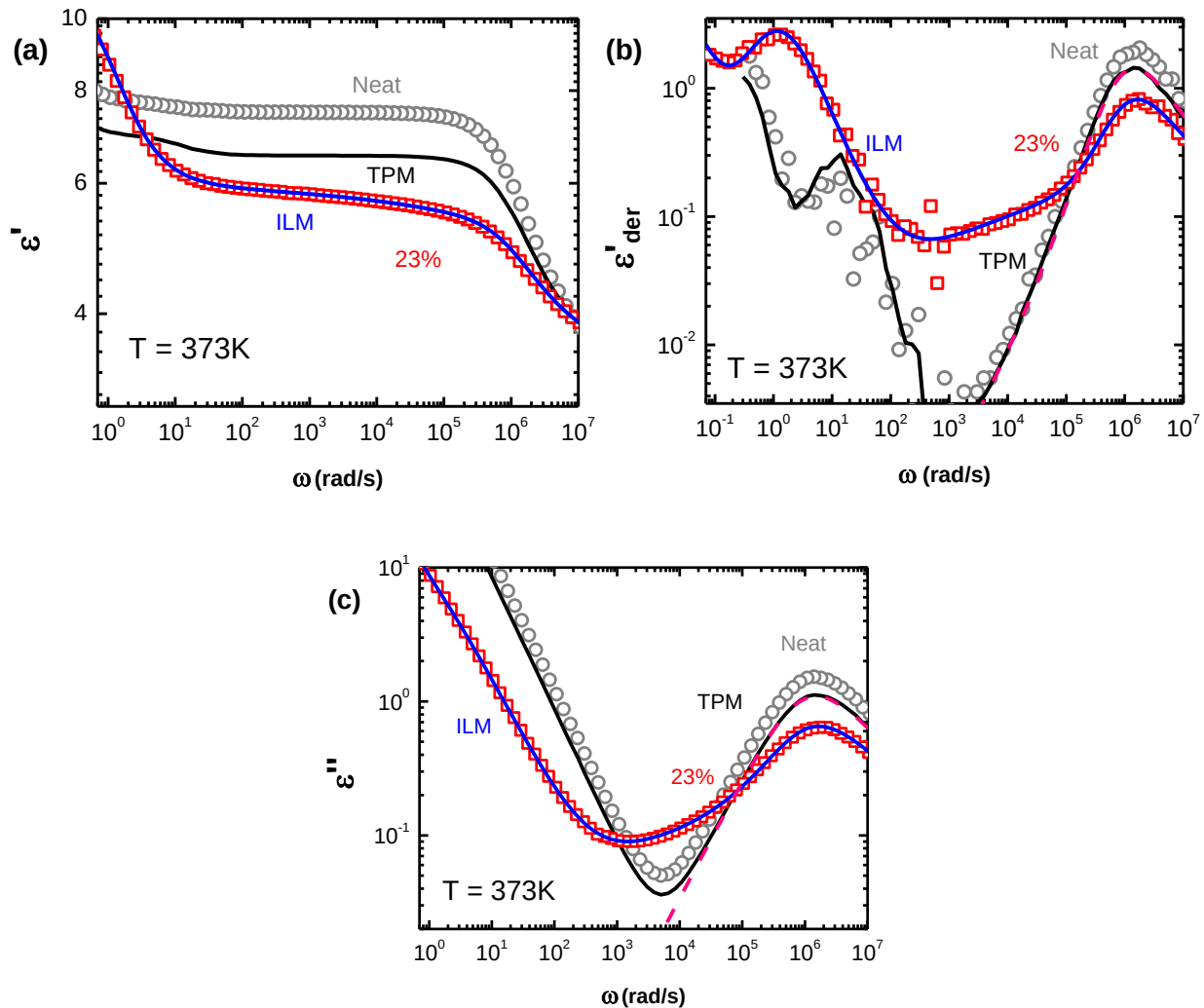


Figure 4.7: The dielectric storage (a), derivative (b), and loss (c) spectra of the neat and PVAc-23% samples (symbols) and their fit using the two-phase model (TPM) (black lines) and interfacial layer model (ILM) (blue lines). Whereas the TPM fails to fit the PNC spectra, the ILM fits it over the entire frequency range.

The remaining free parameters are the interfacial polymer dielectric amplitude and spectral shape, and the bulk dielectric amplitude. Then, let the τ_{int} be set free before also letting the τ_{bulk} be released. This final step ensures that only the spectral shape of the bulk contribution is fixed. This procedure allows φ_{int} to be directly tuned, and as can be seen in Figure 4.8, the fit of the dielectric spectra is very sensitive to slight variations in φ_{int} .

4.4.2. Comparisons of Three Different Approaches

For the single HN function approach, the dielectric spectra can be fit only in a limited frequency range. Even taking fitting results at face value, the bulk polymer fraction is assumed to be $\varphi_{bulk} = \frac{\Delta\epsilon_{bulk}}{\Delta\epsilon_{neat}}$; this relationship would mean the dielectric amplitude of the segmental process would be invariant per unit polymer volume. This scaling of dielectric amplitude with loading is likely unphysical if the interfacial polymer organization is modified at all from the bulk polymer by the presence of nanoparticles. Further, the approach attributes the broadening to an increase in dynamic heterogeneity in the bulk polymer, instead of attributing it to a dynamically and structurally distinct interfacial layer. Finally, this approach does not explicitly account for possible contributions from interference terms, which are expected for heterogeneous PNC systems.

In the two HN functions approach, the dielectric spectra can be fit well over the entire frequency range. The overall dielectric amplitude of PNCs is assumed to be additive, $\Delta\epsilon_{PNC} = \Delta\epsilon_{int} + \Delta\epsilon_{bulk}$. By assuming the interfacial layer and the bulk polymer share an identical Kirkwood–Fröhlich factor, the ratio $\frac{\Delta\epsilon_{int}}{\Delta\epsilon_{PNC}} = \frac{\Delta\epsilon_{int}}{\Delta\epsilon_{int} + \Delta\epsilon_{bulk}}$ determines the interfacial layer volume fraction. Therefore, absolute dielectric amplitude measurements are not needed for this method. The dielectric broadening is taken to be entirely from the existence of the interfacial layer

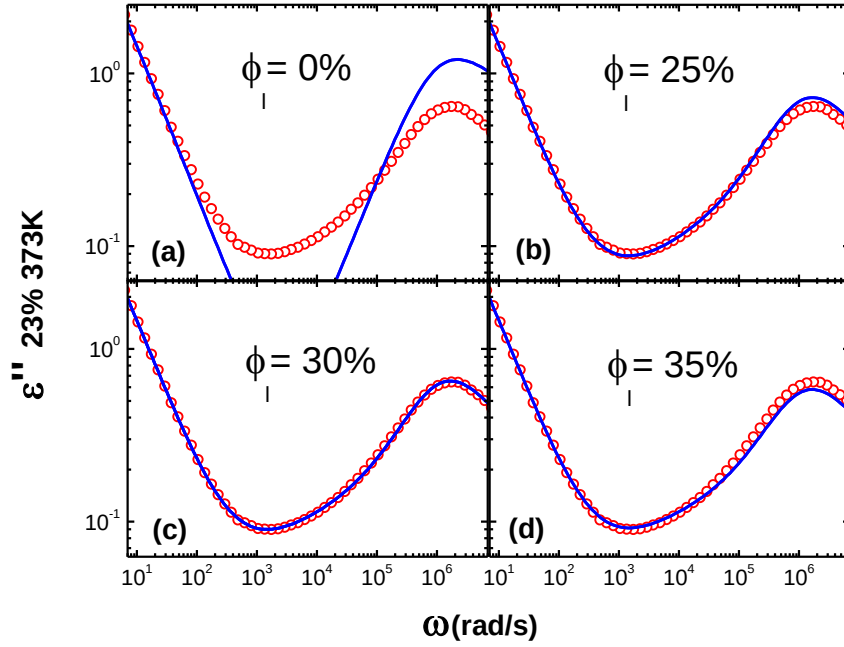


Figure 4.8: Interfacial layer model fit of PVAc-23% at $T = 373$ K with varying interfacial fractions ϕ_{int} of (a) 0%, (b) 25%, (c) 30%, and (d) 35%. The ϕ_{int} , a free parameter in the ILM, is very sensitive to tuning and thus provides a good estimate for the interfacial layer volume fraction.

process, while the bulk matrix relaxation is typically taken to be identical to the neat polymer. This method also does not account for any interference effects in the dielectric response of the heterogeneous PNCs.

The heterogeneous model analysis, on the other hand, explicitly accounts for dielectric contributions from each component and their interference terms. This interference leads to a reduction in the dielectric amplitude and a broadening of the relaxation peak even when the relaxation process remains unchanged as it does for the TPM [86]. The TPM does not accurately fit the PNC spectra in this study, however, so unless otherwise noted we will focus solely on the ILM. This ILM approach, though conceptually and quantitatively most accurate, requires more free parameters to analyze properly. Further, the ILM approach requires accurate absolute

measurements of dielectric permittivity, either through careful measurement or normalization at low temperature. Some reports in the literature use the secondary relaxation spectra to normalize the segmental relaxation data. This procedure assumes (1) the secondary dynamics are invariant with loading and (2) the secondary relaxation amplitude can be scaled with nanoparticle loading. The secondary relaxation spectra in Figure 4.3 shows that these conditions are not always met for PNCs.

Because of the complex geometry of the PNCs, it is difficult to independently measure the dynamics of the interfacial layer in isolation and match them with the results from the outlined analyses. However, a close approximation is possible by extracting the free polymer from the PNCs. By washing the PNCs with a good solvent, only the physically-adsorbed chains will remain [87, 150]. Although the physically-adsorbed polymer layer is different from the interfacial layer [86], a large portion of the physically-adsorbed polymer also belongs to the interfacial layer [9, 86]. After extracting the free polymers from the PVAc-32% PNC, the nanoparticle loading is found to be 47 vol %. If the interfacial layer thickness remains about 3.3 nm at $T = 373$ K, the volume fraction of the interfacial layer is 47 vol % (assuming no overlap). These results imply the bulk-like segments should occupy only ~ 6 vol % in the PVAc-32% without free polymer, meaning this measurement should give a much more pronounced dielectric description of the interfacial layer. Figure 4.9 presents the comparison of the dielectric responses among the neat PVAc, the PVAc-32%, and the effective matrix dielectric response of the PVAc-32% without free polymer at $T = 373$ K. It is clear that the PVAc-32% without free polymers shows a strong suppression of the bulk dynamics, and the features of the interfacial layer dynamics are more pronounced than in the PVAc-32% PNC. Moreover, we can compare the $\varepsilon_{int}^*(\omega)$ of the PVAc-32% PNC fit from the ILM approach (the olive dashed lines) to the $\varepsilon_{int}^*(\omega)$

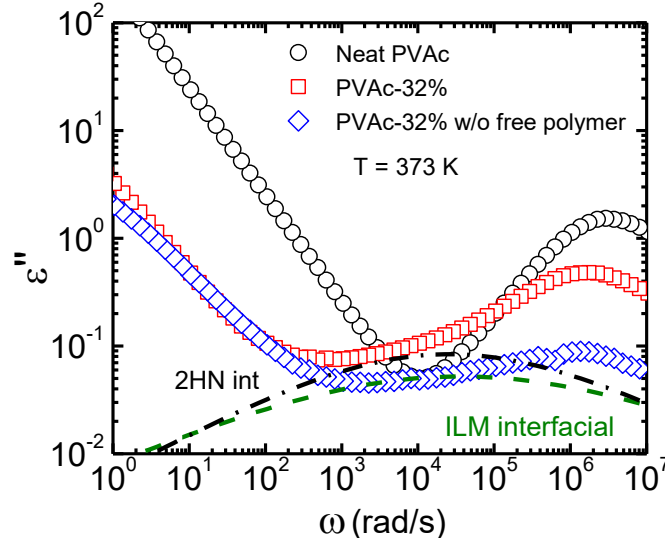


Figure 4.9: Dielectric loss spectra of the neat PVAc, the PVAc-32%, and the effective matrix dielectric function of the PVAc-32% with free polymer removed at $T = 373$ K. The dashed lines represent the dielectric functions of the interfacial layer in isolation from the ILM fit (olive dashed lines) and the two HN functions fit (black dash-dotted lines) of the PVAc-32% nanocomposite (red squares).

of the two HN function (the black dash-dotted lines). We see the ILM $\epsilon_{int}^*(\omega)$ provides a better approximation to the low-frequency shoulder of the PVAc-32% without free polymer (blue), in terms of both the shape and the amplitude. This approximate measurement of the interfacial contribution lends extra support to the robustness of the ILM approach for analyzing PNC spectra.

4.4.3. Characteristic Relaxation Time of the Interfacial Layer Dynamics

The two HN function and ILM approaches give relaxation time information on the interfacial and bulk polymer dynamics [57, 99]. Figure 4.10a presents the temperature dependence of the relaxation time distribution of the interfacial layer, τ_{int} , and the bulk polymer, τ_{α} , of the PVAc-32% sample obtained from these two approaches. A dynamic slowing down in the interfacial layer is evident in both analyses. The T_g of the interfacial layer is ~ 6 – 8 K higher

than that of the bulk-like polymer as determined from a Vogel-Fulcher-Tammann [151] fit of the relaxation spectra. All these characteristics are consistent with recent reports for PNCs with attractive polymer-nanoparticle interactions from both experiments and computer simulations [57, 152]. It appears the τ_{int} estimated from the two HN functions approach is ~ 1.5 times longer than the one obtained using the ILM approach (Figure 4.10b). Still, both approaches demonstrate slower interfacial dynamics that can be quantitatively estimated as a function of temperature.

4.4.4. Dielectric Amplitude of the Segmental Process in PNCs

The amplitude of dielectric signal is expressed by $\Delta\epsilon = g \frac{\mu^2}{3\epsilon_0 k_B T} \frac{N}{V}$ with ϵ_0 , k_B , and μ corresponding to the permittivity of vacuum, the Boltzmann constant, and the dipole moment of a segment, respectively, $\frac{N}{V}$ corresponding the number density of molecules (dipoles), and g being the Kirkwood–Fröhlich factor [12]. The dielectric spectra (Figure 4.11) reveals a much stronger temperature dependence for the amplitude of the α -process in neat PVAc than in PNCs:

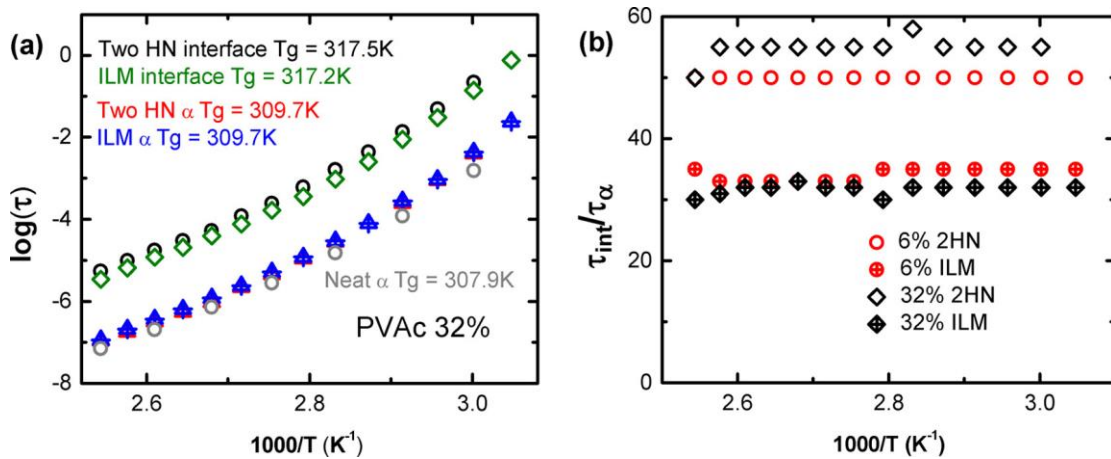


Figure 4.10: (a) Relaxation time distributions for neat PVAc and PVAc-32%. The bulk and interfacial relaxation times from the two HN functions fit and the interfacial layer model fit are shown. (b) The ratio of interfacial and bulk relaxation times obtained from these two models for PVAc-6% and PVAc-32%.

the neat amplitude increases significantly upon cooling in the neat (behavior typically understood with the Curie law), while the PNC amplitude remains essentially constant for PNCs. Despite this difference, the spectral shape is essentially temperature independent in both cases, as seen in their superposition in Figure 4.11c.

Our analysis reveals that the total dielectric amplitude of the segmental peak, $\Delta\epsilon_{PNC} = \Delta\epsilon_{int} + \Delta\epsilon_{bulk}$, in PVAc-silica (red points) decreases with loading stronger than it should when normalized to the nanoparticles' volume fractions (blue points) (Figure 4.12a). This difference is consistent with the earlier observations for glycerol-silica nanocomposites (Figure 4.12b) [99]. The TPM predicts a decrease in amplitude owing to its interference term; indeed, it can describe well the decrease of the dielectric amplitude in glycerol-silica nanocomposites (lines in Figure 4.12b and ref [99]). However, the amplitude and normalized amplitude in PVAc-silica decreases with loading significantly stronger than what is predicted by the TPM (Figure 4.12a). Analysis of the temperature dependence of the dielectric amplitude in PNC, $\Delta\epsilon_{PNC}(T)$, also reveals significantly different variations than those predicted by the TPM for all studied loadings (Figure 4.12c). In contrast, the $\Delta\epsilon_{PNC}(T)$ of the glycerol-silica nanocomposites follows the TPM predictions (Figure 4.12d).

The observed decrease in PNC dielectric amplitude can most plausibly be explained by either a decrease in the amount of active dipoles or a decrease of the Kirkwood–Fröhlich factors. The former explanation would correspond to a “dead” or “glassy” layer with frozen dipoles. However, our TMDSC measurements in Figure 4.1 reveal no signs of a “dead” layer in this system, only a broadening of the glass transition step. It is more plausible to ascribe the reduction in the dielectric amplitude to a change in the Kirkwood–Fröhlich factor for the dipoles in the interfacial layer. At highest NP-loading, we estimate the Kirkwood–Fröhlich factor would be

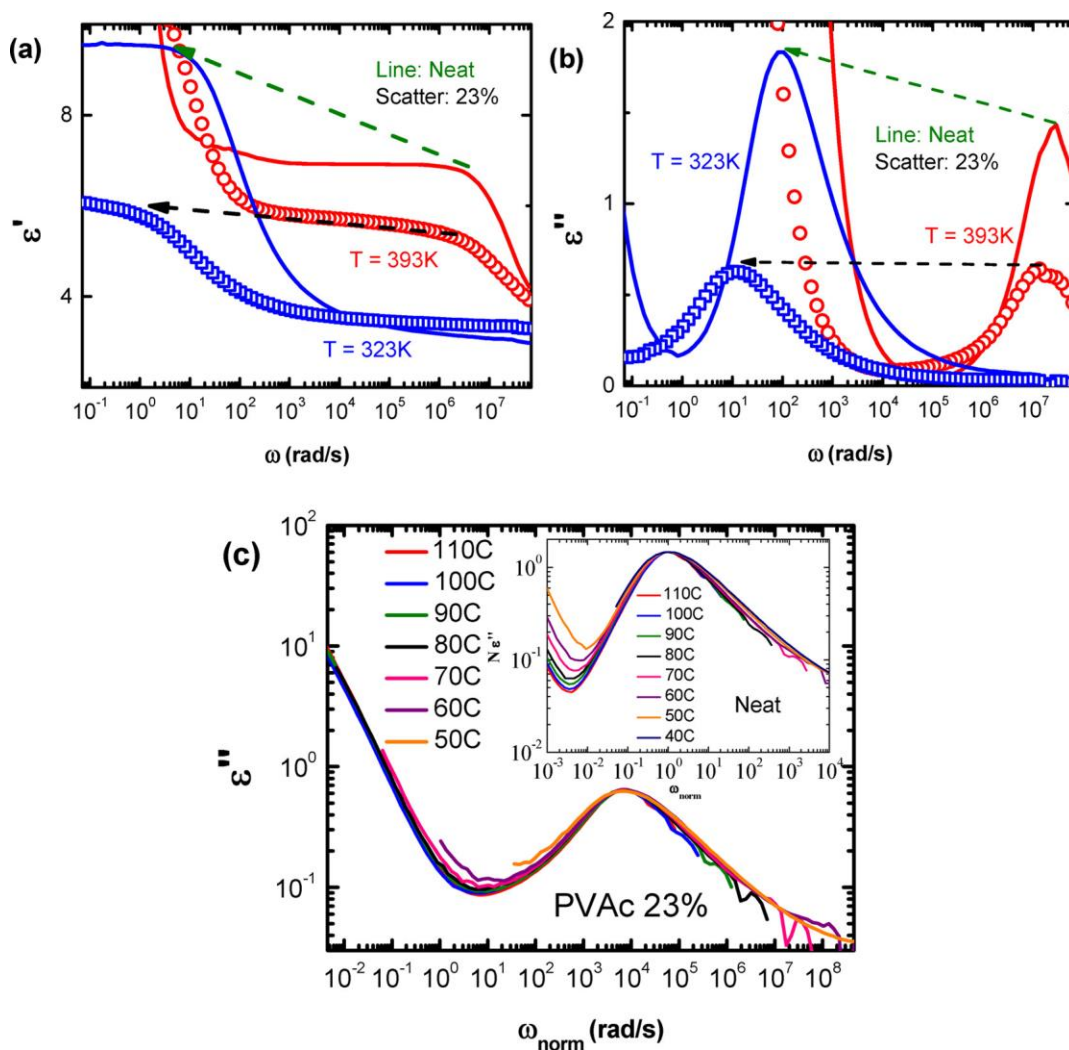


Figure 4.11: Real (a) and imaginary (b) parts of the dielectric permittivity spectra of the neat PVAc (line) and PVAc-23% (symbols) at two selected temperatures. Clearly the temperature dependence of the neat α -process's amplitude is much stronger than that of the PVAc-23%. (c). The PVAc-23% loss spectra normalized to peak frequency. The shape of the spectra does not change with increasing temperature. Inset: the neat PVAc normalized to the peak frequency and amplitude, which again does not have changing spectral shape.

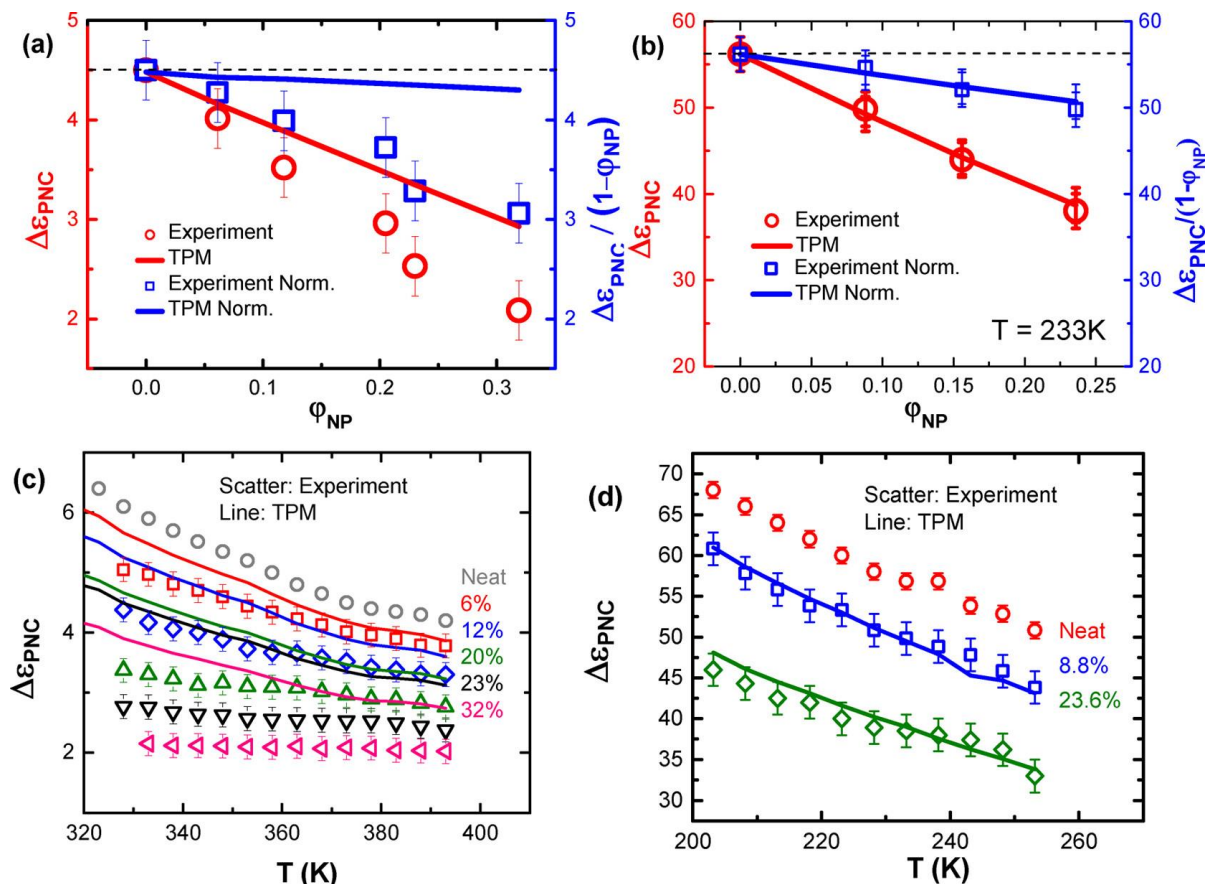


Figure 4.12: Dielectric amplitude of the nanocomposite with NP loading for PVAc-silica (a) and glycerol-silica (b). Plots present both experimental data (left Y-axis, red symbols) and the data normalized to the polymer volume fraction $1 - \phi_{NP}$ (right Y-axis, blue symbols). These amplitudes are compared to their corresponding two-phase model predictions (lines). Temperature dependence of the total dielectric amplitude of (c) neat polymer and PNCs (symbols) and (d) neat glycerol and glycerol-silica composites (symbols), with two-phase model predictions for both (lines) (Taken from [99]).

reduced to $\sim 30\%$ of its original value. This reduction coincides with recent studies of thin supported films which showed a similar reduction in Kirkwood–Fröhlich factor (expressed in terms of the measured dielectric amplitude $\Delta\epsilon$) in the interfacial layer [118]. The reduction in the dielectric amplitude can be as much as 80% depending on the thickness of the thin film [153]. The suppression of the Kirkwood–Fröhlich factor is not observed in the glycerol-silica system where chain connectivity is absent. Therefore, it is highly plausible that the reduction of the Kirkwood–Fröhlich factor can be attributed to chain stretching and alignment in the interfacial region [118], features that are well-known for polymer chains in the interfacial layer of PNCs [65, 88, 93, 154, 155]. This reduction in the Kirkwood–Fröhlich factor would manifest in a change in dielectric amplitude for the interfacial layer. Further, it would seem that these deviations between experiment and TPM prediction grow with NP loading (seen in Figures 4.12a and 4.12c).

4.4.5. Thickness of the Interfacial Layer

The thickness of the interfacial layer, l_{int} , is one of the key parameters defining the macroscopic properties of PNCs. All three approaches provide an estimate of l_{int} from the interfacial layer volume fraction (eq. 4.3). Figure 4.13 shows the temperature dependence of l_{int} obtained from the three different approaches at a given loading $\varphi_{NP} = 23$ vol %.

The two HN approach gives rather low values for the thickness of the interfacial layer. The reason for these low values is the two HN approach assumes the dielectric amplitude per volume is the same for the interface and the bulk; we have shown that the interfacial polymer apparently has a smaller dielectric response per volume owing to a reduced Kirkwood–Fröhlich factor. Combined with the reduced interfacial thickness, the ratio of the dielectric amplitude

between the interfacial layer and the bulk-like polymer varies very little with temperature in the two HN approach since the shape of the PNCs' spectra has only minor changes with temperature (Figure 4.11c). Consequently, the two HN functions approach suggests a negligible increase in l_{int} upon cooling (Figure 4.13a). On the contrary, the single HN and ILM approaches reveal an increase in the interfacial layer thickness resulting from the much weaker temperature variation of PNC dielectric amplitude than neat dielectric amplitude (Figures 4.11 and 4.12). In other words, the ratio $\frac{\Delta\epsilon_{bulk}(T)}{\Delta\epsilon_{neat}(T)}$ decreases with temperature, indicating a decrease in the population of bulk-like polymer segments upon cooling in PNCs. Because the Kirkwood–Fröhlich factor in the bulk-like polymer should be identical to the neat polymer, this result suggests a decrease in the bulk-like polymer fraction upon cooling and a corresponding increase in the interfacial layer fraction. The ILM approach captures this important feature of PNCs (Figure 4.13a). The single HN function also captures this feature; however, this result is likely a coincidence since the fit from a limited frequency range is not reliable. The two HN approach recovers this temperature dependence (see Figure 4.13b) if you take $\Delta\epsilon_{bulk}(T)/\Delta\epsilon_{neat}(T)$ as the fraction of the bulk-like polymer, with the interfacial layer fraction given by $\varphi_{int} = 1 - \varphi_{NP} - \frac{\Delta\epsilon_{bulk}}{\Delta\epsilon_{neat}}$. Justification for this interfacial thickness temperature dependence is observed in computer simulations in PNCs, where the increase in thickness on cooling has been ascribed to an increase of the cooperativity length scale upon cooling [152, 156].

We note that the interfacial layer thicknesses of the PNCs from the ILM approach are in the 3–5 nm range depending on the testing temperature. In a recent study [142], we summarized the interfacial layer thickness of different types of PNCs from previous publications and found an

aggregate thickness range of ~2–6 nm, depending on the polymer chain rigidity, molecular weight, and measurement temperature. This range is in line with this PVAc-silica system.

4.5. Conclusions

Dielectric measurements on a model PVAc-silica polymer nanocomposite (PNC) system revealed clear evidence of an interfacial layer with segmental dynamics much slower than in the neat polymer. The dielectric amplitudes of the PNCs show a much weaker temperature dependence on cooling than for the neat polymer, suggesting a strong increase in the interfacial layer thickness upon approaching T_g . Comparing the three different analysis approaches for the dielectric spectra of PNCs, we found the following conclusions. The single HN function can only fit part of the PNC's spectra and does not provide information on the interfacial layer dynamics. The two HN functions fit provides clear physical meaning of the thickness and dynamics of the

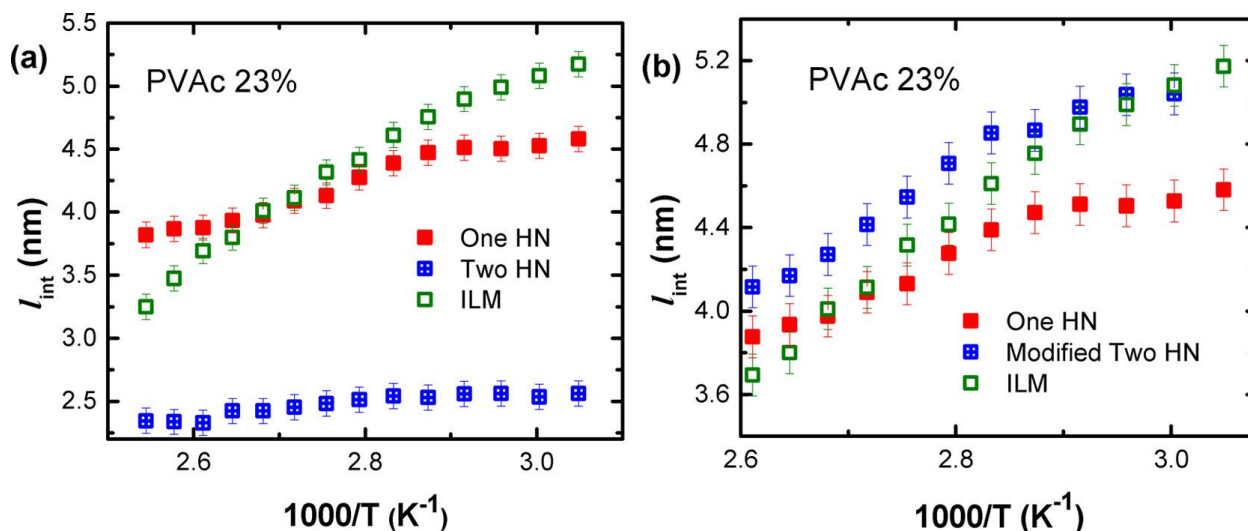


Figure 4.13: (a) Interfacial layer thickness, l_{int} , of PVAc-23% estimated from three different methods: the single HN function (filled red squares), the two HN function (blue squares with crosses), and the interfacial layer model (open squares). (b) The same data, except the two HN fit results use a modified two HN fit method (see *Heterogeneous Model Analysis* in Section IV.1 for details).

interfacial layer; however, it underestimates the thickness of the interface and cannot properly capture its temperature dependence. This approach also does not account for dielectric interference between the different PNC components, so while the two HN functions analysis can provide qualitative descriptions, it cannot be relied on for accurate quantitative estimations. The HMA approach that uses an interfacial layer model (ILM), based on analytical calculations accounting for three distinct dielectric contributions (nanoparticle, bulk polymer, and interfacial layer) as well as their interference terms, provides an excellent fit of the dielectric spectra for the entire frequency range. Moreover, the interfacial layer response from the ILM approach agrees well with the low frequency broadening of the PNC with free polymer removed.

Therefore, the ILM approach captured both the slowing down in interfacial dynamics and the strong temperature dependence of the interfacial layer thickness, providing the most accurate analysis of the dielectric spectra of PNCs. Our analysis also informs that the Kirkwood–Fröhlich factor that decreases for the PVAc chains in the interfacial layer is most probably caused by chain stretching. Our results demonstrate the robustness of both the ILM approach as well as dielectric spectroscopy itself to properly measure the quantitative features of polymer nanocomposites needed for this dissertation.

5. Influence of Chain Rigidity on the Interfacial Layer in Polymer Nanocomposites

In this chapter, the role of polymer chain rigidity on interfacial layer properties of polymer nanocomposites (PNC) is explored for four PNC systems. This chapter utilizes the ILM dielectric analysis methodology outlined in chapter 4. In addition to BDS, the interfacial layer thickness is determined from differential scanning calorimetry and small-angle X-ray scattering, giving a holistic aggregation of interfacial thickness estimates. This measured data is compared with other experimental data as well as computer simulations estimates from the literature. It is found that interfacial layer thickness grows significantly with chain rigidity above a certain threshold. Further, the interface is shown to grow with decreasing temperature at a rate which scales with fragility. Finally, a correlation is proposed between interfacial layer thickness of PNCs and the length scale of dynamic heterogeneity from descriptions of glass dynamics (e.g. Adam-Gibbs).

5.1. Introduction

The goal of this dissertation and polymer research in general is to study the properties of PNCs so they can be rationally designed for desirable technologies. Study of the 2-6 nm interfacial polymer layer surrounding nanoparticles is one of the main components of this research [7, 9, 58]. Experiments [76, 97, 157] and computer simulations [126, 127, 158] have revealed that the macroscopic properties of PNCs are largely determined by the thickness and dynamics of the interfacial layer. What needs to be more clearly elucidated is what specific parameters control this interface. As was covered in the literature review, properties of the

interfacial layer in PNCs depend on the size of nanoparticles [42] the molecular weight of the polymer [86], and polymer-nanoparticle interactions [156]. Another parameter that has yet to be covered experimentally in PNCs is the effect of polymer chain rigidity. Studies on thin films show that an increase in chain rigidity leads to higher ordering away from the substrate [159]. MD simulations [126] and theory [160] argue that a more rigid polymer chain should also affect the extent of polymers with modified dynamics. One of the main obstacles to confirming this effect in experiment is the confusion when comparing quantitative estimates of the interfacial properties from different techniques [9].

Aside from its importance to PNC research, the interfacial layer dynamics and thickness are thought to be closely connected to the general features of glasses, including the length scale of dynamic heterogeneity [23, 161], fragility [19], and the glass transition [14]. For example, Stevenson and Wolynes [162] have shown using calculations from random first order theory (RFOT) [24] that the extent of an interfacial layer with distinct dynamic properties should scale inversely to the configurational entropy of thin films. Further, the thickness of this interfacial layer should be proportional to the characteristic dynamic heterogeneity length scale, ξ . Recent simulations of thin films by Hanakata et al. [125] showed a direct proportionality between interfacial thickness and the characteristic length scale of “string-like” cooperative motion. Given what is proposed from theoretical considerations, the interfacial layer thickness and dynamics could potentially be used to experimentally probe the length scale and temperature dependence of cooperative relaxation. This pertinent information is absent from the literature owing to the previously discussed difficulties in probing the interfacial layer in PNCs.

In this chapter, three experimental techniques will be used to thoroughly characterize the structure and dynamics of the interfacial layer, which should account for potential systematic

discrepancies from an individual technique. These measurements will then be used to calculate molecular parameters of the interface, which will illuminate not only PNC properties but general properties of glasses. Specifically, we apply small-angle X-ray scattering (SAXS), temperature-modulated differential scanning calorimetry (TMDSC), and broadband dielectric spectroscopy (BDS) to study the structural, thermodynamic, and dynamic characteristics of the interfacial layer. Our analysis unambiguously demonstrates an increase in PNC interfacial layer thickness l_{int} with increasing polymer rigidity, which is defined by the characteristic ratio, C_∞ , of the polymer. The l_{int} is again found to increase upon cooling with BDS, and the temperature dependence of l_{int} , $-dl_{int}/d(T/T_g)$, is found to correlate with the fragility of the polymer matrix. These properties of l_{int} would not be observable without the heterogeneous ILM approach outlined in chapter 4. Our analysis also reveals a connection between l_{int} and characteristic dynamic heterogeneity length scale, ξ . These results indicate a potential avenue for experimental verification of theoretical predictions for dynamic heterogeneity and the origin of fragility in glass-forming systems.

5.2. Materials and Methods

Polymer Nanocomposite Preparation

Chain rigidity is quantified through the polymer characteristic ratio, C_∞ , [163] for which four polymers were chosen in this study: poly(propylene glycol) (PPG) ($C_\infty = 5.1$; molecular weight (MW) of 4.0 kg/mol; Scientific Polymer Products, Inc.); poly(methyl methacrylate) (PMMA) ($C_\infty = 7.0$; MW = 65 kg/mol); poly(vinyl acetate) (PVAc) ($C_\infty = 9.4$; MW = 40 kg/mol; Spectrum Chemical MFT, Corp.); and poly(2-vinylpyridine) (P2VP) ($C_\infty = 10.0$; MW = 101 kg/mol; Scientific Polymer Products, Inc.). The poly(methyl methacrylate) (PMMA) was

synthesized through reversible addition-fragmentation chain-transfer (RAFT) polymerization. The detailed characterizations of all these polymers are summarized in Table 1. The silica nanoparticles of a radius $R_{NP} = 12.5$ nm were synthesized by the same modified Stöber method [143] in a suspension of ethanol with a concentration of 15 mg/mL. Four loadings of $\varphi_{NP} = 11.8$, 20.5, 23.0, and 31.9 vol % are included for PVAc-silica to examine the effect of nanoparticle loading (this PVAc-silica data is the same data set as used in Chapter 4). For the three other PNCs, we studied a single loading: PPG-silica, PMMA-silica, and P2VP-silica with $\varphi_{NP} = 18$, 24, and 26 vol %, respectively. For the sake of brevity, the samples are coded by the polymer name followed by the nanoparticle loading φ_{NP} , e.g., PPG-18 is the PPG-silica nanocomposite with nanoparticle volume fraction $\varphi_{NP} = 18$ vol %.

The sample preparation procedures are as follows: PPG-18 and P2VP-26 were prepared by dissolving the polymer matrix in ethanol (0.3 g of polymer in 10 mL of ethanol) before adding the nanoparticle solution. PVAc-based PNCs were prepared in methyl ether ketone (MEK) (ACS grade, BDH solvents-B&H) by following a previous procedure [86]. In order to prepare PMMA-24, the MEK/silica suspension was first prepared by a solvent dialysis that replaces the ethanol of the ethanol/silica solution with MEK. After that, the PMMA-24 were prepared in MEK with the now MEK/silica solution. All the PNC solutions were transferred into 25 mL Teflon dishes and dried in a fume hood at 20°C for 48 h before further drying under high vacuum (10^{-5} bar) for 1 week. The drying temperatures in the vacuum oven were 40 °C for neat PPG and PPG-18, 150 °C for neat PMMA, neat P2VP, PMMA-24, and P2VP-26, and 80 °C for all PVAc samples, neat and PNCs. The extended annealing time is to help remove potential artifacts from sample preparation, which can alter the properties of PNCs [109]. The samples

Table 5.1: Molecular weight, nanoparticle loading, polydispersity (PDI), and characteristic ratio (C_∞) of the different polymer nanocomposites used in this study. Values for C_∞ taken from [163]. The sample names are the polymer hyphenated with the volume fraction of nanoparticles in that sample.

Sample	Molecular weight (kg/mol)	Loading (vol%)	Polydispersity (PDI)	C_∞
PPG-18	4.0	18	1.07	5.1
PMMA-24	31	24	1.13	7.0
PVAc-11.8	40	11.8	1.76	9.4
PVAc-20.5	40	20.5	1.76	9.4
PVAc-23.0	40	23.0	1.76	9.4
PVAc-31.9	40	31.9	1.76	9.4
P2VP-26	101	26	1.07	10.0

were annealed for $10^{13} \tau_\alpha$ to $10^{15} \tau_\alpha$ before any measurements; these times are longer than the characteristic chain desorption time measured in thin films [164].

Thermogravimetric Analysis (TGA)

NP loadings were determined by thermogravimetric analysis (TGA) (TA, Discover Q50) with a heating rate of $20^\circ\text{C}/\text{min}$ from 40 to 800°C under air. The accuracy of this instrument is $2 \mu\text{g}/2 \text{ mg}$ (0.1%). For calculating the volume fraction of nanoparticles, ϕ_{NP} , the mass densities are $\rho_{NP} = 2.40 \text{ g}/\text{cm}^3$ for neat nanoparticles and $\rho_m = 1.01, 1.18, 1.20$, and $1.22 \text{ g}/\text{cm}^3$ for neat PPG, neat PMMA, neat PVAc, and neat P2VP. All the densities are measured at 20°C under 1 atm by pycnometry. The average interparticle surface-to-surface distance, d_{IPS} , is estimated by assuming a random distribution of the nanoparticles [144] and presented in Table 2.

Temperature-Modulated Differential Scanning Calorimetry (TMDSC)

The TMDSC of all samples except neat PPG and PPG-18 was carried out on a TA Q2000. The PNCs were first heated up to 200°C , annealed for 20 min, and then cooled down to -20°C with a cooling rate of $2^\circ\text{C}/\text{min}$ and modulation amplitude of $\pm 0.5^\circ\text{C}/\text{min}$. The TMDSC of

neat PPG and PPG-18 was carried out on a TA Q1000 from 40°C to -120°C with a cooling rate of 2°C/min and modulation amplitude of ± 0.5 °C/min.

Small-Angle X-ray Scattering (SAXS)

The small-angle X-ray scattering (SAXS) measurements were performed using a high-flux SAXS instrument (SAXSess mc2, Anton Paar, Austria) equipped with a Kratky block-collimation system and a sealed-tube Cu K α X-ray generator with a wavelength $\lambda = 0.154$ nm, operating at 40 kV and tube current = 50 mA. All SAXS measurements were performed in a transmission geometry at room temperature. The acquisition time for an individual spectrum was approximately 30 min. The scattered X-ray intensities were measured by a 2D charge couple detector with a spatial resolution of $24 \times 24 \mu\text{m}^2$ per pixel at a sample-to-detector distance of 309 mm. The scattering intensities, $I(q)$, measured as a function of half the scattering angle, θ , were first corrected for X-ray absorption, followed by a transformation to a plot of scattering intensity vs momentum transfer vector, q ($q = 4\pi \sin \theta / \lambda$), using the Anton Paar SAXSquant package.

The q dependence of the scattering intensity, $I(q)$, of polymer nanocomposites can be described by the following equation [92]:

$$I(q) = \int_0^\infty n(r)[P(q)]^2 S(q) dr \quad (5.1)$$

where $n(r)$ is the particle size distribution function, $P(q)$ is the form factor of a spherical nanoparticle, and $S(q)$ is the structure factor of the polymer matrix that accounts for the nanoparticle dispersion state in that matrix. The $n(r)$ is described by a Schulz distribution:

$$n(r) = \frac{1}{N} (z + 1)^{z+1} (r/r_{mean})^z \frac{\exp[-(z+1)r/r_{mean}]}{r_{mean} \Gamma(z+1)} \quad (5.2)$$

where N is the normalization factor, z is related to the polydispersity in terms of the normalized standard deviation via $z + 1 = (\overline{r^2}/r_{mean}^2 - 1)^{-1}$, r_{mean} is the average radius, and Γ represents the gamma function.

For well-dispersed spherical nanoparticles in the polymer melt, a hard-sphere model (without interface) and a core-shell model (with interface) are typically used to fit the SAXS data of the PNCs, as described in the literature review. The form factors are [92]

$$P(q)^2 = \frac{A}{V_c} \left[3V_c(\rho_c - \rho_{solv}) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} \right]^2 + C_0 \quad (5.3)$$

for the hard-sphere model and

$$P(q)^2 = \frac{A}{V_s} \left[3V_c(\rho_c - \rho_s) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} + 3V_s(\rho_s - \rho_{solv}) \frac{\sin(qr_s) - qr_s \cos(qr_s)}{(qr_s)^3} \right]^2 + C_0 \quad (5.4)$$

for the core-shell model. Here, A is a scale factor; $V_c = (4\pi/3)r_c^3$; $V_s = (4\pi/3)r_s^3$; ρ_c , ρ_s , and ρ_{solv} are the scattering length densities of the core, shell, and solvent, respectively; r_c is the radius of the core; $r_s = r_c + l_{int}$ is the radius of the entire core-shell structure with l_{int} being the thickness of the shell; and C_0 is the background. For PNC systems, the core is the silica nanoparticle, the shell is the interfacial layer, and the solvent is the polymer matrix. The structure factor, $S(q)$, which accounts for the particle-particle interactions, is a hard-sphere structure factor in both the hard-sphere model and the core-shell model.

When fitting the SAXS data, many parameters are predetermined to minimize the free variables. The form factor depends on the nanoparticle radius and volume fraction, the shell thickness, and the scattering length densities (SLDs) of the sphere, shell, and polymer matrix; these SLDs depend on the density of the material and its chemical composition. The densities (and thus SLDs) of the nanoparticle and the polymer matrices are determined by pycnometry, the

volume fraction of nanoparticles is determined by TGA, and the nanoparticle size distribution is measured using dynamic light scattering. The fit of the SAXS data describes the dispersion state of the nanoparticles as well as the thickness of the interfacial layer.

Transmission Electron Microscopy (TEM)

The PNCs were first microtomed with a Leica Ultra microtome EM UC7 using a diamond knife at ambient conditions with a step of 50 nm. The TEM measurements for these thin films were performed at ambient conditions on a Zeiss Libra 200 HT FE MC with an operating voltage of 200 kV and an emission current of 230 mA.

Broadband Dielectric Spectroscopy (BDS) Measurements

The BDS measurements in the frequency range 10^{-2} – 10^7 Hz were carried out using a Novocontrol Concept-80 system with an Alpha-A impedance analyzer and a Quatro Cryosystem temperature controller. PNCs films were first melt-pressed at temperatures well above their T_g to form a disc of diameter 14 mm and thickness 0.1 mm. Then the samples were sandwiched between two gold electrodes with a diameter of 20 mm before being transferred into the sample cell. For PVAc-based PNCs, the measured temperatures were from 180 °C with an interval of 20 °C down to 120 °C, then with an interval of 5 °C down to 40 °C, and then with an interval of 10 °C down to –100 °C. For P2VP- and PMMA-based PNCs, we started from 200°C with an interval of 5°C down to 100°C and an interval of 10°C down to 0°C. For PPG-based PNCs, the temperature range started from 20°C with a temperature interval of 5°C down to –120°C. A thermal equilibration of 20 min was performed before each measurement. A couple of temperatures below and above T_g were measured on heating to check for reproducibility. The BDS data was analyzed using the interfacial layer model (ILM) outlined in chapter 4.

Table 5.2: Table 2 Summary of the interfacial layer thickness, l_{int} , from small angle X-ray scattering (SAXS), temperature-modulated differential scanning calorimetry (TMDSC), and broadband dielectric spectroscopy (BDS).

Sample	Core radius (nm)	Shell thickness (nm)	SLD_{shell} ($\times 10^{-5} \text{\AA}^{-2}$)	$SLD_{solvent}$ ($\times 10^{-5} \text{\AA}^{-2}$)	TMDSC (nm)	BDS (T ~ 1.05 Tg) (nm)	BDS (T ~ 1.22 Tg) (nm)
PPG-18	11.3	1.3	0.9086	1.095	1.8	3.5	1.9
PMMA-24	9.03	2.3	0.701	1.093	2.1	N/A	N/A
PVAc-11.8*	9.07	2.14	0.739	1.391	2.5	N/A	N/A
PVAc-20.5*	9.1	2.32	0.890	1.395	2.4	4.7	3.4
PVAc-23.0*	8.91	2.43	0.913	1.400	2.4	5.0	3.8
PVAc-31.9*	8.90	2.30	0.913	1.430	2.2	N/A	N/A
P2VP-26*	15.0	4.7	N/A	N/A	3.4	5.4	3.7

5.3. Results

5.3.1. Small Angle X-ray Scattering (SAXS)

Good nanoparticle dispersion was achieved in all PNCs as evidenced from SAXS data (Figure 5.1a) [57] and the transmission electron microscopy (TEM) images (Figure 5.1b). Figure 5.1a shows the SAXS data for PNCs of similar loading for the four different polymers measured. A fit for the hard-sphere model (dashed dot pink lines) is shown for PMMA-24 and a fit for the polydisperse core-shell model (solid black lines) [92] is shown for each polymer. Several features should be pointed out: (1) The intensity, $I(q)$, does not level off but scales with $q^{-1.5}$ at low q ($q < 0.02 \text{\AA}^{-1}$) in almost all PNCs under study. The expected scattering dependence from NP aggregates at low q is q^{-4} , [165] so this low q scattering here is most likely from polymer matrix scattering that is not completely accounted for in the data reduction. (2) The hard-sphere model cannot fit the PNCs' SAXS data while the polydispersed core-shell model provides a reasonable fit. This result indicates the existence of an interfacial layer, which for SAXS measurements would be described as a polymer layer with modified density from the neat

matrix. The detailed fit parameters are presented in the Table 2. (3) The nanoparticle sizes in PPG-18 and P2VP-26 are slightly larger than in the other two PNCs because they were taken from different NP batches. Though nanoparticle size does affect the interfacial layer thickness, the variation from $R_{NP} = 9$ nm to $R_{NP} = 15$ nm should not be significant [42].

The obtained shell thickness reflects the contrast in density from the interfacial layer polymer in comparison to the neat polymer in PNCs. This “structural” interfacial layer thickness in PVAc-silica, l_{int} , varies from 2.13 to 2.43 nm with nanoparticle loading, an effect seen in a previous study [57]. However, l_{int} varies significantly with the type of polymer: l_{int} (PPG-18) = 1.3 nm, l_{int} (PMMA-24) = 2.3 nm, and l_{int} (P2VP-26) = 4.7 nm. These values of l_{int} estimated from density contrast seem to correlate with the interfacial thickness with the characteristic ratio C_{∞} of the polymer.

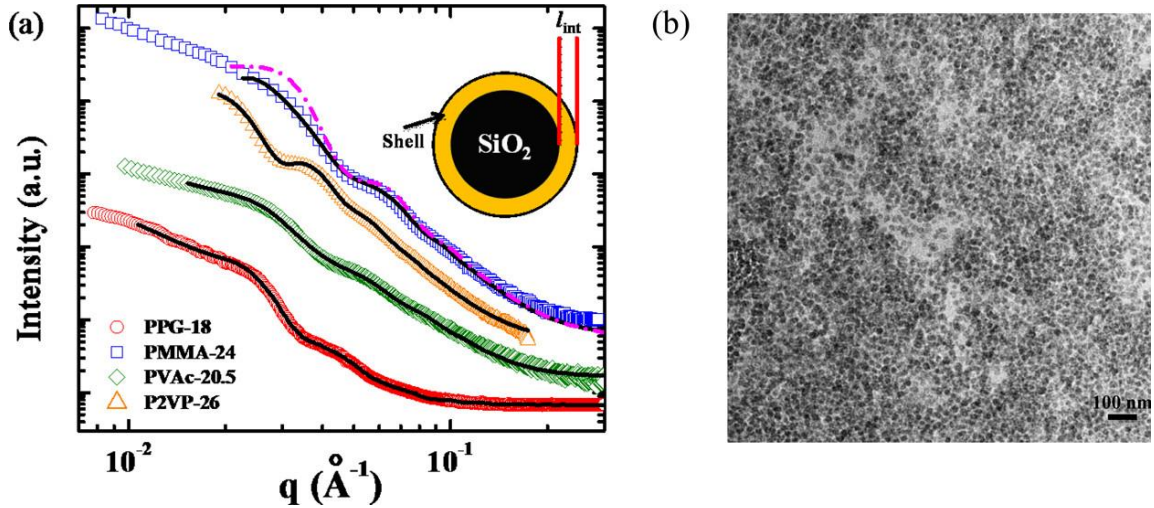


Figure 5.1: (a) Small-angle X-ray scattering (SAXS) measurements for PPG-18, PMMA-24, PVAc-20.5, and P2VP-26 at $T = 293$ K. The dashed-dot pink line is the hard-sphere model fit of PMMA-24, demonstrating the failure of the model to fit the data. The solid black lines are the polydispersed core-shell model fits (geometry shown in inset). The P2VP-26 data and its fit are taken from [57]. The shell thickness, l_{int} , can be extracted by the scattering length density (SLD) contrast between the shell, the nanoparticle, and the rest of the matrix. The fit parameters used are presented in the Table 2. (b) A

representative TEM image for PVAc-23 demonstrating the good nanoparticle dispersion state in the PNCs.

5.3.2. Temperature-Modulated Differential Scanning Calorimetry (TM-DSC)

Separate from structural measurements, the TMDSC analysis procedure described in section III.1 of chapter 4 can provide thermodynamic indicators associated with the interfacial layer [57, 63]. Figure 5.2 compares the normalized specific heat capacity, $C_p^{mat} = \frac{C_p^{PNC} - C_p^{NP} m_{NP}}{1 - m_{NP}}$, of the PVAc nanocomposites for different loadings to the neat PVAc (these data are the same as plotted in Figure 4.1b of chapter 4). The extended tail or shoulder in the glass transition step can be attributed to the presence of the interfacial layer and can be used to estimate the extent of the interfacial layer. The interfacial layer's contribution to the glass transition step, δC_p , can be described by the difference in specific heat capacity at T_g for the neat polymer, ΔC_p , and the normalized polymer matrix heat capacity, ΔC_p^{mat} , given by $\delta C_p = \Delta C_p - \Delta C_p^{mat}$ (more clearly visualized in Figure 5.2). This δC_p can be used to estimate the volume fraction of the polymer belonging to the interfacial layer, since both interfacial and neat polymer components contribute to the polymer glass transition step. The volume fraction of the interfacial layer as well as its thickness can be determined by:

$$\varphi_{int} = (1 - \varphi_{NP})\delta C_p / \Delta C_p \quad \text{and}$$

$$l_{int} = R_{NP} \left(\left(\frac{\varphi_{int} + \varphi_{NP}}{\varphi_{NP}} \right)^{1/3} - 1 \right) \quad (5.5)$$

The error bars from the estimate of l_{int} (inset in Figure 5.2) are sizeable considering the uncertainty of determining ΔC_p and δC_p . These estimates also find negligible differences in l_{int} with NP loading (inset Figure 5.2), consistent with previous reports [57, 99].

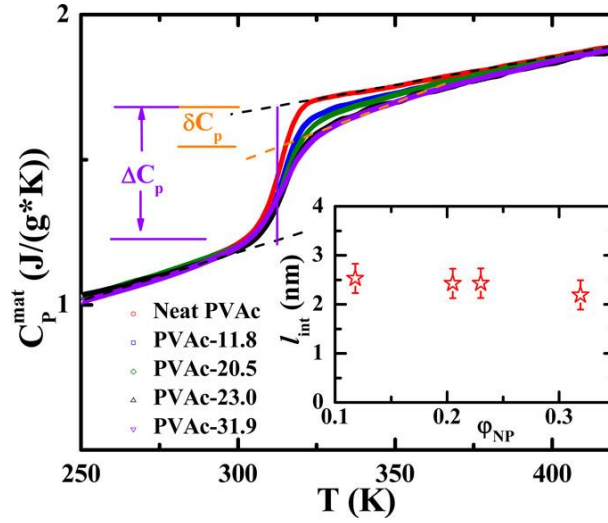


Figure 5.2: Normalized specific heat capacity, C_p^{mat} , of PVAc-based PNCs for different loadings where the data is normalized for silica contribution. The ΔC_p (purple) is the specific heat capacity jump at T_g for the neat PVAc. The contribution of the interfacial layer to the normalized specific heat capacity, δC_p , (shown for PVAc-31.9 in orange) is defined by: $\delta C_p = \Delta C_p - \Delta C_p^{mat}$, where the ΔC_p and ΔC_p^{mat} values are evaluated at T_g . The inset shows the estimate of the interfacial layer thickness, l_{int} , of the PVAc PNCs at different loadings; there is a small decrease with increased loading.

The same analyses are applied to the PNCs with different polymer matrices in Figure 5.3, where the red lines are the neat polymers and the blue lines are the PNCs. Notably, the width of the glass transition, ΔT_g , defined as the gap between the temperature at which the C_p^{mat} and C_p meet and the T_g of the neat polymer (shown more clearly in Figure 5.3), is different for different polymer chain rigidities: $\Delta T_g = 15\text{K}$ for PPG-18, 31K for PMMA-24, 37K for PVAc-23, and 43K for P2VP-26. Further, the fraction of heat capacity step size associated with this broadening, $\delta C_p / \Delta C_p$, increases from 0.11 in PPG-18 to 0.37 in P2VP-26. This effect leads to the following values for thermodynamic interfacial layer thickness: $l_{int} = 1.8\text{ nm}$ for PPG-18, 2.1 nm for PMMA-24, 2.4 nm for PVAc-23, and 3.4 nm for P2VP-26. Once again l_{int} , this time estimated from the TMDSC measurements, increases with increase in chain rigidity, in good agreement with the SAXS data.

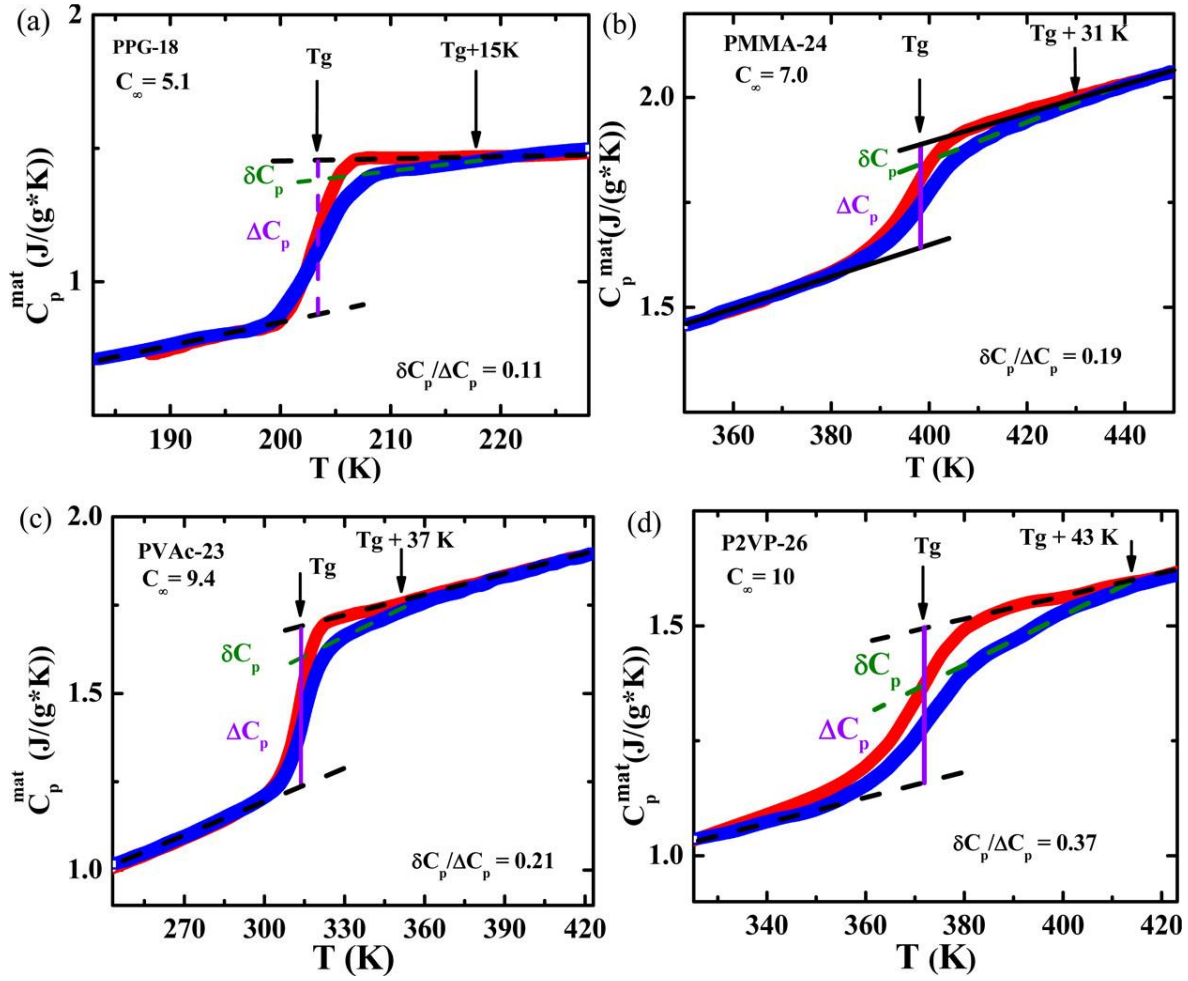


Figure 5.3: Normalized specific heat capacity (blue curves), C_p^{mat} , for the four different types of polymer nanocomposites (PNCs): (a) PPG-18, (b) PMMA-24, (c) PVAc-23, and (d) P2VP-26, with their corresponding neat polymers (red curves). The specific heat capacity step size for the neat polymer at T_g are labeled ΔC_p for each case (purple). The interfacial contributions to the specific heat capacity jump at T_g are labeled δC_p (green). The values of these two quantities at T_g can be used to estimate the thermodynamic interfacial layer volume fraction by $\phi_{int} = (1 - \phi_{NP})\delta C_p / \Delta C_p$.

5.3.3. Broadband Dielectric Spectroscopy (BDS)

The dielectric loss spectra, $\varepsilon''(\omega)$, of the PNC (PVAc-20.5) and the corresponding neat polymer spectra are shown in Figure 5.4a. All the features relating to the presence of the interfacial layer identified in Chapter 4 are noticeable. The interfacial process is also shown in both the derivative spectra, $\varepsilon'_{der}(\omega) = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln \omega}$, and the relaxation time distribution analysis spectra, $\Delta\varepsilon * g(\ln\tau)$, seen in Figure 5.4a and 5.4b.

The interfacial layer model (ILM) [86, 148, 166] outlined in Chapter 4 is applied to each of the polymer nanocomposites to analyze the dynamic features of the interfacial layer. A sample fit of the spectra is included in Figure 5.4a for the neat and the PVAc-20.5 PNC. This method again is used to make estimates of the interfacial layer fraction as well as the characteristic relaxation time of the interfacial process, $\tau_{\alpha'}$. The PMMA-24 is omitted for this analysis because its dominant secondary relaxation process completely engulfs the dielectric signal of the segmental relaxation, preventing conclusive analysis of the interface. Figure 5.4f shows the interfacial layer thicknesses l_{int} for the different polymers as a function of temperature, where the error bars are determined from the uncertainty in the interfacial volume fraction. The inset shows the derivative of the l_{int} vs T/T_g as a function of the fragility taken from a VFT fit of the peak positions. The interfacial layer thicknesses at $T = 1.2T_g$ are $l_{int} = 1.9$ nm for PPG-18, 3.4 nm for PVAc-20.5, and 3.7 nm for P2VP-26, values which increase with cooling (Figure 5.4f). The dynamic l_{int} increases with increasing chain rigidity, similar to structural and thermodynamic interfacial estimates. One might expect a slowing down in interfacial segmental dynamics, $\tau_{\alpha'}(T)/\tau_{\alpha}(T)$, with increased chain rigidity; however, no such slowing down occurs (Figure 5.4c-e). One potential explanation is these polymers differ in polymer-nanoparticle

interaction strength, which recent MD simulations [126] have shown will strongly affect the dynamics. Further, there does not appear to be strong variation of the ratio of the two VFT curves with temperature (Figure 5.4c-e), indicating minimal deviation in the interfacial process's fragility from the neat polymer.

5.4. Discussion

5.4.1. Role of Chain Rigidity

Independent estimates of the interfacial layer thickness were based on three experimental techniques that probe different aspects of the polymer interfacial layer: the structural (SAXS), the thermodynamic (TMDSC), and the dynamic (BDS). All three methods show the same dependence of l_{int} at $T \sim T_g$ with the polymers' values for C_∞ , as can be seen in Figure 5.5a. The three techniques give different values for an individual polymer system; these discrepancies result from limitations in analysis or measurement technique. For instance, the TMDSC model analysis is relatively rudimentary, and would greatly depend on evaluating the slope of the shoulder. Likewise, the SAXS and BDS results are the result of fitting analysis which contains free parameters. Given the high experimental accuracy and broad frequency range, the quantitative values from BDS analysis are probably the most accurate evaluation of interfacial layer thickness. Nevertheless, the trend is clear for all three methods: l_{int} increases with an increasing C_∞ .

Figure 5.5b compares this study's BDS results for l_{int} with literature data taken at temperatures well above T_g ($T = 1.2-1.3T_g$) in order to bolster the argument about chain rigidity. Glycerol is taken to have $C_\infty = 1$ because it is a small molecule with no connectivity. This collection of PNC data suggests the apparent existence of a critical C_∞ . The l_{int} increases

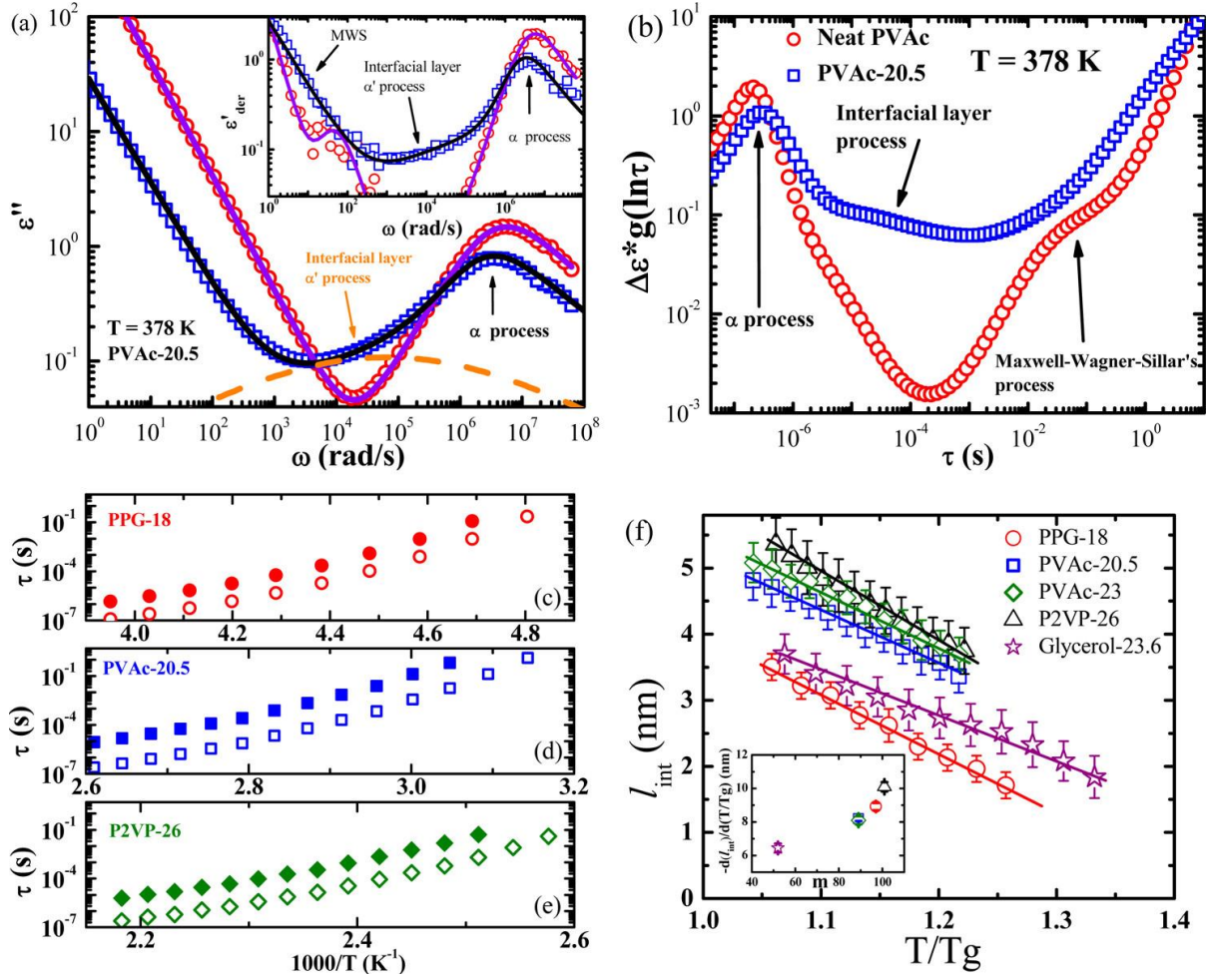


Figure 5.4: (a) Dielectric loss spectra, $\varepsilon''(\omega)$, and the derivative spectra (inset), $\varepsilon'_{der}(\omega)$, of neat PVAc (red circles) and PVAc-20.5 (blue squares) at $T = 378$ K demonstrating the effect of the interface on dielectric spectra. The neat PVAc (purple line) is fit with a single Havriliak–Negami function while the PNC (black line) is fit with the interfacial layer method outlined previously in chapter 4, where the interface (dashed-orange line) has a distinct dielectric function. (b) The relaxation time distribution analysis where the interfacial layer process can be clearly discerned as a shoulder with slower characteristic dynamics. The segmental relaxation time (open symbols), τ_α , and interfacial layer relaxation time (filled symbols), $\tau_{\alpha'}$, of the (c) PPG-18, (d) PVAc-20.5, and (e) P2VP-26. The average interfacial layer slowing down, $\tau_{\alpha'}/\tau_\alpha$, is 12, 35, and 25 for PPG-18, PVAc-20.5, and P2VP-26, respectively. (f) Interfacial layer thickness, $l_{int}(T/T_g)$, estimated using the interfacial layer model. The inset shows the slope of each line, $-dl_{int}/d(T/T_g)$, vs fragility index, m , of the corresponding neat matrices. The data for glycerol-23.6 nanocomposite are taken from [99].

strongly above $C_\infty \sim 5-7$; below this critical value the interfacial layer thickness appears insensitive to chain rigidity. This result is consistent with an earlier coarse-grained MD simulations study [126] for a fixed polymer-wall interaction. In that study, the polymer-wall interaction was chosen to mimic hydrogen bonding in a polymer nanocomposite, with the interfacial layer being defined as the distance at which the wall stops influencing chain motion. The chain rigidity itself was tuned by a chain bending potential. To compare these simulation results to our experimental data directly, we express the characteristic ratio as $C_\infty = 2 l_p / l$, where l_p is the persistence length of the chain and l is the bond length in the simulations. This calculation gives a similar behavior for chain rigidity, including an apparent critical C_∞ (Figure 5.5b).

There are a couple caveats about these conclusions related to the experimental measurements themselves. First, the ideal study would be to only tune the chain rigidity of the polymer, keeping other related parameters (such as polymer-nanoparticle interactions) constant. In real experiments this is impossible because changing the C_∞ in experiments changes the polymer chemistry itself, in turn altering such parameters as the polymer-nanoparticle interactions. We therefore cannot attribute the observed experimental results to chain rigidity with complete certainty. However, molecular dynamics simulations allow easy separation of chain rigidity and polymer-nanoparticle interaction. What these studies [126, 152] show is that the interfacial layer thickness is not sensitive to polymer-nanoparticle interactions, meaning the effect can be solely attributed to the chain rigidity in simulation. The experimental results in Figure 5.5 provide the first experimental test confirming these simulations results.

The second consideration is that the polymers studied here have different molecular weights ranging from 4 kg/mol for PPG to 101 kg/mol for P2VP. This difference is unavoidable

based on the chemistry of these different polymers and what molecular weights can be mixed with nanoparticles. As pointed out in the literature review, an increase in molecular weight in PNCs causes a relatively small decrease in the interfacial layer thickness [86], an effect ascribed to a frustration in chain packing. So even if the molecular weight has a minor effect on the quantitative results, it would only enhance the conclusion since we found a smaller interfacial layer thickness for the shorter chains used in this study (PPG of 4kg/mol). The literature data includes polymers with different molecular weights for the same type of PNC, so the effect of molecular weight is likely relatively insignificant to the final conclusions.

5.4.2. Role of Dynamic Heterogeneity Length Scale

Experimental and computer simulation studies suggest the existence of a critical characteristic ratio below which the interfacial layer thickness is insensitive to changes in C_∞ . This behavior requires a physical explanation in order to fully understand chain rigidity's relationship to macroscopic properties of PNCs. One hypothesis is this minimum interfacial layer thickness is the characteristic length scale of dynamic heterogeneity, ξ , also known from Adam-Gibbs theory as the cooperative rearranging region (CRR) length scale [23]. The value of this length scale is usually $\sim 2\text{--}3$ nm [167] for most of the materials but is known to be larger for rigid polymers [168].

A relationship between the l_{int} and the dynamic heterogeneity length scale ξ has been suggested for polymer thin films in both theory [162] and simulations [125]. This relationship has not been experimentally demonstrated because there are very few direct measurements of the dynamic heterogeneity length scale. Direct measurements can be done with multidimensional NMR [169, 170]; however, an indirect estimate of ξ can also be taken from the low-frequency

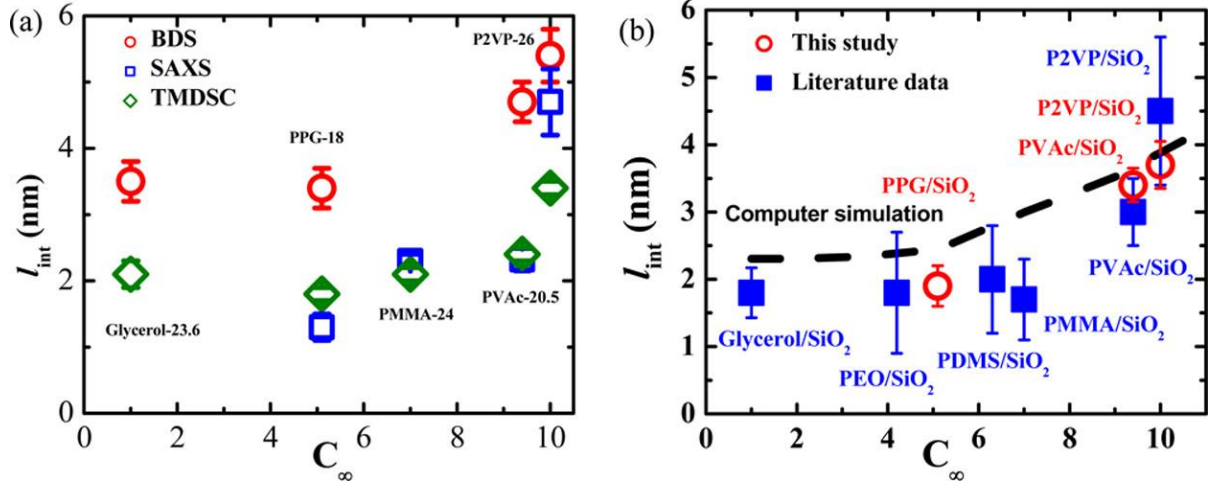


Figure 5.5: (a) The l_{int} vs C_∞ taken for temperatures just above T_g ($T = 1.05T_g$) from the three different techniques in this study. From left to right: glycerol-23.6, PPG-18, PMMA-24, PVAc-20.5, P2VP-26. The glycerol-23.6 nanocomposite data are taken from [99]. (b) The l_{int} vs C_∞ at slightly higher temperature ($T = 1.2T_g$) for PPG-18, PVAc-20.5, and P2VP-26 from left to right (red circles). Blue squares are literature data measured at temperatures ranging from $T = 1.2$ – $1.3T_g$: from left to right, glycerol-silica (refs [99] and [171]), poly(ethylene oxide)-silica (refs [96, 172, 173]), polydimethylsiloxane-silica (refs [174–176]), PMMA-silica (refs [63] and [114]), PVAc-silica (refs [86] and [106, 177]), and P2VP-silica (refs [42], [57], and [65]). The error bars for the blue squares account for measurements done by different groups and from different methods. The dashed-black line gives l_{int} estimates from MD simulations [126], which shows an apparent critical C_∞ above which the l_{int} increases strongly.

collective vibrations of the Boson peak [167]. Figure 5.6 shows the l_{int} at $T = 1.2T_g$ for PNCs plotted versus ξ estimates from both NMR, ξ_{NMR} , and the Boson peak, ξ_{BP} . We see for both direct and indirect estimates of ξ a good correlation with the interfacial layer thickness. Again, there is some dependence of these values of l_{int} on molecular weight and nanoparticle loading and size, so there are sizeable error bars in the vertical direction. There are even larger error bars for the value of ξ measured from experiments. Still, within one order, there seems to be a relationship between l_{int} from PNCs and experimental values for dynamic heterogeneity length scale ξ . These quantitative results, though not exact, suggest that $l_{int} \sim \xi$ for PNCs. This relationship is in contrast with predictions from RFOT theory, which estimate that the propagation of dynamic changes occur as far as $\sim 10-20 \xi$ from the free surface of a glassy material [162].

The proposed relationship between interfacial layer thickness l_{int} and length scale of dynamic heterogeneity ξ is also reinforced by the shared temperature dependence of the two quantities: both increase with cooling [23]. This temperature dependence is echoed in recent MD simulations studies [127, 152, 156], which showed that for attractive polymer-NP interactions, there is enhanced “string-like” cooperative motion with cooling. Moreover, the increase in ξ upon approaching T_g is expected to be stronger in more fragile systems, where there is a steeper slowing down in segmental dynamics upon cooling to T_g . Looking at the inset of Figure 5.4f, we indeed see an increase in the temperature derivative of l_{int} , $-dl_{int}/d(T/T_g)$ with fragility m , taken from BDS measurements. These estimates give strong experimental support to previous theoretical analyses [125, 127] arguing for a direct connection between the length of string-like cooperative motion (which is analogous to the interfacial layer in PNCs) and fragility. Therefore, the presented experimental analysis which is verified using three experimental techniques reveals

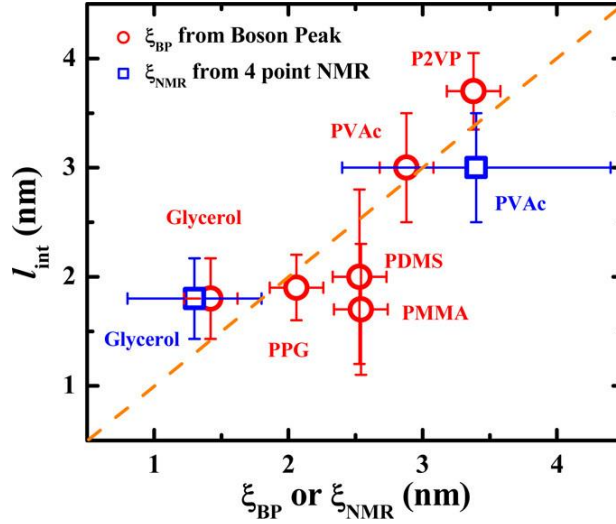


Figure 5.6: The estimated l_{int} for the different nanocomposites shown in Figure 5.6b at $T = 1.2T_g$ vs the dynamic heterogeneity length, ξ , of the corresponding neat polymers. The blue squares (refs [169] and [170]) represent ξ estimates from four point NMR measurements taken at temperatures above T_g , ξ_{NMR} , and the red circles (refs [167] and [168]) represent Boson peak measurements take at T_g , ξ_{BP} . The dashed line shows $l_{int} = \xi$, which has a correlation coefficient of $R^2 = 0.58$ for the presented data.

for the first time a direct link between the interfacial layer thickness and the characteristic length scale of dynamic heterogeneity, both of which depend on polymer chain rigidity and temperature.

5.5. Conclusions

The effect of polymer chain rigidity on interfacial layer thickness and dynamics is probed using three experimental techniques that looked at the structural, thermodynamic, and dynamic signatures of the interfacial layer. The combination of all three methods plus literature data from experiment and computer simulations showed that there exists a critical chain rigidity, as defined by the characteristic ratio, at which the interfacial layer thickness will increase significantly with further increase in rigidity. Additionally, a relationship between the interfacial layer thickness l_{int} in PNCs and the dynamic heterogeneity length scale ξ is experimentally established; this

relationship has been previously proposed in theory and simulations studies. The temperature dependence of the interfacial layer measured from BDS further reinforces this relationship, as both the l_{int} and ξ increase with decreasing temperature towards T_g . The rate of this increase for ξ with temperature is stronger in more fragile systems, and we see that this dependence on fragility also exists for the l_{int} in PNCs. This comparison between the l_{int} and ξ is possible because of the ILM analysis approach, reiterating how accurate BDS analysis can provide new insights for PNC research. The effect of chain rigidity on l_{int} also reinforces the importance of polymer properties at the interface and how they can be probed with different techniques. These results are interesting from the perspective of polymer nanocomposite design as another parameter with which to alter potential macroscopic properties. More broadly useful is a potential experimental approach to verify quantitative details about dynamic heterogeneity as well as the origin of fragility, topics important to amorphous glasses in general.

6. Effect of Chain Ordering on Dielectric Amplitude in Different Polymer Nanocomposite Systems

This chapter explores the dielectric response of three polymer systems: neat polymer, polymer nanocomposites (PNCs), and polymer-adsorbed nanoparticles (ANPs). This third system is made from PNCs where the free polymer is removed. These systems are studied systematically with molecular weight where it is found that the temperature dependence of each system's dielectric amplitude behaves differently. This chapter explores in detail an effect found in chapter 4: while the neat polymer's dielectric amplitude follows the Curie-Weiss law, the PNC and the polymer-adsorbed nanoparticles depart from this temperature behavior. The PNC dielectric amplitude appears roughly constant with temperature, whereas the ANPs' dielectric amplitude decreases with decreasing temperature (a surprising effect opposite from Curie-Weiss behavior). This effect is explained by chain ordering in the system, where stretched or flattened chains have hindered dipole reorientation that becomes less restricted with increasing temperature. A qualitative description is proposed where the energy of interaction between attached chains is related to the dielectric amplitude. This interaction energy for the polymer-adsorbed NP system decreases with molecular weight, coinciding with decreased segmental relaxation times at highest MW. These results demonstrate that composite systems with stretched or flattened chains have modified dielectric amplitude behavior, indicating the potential importance of this parameter for describing the properties of the interfacial layer itself.

6.1. Introduction

The importance of studying the interfacial structure and dynamics in polymer nanocomposites (PNCs) has already been well established [57, 58, 65, 87, 147, 166, 173, 177]. Broadband dielectric spectroscopy (BDS) [12, 106, 140] can be employed to track polymer relaxation processes with temperature which can reveal many properties of polymer nanocomposites with proper analysis [142, 166]. In chapter 4 we discussed spectral shape and relaxation time of dielectric spectra for PNCs, and how these parameters are used to give quantitative estimates of the interfacial layer volume fraction. The use of changes in segmental relaxation time to determine the interfacial volume fraction is commonplace in the literature for PNCs [42, 57, 166, 176]. Another important quantity from the dielectric spectra is the dielectric amplitude, $\Delta\epsilon$. The dielectric amplitude, as discussed in Chapter 3, is given by:

$$\Delta\epsilon = \epsilon_s - \epsilon_\infty = \frac{1}{3\epsilon_0} F g \frac{\mu^2}{k_B T} \frac{N}{V} \quad (6.1)$$

In this equation, μ is the dipole magnetic moment, T is temperature, $\frac{N}{V}$ is the number density of dipoles, F is the Onsager factor, and g is the Kirkwood-Fröhlich factor, the unitless factor related to an individual dipole's relative rotational freedom [12]. For neat polymers, the dielectric amplitude typically follows the Curie-Wiess Law, where the dielectric amplitude increases with decreasing temperature. In chapter 4, we found that for the poly-vinyl acetate (PVAc)-silica PNCs, the dielectric amplitude remains roughly constant with decreasing temperature. Further, by analyzing the decrease in dielectric amplitude with loading, we found the interfacial polymer has a reduced dielectric amplitude from the neat polymer [178]. The physical origin of this suppressed dielectric amplitude with loading was attributed to chain stretching that reduced the

Kirkwood-Fröhlich factor. Other BDS studies have demonstrated the importance of chain organization, where interfacial properties have been shown to change with loading and molecular weight owing to chain packing [86]. It is worthwhile to explore in detail what the dielectric amplitude and its temperature dependence can tell about molecular structure and organization in the interface of PNCs.

This chapter explores this topic by examining the BDS spectra of three P2VP polymer systems with different molecular weights (see Figure 6.3): (1) neat polymer (P2VP), (2) regular PNC of P2VP-silica, and (3) polymer-adsorbed nanoparticles (ANPs) of P2VP-silica, which are made from regularly blended PNCs with the free polymer removed by solvent washing [87]. The polymer layer surrounding the nanoparticle for these polymer-adsorbed NPs will be referred to as the “adsorbed layer”. The temperature dependence of the dielectric amplitude was analyzed for all three systems at different molecular weights. In agreement with previous studies [99, 166], the neat systems followed the Curie-Weiss temperature dependence, whereas the regular PNC show very little temperature variations. The polymer-adsorbed NPs showed behavior opposite Curie-Weiss (dielectric amplitude *decreased* with decreasing temperature) and a significant overall reduction in dielectric amplitude relative to the neat polymer. This behavior is explained by the restricted reorientation of dipoles in stretched or flattened chains, which become freer as temperature increases. This effect is counterbalanced in PNCs by the neat fraction whose lack of dipole ordering results in the expected decrease of dielectric amplitude with temperature. A qualitative model for the polymer-adsorbed NPs is proposed that describes dielectric amplitude in terms of a characteristic interaction energy of a single adsorbed chain with the surrounding chains. This interaction energy is found to decrease with molecular weight, coinciding with the faster segmental relaxation times found in the highest molecular weight

polymer-adsorbed NPs. We argue that changes in the dielectric amplitude with temperature are the result of the restricted motion of dipoles in the polymer chains, and that these effects can be ascribed to the stretching or flattening of chains in the interfacial layer. These dielectric amplitude results have significant implications for estimations of the interfacial layer in polymer systems.

6.2. Sample Preparation and Methods

Sample preparation.

Poly(2-vinylpyridine) (P2VP) of molecular weights 9k, 36k, 101k, and 404k were purchased from Scientific Polymer Products. Table 1 lists the densities and radii of gyration of the different molecular weights, where the densities were measured from a previous small-angle X-ray scattering study [179]. Ethanol, ammonium aqueous solution (30–33 wt %), and tetraethyl orthosilicate (TEOS, >95%) were purchased from Sigma Aldrich and were used as received. A colloidal silica nanoparticle ($D = 20$ nm) suspension in ethanol was synthesized using the modified Stöber method according to previous reports [143, 180].

The polymer nanocomposite (PNC) samples were prepared with the previously described procedure where 0.5 gram of polymer was dissolved in ethanol and the silica-ethanol suspension was added dropwise. The targeted final concentration of nanoparticles was 30wt% for each molecular weight. The nanocomposite solutions were stirred for 6 hours before being poured into Teflon dishes where they evaporated for 12 hours in the hood. The remaining solvent was removed by vacuum drying the samples at 120°C at 1mbar for one week prior to measurement. Neat samples were prepared in a similar manner without the addition of nanoparticle solution. Both the neat and PNC samples are transparent after drying.

The polymer-adsorbed nanoparticles (ANPs) were made with a similar mixing procedure as for the PNCs, where 0.5 g of nanoparticles was targeted for a 30wt% PNC solution. After stirring overnight, the solution was divided into 2mL vials where they were centrifuged for one hour. The free polymer floats to the top of the vial and the precipitate composed of the ANPs is forced to the bottom. The solvent (which should be transparent since it contains only miscible free polymers) is then syringed out and set aside. The remaining precipitate at the bottom of each vial is re-dissolved in 1mL of ethanol via sonication for 10-15 min. The sonication is weak enough that the adsorbed polymer should not detach. This centrifugation procedure was repeated twice meaning the sample was centrifuged or “cleaned” a total of three times. After the final centrifugation, the precipitate was removed from each vial with a small amount of ethanol and the combined precipitates dried in a Teflon dish overnight. The powder that remained was then dried at 120°C at 1mbar for at least one week prior to measurement.

Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) with a Discover Q50 (TA Instruments) was used to confirm the final weight percent of the nanoparticles in the blended PNCs and ANPs after drying. The sample was heated at a rate of 20°C/min to 900°C.

Broadband Dielectric Spectroscopy (BDS)

Broadband dielectric spectroscopy (BDS) measurements were carried out using a Novocontrol Concept-80 system with an Alpha-A impedance analyzer and an active ZGS sample holder, in concert with a Quatro Cryosystem temperature controller with a temperature stability of ± 0.1 °C. All samples were measured between two gold-coated electrodes; the neat polymer and PNC were able to be pressed into films, while the ANPs were ground into a fine powder. A

frequency range of 10^{-2} to 10^7 Hz was used for a temperature range of 180°C to 90°C in cooling steps of 5°C, followed by cooling steps of 10°C for 80°C to -50°C. The samples equilibrated for 20 min at each temperature step prior to measurement.

Table 6.1: Characteristics of polymers used in the PNC study.

Molecular Weight MW [g/mol]	Density $\rho_{polymer}$ [g/cm ³]	Radius of Gyration R_g [nm]	Silica wt% (PNC)	Silica wt% (Polymer-adsorbed NPs)	Polymer-adsorbed layer d [nm]	d/R_g
9k	1.129	2.67	28.3%	73.7%	2.11	0.79
38k	1.194	5.33	28.1%	70.1%	2.33	0.44
101k	1.211	8.89	28.5%	70.4%	2.28	0.26
404k	1.224	17.78	34.8%	58.3%	3.45	0.19

6.3. Results

6.3.1. Thermogravimetric Analysis (TGA)

The silica loading fractions of the PNCs and ANPs taken from TGA are included in Table 1 in weight %. The PNCs have final silica concentrations of approximately 30wt%, whereas the ANPs decrease from 74wt% at 9k to 58wt% at 404k, as seen in Figure 6.1. We can roughly estimate the number of polymer chains per nanoparticle, x , for the ANPs using the following expression:

$$x = \frac{N_{polymer}}{N_{NP}} = \frac{N_A(1-\varphi_{NP})}{MW} \frac{4\pi R_{NP}^3 \rho_{NP}}{3\varphi_{NP}} \quad (6.2)$$

Here $R_{NP} = 10$ nm and $\rho_{NP} = 2.45$ g/cm³ are the radius and density of the nanoparticles, MW and $\rho_{polymer}$ are the polymer molecular weight and density, φ_{NP} is the mass fraction of the

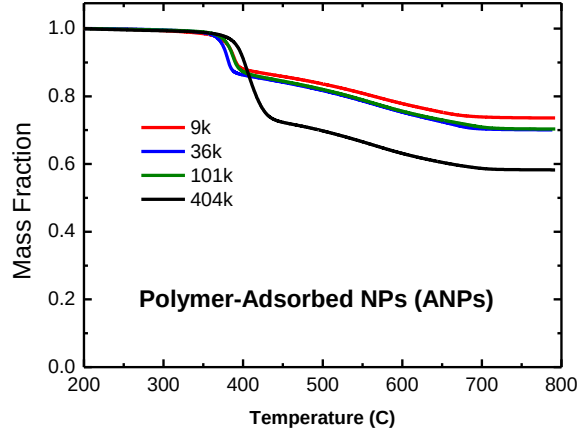


Figure 6.1: Thermogravimetric analysis data for the polymer-adsorbed NPs of different molecular weight.

nanoparticles measured by TGA for the polymer-adsorbed NPs, and N_A is Avogadro's number. These quantities are listed in Table 1. The number of chains per nanoparticle x decreases from a few hundred at 9k to roughly 10 at 404k, as seen in Figure 6.2a. If we assume that the polymer forms a homogeneous layer around the nanoparticle and that the density of the adsorbed layer matches that of the bulk polymer, $\rho_{polymer}$, we can then estimate the expected thickness of the adsorbed layer, d .

$$d = R - R_{NP}$$

$$R = \left(R_{NP} + x \frac{3}{4\pi} \frac{MW}{\rho_{polymer} N_A} \right)^{1/3} \quad (6.3)$$

These calculated values for the adsorbed layer d along with their ratio with the radius of gyration, d/R_g are plotted in Figure 6.2b. The adsorbed layer d grows with increasing MW; however, its ratio with the radius of gyration, d/R_g , decreases significantly with MW. This decrease suggests that the adsorbed layer in ANPs is likely flattened, forming a pancake-like structure. It is also important to point out that assuming the density of the interfacial polymer is

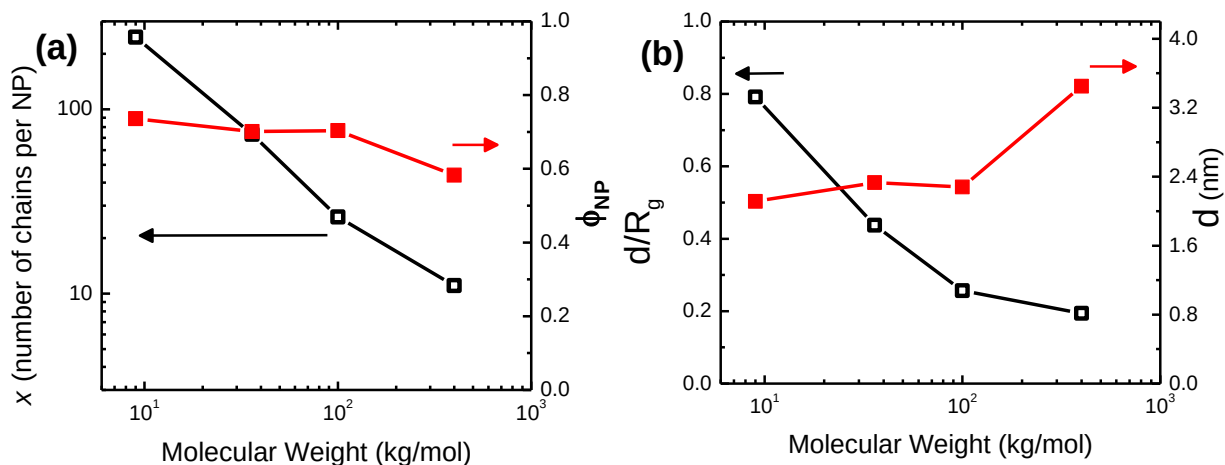


Figure 6.2: (a) The number of chains per nanoparticle (black) and the weight fraction of nanoparticles (red) vs polymer MW. (b) The expected adsorbed layer thicknesses d (red) and its ratio with radius of gyration d/R_g (black) calculated using Eq. (6.2).

the same as the bulk polymer is known not to be true [93], meaning these estimations of d are likely not the real thicknesses of the adsorbed layer.

6.3.2 Broadband Dielectric Spectroscopy (BDS)

The real and imaginary part of the dielectric permittivity spectra for all three systems at 404k molecular weight are shown in Figure 6.3. The α -relaxation process associated with segmental relaxation is clearly observed for the neat, PNC, and ANPs. The presence of nanoparticles causes Maxwell-Wagner-Sillars polarization, and this process is much larger in comparison to the segmental relaxation for the ANPs. The behavior for the remaining molecular weight systems is similar, although for the lower molecular weight polymer-adsorbed NPs, the segmental relaxation process is very suppressed given the large nanoparticle loading.

The progression of the dielectric loss spectra with temperature is shown in Figure 6.4a for the three systems at 404k, where the dielectric loss peaks at two temperatures indicate the

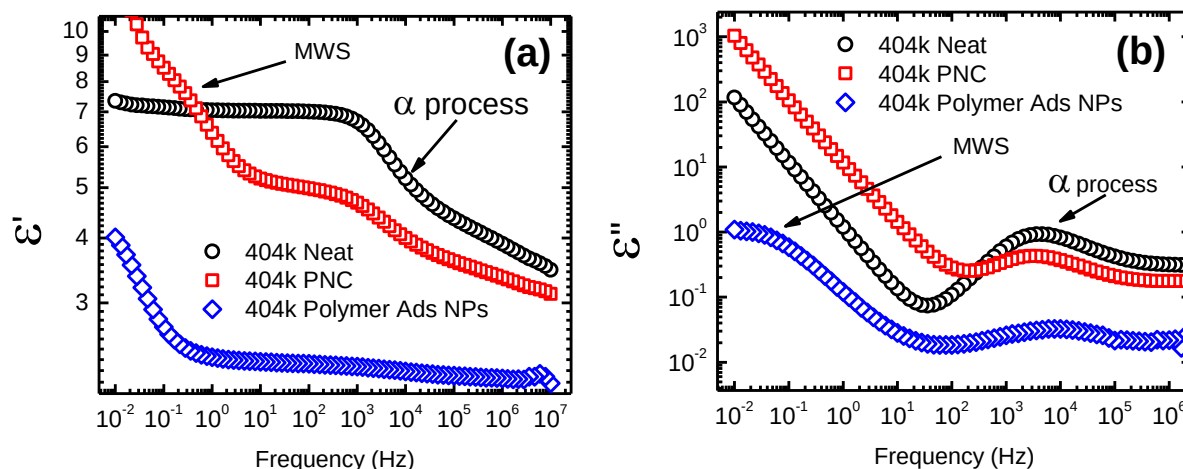


Figure 6.3: Broadband dielectric data of the (a) real and (b) imaginary spectra of 404k neat, polymer nanocomposites (PNC), and polymer-adsorbed nanoparticles (ANPs). The α -relaxation process becomes progressively suppressed with higher silica content. The Maxwell-Wagner-Sillars polarization is present for both PNCs and polymer-adsorbed NPs, where the process is much more pronounced for polymer-adsorbed NPs.

general behavior of the dielectric amplitude. The following behavior is seen for the amplitude of the dielectric loss peak with decreasing temperature: (1) It increases in the neat polymer following the expected Curie-Weiss behavior; (2) It remains roughly constant in the PNC, or at least has a much smaller increase on cooling; (3) It decreases in the polymer-adsorbed NPs. The behavior of these first two points was seen in Chapter 4 for the poly(vinyl-acetate) (PVAc) neat and PNC system [166]. The behavior for the dielectric strength in polymer-adsorbed NPs is unexpected for a polymer system. The nanoparticle's dielectric amplitude does not decrease with decreasing temperature, so the suppression of dielectric amplitude is not simply caused by the nanoparticle fraction [73]. The decrease in dielectric amplitude with temperature is observed for all four molecular weight polymer-adsorbed NPs. Figure 6.4b shows the broadening of the 404k polymer-adsorbed NP relaxation peak at all temperatures superimposed. The spectral shape is relatively unchanged with temperature, indicating the loss in dielectric amplitude cannot simply be attributed to broadening in dynamics.

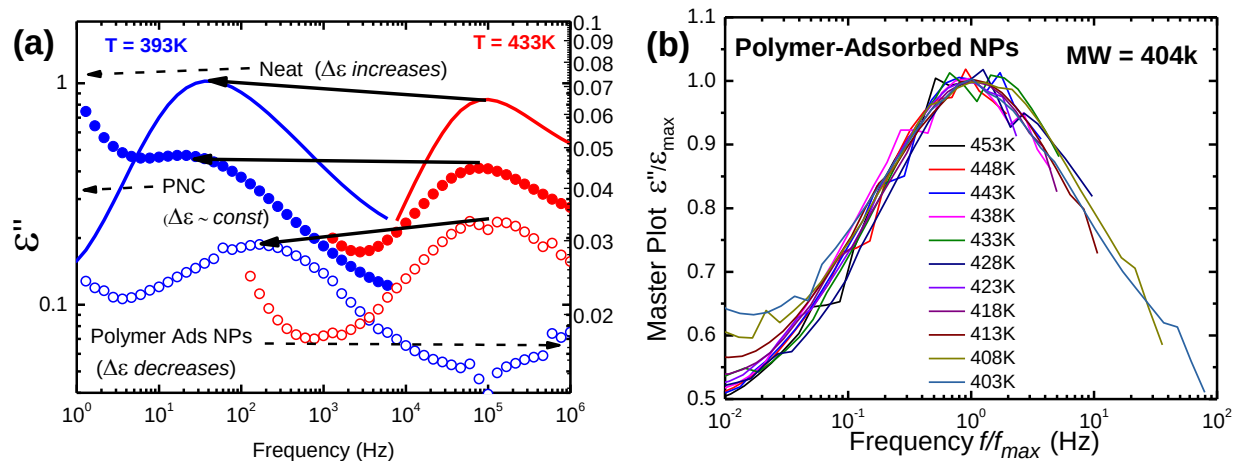


Figure 6.4: (a) Dielectric loss spectra at two temperatures for the 404k neat, polymer nanocomposite (PNC), and polymer-adsorbed NPs. The left axis is the y-values for the neat and PNC systems while the right axis is the y-values for the ANPs. The temperature dependence of the dielectric loss peak is different for all three systems for decreasing temperature: (1) for the neat, it increases; (2) for the PNC, it remains roughly constant; (3) for the polymer-adsorbed NPs, it decreases. (b) Master plot of dielectric losses for segmental relaxation in the ANPs of MW = 404k kg/mol is displayed. This collapse of all temperature measurements onto a master curve indicates the stretching is negligible, meaning the increase in dielectric loss peak cannot be simply attributed to broadening.

6.4. Discussion

6.4.1. Dielectric Analysis

In addition to the unusual decrease of the dielectric amplitude with decreasing temperature, the polymer-adsorbed NPs also have slightly faster segmental relaxation times in comparison to their neat counterpart. Figure 6.5a-d shows the segmental relaxation peak of the three polymer systems for each molecular weight. We see as molecular weight increases, the segmental relaxation of the polymer-adsorbed NPs becomes faster than the neat; this effect essentially disappears at lowest molecular weight, 9k. The PNC system has systematically slower segmental relaxation times, an effect attributed to the attractive polymer-nanoparticle interactions that slow the polymers in the interfacial layer [57, 65, 100, 106, 176]. The enhanced segmental relaxation times for the polymer-adsorbed NPs are unusual, however, given the

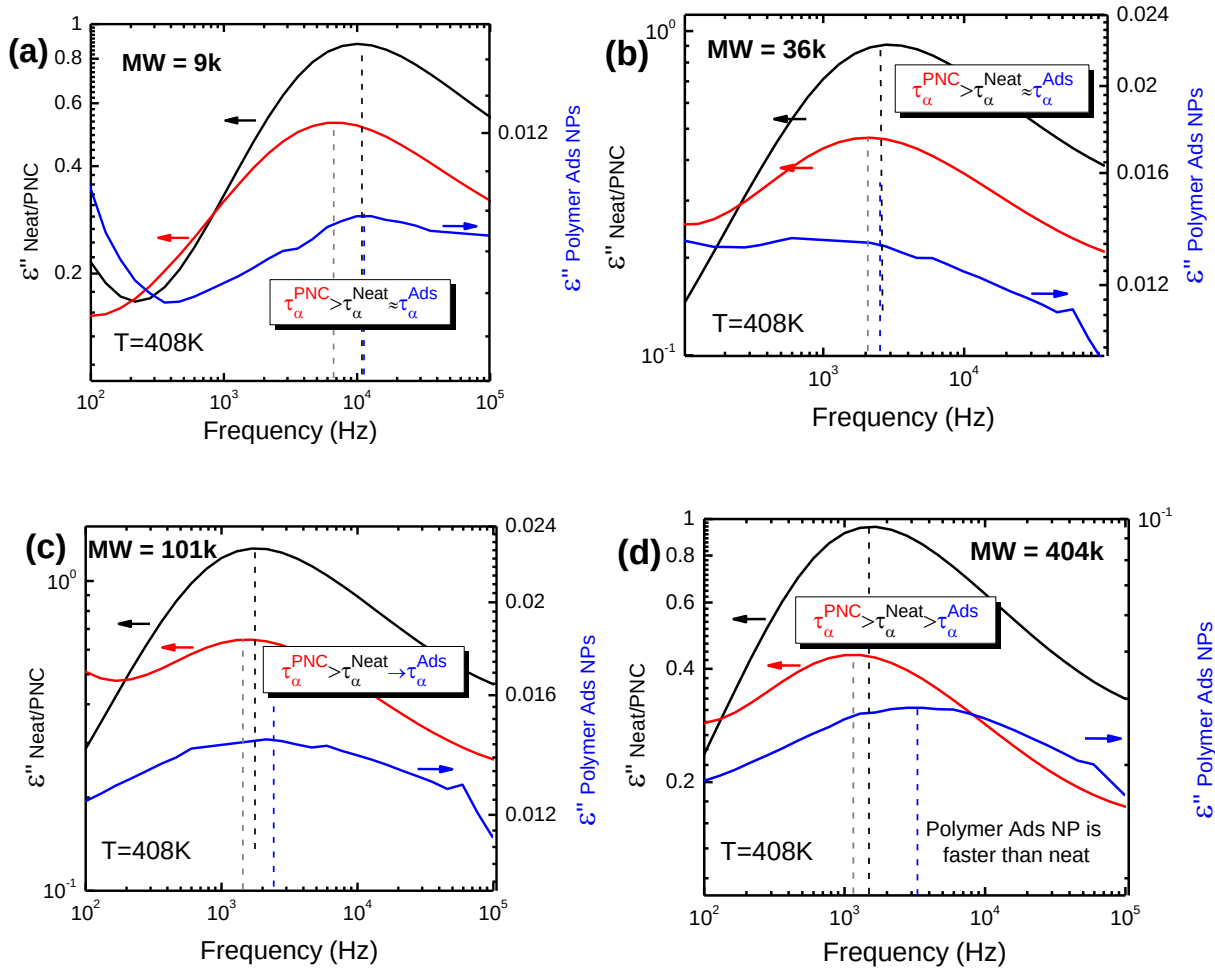


Figure 6.5: Dielectric loss peaks for three systems: neat, PNC, and polymer-adsorbed NPs, for different molecular weight: (a) MW = 9 kg/mol, (b) MW = 36 kg/mol, (c) MW = 101 kg/mol, (d) MW = 404 kg/mol. As the molecular weight is increased, it appears the polymer-adsorbed NPs have faster dynamics than the neat and PNC systems, especially noticeable at 404k.

system has the same attractive polymer-nanoparticle interaction between P2VP and silica that the PNCs have.

A fitting treatment was applied to the spectra to determine exact values for the dielectric amplitude as a function of temperature. These results are shown in Figure 6.6. The neat samples were fit with a single Havriliak-Negami function, a procedure used previously in Chapter 4. The polymer-adsorbed NPs were also only fit with a single Havriliak-Negami function, even though it is a multi-component system. The bulk fraction is very small, especially since the samples were annealed prior to BDS measurement, so the interfacial layer model (ILM) is not applied. Further, the two-phase model analysis is not applicable because the model only works at high loading if there is no interfacial interaction [148]. These models are derived for specific geometries where the bulk polymer is the main contribution, which significantly departs from the polymer-adsorbed NPs picture. The single Havriliak-Negami function can reliably fit the data, so the analysis should give reliable information on the dynamics and dielectric amplitude.

Figure 6.6a demonstrates the temperature dependence of the dielectric amplitude $\Delta\epsilon$ for the neat polymer and the silica-normalized dielectric amplitude $\Delta\epsilon/(1 - \phi_{NP})$. Clearly the amplitude of the neat spectra of all polymers decreases systematically with increasing temperature, while the polymer-adsorbed NPs' amplitudes increase with temperature. This dielectric analysis confirms the trend shown in Figure 6.4a. Additionally, it worth noting that even though the polymer fraction is normalized, the dielectric amplitude for the polymer-adsorbed NPs is noticeably smaller than the neat polymer, by roughly 5-10 times. A decrease in dielectric strength was shown for the interfacial layer contribution to the PVAc-silica PNCs in chapter 4 owing to chain stretching. In addition, many studies on thin polymer films have shown a reduced dielectric amplitude with film thickness and temperature [118, 153, 181]. It can be

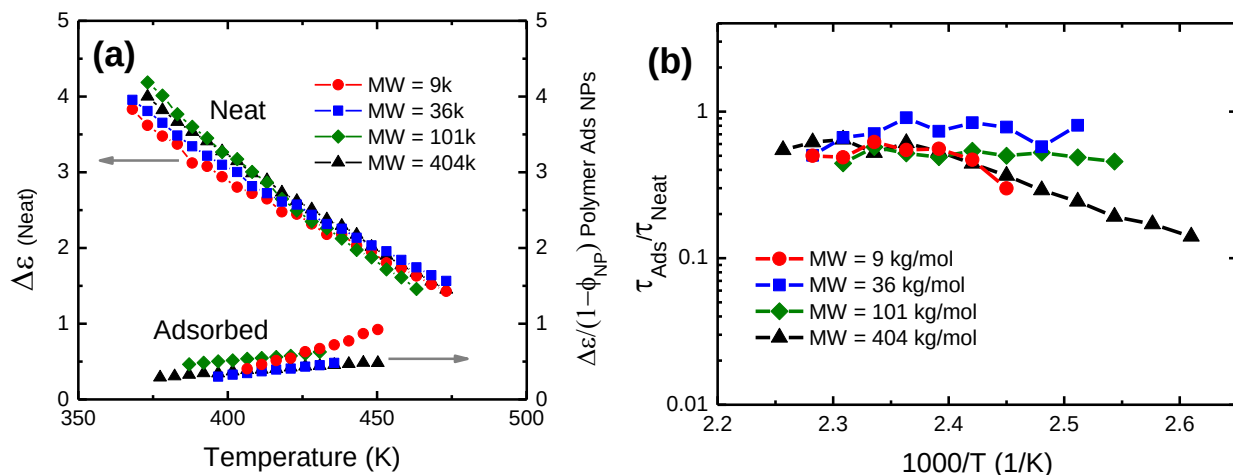


Figure 6.6: (a) The temperature dependences of dielectric amplitude for the neat polymer and polymer-adsorbed NPs. For the polymer-adsorbed NPs, the signal is normalized for the nanoparticle fraction. (b) The ratio of segmental relaxation times for the polymer-adsorbed NPs and the neat polymer, τ_{Ads}/τ_{Neat} , as a function of temperature. The lower molecular weight systems have roughly similar segmental relaxation times, whereas the highest molecular weight has faster segmental relaxation times.

argued that the reduced dielectric amplitude is a general feature of polymer composite systems where the polymer chains are stretched or flattened as a result of their interaction with a surface.

Figure 6.6b shows the ratio of relaxation times between the polymer-adsorbed NPs and the neat polymer as a function of temperature. Each system follows a Vogel-Fulcher-Tammann dependence individually. The ratio of relaxation times approaches 1 for most molecular weight systems; however, the 404k molecular weight system has noticeably faster dynamics for the polymer-adsorbed NPs. The cause of these accelerated dynamics is likely the frustrated packing of long chains in the adsorbed layer which creates increased free volume which facilitates the faster segmental relaxation times.

6.4.2. Theoretical Model for Dielectric Amplitude in Polymer Systems

The polymer-adsorbed NPs have a non-Curie-Weiss temperature dependence for the dielectric amplitude. When we reported similar non-Curie-Weiss behavior in Chapter 4 for the

PVAc-silica composites, we argued that its origin was either from changes in the number density of dipoles or changes in the Kirkwood-Frohlich factor, where the dielectric amplitude was given by equation 6.1. The former argument was dismissed for PNCs since it would imply the dipoles N in the interface would be dielectrically inactive, and numerous studies have suggested that the interface is dynamically alive [9, 57, 100, 145]. There is not a one-to-one correspondence between this argument for PNCs and polymer-adsorbed NPs because the adsorbed layer is different from the interfacial layer, as the latter contains free polymers. One might argue that increasing temperature frees completely frozen dipoles in this polymer-adsorbed NPs system, where this effect is no longer “shielded” by free polymer. However, it is unlikely that the polymer-adsorbed NPs would have completely frozen dipoles in the first place, given that they have the same polymer-NP interaction as PNCs. Further, Figure 6.4b shows no significant broadening with temperature for the polymer adsorbed NPs, broadening which would occur once frozen dipoles were allowed more freedom of motion.

Ruling out changing the number of dipoles, modifying the Kirkwood-Frohlich factor remains a viable explanation; however, it is unclear if the Kirkwood-Frohlich factor description applies to the polymer-adsorbed NPs system. For simplicity, we can instead argue that the total amplitude of the dipole μ is reduced in the polymer-adsorbed NP system resulting from the dipole reorientation being impeded on the timescale of segmental motion. This hindered dipole motion becomes progressively freed as temperature is increased, causing the dielectric amplitude behavior seen in Figure 6.4a. The segmental motion of the chains in polymer-adsorbed NPs may not differ greatly from the neat polymer because of the competing effects of chain adsorption, stretching, and packing. So even though ordered (stretched/flattened) and disordered (neat-like) chains may have similar segmental relaxation times, their dielectric amplitude can be very

different because dielectric amplitude is not completely coupled to the timescale of segmental relaxation. This distinction is important since the literature typically uses changes in segmental relaxation times to estimate the interfacial volume fraction in dielectric spectroscopy. This dielectric amplitude behavior shows that the chains may have very different conformations even though their relaxation dynamics are similar.

Given both the effects of chain adsorption and annealing, the majority of the chains in the polymer-adsorbed NPs are likely going to be in pancake-like structures, especially at high MW, with limited potential conformations [88]. The amplitude of the segmental reorientation is going to be very limited in this flattened structure, especially in the out-of-plane direction. To estimate the observed changes in dielectric amplitude of polymer-adsorbed NPs and their non-Curie-like temperature dependence, we develop a simplified model with restrictions on the amplitude of segmental fluctuations caused by the stretched neighboring chains. Figure 6.7a shows how the tails and loops in the polymer-adsorbed NPs can be treated as individual k loop on a spherical surface, each with their own dipole moment M_k . Figure 6.7a only diagrams the stretched chains, but this model is applicable to pancake-like structures as well. Since the segments will entropically repel each other, we can argue a single segment's motion is that of a free (neat) chain ($U_k = 0$) that is confined in a conic potential wall with angle $2\delta_c$. The interaction energy of the wall, U_k , is defined as the interaction between segments.

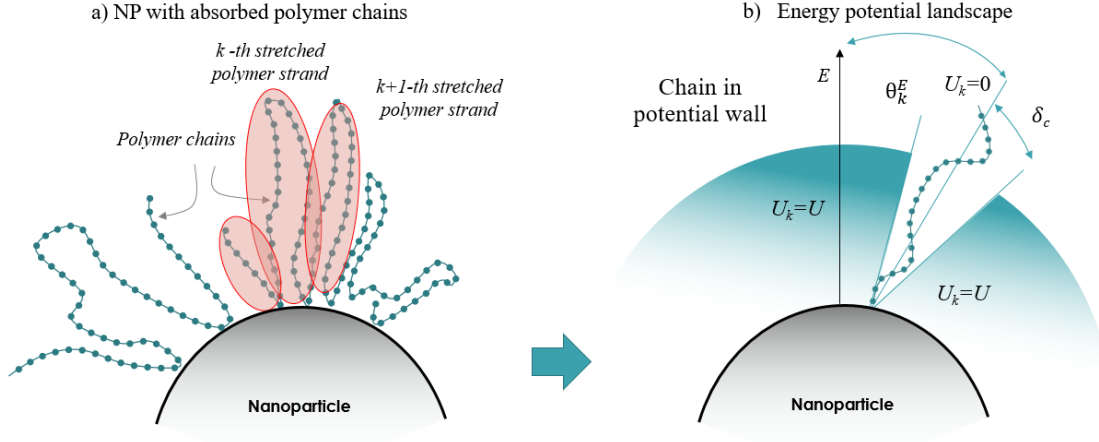


Figure 6.7: (a) Schematic of a polymer chain associated to the NP. Tails or loops are both defined as individual segments (b) Energy potential landscape for an individual k^{th} segment. Inside the conic sector of angle $2\delta_c$, the polymer chain segment is considered a free chain ($U_k = 0$), while outside of the conic well the polymer segment has an interaction with neighboring polymer segments with a potential $U_k = U$.

By definition, the dielectric strength of the adsorbed layer is given by:

$$\Delta\epsilon_{Abs} = (1 - c_{NP}^V) \frac{4\pi\langle M \rangle_{Ads}^E}{VE} = (1 - c_{NP}^V) \frac{4\pi}{VE} \sum_k^N \langle M_k \rangle^E, \langle M_k \rangle^E = \int \frac{(\mathbf{M}_k \mathbf{E})}{E} \Psi(M_k) dM_k^3 \quad (6.4)$$

In this equation, E is the applied electric field, V is volume, c_{NP}^V is the volume fraction of the nanoparticles, $\Psi(M_k)$ is a distribution function in the field that is related to the distribution function for the free chain related by the following expression:

$$\Psi(M_k) = const \cdot \Phi(M_k) \cdot e^{-H_k/k_B T} = const \cdot \Phi(M_k) \cdot e^{-U_k/k_B T} \left[1 + \frac{(\mathbf{M}_k \mathbf{E})}{k_B T} \right], \frac{(\mathbf{M}_k \mathbf{E})}{k_B T} \ll 1 \quad (6.5)$$

By assuming that all potential wells are identical ($U_k = U$), that the dipole moment does not have a large fluctuation value ($\langle M^2 \rangle \approx \langle M \rangle^2$), that there is a large number of chains N , and that the interaction energy between chains is stronger than chain motion, we can approximate that the ratio of the dielectric amplitude of the polymer-adsorbed NPs and the neat, $\Delta\epsilon_{Ads}/\Delta\epsilon_{Neat}$, has an Arrhenius temperature dependence of

$$\frac{\Delta\varepsilon_{Ads}}{\Delta\varepsilon_{Neat}} \sim \exp\left(-\frac{U}{k_B T}\right) \quad (6.6)$$

Ignoring the constants, we can use this equation to fit the data in Figure 6.6a in order to estimate the interaction energy U for each molecular weight of polymer-adsorbed NPs. Figure 6.8 shows the ratio of the dielectric amplitudes of the polymer-adsorbed NPs and the neat polymer in log scale, where the scatter points are the data from Figure 6.6 and the lines are the lines of best fit using equation 6.6. Taking the slope of this fit, an estimate of the interaction energy U can be made. The interaction energy, plotted in Figure 6.8b, clearly decreases with increasing molecular weight, which would imply that shorter chains have a greater neighboring influence on other adsorbed chains' motion.

This molecular weight dependence of the interaction energy mirrors the ratio of the adsorbed layer thickness to the radius of gyration, d/R_g . Though the estimated thickness of the adsorbed layer d increases with molecular weight, the d/R_g decreases with MW, indicating the higher MW adsorbed layers collapse more significantly than low MW. The collapse is likely the result of a reduced density at higher MW resulting from the entropic effects of inefficient chain packing. Additionally, centrifugation better removes weakly adsorbed chains in higher MW systems than lower MW ones, potentially enhancing this packing effect. Therefore, lower MW ANPs, with more efficient chain packing, have higher interaction energies with surrounding adsorbed chains.

The reduced density at higher MW can also explain the enhanced relaxation time effect for the 404k ANPs shown in Figures 6.4 and 6.6b. The ANPs segmental relaxation is a competing effect between the slowing down expected from the polymer association to the nanoparticle, and the faster dynamics expected for a reduced density and smaller interaction

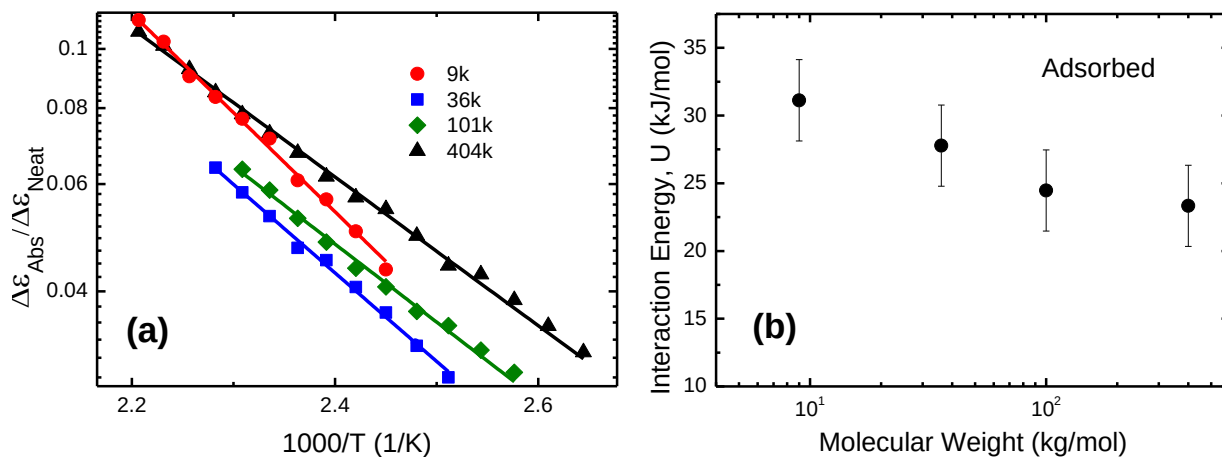


Figure 6.8: (a) The temperature dependence of the ratio of dielectric amplitudes for the polymer-adsorbed nanoparticles and the neat polymer, $\Delta\epsilon_{Abs}/\Delta\epsilon_{Neat}$. (b) The molecular weight dependence of the interaction energy calculated from the data presented in (a) and Eq. 6.6.

energy between chains. This latter effect is most prominent at highest molecular weight, where the ANPs' relaxation is clearly faster than the neat. The enhanced segmental relaxation times are not present in polymer nanocomposites because the presence of the bulk polymer layer prevents the adsorbed chains from having faster dynamics than the bulk, making nanoparticle adsorption the dominant effect.

There is an interesting similarity between the polymer-adsorbed nanoparticles' behavior with molecular weight and PNCs. In both systems, chain ordering plays a crucial role in the dielectric behavior of the polymer chains near the nanoparticle surface, even though the adsorbed layer and the interfacial layer are not physically identical. The mechanism for creating greater free volume in both polymer-adsorbed nanoparticles and PNCs is different, but the source is the same: the entropic effects of how polymer chains are organized on spherical nanoparticles. Both systems have modified chain structure near the nanoparticle surface that changes with molecular weight. Most significantly, the hindered chain reorientation appears to be a universal effect for

polymer composite systems, which suggests that research on the interface needs to carefully account for the dielectric amplitude when estimating the interfacial volume fraction.

6.5. Conclusions

In this study, we compared the dielectric response of neat polymers, polymer nanocomposites, and a free-polymer-removed nanocomposite system, termed polymer-adsorbed nanoparticles (ANPs), for different molecular weights. Analyzing the dielectric spectra, it is apparent that the PNCs' and ANPs' temperature dependences of dielectric amplitude differ from the neat polymer. While the neat polymer exhibits the expected Curie-Weiss behavior with decreasing temperature (the dielectric amplitude increases), the PNCs exhibit almost no temperature dependence, and the polymer-adsorbed NPs exhibit opposite Curie-Weiss behavior, where the dielectric amplitude decreases on cooling. The origin of this dielectric amplitude behavior is the restriction of dipole reorientation for polymer chains in the composite systems (chain stretching in the interfacial layer for PNCs, chain flattening for the adsorbed layer in polymer-adsorbed NPs). These dipoles reorient more freely with increasing temperature. The restricted motion of stretched or flattened chains causes a significant reduction in dielectric amplitude, even though the segmental relaxation times may not change significantly from the neat polymer.

Modeling the polymer-adsorbed NP system as single adsorbed chains interacting with a potential wall, the dielectric amplitude can qualitatively be described by an Arrhenius function with a characteristic interaction energy. The estimated interaction energy between chains decreases with increasing molecular weight, which roughly coincides with the unexpected enhancement of segmental relaxation times for the polymer-adsorbed NPs at high molecular

weight. The cause of this relaxation time behavior is likely due to reduced density at high molecular weight either by frustrated packing or by removal from centrifugation. This research demonstrates the importance of dielectric amplitude for determining the chain organization in the interfaces of polymer composite systems, and how changes in segmental relaxation time do not give a complete picture of how segmental dynamics are modified in the interfacial layer.

7. Striking Properties of Small Nanoparticles in Polymer Nanocomposites

This chapter explores polymer nanocomposites of poly(2-vinyl pyridine) (P2VP) mixed with small ~2 nm nanoparticles and compares the results to polymer nanocomposites with conventional 25 nm silica nanoparticles used in the previous three chapters. The 2 nm nanoparticles are the size of a polymer segment and have a similar hydrogen bonding interaction with P2VP as the 25 nm silica. The ~2 nm nanoparticles have significant changes in glass transition temperature and fragility with loading; however, they have relatively small changes in thermodynamic and viscoelastic properties. These results are significant departures from the behaviors of the 25 nm silica composites. Using MD simulations as a guide, these striking results are attributed to the weak and limited interactions of the small NPs with the polymer. These temperature sensitive bonds reinforce the polymer at low temperatures but desorb easily at high temperatures, resulting in relatively mobile nanoparticles. These results demonstrate that nanoparticle mobility can play an important role in macroscopic properties of PNCs.

7.1. Introduction

Chapters 4 through 6 of this dissertation have investigated the dynamics and structures of polymers in polymer nanocomposites using a variety of techniques. The use of 20-25 nm silica nanoparticles has been a constant for each study; the polymer chains adsorb to the nanoparticle surface which gives the polymer nanocomposites their interesting properties [7-9]. Both the interfacial and adsorbed polymer layer have been investigated in these studies by measuring the

properties of the polymers themselves; the nanoparticles have thus far played a somewhat passive role in the actual measurements. However, the nanoparticles themselves can be a tuning parameter that can potentially control the behavior of PNCs. For nanoparticles between 7 nm and 100 nm, it has been shown that the interfacial layer thickness increases with nanoparticle size [42]. The smaller the nanoparticle size, the larger the expected volume fraction of interfacial layer for PNCs [58]. However, there is likely an optimal size to achieve maximum interfacial thickness; at very small sizes, the nanoparticles plasticize the polymers [80, 81, 83, 182], which speeds up dynamics, reduces T_g , and eliminates the enhanced mechanical properties desirable for PNCs [183]. Further, these small nanoparticles typically have weak or no interaction with the chains, leading to aggregation and dispersion problems which ruin any potentially advantageous results [183]. For these reasons, very few studies have looked at PNCs with well-dispersed, attractive nanoparticles with diameters of 1-2 nm [182, 184-186].

The setup of this study is straightforward: small, ~2 nm octaaminophenyl polyhedral oligomeric silsesquioxane (OAPS) nanoparticles are dispersed in a poly(2-vinyl pyridine) (P2VP) polymer matrix up to high loading. These nanoparticles, whose size is on the order of a polymer segment, are compared to a conventional 25 nm silica in P2VP composite. The P2VP-silica PNC has behavior in line with the PVAc-silica PNCs studied in Chapter 4 and other PNC studies from the literature as well [9, 57, 114, 140, 166, 176]. The two composite systems are compared in different experimental techniques which investigate the thermodynamic, kinetic, and viscoelastic properties of each. The P2VP-OAPS composites have significant changes in glass transition temperature and fragility with loading that are distinct from the P2VP-silica composites. Despite these large changes, the P2VP-OAPS composites have relatively minor changes in specific heat capacity step and high temperature viscoelastic properties. To explain

these seemingly opposing effects, MD simulations are performed so that the polymer-nanoparticle interaction energy can be directly tuned. The MD simulations suggest that the small OAPS NPs have a relatively short polymer desorption time at elevated temperatures, which allows them to detach and move to another chain. This nanoparticle mobility is responsible for the relatively minor changes in thermodynamic and viscoelastic properties not present in silica NPs. At lower temperatures the bonds are not as weak and the OAPS crosslinks the polymer on segmental time scale, causing the enhanced T_g and fragility. Understanding the relationship between interaction energy and particle mobility for small attractive NPs will be important, as these OAPS NPs open a potentially exciting new horizon for PNC research and design.

7.2. Materials and Methods

Sample Preparation

The octaaminophenyl polyhedral oligomeric silsesquioxane (OAPS) nanoparticles were purchased from SES materials and used as received. Poly(2-vinylpyridine) (P2VP) with molecular weight (MW) of 101 kg/mol and polydispersity of 1.07 was purchased from Scientific Polymer Source Inc. The OAPS powder was dissolved in THF at a concentration of 0.15 g/mL. For both OAPS and silica systems, 0.3 g of polymer was dissolved in 10 mL of THF. The OAPS/THF solution was added dropwise under stirring and mixed for 1 h. Next, the P2VP-OAPS nanocomposite solutions were poured into a Teflon dish to dry under a hood for 24 h before being transferred to a vacuum oven (0.1 mbar) under 160 °C for one week. The P2VP-silica composites were prepared in a similar manner except with ethanol as the mixing solvent. All PNC samples were characterized by thermogravimetric analysis (TGA) (TA Instruments Discover Q 50) under air with 20 °C/min heating up to 800 °C and temperature-modulated

differential scanning calorimetry (TMDSC) (TA Instruments, Q2000) with a heating/cooling rate of 2 °C/min and a modulation speed of ± 0.5 °C/min. The mass densities of OAPS, silica NPs, and neat P2VP were 1.4028 ± 0.0019 g/cm³, 2.4057 ± 0.0019 g/cm³, and 1.2249 ± 0.0024 g/cm³, respectively, and were measured by gas pycnometry (Micromeritics Accupyc II 1340). The OAPS and the silica NPs both adsorb to P2VP via hydrogen bonding, where the chemical structure of the OAPS is shown in Figure 7.1b. The size of the OAPS NPs, $D = 1.8$ nm, is roughly the size of a Kuhn segment for P2VP ($l_k \sim 1.7$ nm). The silica NPs are as usual $D = 25$ nm, much larger than the Kuhn segment or even the tube diameter of P2VP.

Small Angle X-ray Scattering

The SAXS measurements were performed at the Duke Shared Materials Instrumentation Facility using a high-flux SAXS instrument (SAXSLab Ganesha), a point collimated pinhole system with a 2D configurable detector, and a Cu 50 kV Xenocs Genix ULD SL X-ray Source. All measurements were performed at room temperature in a transmission geometry where the nanocomposite samples were pressed into thin films. Scattering intensities measured as a function of half the scattering angle, θ , were first corrected for the absorption of X-rays by the sample. The empty cell scattering was then subtracted before the scattering data were transformed to a plot of absolute scattering intensity vs momentum transfer vector, q , where $q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$. The corrected data were normalized to absolute units by scaling to the scattering of water measured in the same geometry. The scattering data were fit with a fuzzy sphere model [92], whose form factor is expressed as follows:

$$P(q) = \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3} \exp\left(-\frac{(\sigma_{fuzzy}q)^2}{2}\right) \quad (7.1)$$

Here, R is the radius of the NP and σ_{fuzzy} is the width of the smeared particle surface.

Broadband Dielectric Spectroscopy

Broadband dielectric spectroscopy (BDS) measurements were carried out using the same Novocontrol Concept-80 system with an Alpha-A impedance analyzer, in concert with a Quatro Cryosystem temperature controller and a ZGS sample holder. The PNC and neat polymers were hot-pressed at 160 °C into 0.08–0.15 mm films inside a Teflon ring with inner diameter of 14 mm and outer diameter of 24 mm. These samples were then sandwiched between two gold-coated electrodes with a diameter of 20 mm and placed in the sample holder. All the measurements were conducted in the temperature range of 200°C to 0°C with a temperature step of 5°C between 200°C and 90°C and 10°C between 90° and 0°C, over a frequency range of 10^{-2} – 10^7 Hz. The samples were thermally equilibrated for 20 min prior to each measurement step.

Rheology

Small amplitude oscillatory shear (SAOS) measurements were conducted on an AR2000ex rheometer (TA Instrument). For the segmental relaxation and glassy modulus measurements, a parallel plate with a diameter of 4 mm and a strain amplitude of 0.05% was used. For the rubbery plateau and terminal relaxation measurements, a parallel plate with a diameter of 8 mm and a strain amplitude of 1.0% was used. The temperature was controlled by an environmental test chamber under nitrogen atmosphere with an accuracy of ± 0.1 °C.

Molecular-Dynamics Simulations

Coarse-grained (CG) molecular dynamics (MD) simulations were performed at the Oak Ridge Leadership Computing Facility (OLCF) using the LAMMPS [187, 188] software package done in collaboration with this work. The polymer nanocomposites were modeled using a

modified Kremer and Grest [189] polymer melt model with sticky nanoparticles dispersed throughout. The simulations contain 500 polymer chains with molecular weight characterized by degree of polymerization $N = 400$. The neat polymer melt is first equilibrated by MD simulations and Monte Carlo bond swaps [190]. The equilibrated melts are then mixed with the sticky NPs for different loadings up to 25 vol%. After slowly moving the NPs occupying polymer segments spots, an equilibration MD run of $10^5 \tau$ and a production MD run of $4 \times 10^5 \tau$ were performed, where τ is the simulation unit of time. The trajectories of the particles were used to calculate the self-intermediate dynamic structure factor, $F_s(t)$, and the cross-correlation function between polymer segments and NPs, $F_{12}(q, t)$. The $F_s(t)$ is given by the equation:

$$F_s(q, t) = \frac{1}{Nm} \sum_{i=1}^{Nm} \frac{\sin(qr_i(t))}{qr_i(t)} \quad (7.2)$$

Here, Nm refers to the total number of polymer segments or nanoparticles, q is the wave vector magnitude, and $r_i(t)$ is the displacement of the i^{th} particle after a time t . The relaxation times of the polymer segments and NPs are taken to be the time when $F_s(q, t) = 0.6$ for each type of particle, which is simulated for different interaction energies. The $F_{12}(q, t)$ is given by:

$$F_{12}(q, t) = \frac{1}{2} \left(\exp[iq(r_p(t) - r_{NP}(0))] + \exp[iq(r_p(0) - r_{NP}(t))] \right) \quad (7.3)$$

Here, $r_p(t)$ and $r_{NP}(t)$ are the vector locations of an individual polymer segment and nanoparticle, respectively, at a given time t . From this equation the dissociation time, τ_{dis} , for polymer segments and nanoparticles is defined as the time when $\frac{F_{12}(q, t)}{F_{12}(0)} = 0.6$.

7.3. Results

Small-Angle X-ray Scattering (SAXS)

Given the small size of the nanoparticles, SAXS is used to determine the dispersion state of the OAPS nanoparticles in the P2VP melt. Figure 7.1a shows the scattering intensity data $I(q)$ of the OAPS in P2VP-OAPS at two loadings ($\phi_{OAPS} = 18$ vol% and 37 vol%). In addition to the procedures outlined in the methods, the polymer fraction scattering contribution has also been subtracted from the P2VP-OAPS scattering intensity. Analysis of the SAXS spectra reveals that P2VP-OAPS composites up to ~27vol% have excellent dispersion that can be fit by the fuzzy-sphere model [92]. The inset of Figure 7.1a shows the static structure factor $S(q)$ of OAPS in P2VP, which was taken from the scattering intensity data $I(q)$ by the following equation [191, 192]:

$$S(q) = \frac{I(q)}{\left(\frac{\phi}{V}\right)(\Delta\rho)^2 P(q)} \quad (7.4)$$

where ϕ is the volume fraction of the OAPS NPs, V is the absolute volume of one OAPS NP, $(\Delta\rho)^2$ is the scattering length density contrast between the OAPS and the polymer, and $P(q)$ is the form factor from the fuzzy sphere model. When this structure factor $S(q)$ is ~ 1 , as it is for P2VP-OAPS 18 vol%, it can be argued that the NPs are individually dispersed. At $\phi_{OAPS} = 37$ vol% and 54 vol% (not shown), there is an increase of scattering intensity at low q ($q < 0.02$ Å⁻¹), which would indicate some level of aggregation and/or kinetic gelation [121]. The samples themselves, however, are optically clear, and it is expected that the aggregation is minimal.

Temperature-Modulated Differential Scanning Calorimetry (TMDSC)

The TMDSC measurements are useful for determining thermodynamic changes in PNCs. Aside from determining the shift in glass transition temperature, we have also shown that they can provide estimates of the interfacial layer when properly normalized for the silica fraction. Like silica NPs, OAPS NPs do not have a transition that occurs in the temperature range of $T =$

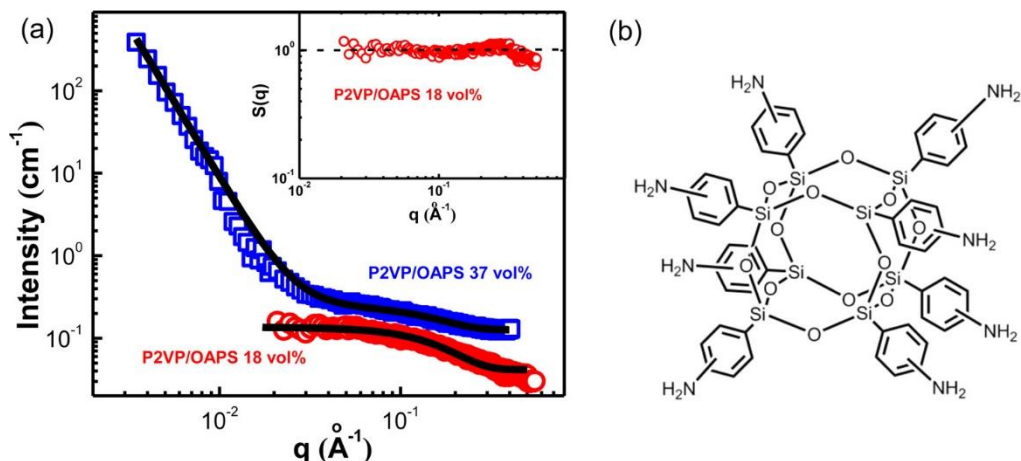


Figure 7.1: The SAXS data for P2VP-OAPS for $\varphi_{OAPS} = 18$ vol % and $\varphi_{OAPS} = 37$ vol %. The black line is a fit with the fuzzy sphere model for $\varphi_{OAPS} = 18$ vol %; for the $\varphi_{OAPS} = 37$ vol % the black line is a combination of a power law and the fuzzy sphere model fit [92]. (Inset) The static structure factor $S(q)$ of the P2VP-OAPS at 18 vol%. A value of $S(q) \sim 1$ indicates individual dispersion (b) The chemical structure of OAPS, where the amine groups can form hydrogen bonds with P2VP segments.

60°C-180°C. Looking at the raw heat capacity data of P2VP-OAPS in Figure 7.2, we see that there is a staggering increase in T_g at 54 vol%, a shift of $\sim 35^\circ\text{C}$. This shift is much more significant than the P2VP-silica data shown in the inset. This $\sim 2\text{-}5^\circ\text{C}$ shift in T_g is consistent with other PNC studies that use 25 nm silica nanoparticles [57, 114, 166]. What is also unusual is the step amplitude of the heat capacity, ΔC_p , for the P2VP-OAPS is almost unchanged, even at a loading of 54vol%. The inset containing the P2VP-silica data clearly shows a strong suppression in ΔC_p at even 35vol%. For conventional PNCs one would expect large changes in the thermodynamic step if the polymer fraction decreases significantly [57, 114, 166].

Broadband Dielectric Spectroscopy (BDS)

Broadband dielectric spectroscopy is employed to measure the segmental dynamics in the PNCs. The dielectric spectra are shown in Figure 7.3a, with several noticeable changes to the α -process peak associated with segmental dynamics: a shift to lower frequency, significant

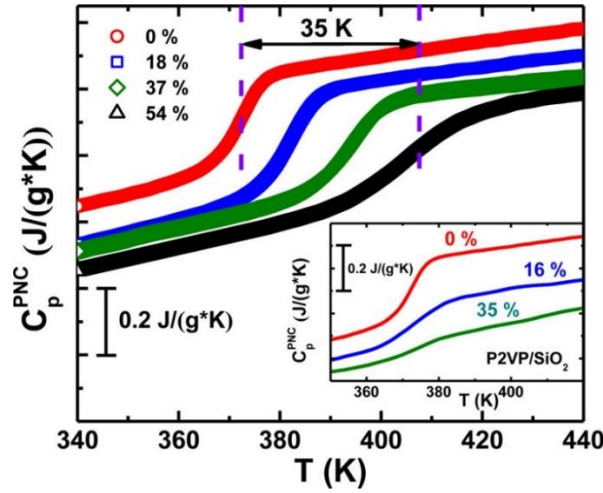


Figure 7.2: Temperature-modulated differential scanning calorimetry (TMDSC) measurements of P2VP-OAPS ($D = 1.8$ nm) nanocomposites (PNCs) with different loadings. The P2VP-OAPS PNCs demonstrate a large ($\sim 35^\circ\text{C}$) shift in T_g with addition of OAPS NPs, despite having relatively minor changes in the heat capacity step, ΔC_p . Contrast these results with the conventional P2VP-silica composites ($D = 25$ nm, inset) where the T_g shift is relatively small and the thermodynamic step is greatly suppressed with the reduction of polymer fraction.

broadening of the peak, and decreased dielectric amplitude. These features are common in conventional PNCs with silica size ~ 10 - 50 nm [166]. However, the slowing down of the segmental relaxation times is unusually strong at lower temperatures (where the dynamics are up to 6 orders slower for highest loading at $T \sim 137^\circ\text{C}$), but not so at high temperatures. The dynamic glass transition temperatures (defined as the temperature where $\tau_\alpha \sim 100\text{s}$) measured from fitting the relaxation time spectra reveal a large shift in T_g with loading, in agreement with the TMDSC data.

Rheology

Rheology is used to compare the linear viscoelastic responses of the P2VP-OAPS and P2VP-silica PNCs by small amplitude oscillatory shear measurements. The master curves of the complex moduli $G'(\omega)$ and $G''(\omega)$ are shown in Figure 7.4, which are made by taking advantage

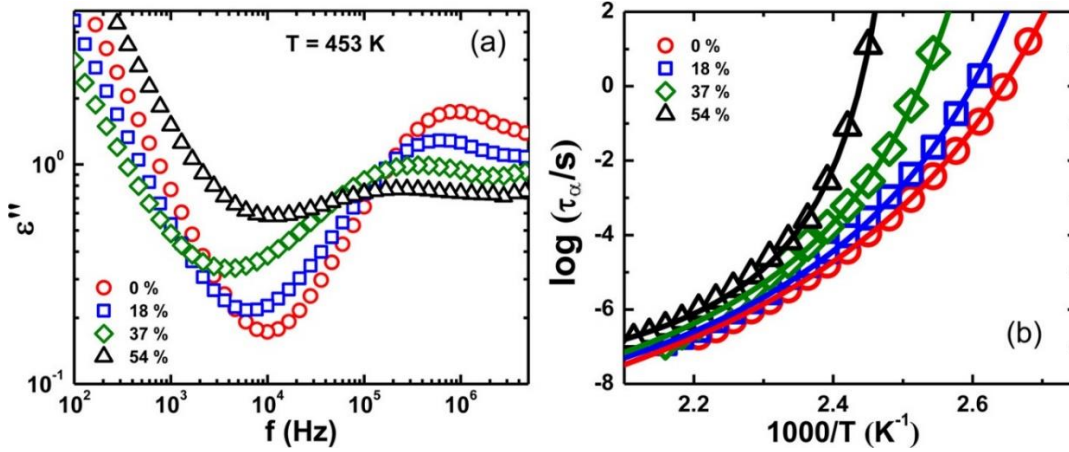


Figure 7.3: (a) Broadband dielectric spectra of P2VP-OAPS with different loadings (in vol %) at 180°C. The addition of the OAPS creates significant changes in segmental peak position, broadening, and peak dielectric amplitude. (b) Temperature dependence of characteristic relaxation times for the segmental relaxation process of the neat P2VP and P2VP-OAPS PNCs at shown loadings, indicating a rapid slowing down in dynamics with cooling for the PNCs at highest loading.

of the time-temperature superposition principle. Figure 7.4a shows the $G'(\omega)$ and $G''(\omega)$ curves of the neat P2VP (red, blue lines), the P2VP-silica at 27vol% (pink, purple symbols), and the P2VP-OAPS at 27vol% (green, black symbols), all at $T = 180^\circ\text{C}$. The P2VP-silica PNCs exhibit the following: typical gelation behavior, characterized by a low-frequency power law $G' \sim G'' \sim \omega^{0.25}$; a strong enhancement of the moduli; and a lack of terminal flow [157]. The P2VP-OAPS PNC is at a similar loading but has very different rheological behavior. First, the entanglement plateau modulus is almost the same as the neat P2VP at high temperature. Further, the entanglement onset time, τ_e , of the PNC is ~ 11 times longer than the neat P2VP even though the segmental relaxation time, τ_α , is only ~ 1.9 times as long. On the other hand, the time scale of terminal flow, τ_d , only increases by a factor of ~ 1.2 . As a result, the breadth of the entanglement plateau, defined by τ_d/τ_e , goes from ~ 700 in the neat P2VP to ~ 70 for the P2VP-OAPS at 27vol%; this ratio is as low as ~ 5 for the 37vol%. This shrinking of the entanglement breadth is

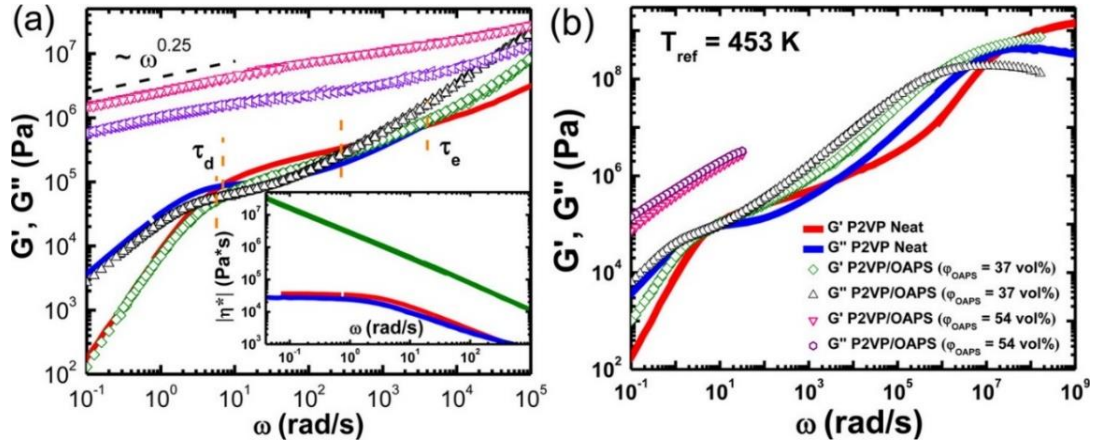


Figure 7.4: (a) Master curves of $G'(\omega)$ and $G''(\omega)$ of P2VP-silica ($\phi_{\text{silica}} = 27\text{ vol}\%$, pink and purple symbols), P2VP-OAPS ($\phi_{\text{OAPS}} = 27\text{ vol}\%$, olive and black symbols), and neat P2VP (red and blue lines) at $T = 180^\circ\text{C}$. The P2VP-silica systems exhibit much higher moduli while the P2VP-OAPS PNCs show rheological behavior similar to the neat. (Inset) The complex viscosity, $|\eta^*|$, of neat P2VP (red), P2VP-OAPS (blue), and P2VP-silica (olive). The neat P2VP and P2VP-OAPS systems have similar complex viscosity behavior at $T = 180^\circ\text{C}$, while the P2VP-silica is much higher and never reaches zero-shear viscosity. (b) Master curves of G' and G'' at $T = 180^\circ\text{C}$ for neat P2VP (red and blue lines), P2VP-OAPS ($\phi_{\text{OAPS}} = 37\text{ vol}\%$) (olive and black symbols), and P2VP-OAPS ($\phi_{\text{OAPS}} = 54\text{ vol}\%$) (pink and purple symbols). The $\phi_{\text{OAPS}} = 54\text{ vol}\%$ PNC exhibits kinetic gelation; the lack of kinetic gelation for the $\phi_{\text{OAPS}} = 37\text{ vol}\%$ is unusual for PNCs loading that high.

tantamount to a disentanglement of the polymer at high loading for P2VP-OAPS. Finally, the complex viscosity, $|\eta^*|$, of the P2VP-OAPS is nearly identical to the neat polymer at higher temperature, as seen in the inset of Figure 7.4a. The P2VP-silica composite in green has a significantly higher viscosity and does not have the same zero-shear-rate plateau that the neat polymer has. The onset of kinetic gelation for the P2VP-OAPS PNCs occurs at a loading of around 43vol%, a threshold much higher than in other conventional PNCs [193].

7.4. Discussion

A summary of the key differences between P2VP polymer nanocomposites with OAPS NPs ($D = 1.8\text{ nm}$, shown in red) and silica NPs ($D = 25\text{ nm}$, shown in blue) is plotted in Figure 7.5. The first column looks at data from TMDSC and BDS, both of which show a significant

increase in T_g of $\sim 35^\circ\text{C}$. By comparison, the T_g shift of conventional silica NPs is only $\sim 2\text{-}5^\circ\text{C}$ (seen in Figure 7.5a). It is clear the OAPS in P2VP do not act as plasticizers as was shown in a different OAPS PNC study [182]. Despite the large shift in T_g , the specific heat capacity step in the P2VP-OAPS, ΔC_p , is nearly independent of loading, in contrast to the P2VP-silica step which decreases significantly with loading (Figure 7.5b). This DSC behavior suggests that the OAPS nanoparticles are somehow taking part in the thermodynamic glass transition, counteracting the decrease in polymer fraction. The relaxation time spectra of BDS reveal a large change in segmental dynamics on cooling, represented by the fragility index, m . The fragility is the slope of the relaxation time spectra with inverse temperature scaled by T_g , given by $m =$

$$\left. \frac{d[\log_{10}\tau(T)]}{d(T_g/T)} \right|_{T=T_g}. \text{The value of the fragility (seen in Figure 7.5c) increases from } m = 100 \text{ for the}$$

neat polymer up to $m = 270$ for $\varphi_{OAPS} = 54\text{vol}\%$; in contrast, the fragility for the P2VP-silica PNCs only increases by about 10%. The value of $m = 270$ for a polymer nanocomposite is the highest reported in the literature for a polymer system [194]. This high fragility indicates the PNCs' dynamic behavior is extremely temperature-sensitive. Explaining this glass transition behavior requires a departure from the typical understanding of polymers and nanoparticle adsorption for 25 nm NP composites.

The second column of Figure 7.5 relates to different characteristic time scales taken from the rheological data, and how the viscoelastic effects of P2VP-OAPS are different from conventional PNCs. We already saw in Figure 7.4 that the P2VP-OAPS nanoparticles do not begin to exhibit kinetic-gelation until around 43vol%, a threshold much higher than for the conventional P2VP-silica PNCs. Looking at Figure 7.5d, the breadth of the entanglement rubbery plateau defined by the ratio τ_d/τ_e decreases almost exponentially with loading. The value of the

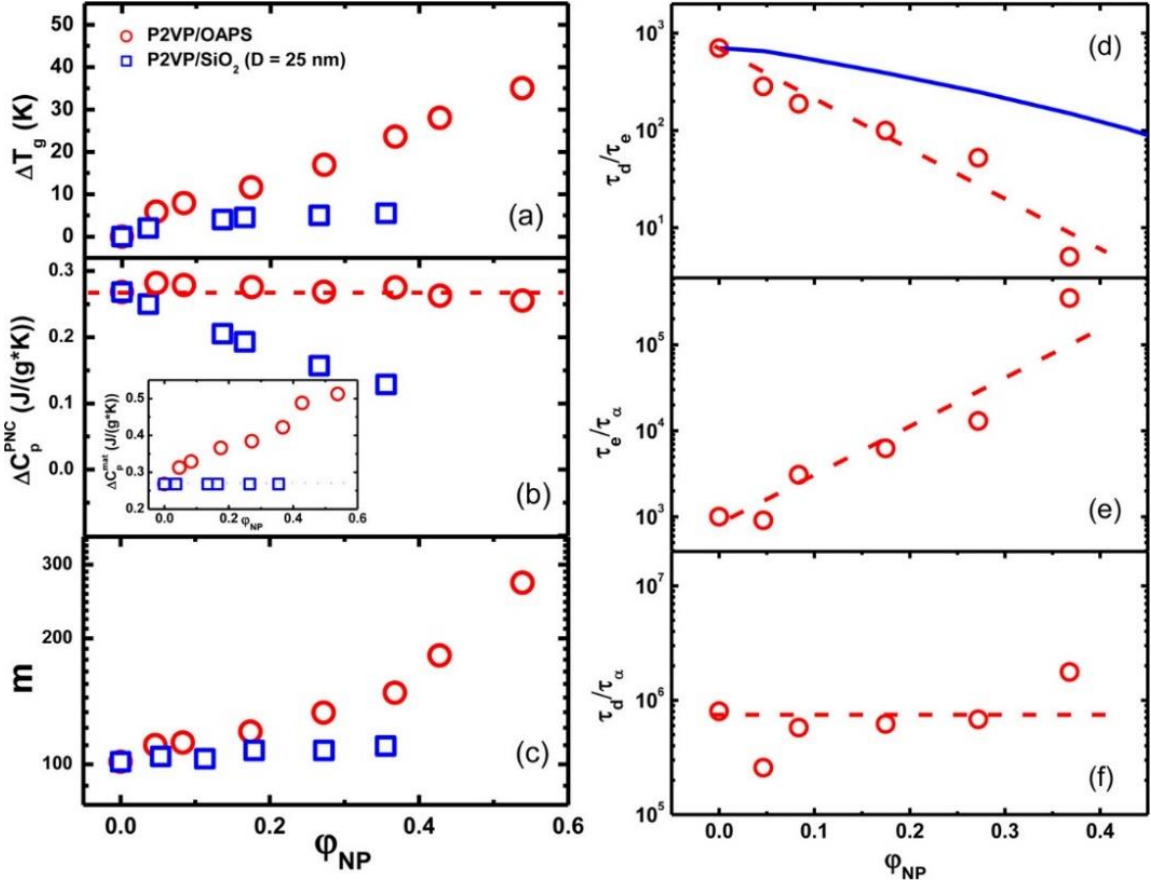


Figure 7.5: (a) Shift in the glass transition temperature, ΔT_g , (b) specific heat capacity jump at T_g , ΔC_p^{PNC} , and (c) fragility index, m , as a function of loading for P2VP-OAPS ($D = 1.8$ nm) (red circles) and P2VP-silica ($D = 25$ nm) (blue squares). There are clear differences for all parameters. (d) Entanglement plateau breadth τ_d/τ_e , (e) ratio of entanglement onset time to segmental relaxation time, τ_e/τ_α , and (f) τ_d/τ_α ratio of P2VP-OAPS PNCs for different loadings. The inset of (b) shows that the ΔC_p of the matrix, $C_p^{mat} = \frac{C_p^{PNC} - C_p^{NP} m_{NP}}{1 - m_{NP}}$, appears to be independent of loading in the conventional PNCs [57], where C_p^{NP} and m_{NP} are the specific heat capacity and weight fraction of the NPs, respectively. This behavior is not the case for P2VP-OAPS, which now overestimates the polymer contribution. The blue line in (d) is the prediction from reptation tube theory [195] for NPs taken to be a solvent or plasticizer.

exponent of this line is $\tau_d/\tau_e \sim \exp(-13\phi_{OAPS})$, a value much larger than what is expected for a solvent or some other plasticizing NPs [195] (this predicted behavior is the blue line in Figure 7.5d). Taking the entanglement onset time and looking at its ratio to the segmental relaxation time, τ_e/τ_α , we see in Figure 7.5e that it increases with loading in an exponential manner, $\tau_e/\tau_\alpha \propto \exp(13\phi_{OAPS})$. This relationship contradicts the assumption that the segmental relaxation and chain relaxation are fully coupled in polymer nanocomposite systems. However, the ratio of terminal flow to segmental relaxation, τ_d/τ_α , is almost loading independent (Figure 7.5f). This result implies that the loading dependence for the flow time and viscosity enhancements is controlled entirely by the segmental relaxation τ_α .

The takeaway from this summary of results is that the P2VP-OAPS PNCs are very different from conventional PNCs [42, 86, 114, 157, 166] and must be modeled using different qualitative pictures. Because the size of the OAPS NPs is roughly the same as an individual polymer segment, it is unreasonable to describe the polymer chains' interaction with them in terms of an interfacial layer. The chemical structure in Figure 7.1b shows that the OAPS has only 8 bonding sites, and it is not realistic to expect chains to wrap around the surface of such small nanoparticles. For this reason, the dielectric analysis outlined in chapter 4 is not applied to the BDS data. Further, it does not make sense to assume the nanoparticles themselves are immobile “anchoring points” that the polymers chains have a one-sided interaction with. Instead, this experimental data suggests that these nanoparticles are much more mobile than 25 nm silica nanoparticles. At the same time, the OAPS nanoparticles reinforce the polymer chains at low temperatures and as such cannot be treated simply as plasticizers. There is a complicated relationship between the polymer chain and the small, attractive OAPS nanoparticles that requires an innovative description.

Direct measurement of OAPS nanoparticle motion will be the subject of chapter 8. For now, we turn to coarse-grained (CG) molecular dynamics (MD) simulations to directly tune the interaction energy between polymer segment and nanoparticle, and how this energy affects the nanoparticle mobility. The nanoparticle and polymer segment are taken to be identical in size with interaction energies of 1, 2, and $4k_B T$. To ensure miscibility, the NP-NP and polymer-polymer interactions are set to be repulsive. The particle trajectories are first used to determine the self-intermediate dynamic scattering function, $F_s(t)$, which gives the characteristic relaxation times of both NPs and polymers for different interaction energies shown in Figure 7.6a. The lines refer to the nanoparticle relaxation times and the points refer to the polymer segmental relaxation times in the composite, where both are normalized to the segmental relaxation time of the neat polymer. The results show that for even the strongest interaction, the NPs and polymer segments have roughly comparable relaxation times, i.e. $\tau_{NP} = 1-2 \tau_\alpha$. This strong similarity in dynamics between segments and NPs is in stark contrast to conventional PNCs where the nanoparticles are essentially immobile on the time scale of polymer segmental relaxation. Figure 7.6b shows the dissociation times of the NPs for different polymer-NP interaction strengths using the dynamic cross-correlation function $F_{12}(q, t)$. The dissociation time, τ_{dis} , is slower than the segmental relaxation process, with a maximum slowing down of $\tau_{dis} \sim 10^2-10^3 \tau_\alpha$. This value is still relatively small compared to silica NPs, which are expected to have a much longer dissociation time of $\tau_{dis} \sim 10^6-10^{12} \tau_\alpha$ [164].

The following physical picture can be constructed in order to resolve the apparent diverging results for the PNCs with small, attractive OAPS nanoparticles. The OAPS cause the large shift in T_g by acting as temporary cross-linkers that can attach to multiple chains. Given the small volume of the nanoparticles, there are many interaction sites spread throughout the melt.

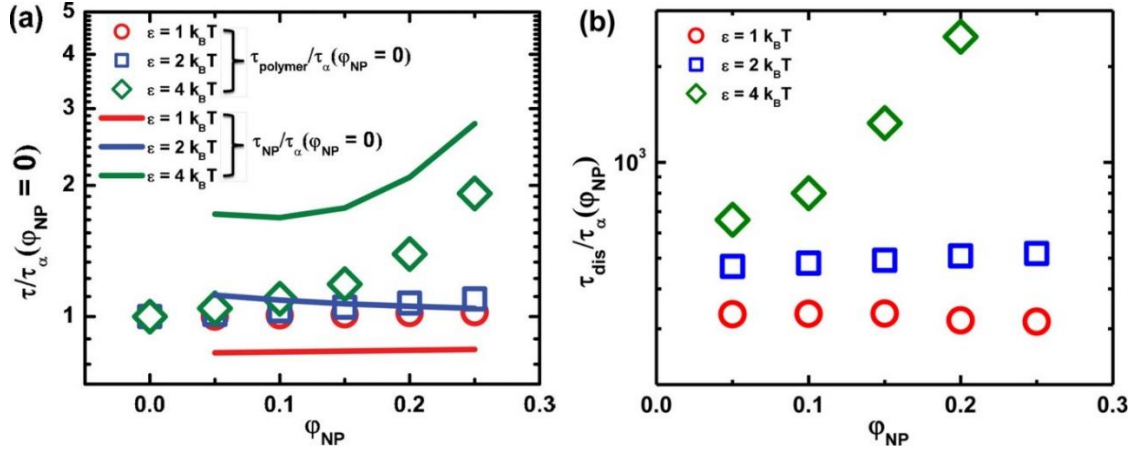


Figure 7.6: Molecular dynamic (MD) simulation results for OAPS NPs in a polymer melt where the NPs and polymer segments are the same size. (a) The normalized alpha relaxation time of polymer segments ($\tau_{polymer}/\tau_\alpha(\phi_{NP} = 0)$, symbols) and NPs ($\tau_{NP}/\tau_\alpha(\phi_{NP} = 0)$, lines), where the alpha relaxation is normalized to the neat polymer relaxation time. (b) The normalized NP-segment dissociation time ($\tau_{dis}/\tau_\alpha(\phi_{NP})$) as a function of loading at different polymer-NP interaction strengths.

These temperature-sensitive bonds are responsible for the large increase in fragility; as loading increases more of these bonds form, and the reinforcement on cooling increases dramatically. At higher temperatures the OAPS, owing to their limited number of bonding sites and weak interactions with polymer chains, can desorb more easily and diffuse throughout the melt before re-attaching elsewhere. This nanoparticle motion is responsible for the negligible change in heat capacity step, ΔC_p , even at high loading where the polymer fraction is reduced. For similar reasons, the complex viscosity and entanglement plateau moduli of the P2VP-OAPS composites closely resemble the neat behavior at elevated temperatures, even at relatively high loading. The actual mechanism of the disentanglement and other details related to the rheological time scales requires further study with different molecular weights. However, what is clear is the need for an experimental understanding of the motion of OAPS nanoparticles in a polymer melt in order to fully explain the behavior of these PNCs with small, attractive nanoparticles.

7.5. Conclusions

This study investigated the experimental properties of PNCs with small ($D = 1.8$ nm) OAPS nanoparticles (NPs) in a polymer melt and compared them to PNCs with conventionally-sized ($D = 25$ nm) silica NPs. The size of the OAPS NP is on the order of a polymer segment, and the size and bonding behavior of the OAPS NPs leads to several striking results. The OAPS nanoparticles provide large shifts in T_g and increase in fragility when mixed in a polymer melt that far exceed those of conventional silica NPs. On the contrary, they have relatively small changes in thermodynamic and viscoelastic properties at high temperature, again opposite to conventional silica PNCs. The source of these striking results is the weak and limited interactions between the OAPS NPs and the polymer chains. At low temperatures, the OAPS NPs act as temporary cross-linkers which reinforce the polymers; the large number of these temperature-sensitive bonds causes the rapidly-slowng dynamics on cooling. At higher temperatures, the NPs can desorb more easily and diffuse throughout the polymer melt, facilitating the neat-like thermodynamic and viscoelastic behavior. The modest change in viscosity from neat at high temperatures is particularly exciting from a PNC processing standpoint. The question posed for further research is how to understand nanoparticle mobility in the context of size and bonding strength so that rational design of PNCs with these exciting properties can be achieved.

8. Diffusion of Small Attractive Nanoparticles in a Polymer Melt

This chapter explores the diffusion of adsorbing nanoparticles in a poly(propylene glycol) (PPG) polymer melt using dynamic light scattering. The diffusion of two nanoparticle sizes, $D = 1.8$ nm (OAPS) and $D = 10$ nm (silica), were measured as a function of PPG molecular weight. These experimental diffusion values are compared to their predicted Stokes-Einstein (SE) diffusion coefficients. For the $D = 10$ nm NPs, the diffusion exhibited slower than SE behavior owing to the adsorbed polymer layer which increased the effective size of the nanoparticle. For the $D = 1.8$ nm NPs, the diffusion was initially slower than SE but crossed over to an enhanced diffusion, up to 20 times faster than SE at highest molecular weight. The non-monotonic diffusion behavior is explained by a vehicle mechanism which dominates at higher molecular weight and is heavily dependent on the polymer-nanoparticle desorption time. A qualitative general description of nanoparticle diffusion is given based on nanoparticle size and polymer-NP interaction strength.

8.1. Introduction

The transport of nanoparticles (NPs) in polymer systems is of fundamental interest for many research disciplines ranging from material science and engineering [37, 78, 196-198] to biological applications such as drug delivery [199, 200] and protein diffusion [201, 202]. For polymer nanocomposite materials, the diffusion of nanoparticles is important for processing as it determines how the nanoparticles organize in the polymer melt or solution [9, 78]. As was discussed in the previous chapter, nanoparticle mobility can also be an asset for PNC design,

where small OAPS NPs caused unexpectedly small viscoelastic and thermodynamic changes to the PNCs while still facilitating enhanced mechanical reinforcement [203].

The classical description for the motion of a spherical NP in a simple liquid is given by the Stokes-Einstein equation:

$$D_{SE} = \frac{k_B T}{6\pi\eta R_{NP}} \quad (8.1)$$

Here R_{NP} is the radius of the NP and η is the liquid medium shear viscosity [1]. This simple description often fails to describe nanoparticle motion in many polymeric systems, where large deviations have been measured in cellular environments [204, 205], polymer melts [81-83], and polymer solutions [206, 207]. The reason the SE relation fails is the macromolecular structure of the polymer has a more complicated interaction with the nanoparticle than a simple (i.e. low molecular weight) liquid would [208]. Further, this description assumes that the size of the nanoparticle is larger than the length scales associated with structural and dynamic relaxation of the fluid, which for polymers is not necessarily the case [1].

The relevant parameters for describing the polymer melt environment surrounding the NPs are the radius of gyration R_g (related to the molecular weight), the polymer segment size, and the tube diameter d_t (related to the entanglement of the chains in melt). These parameters control polymer relaxations across many length scales that are integral to the viscosity in these different regimes. For the local viscosity near the nanoparticle, the polymer-nanoparticle interaction energy becomes a critical parameter as well. Non-attractive (non-adsorbing) nanoparticles can have huge SE violations, $D/D_{SE} > 1$, (where the experimental diffusion is much faster than the SE diffusion) for NPs smaller than the tube diameter [81, 82]. This enhanced diffusion can even occur in the unentangled regime for nanoparticles with a radius that

is less than the radius of gyration. This problem of non-adsorbing nanoparticles in a polymer melt and solution has been well studied from theory [80, 85, 209, 210] and simulation [78, 211].

The diffusion of attractive (adsorbing) NPs, however, is much less understood owing to the more complicated local interaction between polymer and nanoparticle. This system is much more relevant to polymer nanocomposites, however, since the attractive polymer-nanoparticle interaction is what facilitates the interesting macroscopic properties of PNCs [9, 18, 114]. Further, non-adsorbing NPs tend to aggregate and have problems with dispersion, whereas adsorbing NPs can mitigate these problems [208]. The attractive NPs introduce a new critical parameter that is specific to each system: the polymer-NP desorption time, τ_{des} . Nanoparticles with a sufficiently long desorption time should be slowed by the chains adsorbing to the surface, possibly significantly if the melt is highly entangled. This case applies to the PNC studies of Chapters 4 and 5 that used 25 nm silica NPs where NP diffusion was essentially ignored. A recent study [79] measured the NP diffusion for attractive 26 nm silica NPs in a P2VP melt; the experimental diffusion was slower than SE and this suppression grew with increasing molecular weight. This behavior was explained by accounting for the adsorbed polymer layer that created an effectively larger nanoparticle than the bare R_{NP} used in the SE equation. What is unclear is if this picture applies for NPs smaller than d_t and R_g , as is the case for the OAPS NPs that were studied in chapter 7. Some theoretical works have explored this problem, where NP diffusion is described by a combination of hydrodynamic SE and non-hydrodynamic local frictional contributions [80, 85]. This theory gives quantitative estimates for SE violations for different nanoparticle sizes, polymer molecular weights, and polymer-NP interactions. However, the diffusion behavior of small, attractive nanoparticles has yet to be studied experimentally as a function of molecular weight.

This chapter examines a systematic study of the diffusion of adsorbing nanoparticles in a poly(propylene glycol) (PPG) polymer melt of different molecular weights. The two NPs studied, silica ($R = 5$ nm) and octaaminophenylsilsesquioxane (OAPS) ($R = 0.88$ nm), are the same types of nanoparticles studied in Chapter 7. The experimental diffusion is measured with dynamic light scattering and is compared with the SE prediction using the known bare size of the NPs and the macroscopic viscosity of the polymer measured with rheology. For the entire MW range studied, the silica NPs showed slower than SE diffusion ($D/D_{SE} < 1$) that progressively becomes more suppressed with increasing MW. This diffusion is explained with a core-shell mechanism previously described for the large, adsorbing NPs in the P2VP-silica study [79]. The OAPS NPs also initially exhibit slower than SE diffusion for lower molecular weight polymers but cross over to enhanced ($D/D_{SE} > 1$) diffusion at larger molecular weight. The crossover from suppressed to enhanced diffusion occurs for the molecular weight where $R_g \sim R_{NP}$. We describe the non-monotonic D/D_{SE} for the OAPS NPs in PPG using a theoretical framework where the dominant diffusion mechanism crosses over from the core-shell mechanism to a vehicle mechanism. This vehicle mechanism is strongly dependent on the OAPS desorption time τ_{des} , which is argued to be the crucial parameter for understanding the diffusion of small, attractive NPs in a polymer melt. These descriptions are summarized with a general, qualitative description of nanoparticle diffusion in polymer melts.

8.2. Experimental Methods

Polypropylene glycol (PPG) of different molecular weights 76, 425, 1000, 2000, and 4000 g/mol), tetrahydrofuran (THF), and methyl ethyl ketone (MEK) were purchased from Sigma-Aldrich and used as received. The polydispersity index (PDI) of the polymers was estimated from gel permeation chromatography (GPC) and is shown in Table 1. Additional PPG

of molecular weight 12200 and 18200 g/mol were obtained from Catalin Gainaru (TU Dortmund) as a gift. Two different nanoparticles were used: silica ($R = 5.0 \pm 1.3$ nm, purchased from Nissan Chemicals) and OAPS ($R = 0.88 \pm 0.002$ nm, purchased from Mayaterials). The distributions of nanoparticle sizes for silica were estimated by measuring their diffusion in MEK solution using dynamic light scattering. The OAPS sizes were determined from the SAXS measurements [203] of Chapter 7. As before, both silica and OAPS form hydrogen bonds with PPG and are considered to have an attractive interaction with the polymer.

The polymer nanocomposite samples were prepared by first dissolving 4g of PPG at a concentration of 1g/mL in THF for OAPS and MEK for silica. The nanoparticle solutions were added dropwise to these polymer solutions under stirring. After stirring for 20 min, the cap was removed from the vial and the solvent was allowed to evaporate under stirring in the hood at room temperature. Samples were then vacuum-dried for 24 h at room temperature with an Isotemp Model 280A (Fisher Scientific) vacuum oven at a vacuum of 10^{-6} mbar. After drying both, the PPG-OAPS and the PPG-silica were filtered using a 0.02 μm Anotop and 0.1 μm PTFE syringe filter, respectively, using a custom-built filtering device. The final concentration of nanoparticles does not exceed ~ 1 wt % (~ 0.7 vol %) for PPG-OAPS samples. For the PPG-silica PNCs, the concentration was significantly lower than ~ 1 wt % because of the filtering as well as the need to prevent NP aggregation. We were not able to measure the silica NPs' diffusion in the 12200 and 18200 PPG MWs because the remaining NPs aggregated.

Dynamic light scattering (DLS) was used to measure the translational diffusion coefficient of the nanoparticles in PPG melts at 291K. A HeNe laser (Newport R-31425, 632.8 nm, 35 mW) with vertically polarized light was employed to scatter light off the sample. At an angle of 90° from the incident laser, the scattered light was collected, passed through an analyzer

with VV polarization, and filtered using a Semrock 632.8 nm MaxLine cleanup filter to suppress Raman and fluorescent signals from the sample. The filtered light was collected with an ALV static and dynamic enhancer and passed through a beam splitter, which divided the beam into two equal light signals that are detected by two avalanche photodiodes (Pacer SPCMAQRH-14-FC). An ALV-7004 digital correlator took this scattered light intensity data from the photodiodes and calculated a cross correlation function whose decay time is used to determine the experimental diffusion coefficient. The value of the decay time and diffusion coefficients are listed in Table 1.

Rheological measurements of neat PPG, PPG-OAPS, and PPG-silica were performed on an AR-2000ex rheometer (TA Instruments) with a cone-plane geometry in an environmental chamber. The cone has a diameter of 25 mm, a cone angle of 2°, and 58 µm in truncation. Viscosities were measured at T = 291 K in flow mode at a continuous shear rate of 10 s⁻¹. Because of their relatively low NP loading, the viscosities of the PNC systems were the same as the neat polymers. These values are listed in Table 1.

8.3. Experimental Results

Dynamic light scattering measurements provide the intensity correlation functions shown in Figure 8.1a for the PPG-OAPS system which are used to determine the diffusion coefficients. The data are fit with an exponential decay function shown below, from which the decay times can be used to calculate the diffusion coefficient:

$$g_1(t) = [A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}]^2 + \text{constant} \quad (8.2)$$

Each of the decay processes has a distinct decay time τ and signal amplitude A . The main decay process used to calculate nanoparticle diffusion is the second fastest exponential function, with

Table 8.1: Results for OAPS and silica nanoparticle diffusion in PPG melts: molecular weight M_w , polydispersity index (PDI), shear viscosity η , dynamic light scattering decay time τ , chain radius of gyration R_g based on characteristic ratio $C_\infty = 5.1$ [212], nanoparticle (NP) diffusion coefficient D , the expected value of D_{SE} using the bare NP radius, the ratio of NP to SE diffusivities D/D_{SE} , and the number of entanglements N/N_e assuming a molecular weight between entanglements of $M_E = 2832$ [212]. The PPG tube diameter is $d_t = 4.9$ nm [212].

Name	M_w g/mol	PDI	η Pa·s	Decay τ s	R_g nm	D m ² /s	D_{SE} m ² /s	D/D_{SE}	N/N_e
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OAPS

1	76(PG)	1	0.04322	4.60E-4		5.39E-12	5.61E-12		0.026
2	425	1.27	0.134	0.00181	0.65	1.34E-12	1.81E-12	0.74	0.15
3	1000	1.12	0.18662	0.00291	0.99	8.31E-13	1.30E-12	0.64	0.35
4	2000	1.05	0.385	0.00524	1.41	4.61E-13	6.29E-13	0.73	0.71
5	4000	1.03	1.25172	0.00751	1.99	3.21E-13	1.94E-13	1.66	1.41
6	12200		8.05	0.01042	3.47	2.31E-13	3.01E-14	7.68	4.31
7	18200		28.5	0.01494	4.24	1.61E-13	8.50E-15	18.92	6.43

Silica

1	76(PG)	1	0.04322	0.00253		9.81E-13	9.87E-13		0.026
2	425	1.27	0.134	0.0079	0.65	3.07E-13	3.18E-13	0.96	0.15
3	1000	1.12	0.18662	0.0116	0.99	2.09E-13	2.29E-13	0.91	0.35
4	2000	1.05	0.30898	0.02034	1.41	1.06E-13	1.38E-13	0.77	0.71
5	4000	1.03	1.25172	0.102	1.99	2.37E-14	3.41E-14	0.70	1.41

characteristic time τ_2 . In some cases, this one exponential function is sufficient to fit the data. However, a weaker, slower decay process is present in some spectra that is attributed to NP aggregation that was not large enough to be filtered out; this decay process is the τ_3 function. In several molecular weights a third process is needed to fit the data. This fastest but smallest τ_1 process is likely polymeric in origin. The introduction of two additional decay processes could produce multiple solutions and generally muddy the description of NP diffusion; however, the amplitude of the τ_2 process is always the largest of the three. The amplitude of τ_3 is also augmented by the larger intensity expected for aggregated NPs, which scales as $I \propto r^4$. This relationship indicates the number of NPs sampled for the τ_2 decay function is more significant than its amplitude ratio with the τ_3 process.

The experimental diffusion coefficient is calculated as follows:

$$D = \frac{1}{q^2\tau_2}, q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (8.3)$$

Here q is the scattering wave vector, λ is the laser wavelength ($\lambda = 633$ nm), and θ is the scattering wave vector, which is 90° for this laser setup. The obtained diffusion coefficients of the silica (black) and OAPS (red) NPs in PPG are shown Figure 8.2 as a function of PPG MW. At low MW, the diffusion of the two NPs appears to follow a similar power law dependence with molecular weight. As the MW crosses the entanglement MW, M_E , the silica diffusion appears to diverge from the OAPS diffusion, albeit for only the final data point. This sharp decrease in silica diffusion above M_E is contrasted with the OAPS diffusion, whose diffusivity appears to level off in the entangled regime. Whether this OAPS diffusivity will reach MW-independence (where diffusivity is completely constant) in the entangled regime is unclear. We can compare this OAPS diffusivity with the center-of-mass (CM) diffusion of PPG chains (blue) in melt

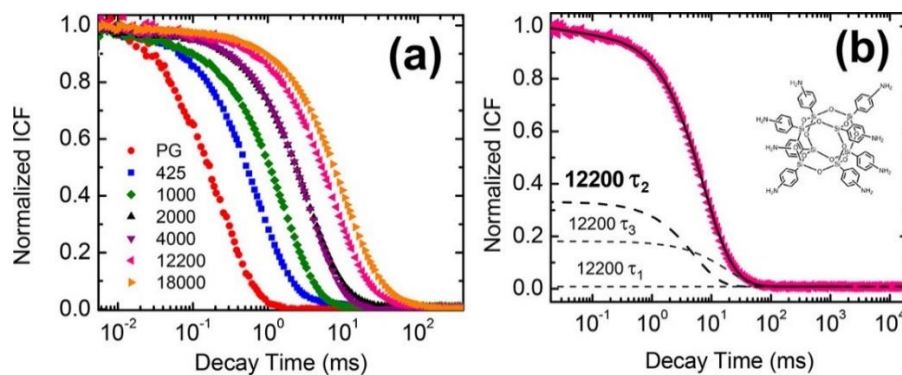


Figure 8.1: (a) Intensity correlation functions taken from dynamic light scattering measurements for OAPS particles in PPG of molecular weights shown (g/mol) (b) The intensity correlation function for the OAPS in PPG with MW = 12200 g/mol (symbols) where it is fit by a three-exponential decay function (solid line). Dashed lines show the three processes separately. The τ_2 decay functions are taken to be the single particle diffusion used for the experimental diffusion. The τ_1 and τ_3 decay functions are taken to be polymer relaxations and aggregated NP diffusion, respectively.

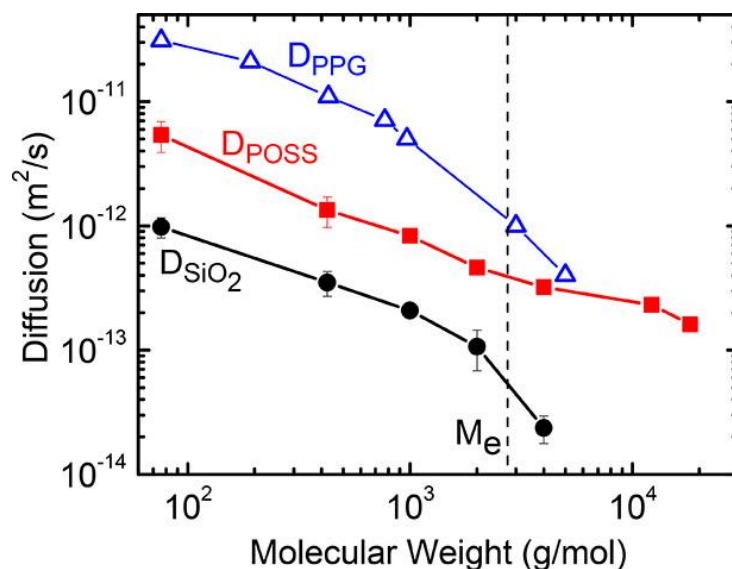


Figure 8.2: Diffusion coefficient for OAPS (red squares) and silica (black circles) nanoparticles as a function of PPG molecular weight. The center of mass diffusion coefficient of PPG chains in melt (blue triangles) taken from [35] is presented for comparison, where the error bars for this PPG melt diffusion (blue) are not known. The error bars for the nanoparticle diffusion that are not visible are smaller than the symbol size. The dashed line marks entanglement MW, taken to be $M_E = 2832$ g/mol from [212].

measured in a different study [35]. At low MW, the PPG chains clearly have a faster diffusivity than the OAPS NPs; however, the two approach the same value at a MW ~ 6000 g/mol $\sim 2M_E$.

8.4. Simulation and Theory Methods

These experimental diffusion results require sophisticated theoretical modeling in order to completely explain the NP behavior in a general, quantitative sense. Published theoretical models have accounted for the importance of nanoparticle size, degree of entanglement, and tube diameter for describing NP motion in a polymer melt [80, 209]. The diffusion behavior of the silica NPs can be roughly described with previously published descriptions of an adsorbed layer [79]. As was outlined in Chapter 7, however, the OAPS NPs are qualitatively different from other NPs in polymer nanocomposites: they have more limited binding sites and generally have a weaker interaction with polymer chains. As a result, it will be necessary to account for the segment-NP desorption time in order to describe their diffusion. Because it is very difficult to measure the desorption time experimentally, molecular dynamics (MD) simulations were performed in collaboration with this work which can directly tune the interaction strength between polymer and NP. The particle trajectories from these simulations can be used to calculate the diffusion behavior with molecular weight for different interaction energies. Additionally, these MD simulations, in combination with density functional theory (DFT) calculations, will provide estimates of the desorption time for this system. The desorption time estimates will justify a simple OAPS diffusion description that uses a single fitting parameter. A more quantitatively rigorous discussion of the OAPS diffusion is described by the primary authors of this section in a separate theory paper [213], but this work is outside the scope of this thesis.

Molecular Dynamics (MD) Simulations

Coarse-grained molecular dynamics (MD) simulations are used to predict the diffusion coefficients for different PPG-OAPS interaction strengths as a function of chain length. MD simulations are not performed on PPG-silica because the computation time is too long for such large nanoparticles. The parameters of the simulations are set in such a way to mimic the PPG-OAPS system; the basic principle is the same as the MD simulations in Chapter 7 for P2VP-OAPS. The polymer is described by a Kremer and Grest [189] bead-spring model with chain lengths $N = 10, 30, 90, 200, 400$, where the bonding angles are set such that the entanglement length is $N_E = 45$. The nanoparticles are modeled as icosahedrons with a size 1.8σ , where σ is the bead size, and dispersed in the melt. The nanoparticle volume fraction is extremely low, $\phi_{NP} \sim 0.0014$; this low loading is chosen so that the NP diffusion is not influenced by other NPs. The polymer-NP interaction is tuned for different interaction strengths ranging from $\varepsilon \sim 2k_B T$ to $\sim 32k_B T$, where the simulations are performed at $T = 291\text{K}$.

The diffusion coefficients are directly calculated from the particle trajectories for both polymer and nanoparticle. The plot of polymer segment and NP diffusion for different interaction energies as a function of chain length is shown in Figure 8.3. The N -dependence of the polymer segment diffusion (solid, square points) is similar for all interaction energies, which is expected in the dilute NP limit. In general, at lower N the NP diffusivity (line and scatter points) is slower than the polymer segment diffusivity; this behavior changes when the NP diffusion levels off at higher N . The N where this levelling-off occurs depends on the interaction energy: higher interaction strength ε means higher N for the onset of N -independence.

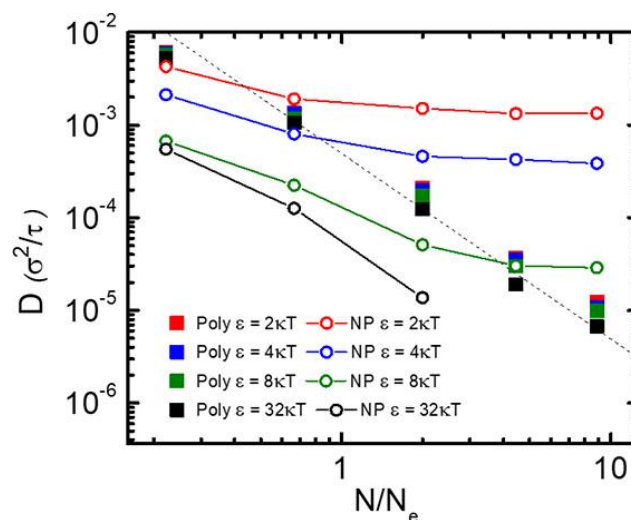


Figure 8.3: Molecular dynamics (MD) simulation results (open symbols + lines) for the diffusivity of small, attractive NPs modeled after OAPS. The diffusivities are calculated for different polymer-NP interaction strengths ε for different chain lengths N scaled by the entanglement molecular weight N_E ($N_E = 45$). The center of mass (CM) diffusion coefficient for the polymer segments is also presented (filled symbols). The dashed line shows the expected polymer chain diffusion for the entangled regime, M^{-2} . In general, the NP diffusion is slower than chain diffusion at low N , followed by the NP diffusivity leveling off and becoming faster than the chain diffusion at a characteristic N . Where this crossover occurs depends on the polymer-NP interaction strength, where a stronger ε means this levelling off occurs at higher N .

Density Functional Theory (DFT) Calculations

The coarse-grained MD simulations can predict diffusivity for different interaction energies, but it is not immediately apparent which energy value corresponds to the actual PPG-OAPS interaction energy. To estimate this interaction energy, spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio simulations package (VASP) package [214]. The details of the calculations are presented here [215]. The monomer-OAPS interaction energies are calculated by computing the difference between the total energy of the PPG-OAPS system and its individual molecular constituents. These DFT calculations suggest the effective monomer-OAPS attraction energy is ~ 15 kJ/mol, or $\sim 6k_B T$ at $T = 291$ K.

Theory for Attractive Nanoparticle Diffusion

Using the experimental data and MD simulations, in concert with previous models for nanoparticle diffusion in a polymer melt, we can generally describe the diffusion of attractive nanoparticles by the sum of two competing diffusion mechanisms:

$$D_{NP} = D_{core-shell} + D_{vehicle} \quad (8.4)$$

The core-shell mechanism is the dominant diffusion mechanism when the nanoparticle radius $R_{NP} > R_g$. For these large attractive nanoparticles, the polymer chains form an adsorbed layer on the nanoparticle and alter the effective size of the NP, with $R_{eff} \sim R_{NP} + R_g$. This core-shell mechanism can be expressed straightforwardly with a modified Stokes-Einstein relation for the silica NPs:

$$D_{silica} = \frac{k_B T}{6\pi\eta R_{eff}} \quad (8.5)$$

In this expression, η is the macroscopic viscosity and R_{eff} is the effective radius of the NP with an adsorbed layer proportional to R_g . This procedure was used previously in the diffusion study on P2VP-silica [79] with a comparable $R_{NP} > R_g$. For the silica nanoparticles the desorption time is extremely long, so the vehicle contribution can essentially be ignored. The silica NPs remain in the $R_{NP} > R_g$ regime for all MW studied.

For the $R_g \gg R_{NP}$ regime, the vehicle diffusion term becomes the dominant mechanism of NP mobility [213]. Here, the polymers act as carriers of adsorbed nanoparticles, which can desorb and move to different chains. This vehicle mechanism will become molecular weight independent for long enough chains if the desorption time is less than the Rouse time of the chains themselves. If the desorption time is longer than the Rouse time, then the vehicle

diffusion should have a slight molecular weight dependence [213]. The OAPS NP spans both $R_{NP} > R_g$ and $R_{NP} < R_g$ regimes in this study, so a continuum description of the diffusivity is necessary. The following expression is used which contains a single adjustable parameter:

$$D_{NP} = D_{core-shell} + D_{vehicle} = \frac{k_B T}{6\pi\eta R_{eff}} + D_v \quad (8.6)$$

In this expression the $D_{core-shell}$ is the same description as for the silica; the D_v is the diffusion constant for the vehicle mechanism which for this OAPS system is set as a free parameter. The exact description of the vehicle contribution can be found in this companion paper [213]. For the purposes of this thesis, however, this D_v is simply taken to be a molecular weight independent constant that is material-specific to OAPS and PPG.

8.5. Discussion of Experimental Diffusion Measurements

Equipped with the MD simulations and theory descriptions, we can now explain the experimental diffusion results of the two NP systems studied. The silica NP theoretical description is more straightforward. The silica hydrodynamic radius measured in MEK solvent is $R_{NP} = 5.0 \pm 1.3$ nm; this size corresponds to a diameter that is (1) about twice as big as the PPG tube diameter, $d_t \sim 4.9$ nm, and (2) larger than the R_g of the highest MW PPG (4000 g/mol, $R_g \sim 2$ nm) used in experiments with silica NPs. The experimental diffusion of the silica NPs is observed to be slower than the predicted SE diffusion, i.e. $D/D_{SE} < 1$; as seen in Figure 8.4a, this SE violation grows with increasing MW. Using equation 8.5, the SE violations of the silica NPs in PPG are well described by the core-shell mechanism, where the NP follows the SE behavior but with a larger effective radius R_{eff} , owing to an adsorbed layer $\sim R_g$. This description is applicable for both unentangled and entangled polymer systems so long as the silica radius

$R_{NP} > R_g$ and the NP desorption time is sufficiently long, which is the expected case for this PPG-silica system.

The dramatic slowing down of silica diffusivity at high molecular weight is the cause of both the suppression of thermodynamic step seen in differential scanning calorimetry and for the gelation measured in rheology for the silica nanocomposites seen in previous chapters. The slow nanoparticle diffusion of these silica nanoparticles, especially for the adsorbing case, is why the NP diffusion generally is not considered when describing the behavior of PNCs. Though these nanoparticles are nanoscale and are responsible for changes in macroscopic properties of PNCs, it is not until the NP size is smaller than R_g that NP diffusion becomes a factor.

The SE violations of the OAPS nanoparticle of size $R_{NP} = 0.88 \pm 0.002$ nm [203] are distinct from the silica, as seen in Figure 8.4b. At the lowest MW, the OAPS show suppressed diffusion where the SE violations are below 1. For these low MWs, we can apply the same core-shell mechanism from equation 8.5 (this diffusion mechanism is the dashed line in Figure 8.4b). However, the D/D_{SE} reaches a minimum and crosses over to an enhanced diffusion where the D/D_{SE} increases rapidly with MW, up to a factor of ~ 20 times larger than the SE value. This enhanced diffusion is facilitated by the vehicle diffusion mechanism described in theory, where the D is either constant or weakly MW-dependent for sufficiently short segmental desorption time, τ_{des} .

Making the assumption that the D is essentially MW-independent, we can fit the curve using equation 8.6 to get a constant value of $D_{vehicle} \sim 2 \times 10^{-13}$ m²/s, which reasonably fits the data over the entire MW range shown (dotted line in Figure 8.4). The apparent crossover from the core-shell- to vehicle-dominated regime occurs at the MW where $R_g \sim R_{NP}$, as seen in Figure

8.4b. From a physical point of view, the R_g needs to be much larger than R_{NP} for the vehicle description to make sense; however, the crossover need not occur at precisely $R_g \sim R_{NP}$ for each system and is likely strongly affected by the desorption time τ_{des} which varies from system to system.

The MD simulations in Figure 8.3 show the existence of an N -independent regime for the OAPS NP diffusion whose onset begins at higher N with increasing interaction strength ε , a parameter directly related to τ_{des} . We do not have a way to estimate the τ_{des} using dynamic light scattering. We can compare the general behavior of the OAPS diffusivity to the simulations data and expectations from theory. First, we should expect the PPG chain diffusion to be faster than the OAPS diffusion so long as the desorption time is faster than chain reptation [213], $\tau_{des} < \tau_{rep}$. Comparing the PPG chain diffusion (blue in Figure 8.2) and the OAPS diffusion (red), we see the diffusivities meet at MW ~ 6000 , which for the simulations corresponds to $N/N_E \sim 2$. The crossover where chain and NP diffusion meet in the simulations occurs at $N/N_E \sim 0.7$ for $\varepsilon = 4k_B T$ and $N/N_E \sim 4.4$ for $\varepsilon = 8k_B T$. We can therefore roughly estimate that the crossover of diffusivities of OAPS and PPG chains occurs experimentally around $\varepsilon \sim 6k_B T \sim 15$ kJ/mol (taken at $T = 291$ K). This value is consistent with the DFT calculations for the PPG-OAPS system and suggests that an OAPS particle has exactly one hydrogen bond per adsorbed PPG molecule. Using this value, we can calculate the desorption time as $\tau_{des} \sim \tau_{seg} \exp 6 \sim 400\tau_{seg}$, where τ_{seg} is the PPG segmental relaxation time. Analysis of dielectric spectra for PPG in melt [35] shows that the segmental relaxation time is 3 orders faster than the chain relaxation time for MW ~ 5500 g/mol. This separation would suggest that indeed $\tau_{des} < \tau_{rep}$ and that the OAPS diffusion is firmly in the vehicle regime. This analysis and the diffusion results in Figure 8.2 support the proposed explanation for the P2VP-OAPS results in Chapter 7 that were attributed to

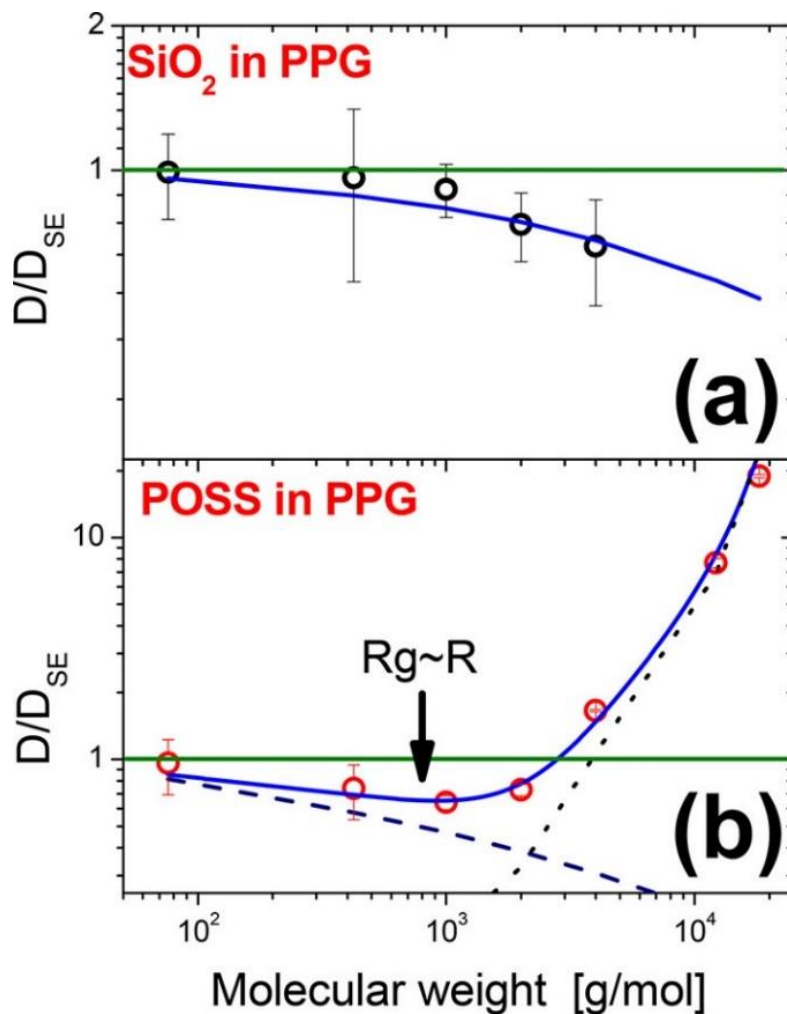


Figure 8.4: (a) Diffusion of silica NPs in PPG melts scaled by D_{SE} (symbols) vs MW of the polymer chains. The solid curve is the core-shell mechanism description where the polymer chains are taken to form a layer around the NP, giving an effective size of $R_{eff} \sim R_{NP} + R_g$. (b) Diffusion of the OAPS NPs in PPG melts scaled by D_{SE} (symbols) vs MW of the polymer chains. The black dashed curve is the same core-shell mechanism, while the black dotted curve corresponds to the diffusion of the vehicle mechanism predicted for sufficiently short desorption time τ_{des} . The solid blue curve is the sum of these two diffusion mechanisms. The arrow marks the molecular weight when $R_g \sim R_{OAPS} \sim 0.9$ nm. The error bars are of the order of the symbol size when not visible.

the OAPS NPs' mobility. Though it is not completely clear if the OAPS diffusion in Figure 8.2 becomes MW-independent, the fact that it can exceed the PPG center of mass diffusion (reptation) shows that sufficiently small NPs can have mobility that approaches the timescale of polymer motions.

8.6. General Picture for Nanoparticle Diffusion

Constructing a general quantitative theory to describe all nanoparticle diffusion scenarios (attractive vs non-attractive interactions, entangled vs unentangled melts) is a very difficult task. A theory which describes the continuous crossover from a core-shell mechanism to a vehicle mechanism is challenging given the disparity in even the qualitative pictures (an NP with a concentric polymer shell diffusing versus a small NP being dragged by a chain and potentially desorbing). The concept of the core-shell NP diffusion with an “effective” NP radius is overly simplistic and does not make physical sense when $R_{NP} < R_g$. The effective polymer shell for the core-shell regime should still have a desorption time dependence that is enhanced for smaller NPs with fewer bonding sites. For now, what can be offered is a qualitative description which provides a general framework for theoretical description of nanoparticles in a polymer melt. This general framework is plotted in Figure 8.5 for the diffusion (Figure 8.5a) and the SE violations (Figure 8.5b).

The simplest case is for nanoparticle size $R_{NP} > R_g$, where the NP diffusion should follow the SE prediction with an effective radius equal to R_{NP} for the nonadsorbing case (thick black line) and $\sim R_{NP} + R_g$ for the strongly adsorbing case (thick blue line). The diffusion description is more complex for when $R_{NP} < R_g$, especially when $R_{NP} < d_t/2$. The diffusion behavior for the non-adsorbing case is well described by current theories [80, 209] where the NP

diffusion can be much faster than the SE prediction, especially so for sizes $R_{NP} < d_t/2$ and in strongly entangled melts ($N \gg N_E$). For adsorbing nanoparticles of size $R_{NP} < R_g$, the description becomes more complicated owing to the dependence of the desorption time. For a very long τ_{des} , the NP diffusion will be controlled by the dynamics of the adsorbed chains [216, 217] (shown as red dashed lines in Figure 8.5). This NP behavior is exhibited by the lime-green lines in Figure 8.5; at low MW the diffusion follows the core-shell behavior (suppressed SE violations) while at high MW the diffusion will follow the chain diffusion (red dashed line). In the case of a desorption time shorter than chain reptation time, $\tau_{des} < \tau_{rep}$, the NP diffusion will become entirely or mostly MW independent at higher MW (seen in the thin blue line). The qualitative behavior of the diffusion will resemble the nonadsorbing case (thin black line), with the diffusion being slower in proportion to some dynamic “effective layer” which is defined by the desorption time. More rigorous theoretical descriptions are necessary to describe this dynamic effective layer, which requires a quantitative estimate of the desorption time along with an understanding of its relation to different polymer relaxation times.

8.7. Conclusion

Dynamic light scattering measurements were used to measure the diffusion coefficients in PPG melts for two nanoparticle sizes with an attractive interaction, $D = 10$ nm (silica) and $D = 1.8$ nm (OAPS). The silica NPs exhibit slower than SE diffusion for the entire MW range studied (where the NP size $R_{NP} > R_g$ for all MWs), which can be explained by a modified SE equation where the NP has an effective larger size $R_{eff} \sim R_{NP} + R_g$. The OAPS NP has initially this same slower than SE behavior but crosses over to an enhanced diffusion at a MW where $R_{NP} \sim R_g$. Using MD simulations and theory, this crossover is explained as a transition from a core-shell

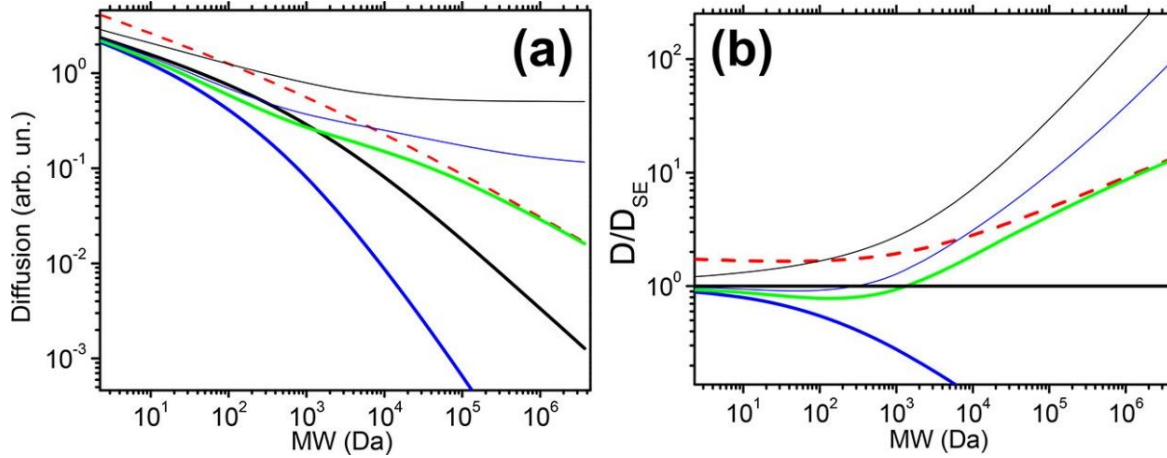


Figure 8.5: (a) Qualitative description for a general framework for nanoparticle diffusion vs polymer molecular weight in concentrated polymer solutions and melts. For the case of nonadsorbing chains, standard Stokes-Einstein behavior (thick black line) is expected for $R_{NP} > R_g$; when $R_{NP} < R_g$ for nonadsorbing chains, the diffusivity levels off to a MW-independent regime at high enough MW (thin black line). For adsorbing chains, the behavior becomes more complicated. For $R_{NP} > R_g$, the diffusion follows the SE description but with an effective radius $R_{eff} = R_{NP} + R^*$ where $R^* \sim R_g$ (thick blue line). In the case of $R_{NP} < R_g$, this same effective radius is used but with R^* defined by the polymer-NP desorption time (thin blue line). When this polymer-NP adsorption is very strong for these $R_{NP} < R_g$ sized NPs (thick green line), diffusion follows the polymer chain diffusion (shown independently as a red dashed line) at higher MW (b) The same curves showing the ratio of diffusion to the classical SE prediction, D/D_{SE} .

dominated diffusion (where the adsorbed polymer is described as a shell on the nanoparticle) and a vehicle-dominated diffusion (where the polymer chain is much larger than the NP and controls its motion). The vehicle diffusion mechanism is controlled by the strength of the polymer-NP interaction, which is defined by the segmental desorption time. For strong adsorption the NP diffuses with the chain and is essentially “along for the ride”; for weaker adsorption the NP detaches and diffuses in a MW-independent manner. The crossover to this MW-independent regime is critically related to desorption time but to predict it quantitatively requires knowledge of other factors like tube diameter, degree of entanglement, and NP size. A qualitative, general picture of nanoparticle diffusion in a polymer melt is given which describes the diffusion behavior in terms of polymer-nanoparticle interaction and NP size. These two quantities are both related to the polymer-NP desorption time, which will be important to measure experimentally so that a complete understanding of NP diffusion can be achieved. This experimental verification of OAPS mobility in a polymer melt is important for supporting the results measured for P2VP-OAPS in Chapter 7. Further, these OAPS studies motivate a new direction for nanocomposite research, one different from previous 25 nm silica studies, where nanoparticle mobility can be exploited for advantageous PNC properties.

9. Concluding Remarks

A brief summary of the thesis chapters is reviewed in the context of their importance to polymer nanocomposite research. An outlook on future research this work motivates is also discussed.

9.1. Conclusions

Polymer nanocomposites (PNCs) are an important class of hybrid polymeric materials where nanometer-size fillers are used to reinforce polymers for enhanced mechanical, electrical, optical, and transport properties. The study of PNCs is not only useful for lightweight, high strength materials but can also be extended to polymer electrolytes, membrane separation, and even biological applications such as drug delivery and tissue engineering. The interaction between filler and polymer, augmented by the nanometer size of the fillers, is what controls these unique properties. This interaction creates the interfacial polymer layer that extends 1-5 nm away from the nanoparticle surface; this interfacial polymer is shown to have modified structure and dynamics from the neat polymer. The goal of PNC research is to understand what controls this interfacial layer and how can these parameters be manipulated towards rational design. This dissertation answers this broad question by focusing on polymer dynamics and local structure near the nanoparticle surface, and how both polymer and nanoparticle characteristics control these properties.

Chapters 4 and 5 of this thesis involved a more conventional approach to studying polymer nanocomposites, where the interfacial polymer layer was investigated with combined experimental and analytic methods. Chapter 4 analyzed broadband dielectric spectra of a model PNC system and determined a heterogeneous interfacial layer model produced distinct results

that reveal important properties of PNCs. Namely, we found the PNCs have a reduced dielectric amplitude with loading and temperature, an effect attributed to chain stretching in the interface. The interfacial layer thickness was also found to increase with decreasing temperature, a relationship we argue is related to the increase of cooperativity length-scale upon cooling to T_g predicted from Adam-Gibbs theory for glasses.

Chapter 5 used these analysis methods on an experimental study which systematically investigated the effect of chain rigidity on the interfacial layer thickness in PNCs. Three different experimental techniques measured the dynamic (BDS), static (SAXS), and thermodynamic (TM-DSC) interfacial layers for four different PNC systems of varying chain rigidity, defined by characteristic ratio C_∞ . All three techniques showed that the interfacial thickness grows with chain rigidity above a critical C_∞ . These results show that adsorbed, rigid chains alter polymer dynamics and structure away from the NP surface to a greater extent than flexible chains. These two chapters demonstrate how polymer-specific properties directly alter the dynamics and local structure of the interfacial layer, which can be detected and quantified from measurement and analysis.

Chapter 6 explores in more detail the temperature dependence of the dielectric amplitude of PNC systems. A BDS comparison of neat, PNC, and a PNC system with the free polymer removed (termed polymer-adsorbed NPs) was done for different molecular weights. We determined that the dielectric amplitude decreases with decreasing temperature for systems with dipole ordering at the NP surface caused by chain packing; meanwhile, dielectric amplitude increases with decreasing temperature for the neat polymers with disordered dipoles throughout. This disordering effect is augmented by molecular weight; higher MW systems with less efficient chain packing and faster segmental dynamics do not have as large of an increase in

dielectric amplitude with T as compared to lower MW systems. These results reiterate how molecular weight and entropic effects alter the chain organization on the NP surface, and specifically how this structure is manifested in distinct measurable properties.

Chapter 7 takes a different approach to studying polymer dynamics at the NP surface by using a smaller nanoparticle of size comparable to a polymer segment. This size regime produces vastly different results from conventionally sized NPs. These small NPs produce greatly enhanced T_g shifts and fragility with NP loading; however, they still produce relatively small changes in thermodynamics and viscoelasticity. Backed up with results from MD simulations, these effects are attributed to the mobility of the small NPs. The previous chapters' description of an interfacial layer surrounding an immobile nanoparticle is no longer applicable; instead, we argue that NPs act as temporary crosslinkers which can reinforce the polymer chains at low temperature but desorb and diffuse at higher temperatures.

Motivated by these striking results, the motion of NPs in a polymer melt were studied in Chapter 8 as a function of the polymer molecular weight. The conventionally sized NPs have a diffusion that slows with increasing molecular weight, especially in the entangled regime. The smaller NPs used in Chapter 7, however, have a diffusion that appears to level off in the entangled regime, eclipsing the chain diffusion itself. This enhanced diffusion is argued to be controlled by the desorption time of the NP, which is expected to become a more dominant effect as nanoparticle size decreases.

9.2. Future Research

The results from these polymer nanocomposite studies, aside from their explicit conclusions, illustrate a couple broad points about PNC research. First, they demonstrate how

intrinsic properties of the polymer chains alter their structure and dynamics at the interface extending from the nanoparticle surface. Second, they demonstrate the importance of nanoparticle size, which for small, segment-size nanoparticles can drastically alter mechanical reinforcement while maintaining sufficient mobility for easy processability.

Future polymer nanocomposite research can expand the design landscape by focusing on nanoparticle aspects in addition to polymer characteristics. Nanoparticle mobility should be investigated even further to better understand polymer-NP desorption time, as well as NP diffusion's temperature- and q -dependence. The polymer-nanoparticle interaction can be modified by mixing different NP and polymer systems, by chemical modification, or by introducing new polymer and NP geometries. Another potential avenue for PNC study is to modify the chemistry of the nanoparticle itself: polymeric "soft" nanoparticles that could potentially be great for dispersion, processing, and hierarchical organization. The structure and dynamics of these polymeric NPs could produce some interesting effects that may unlock novel properties of PNCs not available to rigid NPs. Nanocomposite research will continue to design filler and polymer relationships where both species' utility is maximized towards creating novel and advantageous materials.

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Vita

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