1. Summary and Introduction / Zusammenfassung und Einleitung

1.1 Structural and Dynamical Properties of Atactic Polystyrene in the Interface and Interphase Region Surrounding Grafted and Ungrafted Silica Nanoparticles

The composite industry has long achieved enhanced material properties by mixing micro sized inorganic filler particles with a polymer matrix[1,2]. This is because the combination of two or more different materials can have a synergistic effect on the overall composite material properties imparting advantages that are absent in the individual constituents. A well-known example is that of adding carbon black as reinforcing material to increase tire strength, toughness, and resistance to tear and abrasion[3,4]. To achieve improved materials performance, the design of conventional composites has typically focused on reducing the dimensions of the filler particles. This is done in order to increase the filler surface area to enable greater interaction with the polymer matrix. Consequently, these efforts have received a significant boost with the dawn of the 'nano era'. Wherein experimental methods and tools are now used to synthesize, characterize, and investigate matter at the nano-scale level [10^{-9} m] which is close to molecular and atomic dimensions. The advent of such methods is exciting as it suddenly offers new possibilities of creating novel materials that can be tailored at very small dimensions. This expectation has been derived from the notion that the behavior of materials at their nanoscale level directly influences their microscopic properties and consequently their bulk macroscopic characteristics. As is typical in any emerging field, the challenge is to understand the fundamental aspects that control the final observable properties of these composite materials.

In contrast to the behavior of materials in conventional composites, recent experimental observations of polymer nanocomposites have demonstrated multifunctional changes in their properties. Examples include - but are not limited to - the decrease in the polymer viscosity[5], shifts in the polymer glass transition temperature[6,7], and changes in the composite material's thermo-mechanical[8,9] properties. However, what is still lacking and remains unclear are the fundamental explanations for the differences in the behavior between conventional composites and nanocomposites. In order to address questions pertaining to these differences, this PhD work was part of a large European Union consortium of universities and industrial partners, NanoModel. The aim of the group was to develop a unified scientific understanding from both experimentalists and theoreticians on the behavior of polymers in the presence of a surface. Such understanding of the important controlling parameters would ultimately support the design of industrial polymer nanocomposite materials. Therefore, both

the structural and dynamical investigations always sought to address some of several important open questions that necessitated this work. These questions include among other things: (1) Does a nanoparticle influence the behavior of the surrounding polymer? (2) Since the dispersion state of the nanoparticles is known to control the resulting nanocomposite properties, which controlling parameters are important in obtaining a well-mixed polymer nanocomposite? (3) What role does the size/dimension of the nanoparticle play? (4) Is it necessary to graft or attach polymers to the filler particles, in other words, functionalizing the nanoparticles to facilitate their dispersion in the polymer melt? (5) How long should the grafted polymer chains be relative to the bulk polymer and which grafting density is optimal to achieve a good dispersion state? (6) To what extent are the polymer properties in the interface (next to the surface) and interphase (where grafted and bulk free polymer chains mix) region changed if they are at all? (7) Which parameters influence the width or extent of both the interface and interphase region? (8) Can we observe the same phenomena or changes by employing both experimental and theoretical approaches?

Therefore, the contribution of this PhD thesis within the NanoModel framework was to investigate the structural and dynamical properties of atactic polystyrene in the vicinity of a silica nanoparticle as a model system for polymer nanocomposites at the atomistic level (see Figure 1.1 for a simulation snapshot). This model system was chosen because of its importance to the NanoModel partners since bulk polystyrene is an important, largely used, and well characterized polymer while silica is a typical traditional filler particle. Naturally, consortium partners like BASF would find it invaluable to produce new tailored plastics with superior properties to the traditional ones. At the same time, partners like BOSCH and CRP-FIAT would benefit from knowing the nanoparticle effect on the mechanical properties and the processing of the nanocomposite which directly impacts their injection molding processes for example. On the experimental front, Fribourg University, Juelich, and Epidoris were involved in nanocomposite sample preparation and characterization. These experimental results validated those obtained from computational studies from TU Darmstadt, National University of Athens, Trieste University, and BASF. Therefore, the influence of the nanoparticles of various diameters (3.0, 4.0, and 5.0 nm) and grafting states (0.0, 0.5, and 1.0 chains/nm^2) on atactic polystyrene was studied. To perform this work, a computer molecular dynamics (MD) simulation tool, YASP[10], was employed. This tool numerically solves Newton's equations of motion for a system of interacting atoms to generate a trajectory of their movements. Following this, the resulting trajectories can be analyzed for different properties that characterize the structure, dynamics, and thermodynamics of the system.
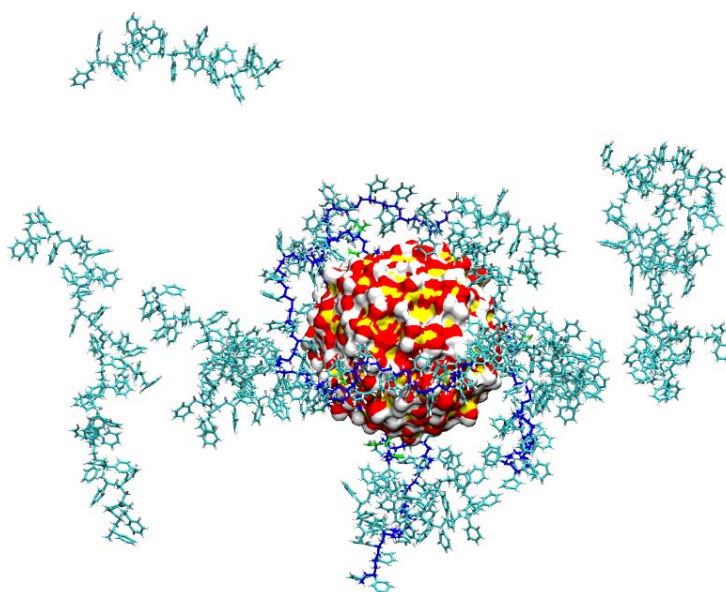
Figure 1.1. Schematic representation of the spherical silica nanoparticle, grafted (shown by the blue backbone carbon atoms) and free (all in cyan) atactic polystyrene chains. Note: There are more grafted and free chains in the simulation which are not shown to improve the clarity of the figure.

The use of atomistic MD simulations has the advantage of being able to investigate both static and dynamic properties of a system in fine detail. The ensuing results have the benefit of being related to experimental observations such as those probed by nuclear magnetic resonance[11] (NMR) and dielectric spectroscopy[12] (DS) studies. Additionally, other experimental techniques like neutron, x-ray, and light scattering now allow the determination of the atomistic structure of a material. Thus, computer modeling techniques interface with and complement experimental methods in understanding the link between structural and dynamical properties of polymers. While many experimental[5,6,9,13-20] investigations have been performed to study the behavior of polymers at surfaces, very few atomistic[21-25] computer modeling studies have been done. This necessitates the development a unified theoretical and experimental understanding of the polymer static and dynamic modifications in the presence of a surface. This is important because such changes determine in part the overall material properties. Examples of these material properties include their mechanical strength, appearance, how well they can be processed, and the duration of the polymer aging process. Additionally, this work sets a foundation for coarse-grained simulations, which investigate longer polymer chains and bigger systems.

Static and dynamic properties of polymers determine whether nanoparticles form clusters or are well dispersed in a polymer melt. This is a pivotal challenge in experimental techniques because it is difficult to control the dispersion of nanoparticles, which finally determines the resulting material

properties. Parameters that influence the static, dynamic, and nanoparticle dispersion state include - but are not limited to - the nanoparticle size, grafting density, the ratio of the length of grafted to free chains, and surface-polymer interactions. Therefore, developing an understanding of how these parameters interplay with each other will aid in the control and tailoring of the final nanoparticle dispersion state.

The first half of this cumulative PhD thesis, chapter 2, presents results of the atactic polystyrene structure around the nanoparticle. The quantities of interest were the polymer density, radius of gyration, and its orientation relative to the nanoparticle surface. The analysis of the computer simulation output trajectory files resolved these polymer properties as a function of distance from the nanoparticle surface to quantify the surface effect. Varying both the polymer grafting density and the nanoparticle surface curvature enabled the understanding of how these two parameters interplay and influence the polymer's structural properties. For instance, the extents of the polymer density modifications under the influence of the nanoparticle surface indicate the wettability of the surface by the polymer. This is important in mitigating adhesive failure and mechanical stress distribution in the nanocomposite material. At the same time, the density changes directly influence the polymer dynamical properties like the glass transition temperature and polymer aging processes. Therefore, understanding and being able to control these changes is vital since polymer properties like the elastic modulus and conductivity amongst many other physical properties change significantly around the polymer glass transition. These observations underscore not only the importance of the polymer in the interface region but also the width of the interphase region. The latter is influenced by the nanoparticle grafting state and the nanoparticle curvature as investigated in this work but also on the length ratio between the grafted and free polymer chains. While changes in the polymer radius of gyration give a measure of how stretched a polymer coil is, this has the effect of directly influencing the packing of polymer chains and their orientation. Additionally, the induced orientation of the polymer and its segments is important in processes that depend on transport properties such as electrical and thermal conductivity. Therefore, the different polymer structural properties are interlinked and understanding their cause-and-effect gives tuning parameters in the design of polymer nanocomposites.

Complementary to structural properties discussed in chapter 2, chapter 3 forms the second half of this thesis and discusses the dynamical properties of the polymer. These included the mean-squared displacement (MSD) of the polymer chain center-of-mass and reorientational dynamics of intramolecular segment vectors. These quantities were also calculated under different nanoparticle grafting states and surface curvature. Changes in the polymer chain MSD and the reorientation of its end-to-end vector have given a measure of the global polymer mobility. To understand the local

dynamics at the monomer level, the reorientation of a three-monomer and the C_α-C_{para} segment vector as well as the backbone C_α-H bond vector was investigated (see Figure 1.2). The advantage of obtaining such a local resolution is that it allows for comparison with experimental NMR and DS studies which probe the C-H bond vector and the C_α-C_{para} segment vectors, respectively. To develop a unified understanding, explanations of the dynamical property changes were linked to the previously observed structural properties either in the interface or interphase region, see chapter 2.
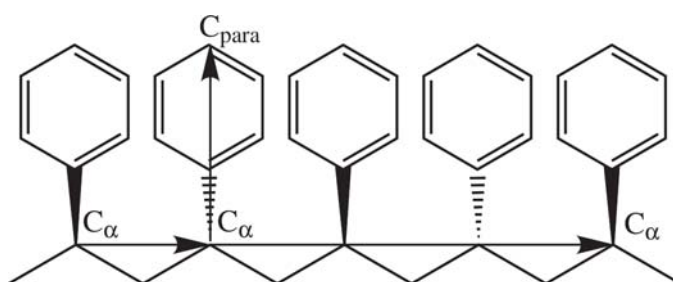

Figure 1.2. This schematic diagram is of a 5 monomer polystyrene chain to show the one monomer (C_α-C_α), three monomers (C_α ... C_α), and C_α-C_{para} segment vectors considered in the study of chain segmental dynamics.

The objectives to this thesis were to use the molecular dynamics simulation tool (YASP), setup the model system under investigation, perform the simulations, and write analysis programs to determine the different polymer properties. Therefore, I interpreted, understood, and explained my results in light of their interconnectedness as well as results from other simulations and experimental work on polymer nanocomposite systems. Finally, this work ends with chapter four which encompasses the conclusions and an outlook for further investigations.