

**The Effect of Composition and Architecture on Polymer
Behavior in Homopolymer Blends and Inter-filament Bonding in
3D Printed Models**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

**Edward Roy Duranty
December 2015**

Copyright © 2015 by Edward R. Duranty
All rights reserved.

DEDICATION

This dissertation is dedicated to my loving fiancée Sarah Camp. Without her patience and guidance I would surely have gone mad many years ago and the work presented here would never have been finished. I would also like to dedicate this work to my parents Ed and Paige Duranty who supported me throughout this entire ordeal and were always available with an ear to listen and a shoulder to cry on.

ACKNOWLEDGEMENTS

I would like to acknowledge the financial and academic support of Dr. Mark Dadmun without which this dissertation would have never been possible. I would like to thank my committee members Dr. Mike Kilbey, Dr. Frank Vogt, and Dr. Chad Duty for their time and consideration during this long process. I would additionally like to thank all my colleagues in my current research lab for their companionship over the past few years including Ms. Halie Martin, Dr. Brad Miller and Mr. Jason Lang. I would specifically like to thank Dr. Adam Imel and Mr. Brian Morgan for the extended sessions on the therapy couch that kept me sane. Additionally I would like to thank all of the graduate students who came through graduate school before me and provided a source of hope and inspiration, especially Dr. Jeremiah Woodcock, Dr. Bo Luttrell, Dr. Lesley Thompson, Dr. Rebecca Horton, and Dr. Stephen Gibson. Finally, I would like to thank all of the people outside of the University of Tennessee who have remained by my side and believed in me for all of these years including but not limited to: Richard and Dana Camp, Bobbie and Richard Adams, Tom and Caitlin Ramon, the family of Andy and Shelly Thomas, the family Joe and Bev Cofelice, Daniel Peck, and Derek Henderson.

ABSTRACT

This dissertation presents work that increases our understanding of the effects of composition and architecture on copolymer structure and dynamics and how they affect material diffusion between filaments in a 3D printed model.

Copolymers are polymer chains made up of at least two different monomers.

The ordering and arrangement of the two monomer species within a copolymer can have drastic effects on the behavior and properties of the copolymer.

The first chapter of this dissertation examines how the copolymer composition affects the structure and dynamics of the chain in a homopolymer blend. This study used a modified Monte Carlo BFM to simulate random polystyrene(PS)-polymethymethacrylate(PMMA) copolymers in a PMMA matrix. The results suggest that the faster moving PS segments in the copolymer chain dominate the chain's motion. However, concentration fluctuations in the local volume around segments of the chain ultimately slow the chain down. This work sheds light into why a randomly distributed copolymer will move faster than a di-block copolymer of the same monomer composition.

The next project focused on the effect of copolymer architecture on the structure and dynamics of branched polymers in a homopolymer matrix using a Monte Carlo simulation. In these simulations, branched polymer consisted of a backbone and the side-chains being unlike monomer species. The number and the molecular weight of the branches was varied to study the effects of branch packing densities on homopolymer copolymer comb structure and motion.

Additionally, the temperature varied to determine the effect of available thermal energy on each architectural copolymer configuration. The results of this project concluded that the structure and motion of a branched polymer are a result of the balance in the thermodynamic environment surrounding the copolymer.

Finally, the effect of inter-filament heat and copolymer diffusion on inter-filament bonding in 3D printed part was examined. In this study the importance of thermal history in the print environment was determined quantitatively and its effect on the adhesion between acrylonitrile-butadiene-styrene (ABS) copolymer filaments was probed. Additionally, the interface between ABS filaments was improved using a chemical cross-linker. These studies provide insight into improving the mechanical strength of 3D printed parts.

TABLE OF CONTENTS

Chapter 1 : Introduction	1
The Role of Copolymer Compatibilizers in Polymer Blends	2
The Thermodynamics of Polymer Blends	4
Compatibilization	8
Effects of Copolymer Sequence and Structural Configuration on Interfacial Modification.....	11
Polymer Diffusion in the Melt	13
The Use of Coarse-grained Monte Carlo Simulations to model Polymer Dynamics	16
Dynamic Monte Carlo Theoretical Basis.....	18
Coarse-Grained Monte Carlo Simulation Models.....	20
Continuum-Based Models	21
Lattice-Based Models	22
Modifying the BFM with an Monomer Overlap Penalty.....	27
Chapter 2 : Modeling Copolymer Dynamics in Copolymer/Homopolymer Blends via a Modified Bond Fluctuation Monte Carlo Simulation.....	30
Abstract	31
Introduction	32
Model & Simulation Details	35
Results	40
Structure	40
Dynamics.....	42
Discussion	46
Conclusion	54
Acknowledgements	55
Chapter 3 : A Study of the Effects of Branching on polymer Combs using a BFM Monte Carlo Simulation.....	56
Abstract	57
Introduction	59
Model and Simulations Details	62
Results	65
Constant Backbone/Branch Ratio with Varying Temperature	65
Variable Branch/Backbone Ratio at Constant Temperature	71
Discussion	77
Structure	77
Dynamics.....	82
Conclusion	85
Acknowledgements	86
Chapter 4 : Introduction to 3D Printing with Polymeric Materials and Fused Deposition Modeling	87
Extrusion Based Additive Manufacturing using Polymeric Materials via Fused Deposition Modeling.....	88

Fused Deposition Modeling	88
Materials Used in FDM	89
Overview of the FDM Process	91
Strength of FDM Printed Parts	94
Chapter 5 : Understanding and Improving the Quality of Inter-filament Bonding in FDM 3-D Printing	96
Abstract	97
Introduction	99
Experimental	104
Sample Production	104
Thermoplastic Characterization	106
Bed Temperature Profiles	108
Interfacial Adhesion Measurements.....	111
Results	115
Characterization of ABS	115
Bed Temperature Profiles	117
Dynamic Mechanical Analysis	120
Interfacial Adhesion Measurements.....	120
Discussion	125
Correlating Inter-filament Bonding to Heat and Material Transfer	125
Chemical Interlayer Bonding.....	132
Conclusion	136
Chapter 6 : Conclusions and Future Work	138
Modeling Structure and Dynamics of Polymer Systems Using Monte Carlo Simulations.....	139
Modeling Dynamics of Copolymer Systems	139
The Effects of Branching on Polymer Combs	140
Future Work.....	141
Inter-filament Bonding in FDM Printed Materials	142
References	144
Vita.....	155

LIST OF TABLES

Table 2.1: Diffusion Coefficients based on %MMA copolymer loading measured from A-type and R-type simulations.....	44
Table 5.1: Temperature Program for the Degradation of Different Components in ABS Samples.....	107
Table 5.2: Temperature of the top layer of the bottom half of the printed t-peel part after print pause.....	124

LIST OF FIGURES

Figure 1.1: Plot of the change in free energy of mixing with the composition of blend component 1. ¹¹	7
Figure 1.2: Phase diagram for a two component mixture featuring an UCST and an LCST not predicted by FH theory. ¹⁶	9
Figure 1.3: (Left) Examples of possible moves in the SAW. (Right) Example of forbidden move in the BFM.....	23
Figure 1.4: Illustration depicting two monomers overlapping at one corner, incurring an overlap penalty.....	29
Figure 2.1: Radial Pair Distribution functions for styrene-MMA, styrene-styrene, and copolymer MMA-matrix MMA monomer pairs for both the A- and R- type simulations at $f(\text{MMA})=0.60$	41
Figure 2.2: Styrene-styrene radial pair distribution functions for A- and R-types at varying MMA copolymer loadings.	43
Figure 2.3: Semi-log plot of the effective chain friction factor with respect to copolymer MMA composition for the A- and R- type motions. The red line indicates the predicted linear power law response.	45
Figure 2.4: Effective local concentrations of Styrene in the A- and R-type simulations where the line represents the predicted effective local concentration using Lodge-McLeish theory.	53
Figure 3.1: Radius of gyration of the branched copolymers for different temperatures at constant molecular weight. As T^* decreases, the copolymer chain starts to collapse in order to reduce thermodynamic interactions. Inset: Plot of R_g of combs with branch sizes equal to 4 vs reduced temperature. .67	67
Figure 3.2: The average radius of gyration for individual branches on each comb from Figure 1 at various temperatures. There does not seem to prevalent trend with temperature.....	69
Figure 3.3: Diffusion coefficients for polymer combs in Figure 1 at different temperatures. The combs at $T^*=2$ exhibit a near linear dependency on branch size.	70
Figure 3.4: A log-log plot of the radius of gyration of individual branches in combs of different molecular weights.....	72
Figure 3.5: Log-log plot of the radius of gyration for the polymer combs described in figure 4. At lower branch density (the black colored data points), the chain is much more condensed.....	73
Figure 3.6: Log-log plot of the diffusion coefficient for the series of polymer combs from Figure 3. These combs feature a -2 power law dependence on molecular weight suggesting they are reptating.....	75
Figure 3.7: Log-log plot of the diffusion coefficients of the linear analogues of the combs in Figure 5. These combs exhibit a -1.3 power law dependence on molecular weight.....	76

Figure 3.8: Diffusion coefficients for linear polymers with an infinite overlap penalty. These chains exhibit the expected -1 power law dependency on molecular weight for polymers below the entanglement length.....	78
Figure 5.1: Diagram of a commercial desktop 3D printer.....	105
Figure 5.2: 3D rendering of H (left) and Z (right) 3D printed samples used in the bed temperature and DMA experiments mentioned above.....	110
Figure 5.3: (Left) 3D diagram of t-peel sample that is sliced into gcode. (Middle) The bottom half of a t-peel sample including samples. (Right) T-peel sample being peeled.	112
Figure 5.4: Chemical structure of 4,4'-diaminodiphenylmethane, the diamine used for covalent crosslinking in the interfacial adhesion experiments above	114
Figure 5.5: TGA data for both ABS samples used in this work (ABS White and New White), pre- and post-extrusion ABS samples from MDF (MDF and Post MDF), two SAN samples (Sparkle 29 and SAN 56.4), and pure PB and pure PAN samples.....	116
Figure 5.6: TGA data for pre-extruded ABS copolymer (green) and post-extruded printed ABS samples obtained from MDF at ORNL.....	118
Figure 5.7: Bed temperature profiles for 80°C (top left), 100°C (top right), and 120°C (bottom).	119
Figure 5.8: The storage modulus (E') as of samples printed in the H geometry at 100°C (red) and 120°C (blue).	121
Figure 5.9: Interfacial adhesion (G_a) measured for the neat ABS printed samples (black square), samples treated with DADPM cross-linker (red circle), and samples treated with CuSO ₄ cross-linker (blue triangle).....	122
Figure 5.10: Cross-section of a Z orientation sample notice the gap in the middle decreases as more layers are deposited towards the top right in addition to more definitive filament. The black arrow points in the direction of material deposition.	128

CHAPTER 1 : INTRODUCTION

The Role of Copolymer Compatibilizers in Polymer Blends

In the past few decades, the blending of various polymer and chemical systems that include modification of surfaces or interfaces between two chemically different environments has become very popular. By blending two physically or chemically dissimilar systems, new materials can be created that combine physical properties contributed from each component, resulting in a single blend that exhibits desired properties. In order to accomplish this blending a compatibilizer is often required to chemically facilitate mixing between the multiple disparate parts of the blend. Most often without a chemical compatibilizer the blend will separate into two distinct phases partitioned by a weak interface due to the incompatible thermodynamic nature of the components in a polymer blend. In the case of an immiscible blend between two polymers, without a copolymer compatibilizer comprised of components from each blend constituent at the interface of the two polymer systems, the blend will phase separate much like oil and water. Branched polymer combs consisting of a backbone with long side chains have been similarly used as polymer blend compatibilizers^{1,2} as well as surface modifiers.^{3,4} For each of these applications, the compatibilizer is essential to strengthening a well-defined interface between two chemically dissimilar materials that promotes dispersion between them. Since compatibilizers play such an important role in the creation of robust interfaces between dissimilar materials, the process of getting the compatibilizer to the interface becomes important. Fortunately, due to the chemical nature of a

compatibilizer, whether it is a linear copolymer or a branched polymer, will selectively segregate to the interface between two thermodynamically incompatible phases.^{5,6} However, the time required for the compatibilizer to diffuse through the bulk phase to the interface is dependent on the chemical architecture of the materials being blended. As a result, the diffusion of the interfacial modifier plays a vital role in the effectiveness of a chosen compatibilizer. The faster the compatibilizer diffuses through the bulk components of the blend, the higher probability it reaches the interface between the bulk components ensuring compatibilization.

However, the dynamics of polymer chains within multicomponent homopolymer/copolymer systems are not well understood or easily predicted because the role of connectivity within an individual polymer chain on the mobility of the different components is not well understood. Moreover, the impact of connectivity on polymer chain dynamics, including the connectivity of side-chains in branched polymers, affects the bulk properties of the blends and therefore the potential uses for the systems. A more profound understanding of the diffusion of a compatibilizer is required in order to more rationally choose an appropriate compatibilizer for a given blend. In order to investigate the diffusion process of polymers within a blend, an introduction into the thermodynamic environment within a polymer blend is needed.

The Thermodynamics of Polymer Blends

The thermodynamic environment of chemical blends is best explained in terms of the change in the Gibb's free energy of mixing ΔG_m presented in **Equation 1.1** when two species are blended together. The mixing process results in changes in the enthalpy and entropy of the system. The potential thermodynamic repulsive and attractive interactions are accounted for in the ΔH_m term, while possible arrangements of the two polymers is incorporated in the ΔS_m term at a given temperature T .⁷ When this process results in a negative net change in ΔG_m , the balance of the enthalpic ΔH_m term and the entropic ΔS_m results in a more favorable configuration of the system, which means the two components are miscible, forming a homogenous mixture. When ΔG_m becomes positive, usually either the enthalpic term increases or the entropic term decreases to the point of becoming dominant. If the chemical nature of the two components is too dissimilar, such as nonpolar oil mixing with polar water, the enthalpic term greatly increases. In the case that the number of possible configurations the system can take is restricted, such as when a polymer is blended with a large, hard nanoparticle that restricts motion, the entropic term decreases. In both of these cases, the separation of the two components into two distinct phases is most probable.

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \text{Equation 1.1}$$

However, this simple explanation is not quite accurate for polymer blends because Equation 1.1 was developed with small molecule systems in mind where ΔS_m is usually very large due to the large number of configurations that unconnected small molecules can arrange themselves in. In polymers, where individual monomers are bonded in a chain resulting in very large molecular weights, the number of arrangements is much lower, greatly decreasing the entropic ΔS_m term. Therefore, Flory and Huggins independently developed a modification to Equation 1.1 that applies to polymers and is presented as:

$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12}]^8 \quad \text{Equation 1.2}$$

In Equation 1.2, n_i and ϕ_i are the number of molecules and volume fraction of component i of the blend. Together, the first two terms in the bracket of Equation 1.2 represent the entropy of mixing between the two blend components. The enthalpy of mixing corresponds to the third term in Equation 1.2, where χ_{12} is the polymer-polymer interaction parameter for the polymer blend, which is related to the solubility parameters or cohesive energy of each polymer. In slightly polar or nonpolar systems, such as many polymers, Hildebrand solubility parameters can be used to determine χ_{12} ⁹, while in more energetically complicated polar systems the Hansen solubility parameters can be used to determine χ_{12} .¹⁰

In binary polymer mixtures, Flory-Huggins theory can be used to predict the range in ϕ_1 (and therefore $\phi_2 = 1 - \phi_1$) where the two components will phase separate. In a two phase system, the chemical potentials of the two phases are

equal. This translates to two points in the ΔG_m vs composition curve where the 1st derivatives of the curve at those points are equal; these two points are represented as A and B in Figure 1.1. Any mixture with a composition between points A and B will decompose into two separate phases, while mixtures with compositions between A and C or D and B will exist in a metastable state where any perturbation in energy in the system will cause the mixture to phase separate. In the composition regions between 0 and A and B and 1, the mixture will be stable, and will not phase separate.

The compositional boundary between the single and two phase regions is a curve where the first derivative of the ΔG_m is equal to zero, which is known as the binodal. The boundary between the two phase region and the metastable region can be described by a curve where the second derivative of the ΔG_m curve is set equal to zero, resulting in the spinodal. The point where the derivative of both binodal and the spinodal curves is zero corresponds to point X on the ΔG_m curve in Figure 1.1 and at this point the third derivative of the ΔG_m curve is also equal to zero. This point in the ΔG_m curve, point X in Figure 1.1, is known as the critical point. Using FH theory, the critical point where the binodal and spinodal meet is called the upper critical solution temperature and is labeled as UCST in Figure 1.2. Unfortunately, FH theory ignores free volume effects and therefore does not predict the existence of the lower critical solution temperature or LCST, which is depicted in Figure 1.2, where at higher temperatures the mixture starts to decompose into its separate components, a phenomenon that is common in

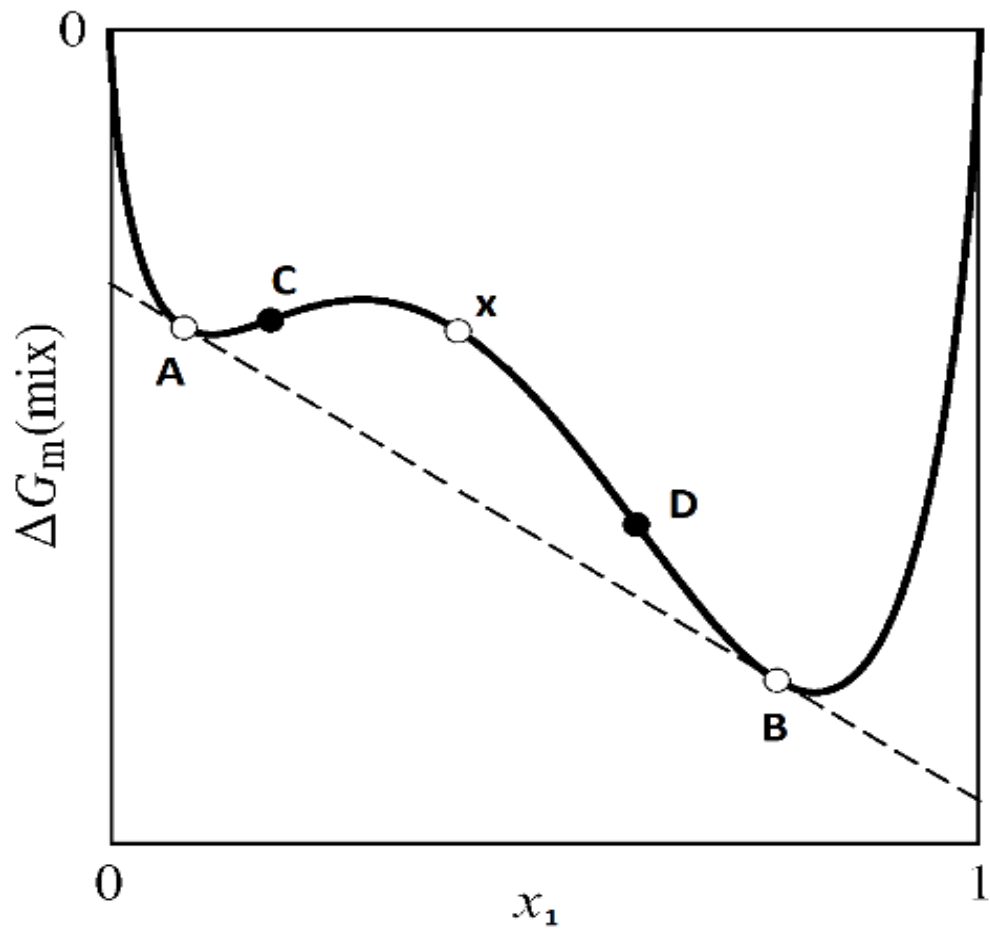


Figure 1.1: Plot of the change in free energy of mixing with the composition of blend component 1.¹¹

homogeneous mixtures of polymers. At higher temperatures free volume effects start to increase, leading to unfavorable mixing conditions that lead to the upper spinodal and binodal curves featuring an LCST in Figure 1.2.

Compatibilization

Often the chemical nature of polymers that exhibit desirable physical properties ensures that mixing with other polymers into a blend is thermodynamically improbable. As mentioned previously, in the case of immiscible or only slightly miscible blends, compatibilizers are often utilized to increase dispersion between two chemically incompatible by altering the thermodynamic landscape of a mixture and strengthen the interface thereby inhibiting coalescence. Compatibilizers must be able to minimize the coalescence of phases and the phase domain size within the blend while strengthening the interface between the phases of the blend. Therefore, the compatibilizer must somehow be thermodynamically compatible with each phase such that it is able to “anchor” itself in each phase and thereby establish a strong interface between the phases in the blend. In polymeric systems, this usually means that the compatibilizer must have favorable interactions to form entanglements with each phase at the boundary between them.^{12–15}

Di-block copolymers are common compatibilizers in polymer systems because they are made up of two blocks that can each be chosen to thermodynamically match a certain target phase. As a compatibilizer, di-block

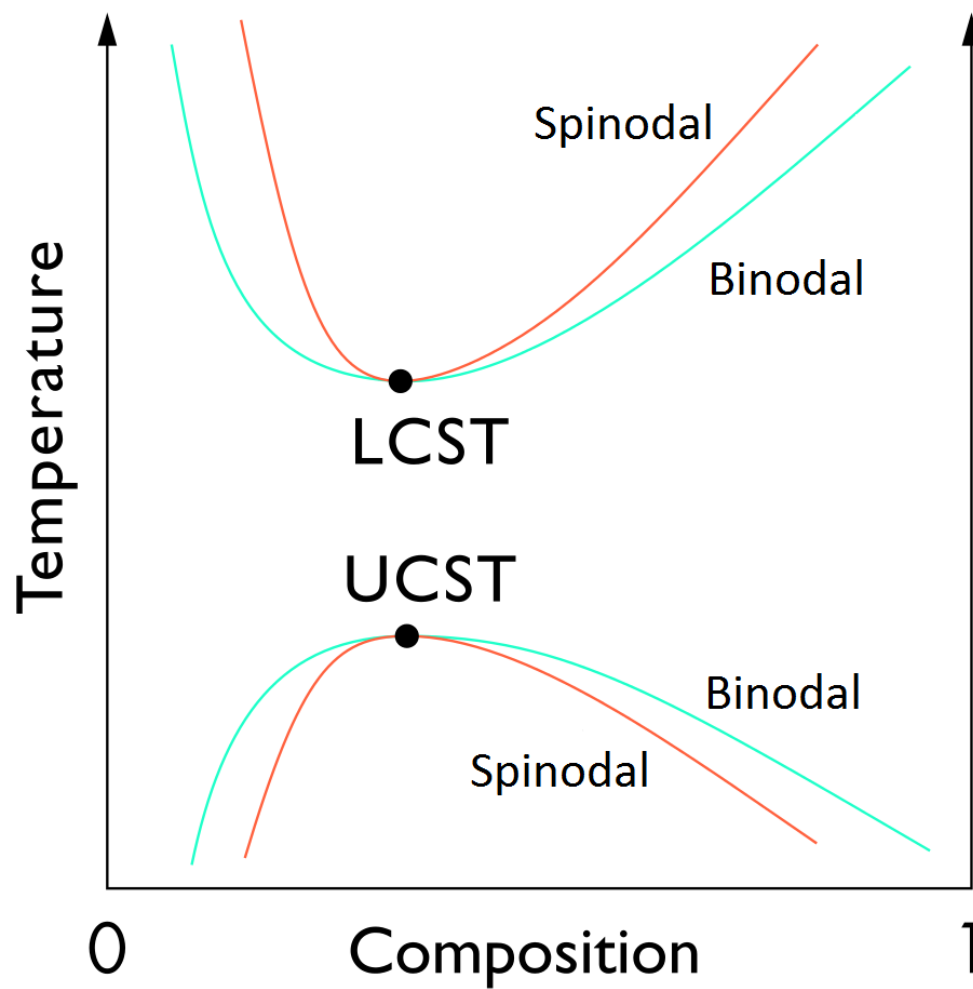


Figure 1.2: Phase diagram for a two component mixture featuring an UCST and an LCST not predicted by FH theory.¹⁶

copolymers can act much like surfactants, such as detergent in an oil and water blend, or lipid membranes, which is the membrane layer between parts of a biological cell, and can modify the interface between the two phases of a polymer blend. In such a capacity, the di-block copolymer acts to minimize the coalescence of large domains of each phase, increasing the surface area of the interface between the phases and ensuring a fine dispersion of one phase in another. The di-block copolymer also widens the interface between the two polymeric phases by entangling with each phase and reducing the unfavorable thermodynamic interactions caused by direct contact between the two phases.^{17–21} It has been experimentally demonstrated that the addition of an A-B di-block copolymer to the interface between an A-B polymer blend improves the physical properties of the phase separated system.^{22–27} When the di-block copolymers are placed at the interface between the two phases and the whole system is annealed, the di-blocks segregate into and entangle with each phase. The result is a much stronger interface and a total improvement of the blend properties over the properties of the individual blend components.

Another process by which di-block copolymers are used as compatibilizers is by forming a mixture of a di-block copolymer with a single homopolymer, and then blending the di-block/homopolymer mixture with another homopolymer to form a ternary mixture. In this system, the di-block copolymer would ideally diffuse to and reinforce the biphasic interface between the two homopolymers in the blend.^{14,15} Again, by using the di-block copolymer as a compatibilizer

between the two homopolymer phases, the mechanical properties of the of the blend are increased relative to the properties of the blend of the individual components. However, di-block copolymers are known to self-assemble into micelles in these systems, which can limit the mobility of the copolymer to the interface, which is crucial for compatibilization to be successful. If the di-block copolymer does not segregate to the biphasic interface, then compatibilization does not occur, and the remaining two phases in the ternary system will phase separate while the di-block copolymer remains in its thermodynamically preferred micelles. As a result, the immiscibility of di-block copolymers can limit their use as compatibilizers due to their tendency to self-assemble into micellar structures, thereby remaining in only one phase. Due to this tendency, understanding how the sequence distribution of the monomers within a copolymer affects the motion of the copolymer within a polymer blend becomes a vital key to developing new copolymers that can be used as compatibilizers for polymer blends.

Effects of Copolymer Sequence and Structural Configuration on Interfacial Modification

As discussed above, the structural and sequential arrangement of the monomers within a copolymer chain play an important role in how effective a copolymer might be as a blend compatibilizer. Copolymers containing monomers A and B can have different distributions of each monomer type in a linear chain, or can have side branches made up of A or B in a variety of distributions. Different sequence distributions and structural configurations can change the copolymer's properties including potential interactions with a

homopolymer matrix. The sequence of A and B monomers can be quantified based on how close the sequence is a random distribution using Equation 1.3. In Equation 1.3 P_x represents the normalized probability that two neighboring monomers on a copolymer chain are of a different type where P_{AB} is the percentage of AB dyads in the copolymer, P_A is the percent of A monomers and P_B is the percent of B monomers in the copolymer chain.²⁸ When P_x is close to zero the copolymer chain almost entirely consists of AA or BB monomer diads, while a value of one represents a randomly distributed copolymer chain, and finally a value of two indicates the copolymer chain is purely alternating. For example, a block copolymer would have a P_x value close to zero while a randomly distributed copolymer that was not quite purely alternating would have a P_x between one and 2.

$$P_x = \frac{P_{AB}}{P_A P_B} \quad \text{Equation 1.3}$$

The structural architecture of a copolymer chain can also affect a polymer's physical properties. Branched copolymers can come in many shapes and monomer sequences, where the number of side-chains, the molecular weight and the composition of these side chains can have a significant impact on the behavior and properties of the polymer. Examples of branched copolymers include: star copolymers which have a number of side-chains attached to a central point; grafted polymers such h-copolymers or pom-pom copolymers where side chains are attached to the ends of a linear backbone, and comb copolymers where side chains are distributed along a linear backbone. Each of

these polymer chain architectures offer different sets of properties that can be exploited as strategies for increasing the effective compatibilization of a copolymer for a given multi-component polymer blend.

Theoretical and experimental studies have determined that di-block copolymers arrange themselves at an interface between two phases such that the block most compatible with each phase extends out into that phase. While compatibilization using a di-block copolymer has been shown to increase the interfacial strength between the phases, studies have also shown that interfacial strength increases with the number blocks in a multi-block copolymer that is used as a compatibilizer.²⁹ Theory^{30–35} and resulting simulations^{31–33} have shown that the more times a copolymer compatibilizer is able to cross back and forth across the interface, the larger its effect on the interfacial strength. The results suggest that copolymers that feature many side-chains or branches that can be extended across the interface multiple times for each polymer chain and copolymers that featuring alternating regions of varying composition such as alternating or even random copolymers would act as effective compatibilizers in polymer blends.

Polymer Diffusion in the Melt

The random motion of small unconnected molecules in solution that is the result of collisions with other moving small molecules is referred to as Brownian motion and can be described using Equation 1.4 where $f(t)$ represents the random force due to collisions with time, ξ is the friction coefficient and $dx(t)/dt$ represents the change in position as a function of time t . The relationship in

Equation 1.4 yields a direct linear dependence of the mean-squared displacement of a particle undergoing Brownian motion with time. In polymeric systems where the constituent molecules within a polymer chain are connected, the motion of the chain becomes dependent not only on the random motion due to collisions as a function of time, but also on the molecular weight of the chain. The Rouse model describes the motion of a polymer chain within an unentangled melt by treating the polymer chain as a series of beads connected by harmonic springs that is arranged in an ideal Gaussian coil.³⁶ Equation 1.5 describes the motion of the polymer chain according to the Rouse model, where κ is the spring constant of the harmonic spring between each bead. The motion that is a result of the Rouse model yields a 0.5 dependence of the mean-squared displacement of the center-of-mass of the polymer chain on time, meaning that unentangled polymer chains move more slowly than free small molecules undergoing Brownian motion.

$$\zeta \frac{dx(t)}{dt} = f(t) \quad \text{Equation 1.4}$$

$$\zeta \frac{dx(t,n)}{dt} = \kappa \frac{\partial^2 x(t,n)}{\partial^2 n} + f(t) \quad \text{Equation 1.5}$$

Polymer chains that are above the entanglement molecular weight N_e are furthered slowed from Rousian motion due to the increased probability of entanglements between the moving polymer chain and the polymer matrix surrounding it in the melt, increasing its hindrance to motion. Since this center-of-mass Rouse-like motion for an entangled polymer is high improbable, motion

is restricted to short distances along the backbone of the polymer.³⁷ These topological restraints due to the surrounding polymer matrix constrain this motion to a tube-like region around the moving polymer chain's backbone.³⁸ The resulting diffusion process for entangled chains is known as reptation, and the diffusion coefficient for the center-of-mass for an entangled polymer chain, D_G , is expressed in Equation 1.6. This diffusion coefficient can also be expressed for a Rouse chain that remained untangled that was derived from Equation 1.5, D_{Rouse} . The product of the relationship in Equation 1.6 is that the diffusion of entangled polymer chains exhibit a -2 power law dependence on molecular weight, while the Rouse chain only exhibits a -1 dependence.

$$D_G = \frac{k_B T}{3N^2 \zeta} = \frac{D_{Rouse}}{3N} \quad \text{Equation 1.6}$$

The Effect of Copolymer Composition, Sequence and Structural Configuration on Dynamics

While it has been suggested that linear and branched copolymers may be effective compatibilizers at the phase interfaces in blends of homopolymers, the copolymer must reach the phase boundaries in order to successfully function as compatibilizers. Ergo, the dynamics of the copolymer within the homopolymer becomes vital to the process of ensuring good compatibilization. While many studies have been completed to examine the effect of copolymer sequence and branching on phase behavior, comparatively little work has been completed concerning the dynamics of these polymers in a blend with a linear homopolymer matrix. This is mainly a result of the difficulty in understanding the dynamics of

multi-component polymers systems that are complicated by the connectivity among the monomers in the copolymer. The effect of this connectivity on the dynamics of the entire chain is not well understood, therefore a course of study is required that correlates the dynamics of these polymers in a homopolymer matrix with the parameters space that is the result of the flexibility in sequence distribution and structural arrangement available in copolymers.

The Use of Coarse-grained Monte Carlo Simulations to model Polymer Dynamics

Computer simulations have been used in chemistry for many years to probe physical concepts that are not readily available experimentally such as the bond formation between two atoms and dipole-dipole interactions in chemical solutions. It is possible for simulations of chemical systems to be accurate down to the atomistic scale, however computational limitations such as processing time and available memory often impose the use of approximations in scope on simulations. In polymer science, where polymers are repeat monomeric units arranged in connected chains that exceed the size of the individual unit by orders of magnitude ($\sim 10^3 \text{\AA}$), the fine atomistic details between individual atoms becomes less important in defining the desired physical properties than the potential interactions and correlations between segments of monomer units.^{39,40} For these types of systems, interesting physical properties can be studied using simplified “course-grained” models in computer simulations.

Course-grained simulations are generally separated into two categories: Molecular Dynamics simulations and Monte Carlo simulations. Molecular Dynamics simulations numerically integrate the Newtonian equations of motion of the system thereby reliably simulating its classical dynamics. In polymer systems, relaxations of the polymer chain can occur at a very wide array of times ranging from the very fast local motion of the individual monomers and slow large-scale motions of the whole polymer chain. As a result of the large spatial and temporal range that has to be accounted for, reaching equilibrium in polymer systems using MD models is very tedious and in some cases convergence is computationally impossible. The resulting computational limitations place restrictions on the size and number of the polymer chains that can be studied within a MD simulation.

Monte Carlo methods provide an alternative to MD simulations for larger polymer systems because in Monte Carlo simulations chain segments or “effective monomers” are represented within the simulation usually as Kuhn segments instead of individual monomers. As a result of this abstraction, motion within a MC simulation is not local and alters larger portions of the chain, decreasing the total computation time needed for equilibration. MC methods are therefore better suited for systems containing a larger number of polymers of larger chain lengths since individual chain convergence is more efficient.⁴¹

Dynamic Monte Carlo Theoretical Basis

$$\langle A \rangle = \int d\mathbf{x} A(\mathbf{x}) P_{eq}(\mathbf{x}) = \frac{1}{Z} \int d\mathbf{x} A(\mathbf{x}) e^{-\beta U(\mathbf{x})} \quad \text{Equation 1.7}$$

$$\bar{A} = \frac{\sum_{m=1}^M A(\mathbf{x}_m) e^{-\beta U(\mathbf{x}_m)} / P_s(\mathbf{x}_m)}{\sum_{m=1}^M e^{-\beta U(\mathbf{x}_m)} / P_s(\mathbf{x}_m)} = \frac{\sum_{m=1}^M A(\mathbf{x}_m) W(\mathbf{x}_m)}{\sum_{m=1}^M W(\mathbf{x}_m)} \quad \text{Equation 1.8}$$

Dynamic Monte Carlo methods provide a numerical approach using equilibrium statistical mechanics for solving Equation 1.7 where $A(\mathbf{x})$ is some observable thermodynamic property in the canonical ensemble (where temperature is constant). A sample configuration is generated $\mathbf{x}_1, \dots, \mathbf{x}_m, \dots, \mathbf{x}_M$ with some distribution $P_s(\mathbf{x})$ and $A(\mathbf{x})$ is estimated using Equation 1.8 where the “weight” $W(\mathbf{x}) = P_{eq}(\mathbf{x})/P_s(\mathbf{x})$ is introduced.^{42–44} In Equation 1.8, $\bar{A}$ is a random variable while $\langle A \rangle$ is a number and whether or not $\bar{A}$ is a good estimate for $\bar{A}$ is dependent on the total number of configurations used M and on the choice of $P_s(\mathbf{x})$. As a result, $P_s(\mathbf{x})$ should resemble $P_{eq}(\mathbf{x})$ as much as possible in order to generate relevant results from an MC simulation.⁴¹

To this end, in most MC simulations a dynamic method called the Markov process is used to randomly generate a sequence of correlated configurations that which has $P_{eq}(\mathbf{x})$ as its equilibrium distribution.^{43,44} In the Markov process, the probability distribution for the next configuration in the process is only dependent on the current configuration and not on a configuration the system may have had in the past. Assuming the Markov process evolves in some discrete time step Δt , Equation 1.9 represents the probability for finding the system in configuration $\mathbf{x}$ at time t . In Equation 1.9, $w(\mathbf{x}|\mathbf{x}')$ represents the

probability of transitioning from x' configuration to the x configuration. Equation 1.9 represents the balance between the transition of all other states x' towards state x which increase $P(x)$ and the transition of states away from x where $x \neq x'$. Since the transition from x' to some state x will occur with certainty, the summation of the probability of transition across all states x' is equal to 1, which can be substituted into Equation 1.9, resulting in Equation 1.10.

$$P(x, t + 1) - P(x, t) = \sum_{x' \neq x} [w(x|x')P(x', t) - w(x'|x)P(x, t)] \quad \text{Equation 1.9}$$

$$P(x, t + 1) = \sum_{x'} w(x|x')P(x', t) \quad \text{Equation 1.10}$$

In order for the results of Equation 1.9 to be physically relevant, $P(x, t)$ must converge to a unique stationary distribution that is independent of the initial configuration of the system at large t and this distribution must be the canonical equilibrium distribution $P_{eq}(x)$. Therefore, the right-hand side of Equation 1.7 must go to zero for $P(x', t) = P_{eq}(x')$. If each term in the sum goes to zero separately, this condition is met leading to the condition of “detailed balance” in Equation 1.11.^{42–45} In order to accomplish this in MC simulations, the transition probability is split into two independent parts where a transition from x' to x according to some probability $P_{proposed}(x' \rightarrow x)$ is accepted or rejected with probabilities $acc(x' \rightarrow x)$ and $1 - acc(x' \rightarrow x)$ respectively. These definitions result in the relationship presented in Equation 1.11. To determine the probability that the transition will be accepted, Equation 1.12 must be solved for $acc(x' \rightarrow x)$ so we set the acceptance probability equation to result in some

function $F(\mathbf{x})$ that depends on the ratio of the product of the proposed distribution probability $P_{proposed}(\mathbf{x}' \rightarrow \mathbf{x})$ and the transition probability $acc(\mathbf{x}' \rightarrow \mathbf{x})$ for $\mathbf{x}' \rightarrow \mathbf{x}$ with the $P_{proposed}(\mathbf{x} \rightarrow \mathbf{x}')$ and $acc(\mathbf{x} \rightarrow \mathbf{x}')$ for the $\mathbf{x} \rightarrow \mathbf{x}'$ transition, resulting in Equation 1.13.⁴⁶ A common solution for $F(\mathbf{x})$ and the solution used in this work is expressed in Equation 1.14 and is known as the “Metropolis criterion”.⁴⁷ The Metropolis criterion is the basis for ensuring the detailed balance described above and ensures that the simulation results are independent of the initial configuration and converges to the canonical equilibrium distribution.

$$w(\mathbf{x}|\mathbf{x}')P_{eq}(\mathbf{x}') = w(\mathbf{x}'|\mathbf{x})P_{eq}(\mathbf{x}) \quad \text{Equation 1.11}$$

$$\frac{w(\mathbf{x}|\mathbf{x}')}{w(\mathbf{x}'|\mathbf{x})} = \frac{P_{pro}(\mathbf{x}' \rightarrow \mathbf{x})acc(\mathbf{x}' \rightarrow \mathbf{x})}{P_{pro}(\mathbf{x} \rightarrow \mathbf{x}')acc(\mathbf{x} \rightarrow \mathbf{x}')} = e^{-\beta U(\mathbf{x})} \quad \text{Equation 1.12}$$

$$acc(\mathbf{x}' \rightarrow \mathbf{x}) = F \left(\frac{P_{proposed}(\mathbf{x} \rightarrow \mathbf{x}')}{P_{proposed}(\mathbf{x}' \rightarrow \mathbf{x})} e^{-\beta[U(\mathbf{x})-U(\mathbf{x}')]}\right) \quad \text{Equation 1.13}$$

$$acc(\mathbf{x}' \rightarrow \mathbf{x}) = \min \left(1, \frac{P_{proposed}(\mathbf{x} \rightarrow \mathbf{x}')}{P_{proposed}(\mathbf{x}' \rightarrow \mathbf{x})} e^{-\beta[U(\mathbf{x})-U(\mathbf{x}')]}\right) \quad \text{Equation 1.14}$$

Coarse-Grained Monte Carlo Simulation Models

Coarse-grained Monte Carlo simulations of polymer systems are usually divided into two separate groups that are either lattice models or models on a continuum. Lattice models offer usability at the cost of spatial accuracy while continuum models are highly spatially accurate, however keeping track of monomers spatially and monomer “accounting” can be computationally challenging. Examples of on-lattice models are the Self-Avoiding Walk (SAW) developed to simulate a linear polymer in a good solvent and the Bond

Fluctuation Model (BFM), a lattice model that offers spatial flexibility similar to that of a continuum model. The BFM was used in both simulation experiments described below.

Continuum-Based Models

While continuum-based models are most commonly associated with molecular dynamics simulations, bead-spring models have been successfully used in Monte Carlo simulations.^{48,49} In these models, monomers that are connected along a polymer chain are bonded to one another via a finitely extendible non-linear elastic (FENE) potential that is expressed in Equation 1.15 and all monomers regardless of bonding interact with each other by the truncated and shifted Lennard-Jones (LJ) potential in Equation 1.16.⁴¹ The values of l_{max} and k in the FENE potential must be chosen such that bond crossing does not occur. The LJ potential in Equation 1.16 contains $C(r_{cut})$ that attenuates the effect of the potential as it approaches a cut-off parameter r_{cut} , ensuring the LJ potential is short-ranged and ϵ which represents the interaction energy and a length scale σ . Unlike in lattice models, in continuum models such as the Kremer-Grest model, monomer overlap is not strictly forbidden, and is controlled by both the FENE and LJ potentials. In the Kremer-Grest model, the parameters $r_{cut} = 2^{\frac{1}{6}}$ and $\sigma = 1$ are set so that monomer-monomer interactions become repulsive, simulating the effect of a good solvent, with starting bond lengths $l = 0.97$ to prevent monomer overlap.⁴⁹ The careful adjustment of these parameters is required to obtain physically relevant results in addition to the increased

difficulty of record keeping of monomer positions relative to the two field potentials are weaknesses of the continuum based Monte Carlo methods.

$$U_{ij}^{ch} = \begin{cases} -0.5kR_0^2 \ln \left[1 - (r_{ij}/R_0)^2 \right], & r_{ij} \ll R_0 \\ \infty, & \text{else} \end{cases} \quad \text{Equation 1.15}$$

$$U_{ij}^{LJ} = \begin{cases} 4\epsilon \left[\left(\sigma/r_{ij} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + C(r_{cut}) \right], & \text{for } r \leq r_{cut} \\ 0, & \text{else} \end{cases} \quad \text{Equation 1.16}$$

Lattice-Based Models

The Self-Avoiding Walk

The self avoiding walk (SAW) was developed as a model to describe polymer chains in good solvent and is defined on a discrete lattice, usually a square(2D) or cubic(3D) lattice. In the SAW, a monomer occupies exactly one lattice site and the bonds between connected monomers is equal to the space between each lattice site known as the lattice constant. The bond angles between each connected monomer in the SAW are a function of the lattice geometry and by the restriction on monomer overlap. This results in only a few possible motions in both two and three dimensions, examples of which are shown in Figure 1.1. Attractive interactions between monomers or monomer and solvent can be incorporated based on the nearest neighbors around a given monomer. All monomer motions are accepted or rejected based on the Metropolis condition.

As a result of the restriction on bond angles and the constant size of the bonds in a SAW, the dynamics of a given polymer chain are artificially slowed.

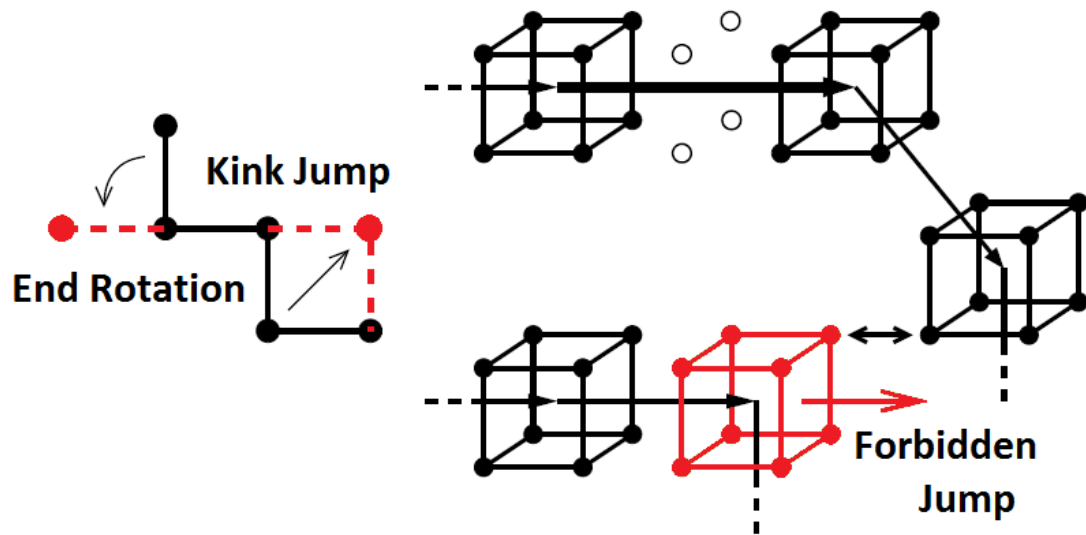


Figure 1.3: (Left) Examples of possible moves in the SAW. (Right) Example of forbidden move in the BFM.

The result of the combined restrictions is that polymer chain motion can only occur through the chain end greatly decreasing the ergodicity of the system undergoing a SAW.⁵⁰ While this result is most prevalent in two dimensional simulations, three dimensional simulations are also possible. In addition, the implication of the reduced possible bond angles prevents branched objects from being simulated using the SAW.⁵¹ As a result of these complications, dense configurations featuring long polymer chains undergoing a SAW can completely “freeze up” where these chains cannot move result in a highly non-random system where the resulting configuration from a SAW step is exactly the same as the previous configuration.⁴¹

The Bond Fluctuation Model

The Bond Fluctuation Model (BFM) was developed to deal with the restrictions of the SAW model by moving a polymeric object with local jumps of the monomers within a polymer chain. These moves do not conserve the set of bond vectors, or bond orientations, of the object but do conserve the number of bonds by allowing the bonds to have a variable bond length. The features are all implemented in the BFM that improve ergodicity while remaining on a lattice, preserving the ease-of-use of a lattice based model while providing bond flexibility normally associated with continuum based models.⁵¹

As a result of the flexibility of the BFM, there are many possible bond vectors between two monomers in a polymer chain. In order to implement varying bond lengths that are not simple multiples of the lattice constant l , the

size of a monomer representing a Kuhn segment is increased from a single lattice site to a whole unit cell of the lattice, which translates to either a square in 2D or a cube in 3D. The number of bond vector permutations is only restricted by two factors: the first is the restriction on bond overlap, and the second prevents bonding kinking, or two bonds intersecting one another, by forbidding monomer overlap using a hard-core monomer-monomer interaction. This imposes a range of possible bond lengths that is dependent on d or the number of dimensions represented in the simulation. In 2D, the restrictions only place a limit on the upper bound of the bond distance where $l_{max} = \sqrt{13}^{51,52}$ and while technically there is no lower bound in two dimensions, the hard-core monomer-monomer interaction imposes a *de jure* lower bound equal to the lattice constant l . For $d = 3$, the range of possible bond distances is $l \leq l_{max} = \sqrt{10}$ where this range is affected by the larger size of the monomer in the BFM which excludes some of the smaller bond vectors.⁵³ The resulting sets of possible bond vectors for 2D and 3D are presented in Equation 1.17 & Equation 1.18 respectively where $[x, y, z]$ represents a bond class of the same magnitude but may vary in direction. These sets of bond classes result in 41 possible bond angles in two dimensions⁵⁴ and 86 possible bond angles and a total of 108 possible bond vectors in 3D.⁵³

$$2D: \{\mathbf{b}\} = [2,0][2,1][2,2][3,0][3,1][3,2] \quad \text{Equation 1.17}$$

$$3D: \{\mathbf{b}\} = \{2,0,0\}\{2,1,0\}\{2,1,1\}\{2,2,1\}\{3,0,0\}\{3,1,0\} \quad \text{Equation 1.18}$$

During the course of the BFM, a single monomer is selected to move and a distance and a direction within the lattice is chosen as a possible move. If the attempted jump satisfies the bond distance requirement and the excluded volume interaction, meaning it does not overlap an existing monomer, the move is accepted. Additionally a finite interaction energy is usually implemented between monomers within the system which is usually implemented as a pairwise interaction potential between similar and dissimilar monomer types, allowing for use of the BFM in copolymer/homopolymer blends. Using such an interaction, the energy change in a local volume within a distance of $2 \leq r \leq \sqrt{6}$ around a given monomer is calculated and is used as the basis for acceptance using the Metropolis criterion. This distance r correlates to all of the monomers within a local volume that contribute to the first peak of the pair-distribution function⁵⁵ in a dense polymer system.⁵³

The BFM minimizes the ergodicity problems that the single-site SAW struggles with. Since the local jumps that monomers undergo during the course of the BFM allow the bond vector to change bond class, the algorithm allows chains to escape from the “frozen” configurations that can result from the SAW algorithm. Thus, the BFM provides a reliable framework for simulating a large number of long polymer chains without the ergodic pitfalls of a SAW and the prohibitive computational requirements of continuum-based molecular dynamics simulations.

Modifying the BFM with an Monomer Overlap Penalty

Wittmer *et. al.* have suggested modifying the BFM such that the restriction on monomer-monomer overlap is relaxed permitting monomers to overlap according to some finite energy penalty ε .⁵⁶ The purpose of attenuating the hard-core monomer-monomer interaction is so that the strength of density fluctuations in dense solutions and polymer melts can be varied to study their effects on static and dynamic properties of these systems.^{56,57} The dimensionless compressibility g can be calculated directly from the results of a MC simulation from the low-wave vector limit of the total monomer structure factor, the expression for which is presented in Equation 1.19. By adjust the parameter ε , the compressibility of the monomers in the system can be varied and the presence of long-range correlations that have been found in incompressible melts^{58–62} were studied in compressible systems.

$$G(q) \equiv \frac{1}{n_{mon}} \sum_{n,m=1}^{n_{mon}} \exp(-i\mathbf{q} \cdot (\mathbf{r}_n - \mathbf{r}_m)) \xrightarrow{q \rightarrow 0} g \equiv T\kappa_T\rho \quad \text{Equation 1.19}$$

In the modified BFM developed by Wittmer *et. al.* the monomer overlap penalty is implemented during the calculation of the total energy used in the Metropolis criterion for a given configuration. In addition to the change of energy incurred during the transition from configuration $\mathbf{x}'$ to $\mathbf{x}$ that is a result of the interaction potential between monomers, a positive energy penalty is assessed on a monomer-by-monomer basis for each of the eight corners that a given monomer overlaps with another monomer. In other words, for each of the

vertices on the lattice that a monomer overlaps with another, $\varepsilon/8$ is added to the total energy of the monomer, an illustration of this implementation can be found in Figure 1.1Figure 1.4. The parameter ε is referred to as the overlap “penalty” because it increases the total energy of a given configuration, decreasing the probability that the configuration will be accepted.

Wittmer *et. al.* performed a series of simulations where the value of ε was varied such that the dimensionless compressibility g ranged across four orders of magnitude.⁵⁶ It was found that the value of ε below which acceptance rate and monomer mobility are most effected is the range $1 \leq \varepsilon \leq 10$ where the simulation acceptance rate and monomer mobility decrease monotonously with ε . Above this range, the monomer mobility and therefore the acceptance rate becomes constant and the probability of movement becomes prohibitively low. At values of ε below this range, monomer mobility and acceptance rate reach a constant value that is independent of ε .⁵⁷ As a result of the increased monomer mobility associated with a lower value of ε , the overlap penalty modified BFM converges much more efficiently than the traditional BFM that has an effective overlap penalty of $\varepsilon = \infty$.

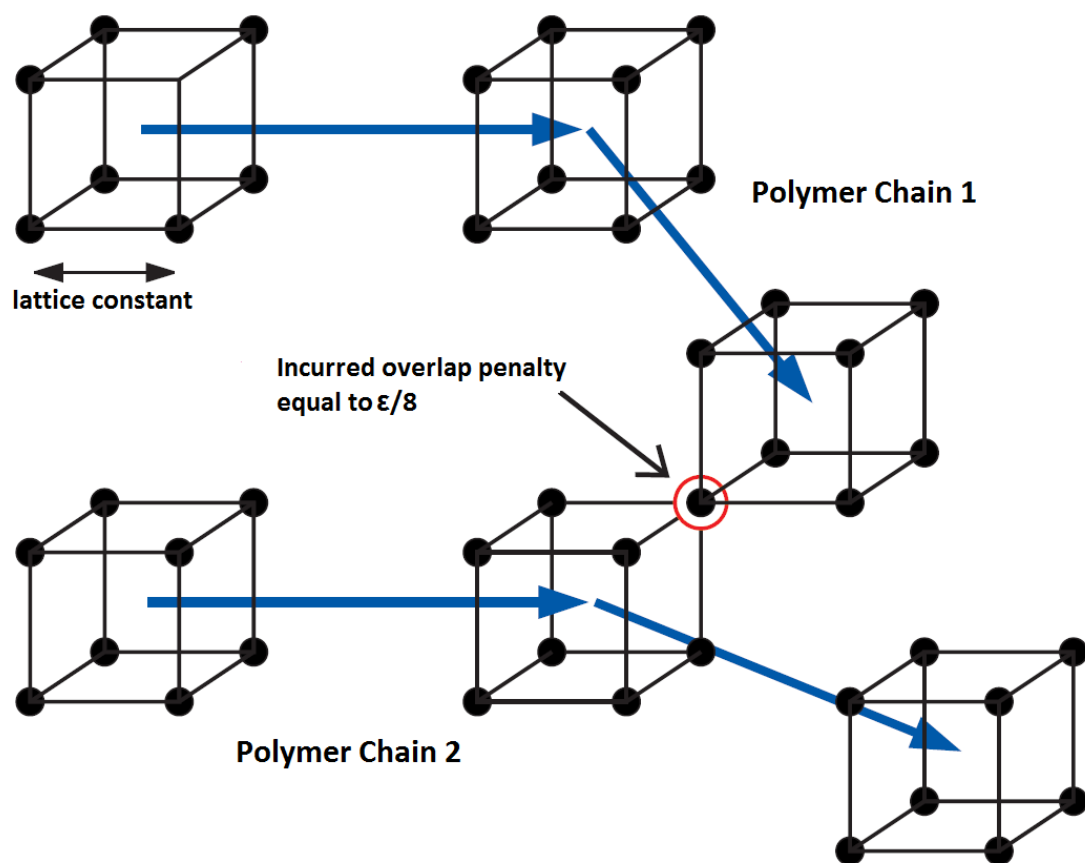


Figure 1.4: Illustration depicting two monomers overlapping at one corner, incurring an overlap penalty.

**CHAPTER 2 :
MODELING COPOLYMER DYNAMICS IN
COPOLYMER/HOMOPOLYMER BLENDS VIA A MODIFIED BOND
FLUCTUATION MONTE CARLO SIMULATION**

Abstract

Copolymers are commonly used as interface modifiers that allow for the compatibilization of polymer components in a blend. For copolymers to function as a compatibilizer, they must diffuse through the matrix of the blend to the interface between the two blend components. The diffusivity of a copolymer in a blend matrix therefore becomes important in determining good candidates for use as compatibilizers. In this work, coarse-grained Monte Carlo simulations using the bond fluctuation model (BFM) modified with an overlap penalty have been developed to study the diffusive behavior of PS/PMMA random copolymers in a homopolymer blend. The simulations vary the connectivity between different monomers, the thermodynamic interactions between the monomers which manifest within a chain and between copolymer and homopolymer matrix, and define the monomer friction coefficient of each component independently, allowing for the determination of the combined effect of these parameters on copolymer chain diffusion. The results of this work indicate that PS-r-PMMA copolymer diffusion is not linearly dependent on the copolymer composition on a logarithmic scale, but is kinetically affected by the dominant motion of the faster styrene monomers and thermodynamically affected by the concentration of styrene monomer within a given monomer's local volume.

Introduction

Blending multicomponent miscible polymer systems has proven to be a cost effective method for developing unique materials that feature a mixture of chemical and physical properties. However, many polymer mixtures that are predicted to have desirable properties are not miscible in one another and, as a result, blending these materials requires a copolymer compatibilizer composed of the molecular components of each individual homopolymer. This compatibilizer selectively segregates to the interface between the two immiscible homopolymers thereby creating a defined interface and therefore promoting dispersion among the two materials.^{5,6} The speed of this segregation process plays a crucial role in the effectiveness of a chosen copolymer as a compatibilizer; the faster the copolymer diffuses through the homopolymer matrix, the higher the probability it reaches this interface. The copolymer must be able to reach the interface between the immiscible homopolymers within an appropriate time period, as defined by the processing conditions, in order to ensure compatibilization.

The dynamics of polymer chains within multicomponent homopolymer/copolymer systems are not easily predicted because the role of connectivity on the motion of the different components within an individual polymer chain is not well understood. Moreover, the impact of connectivity on polymer chain dynamics affects the bulk properties of the blends and therefore the potential uses for the system. Recent work studying the impact of

connectivity of segments in partially miscible homopolymer blends^{63–65} and multi-block copolymers^{66,67} suggests that a potential driving force that controls the dynamics of individual chains in a polymer blend is the local concentration of the segments around a given polymer chain. However, many of these studies only account for the connectivity between polymer segments and bulk composition fluctuations in the blend, while neutron reflectivity experiments⁶⁸ suggest that the sequence distribution of the segments within an individual copolymeric chain plays a crucial role in the local concentration around the polymer. Simulations studies of homopolymer/copolymer systems have shown that the thermodynamic interactions between interacting monomer segments have a critical impact on the local structure of the copolymer and the composition of its local environment, and thus dynamics of the copolymer.^{69,70}

In viscosity and tracer diffusion studies on styrene-MMA block copolymers,⁷¹ the effective chain friction factor ζ_{eff} was experimentally measured and compared with the predictions of two different mixing rules: the first assumes a composition weighted average of the friction factor of pure PMMA and PS melts; in the second, local motion of a given monomer is dependent on its friction factor attenuated by the composition of its local environment. For example, using the first set of mixing rules, a given styrene monomer will move at the same speed regardless of the composition of the volume around it while using the second set of rules, the presence of a MMA monomer in the moving styrene's local volume will slow the styrene down.

While neither of these two models exactly describes the resulting experimental data, the data appear to exhibit a nonlinear dependence of ζ_{eff} on copolymer composition, in general agreement with the neutron reflectivity experiments mentioned above. The combined results of these studies demonstrate that both the connectivity and thermodynamic interactions between the different monomer components impact the local concentration fluctuations around a copolymer. Therefore, connectivity and thermodynamic interactions become important driving forces that govern the dynamics of copolymers, including copolymer diffusion, in homopolymer blends.

In this work, we have developed a Monte Carlo simulation that monitors the diffusion of a copolymer containing two different monomers and examined the importance of their thermodynamic interactions on the diffusion of the copolymer in a homopolymer matrix. In this study, the variation of the effective friction factor, ζ_{eff} , of each monomer is also accounted for. These features allow us to adjust the connectivity between different monomers, the thermodynamic interactions between the monomers which manifest within a chain and between copolymer and homopolymer matrix, and define the monomer friction coefficient of each component independently, allowing for the measurement of the combined effect of these parameters on copolymer chain diffusion. Using this technique, we have developed a method to implement computer simulations in a single experiment to probe the combined effect of both the connectivity among different monomers in the copolymer chain along with changes in local

composition fluctuations on the dynamics of each component in multicomponent polymer blends.

Model & Simulation Details

The model used in this work is the Bond Fluctuation Model which has been successfully used in previous studies to simulate dynamics in polymer blends.^{72–76}^{53,72–75} In the three-dimensional version of the bond-fluctuation model⁵¹ each monomer represents a Kuhn segment and occupies eight sites on a simple cubic lattice. Monomers on a chain are connected with one another by bonds whose lengths vary in the range $2 \leq l \leq \sqrt{10}$. Only six possible bond classes are allowed: [2,0,0], [2,1,0], [2,1,1], [2,2,1], [3,0,0], [3,1,0], where [] implies all permutations of the coordinates with either positive or negative signs. This restriction leads to 108 possible bond vectors and prevents chain kinking. As a result of these restraints, the bond fluctuation model incorporates some of the flexibility associated with an off-lattice model while maintaining the advantages of working on a lattice. Previous studies indicate that the model can effectively capture the dynamics of polymer melts, as well as blends.^{56,69}

The modified model used in this study varies from the standard bond fluctuation model by allowing the monomer segments to overlap, but this overlap incurs a thermodynamic penalty. This model has been used to simulate finite excluded volumes effects in simulations of polymer melts on a lattice.^{56,57} To incorporate this into the model, an overlap penalty is assigned to the monomer segment attempting to move and varies depending on the degree of overlap.

Overlapping one corner of another monomer incurs a penalty of $\frac{\epsilon}{8}$ where ϵ is the penalty for complete overlap, which is not allowed. This energetic penalty is added to the energy of the respective monomer during the calculation of the total change in energy used in the Metropolis sampling of that Monte Carlo step. A result of this condition is that the minimum bond length between monomers in the simulation is lowered to 1, a distance that corresponds to an overlap penalty of $\frac{\epsilon}{4}$.

The systems in each of the simulations in this study consist of 1728 polymer chains, where 10% are tagged as copolymers, of chain length $N=32$ in a cubic lattice of 96 units in length, resulting in an average monomer density of $\rho=0.5$. Thermodynamic interactions between monomers have been implemented by tagging each monomer as type A or type B, which represent MMA and styrene respectively in this study. The thermodynamic interactions between monomers are represented by the pairwise interactions $\epsilon_{AA} = \epsilon_{BB} = -1$ and $\epsilon_{AB} = 1$. Non-bonded interactions were applied to pairs of monomers that have bond vectors of $[2,0,0]$, $[2,1,0]$ and $[2,1,1]$, which results in a $\sqrt{6}$ radius containing 54 possible neighboring lattice sites. The temperature in these simulations was defined as $T^* \stackrel{\text{def}}{=} \frac{k_B T}{\epsilon}$ and were carried out using a standard Metropolis algorithm. These parameters and conditions are consistent with previous studies of polymer melts using the bond fluctuation model.^{77,78}

The initial configurations were generated by filling the simulation box with homopolymer chains that are parallel to the z-axis, where all bond lengths are equal to 2, which is the minimum bond distance allowed using the unmodified

bond fluctuation model. An appropriate number of the initial homopolymer chains were then tagged as copolymer chains depending on the total copolymer chain loading. The monomer sequence of each copolymer chain was determined by an algorithm using the reactivity ratios of MMA and styrene monomers in a free radical polymerization.⁷⁹ The monomer segments of the chosen copolymer chain were then retagged using this generated copolymer sequence.

The monomer friction factor ζ_{eff} of MMA is much larger than that of styrene, where this variation is included in the model by incorporating an additional barrier to monomer motion, which was employed on a step-by-step basis. Two methods to implement the barrier to motion were used to explore how the detailed model of monomer motion attenuation alters the global diffusion of the copolymer chains. The first method is analogous to a mean field approximation where the probability of movement of a given monomer is proportional to the friction factor of the monomer that is moving and is weighted by the global blend composition. In the second method the probability of monomeric motion is determined based on the friction factor of that monomer weighted by the instantaneous local composition that exists around the moving monomer. The first method, which we term the A-type method, determines the probability of movement of a monomer solely on the type of monomer moving, where the local friction factor of MMA is ~3077 times greater than that of styrene, as shown in Equation 2.1.

$$\frac{\zeta_{MMA}}{\zeta_S} \approx 3077 = \exp\left(\frac{(\tilde{B}_{0A} - \tilde{B}_{0B})}{T}\right) \quad \text{Equation 2.1}$$

Thus, when an MMA monomer is chosen to move, the move is allowed with the probability given in Equation 2.2:

$$P(MMA) = \frac{(\tilde{B}_{0A} - \tilde{B}_{0B})}{T} = \ln 3077 \quad \text{Equation 2.2}$$

However, when a styrene monomer is moved, the move's probability is always unity. The movement probability for a given monomer is calculated on a move-by-move basis and is in addition to the Metropolis condition determined by the configuration's total change in energy. This results in a pseudo mean-field approximation with respect to the local friction factors of each monomer type.

The second method, which we term R-type motions, determines the probability of motion of a given monomer as a product of the friction factor of the type of monomer attempting to move and the composition of the immediate neighborhood around it. The probability of MMA movement in this method is similar to the probability of MMA movement in the A-type method, but the barrier to motion is offset proportionally by the number of styrene monomers within a local volume surrounding the moving MMA monomer, as shown in Equation 2.3. Similarly the styrene movement probability is unity but is also offset by the number of MMA monomers nearby, as described in Equation 2.4.

$$P(MMA) = \frac{(\tilde{B}_{0A} - \tilde{B}_{0B})}{T} - \frac{B_{AB}}{T} \frac{1}{2z_{nn}} [N_{AB}(c) + N_{AB}(c')] \quad \text{Equation 2.3}$$

$$P(S) = \frac{B_{AB}}{T} \frac{1}{2z_{nn}} [N_{BA}(c) + N_{BA}(c')] \quad \text{Equation 2.4}$$

In the above Equations, the B_{AB} term represents a barrier to movement that is equal to $\tilde{B}_{0A} - \tilde{B}_{0B}$, and is the barrier to MMA motion in the A-type method as described in Equation 2.4, z_{nn} represents the total number of neighboring monomers in the local configuration, and $N_{AB}(c)$ and $N_{AB}(c')$ represent the number of styrene or MMA monomers that are in contact with the moving monomer in the pre-move configuration and the post-move configuration, respectively.

To implement these algorithms in a coarse grained simulation, two computer programs were constructed from the ground up utilizing the object-oriented nature of the C++ programming language. The resulting source code was compiled using the GCC compiler for the Linux system environment based on an x86_64 architecture. The compiled executables were run on a single quad-core Intel Xeon processor-based system at the University of Tennessee or on the ORNL Institution Cluster (OIC) at Oak Ridge National Laboratory.

Once all of the chains were placed in the simulation box and their monomer segments were properly tagged, the simulation was carried out at a reduced temperature $T^* = 10$ and the mean-squared center-of-mass, $\langle r_{cm}^2 \rangle$, and the radius of gyration, R_g , for each chain was recorded as the simulation was allowed to equilibrate. Equilibrium was defined as the point in time where the homopolymer and copolymer chain motion was diffusive, $\langle r_{cm}^2 \rangle \sim t^1$, and the R_g converges to a constant value. The structure of the resultant blend was

monitored by calculating the radial pair distribution functions for both blend components. System dynamics were quantified by calculating the diffusion coefficient D of the various polymers in the system as the $\lim_{t \rightarrow \infty} \frac{\langle r_{cm}^2 \rangle}{6t}$ where t is time defined in the number of Monte Carlo steps (MCS). Finally, an effective monomer friction factors, ζ_{eff} of the polymer and copolymer were calculated from the diffusion coefficient using the Stokes-Einstein relationship.

Results

Structure

The structure of the copolymer chains contained within the simulation box was probed by measuring the radial distribution profile of the following pairs of monomers: the distance between an MMA monomer that is in a copolymer and surrounding MMA monomers that are in a homopolymer; the distance between a styrene monomer (that must be in a copolymer) and surrounding MMA monomers that are in a copolymer, and the distance between two styrene monomers, which both must reside in a copolymer. The resultant radial pair distribution functions, (rdfs), provide insight into the structure and packing of the monomers within a local volume. Figure 2.1 plots the rdf of a blend that contains a ~60% MMA copolymer chain for systems that are equilibrated using the R-type or A-type models. These plots demonstrate that there is very little difference between the structural packing around each of the three possible monomer pairs between the two movement protocols, the A-type and R-type. This is not unexpected since there is no explicit difference in structural limitations between

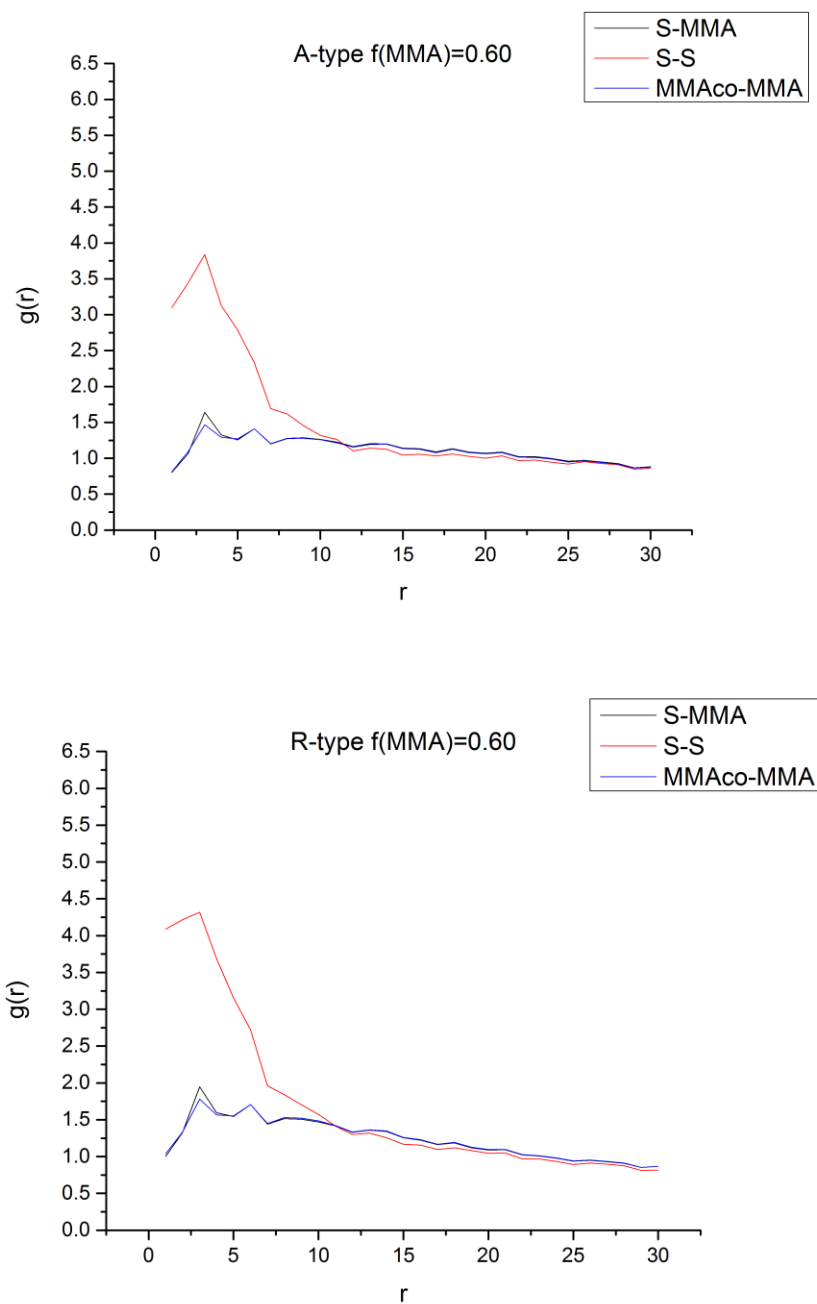


Figure 2.1: Radial Pair Distribution functions for styrene-MMA, styrene-styrene, and copolymer MMA-matrix MMA monomer pairs for both the A- and R- type simulations at $f(\text{MMA})=0.60$.

the two models and this parallel is reinforced by the similarity of the rdfs in Figure 2.2, which shows the rdfs of the systems with a variation in the copolymer composition. Moreover, all chains in each simulation exhibit an average R_g of ~ 6 lattice units, which is in agreement with previous the bond-fluctuation studies.^{51,69,70,73}

Dynamics

For this study, a simulation box contains a total of 1555 homopolymer chains of MMA type, and 173 copolymer chains, where the distribution of MMA and styrene monomers within the copolymer was determined using the algorithm described above. The average effective chain friction factors of the copolymer chains that are calculated from the diffusion coefficients listed in Table 1 are presented in Figure 2.3 where the error bars are smaller than the size of the symbols. The black data points in this figure represent the average effective chain friction factor of a styrene homopolymer and MMA homopolymer melt of the same degree of polymerization. The line fit between these two points predicts the effective friction factor assuming a linear power law dependence on the composition of MMA in the copolymer with this representation of the data. The data gathered for both the A-type and R-type motion models indicate that these copolymer chains are both faster than the linear approximation would suggest and that the dependence of ζ_{eff} on copolymer composition for both the A- and R-type motions are non-linear, with the A-type model demonstrating a very

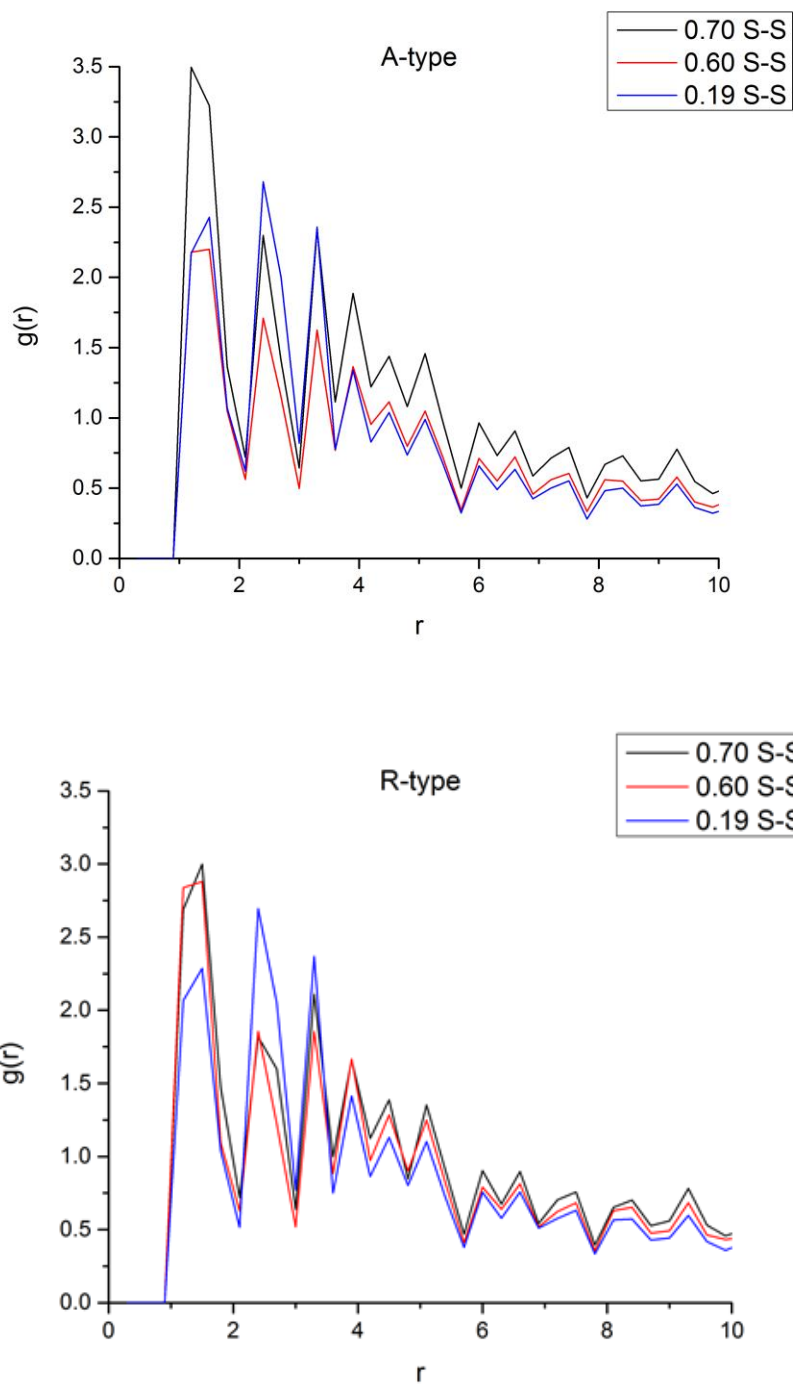


Figure 2.2: Styrene-styrene radial pair distribution functions for A- and R-types at varying MMA copolymer loadings.

Table 2.1: Diffusion Coefficients based on %MMA copolymer loading measured from A-type and R-type simulations

<u>%</u> <u>MMA</u>	<u>A-type</u> <u>(lattice cube units²/Monte Carlo Step)</u>	<u>R-type</u> <u>(lattice cube units²/Monte Carlo Step)</u>
0.98	0.00112	6.41708E-4
0.90	0.00177	8.06772E-4
0.78	0.00281	0.00118
0.70	0.00346	0.00154
0.60	0.00468	0.0021
0.48	0.00621	0.00339
0.39	0.00712	0.00406
0.31	0.00782	0.00463
0.18	0.00902	0.00512

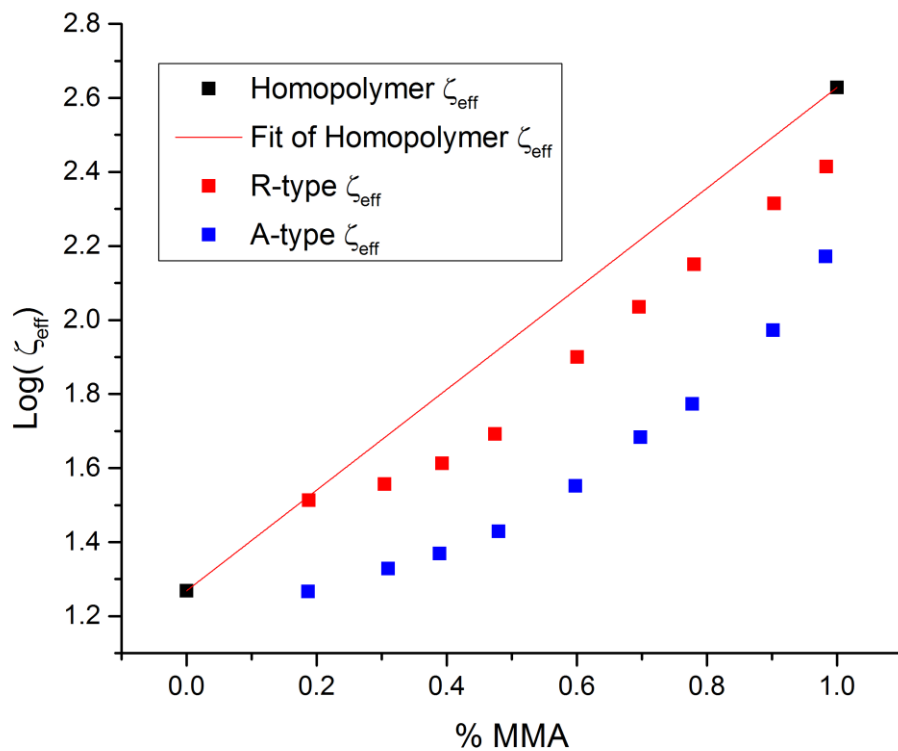


Figure 2.3: Semi-log plot of the effective chain friction factor with respect to copolymer MMA composition for the A- and R- type motions. The red line indicates the predicted linear power law response.

strong non-linearity. The dependence of the chain friction factor on copolymer composition exhibits an inflection point between 0.5 and 0.6% MMA.

Discussion

Copolymer compatibilizers are important components of polymer blends of immiscible homopolymers and in order to act as compatibilizers, these copolymers must readily diffuse throughout the target homopolymer matrices towards a biphasic interface. A primary goal of this work is to study how the connectivity of the copolymer chain, a significant difference in the friction factor of the two monomers in the copolymer, and thermodynamic interactions between the two monomers impacts the global motion of the copolymer chains. This global motion is parameterized by the effective friction factor of the copolymer chain, which is derived from the diffusion coefficient of the copolymer chains.

Our simulation results indicate that the conformation and radii of gyration of both the homopolymer and copolymer chains is independent of the method by which the variation in friction factors is incorporated in the simulation model. The rdf curves that describe the copolymer chain configurations also suggest that the packing of the final copolymer monomer is very similar for the A- and R- type movement models. There is an increase in styrene clustering in copolymers that are rich in styrene (i.e. lower MMA composition copolymers), implying that the thermodynamic environment resulting from the repulsive interactions between the styrene and MMA do alter the local structure of the copolymer in some systems. The largest factor that impacts the rdf curves is the compressibility of

the monomers in the melt, which reduces the average excluded volume. These data confirm that the method by which the variation in monomer friction factor is incorporated into the simulation technique modeling does not impact the final structure and packing of the copolymer chains in the homopolymer matrix. This, however, does not necessarily imply that the composition fluctuations that arise from the variation in friction factors do not affect local monomer packing during the simulation convergence.

As Figure 2.3 shows, the effective local friction that is experienced by the copolymer chain, ζ_{eff} , differs between the two movement types and both exhibit an unexpected nonlinear log-log dependence on copolymer composition. This nonlinear log-log dependence generally follows the copolymer composition dependence of the experimentally determined viscosity and copolymer tracer diffusion coefficient of PS-*b*-PMMA in a PMMA matrix as reported by Milhaupt, et. al. and similar non-linearities in the copolymer composition dependence of the diffusion coefficient of PS-*ran*-MMA copolymers in a PMMA matrix reported by our group.⁶⁸ The inflection point of the curve around 0.55 MMA loading also matches these data.

We believe this nonlinear logarithmic scale dependence on composition is a result of the connectivity between dissimilar styrene and MMA monomers within the copolymer chain and the resulting thermodynamic environment within the copolymer's local volume which result in composition concentration fluctuations. In a solution of MMA and styrene small molecules, where there is no

connectivity between the individual particles, these local composition fluctuations are dependent almost entirely on the thermodynamic interaction potential between the styrene and MMA monomers. In such an untethered system, the average monomer diffusion coefficient in the blend can be represented as a mean-field approximation determined by the compositionally weighted average of the diffusion coefficients of the MMA and styrene monomers.. Since the diffusing movement is not tethered, the movement of fast-moving styrene monomers allows for concentration fluctuations that form and dissipate very fast timescale quickly around a particular local volume, which corresponds to the expected linear log-scale trend in ζ_{eff} . However, the segments in a copolymer are connected, and the faster moving styrene monomers are tethered to the slower moving MMA monomers. This connectivity, in turn, dampens the dissipation (and formation) of local concentration fluctuations. The results presented above can thus be explained based on this connectivity, indicating that the fast-moving styrene monomers dominate the motion of the copolymer chain, dragging the slow moving MMA monomers along with it. This outcome has the effect of decreasing the effective friction factor, ζ_{eff} , of the copolymer below the weighted average of the copolymer composition and as a result the copolymer chain moves faster than the mean field average based on the copolymer composition.

This comparison of the dynamics of copolymers to that of a free particle system provides insight as to why the ζ_{eff} of the copolymers that are moved by the A-type motion is much lower than the expected mean field average. The

increased mobility of these chains can be ascribed to the fact that the A-type motion only depends on the composition of the copolymer, but does not take into account the composition of the local volume around the polymer. Because movement in the A-type system is not dependent on the local environment surrounding the copolymer, the motion of the faster moving styrene monomers dominates the motion of the copolymer chains. Consequentially the diffusion of the copolymer chains in the A-type system becomes a kinetic effect. This interpretation is also consistent with the fact that the A-type copolymer chains are faster than the R-type copolymers with the same styrene loading in Figure 2.3.

The implementation of the R-type model introduces an extra layer of complexity that is not present in the A-type system. In the R-type model, the motion of any given monomer depends on the local composition of the moving monomer. Thus, in the R-type system, the probability that a styrene monomer will move can be attenuated by the statistically probable presence of a neighboring MMA monomer. Similarly, the presence of neighboring styrene monomers can speed up the motion of MMA monomers. As a result, styrene monomers that move by the R-type model do not move as fast as those that move by the A-type model; while the motion of R-type MMA monomers will be faster than their A-type counterparts. However, since the monomeric friction factor for styrene monomers is an order of magnitude less than that of the MMA monomers and given the abundance of MMA monomers within the system,

attenuation of the rate of styrene monomer motion greatly dominates the copolymer chain movement.

The decrease in styrene motion slows the formation and dissipation of concentration fluctuations within the copolymer's local volume, which further dampens the effect of the thermodynamic interactions on copolymer chain diffusion relative to the copolymer in the A-type system resulting in an increase in the copolymer chain effective friction factor ζ_{eff} . Therefore, the R-type copolymers exhibit a weaker log-log nonlinearity in chain ζ_{eff} than in A-type model in Figure 2.3 due to the decreased movement of the copolymer styrene monomers, which in turn increases the local concentration of the styrene in the volume around the copolymer chain. This interpretation is also consistent with the increased styrene-styrene contacts at smaller distances in the rdf data in Figure 2.1 and Figure 2.2.

$$\varphi_{eff} = \phi_s + (1 - \phi_s)\phi \quad \text{Equation 2.5}$$

$$\phi_s = \frac{C_\infty M_0}{k\rho N_{av}V} \quad \text{Equation 2.6}$$

Given the known importance of the local composition of a moving monomer on its motion, one explanation for the decrease in the effective friction factor of the copolymers as shown in Figure 2.3 is that the local composition of the copolymer is richer in styrene than the mean field average. To test this hypothesis, we correlate the results of our simulations with predictions from Lodge-McLeish (LM) theory on dynamics in multicomponent systems. LM theory stipulates that the local environment around a polymer chain in a blend controls

the dynamics of the chain, where the connectivity of the polymers creates a local composition that differs from that of the average composition of the blend.

Therefore LM theory states that the local environment around the two blend components will differ from the average composition even for very miscible blends, with the effect of this local composition on the chain dynamics increasing if the two blend components exhibit distinctly different friction factors. The determination of the local composition in the LM theory is ascribed solely to the chain connectivity in polymer chains and completely disregards the thermodynamic interactions between the components.

To evaluate the impact of the thermodynamic interaction on the local composition of the copolymer in our simulation, the local concentration is determined for the simulated copolymer/homopolymer blends and compared to predictions of the LM theory. According to the LM theory, the effective local concentration ϕ_{eff} around a monomer is given by Equation 2.5 where ϕ_s , the self-concentration of the minor components, describes its excess concentration within a local volume relative to the average matrix composition, and φ is the bulk composition for the two component blend. The self-concentration ϕ_s in Equation 2.6 is calculated from the characteristic ratio C_∞ , monomer molecular mass M_0 , monomer density ρ , the number of backbone bonds per Kuhn segment, κ , the average number of monomers per repeat unit N_{av} , and the volume around a Kuhn segment V . We have calculated values for ϕ_{eff} and ϕ_s for a monomer on the copolymer chains in our simulations assuming values of these parameters for

the copolymer chains that are compositional averages of the corresponding values for PS and PMMA. The ϕ_{eff} values calculated using LM theory for the copolymer chains in our simulations are presented in Figure 2.4 as the solid black line. Since our simulations provide the positions of the monomers of the copolymer chains and their respective types, we can directly measure the number of styrene monomers in the same volume as the local volume in Equation 2.6 in the simulation. These values, which we term ϕ_{eff}^s , are presented for the A- and R-type simulations in Figure 2.4 as the green squares and brown circles respectively. According to the results in Figure 2.4, the Lodge-McLeish model consistently under predicts the local concentration of the styrene component near the copolymer.

This result is not entirely surprising since the Lodge-McLeish theory does not explicitly account for the repulsion or attraction between monomers due to thermodynamic interactions in estimating the local composition around a copolymer. LM theory assumes the correlation-hole effect, which states that each monomer is essentially guaranteed to be surrounded by a certain number of identical monomers as a result of the polymer chain connectivity. While this assumption is valid for some homopolymer blends, our results clearly indicate that this assumption is of questionable validity in a copolymer/homopolymer blend, where that local composition in blends containing copolymers depends on both monomer connectivity and the thermodynamic potential between the connected monomers. These concentration fluctuations, which are the result of

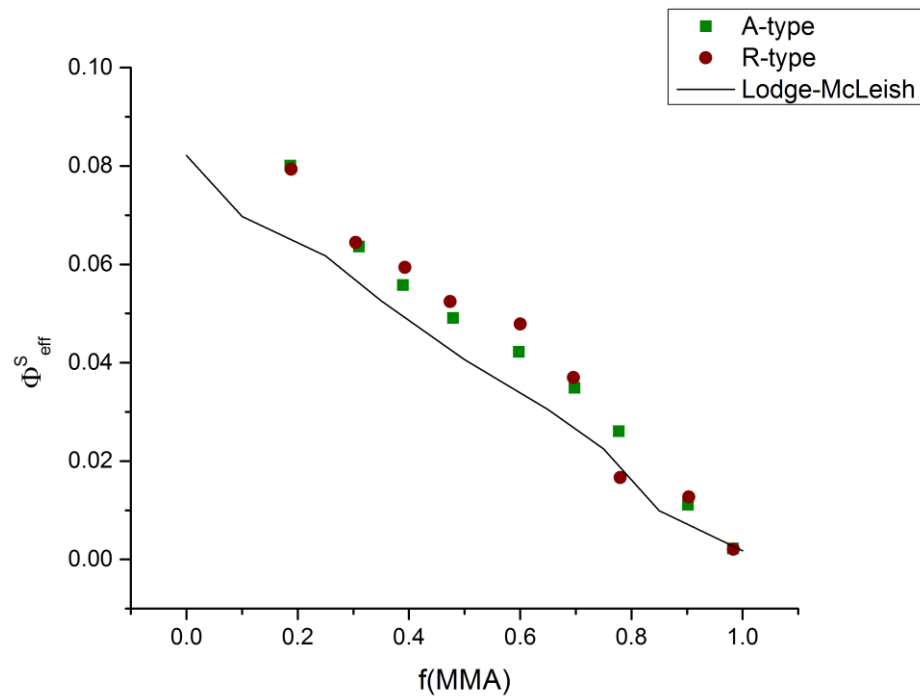


Figure 2.4: Effective local concentrations of Styrene in the A- and R-type simulations where the line represents the predicted effective local concentration using Lodge-McLeish theory.

the kinetic variation of the speed of styrene monomer diffusion relative to that of MMA, as well as the thermodynamic interactions between MMA and styrene monomers that are inherent to both the A- and R-type methods used in our simulations. Thus, the copolymers exhibit a higher local concentration of the faster styrene monomers within the copolymer local volume than LM theory predicts. This increased concentration of styrene in the local volume increases the probability of motion for the copolymer chain, increase their speed and decreases the average effective chain friction factor for copolymers in both A- and R-type from the linear power law dependence with composition.

Conclusion

The effect of connectivity and thermodynamic interactions between components on chain copolymer dynamics in partially miscible homopolymer-copolymer blends was studied using a Monte Carlo simulation featuring a modified bond-fluctuation model. Our studies have confirmed that copolymer connectivity, composition distribution and heterogeneity of the monomer friction factors in the blend impact concentration fluctuations within the copolymer local volume, which in turn effects the diffusion of the copolymer within the homopolymer matrix. These effects can be quantified by measuring the effective chain friction factor of the copolymers thereby measuring the diffusion of the copolymers throughout the homopolymer melt. Our results demonstrate that copolymer diffusion does not have a linear power law dependence on the copolymer composition, but is kinetically affected by the dominant motion of the

faster monomer and thermodynamically affected by the concentration of the minority monomer component within a given monomer's local volume.

The configuration of our simulations reveal this effective local concentration of styrene is larger than what Lodge-McLeish theory predicts. Since the minority component has a monomeric friction coefficient that is three orders of magnitude lower than that of the majority component, this process results in the development of local volumes that are richer in the minority component throughout the blend, which in turn results in faster copolymer diffusion. This kinetically driven motion is attenuated by the aforementioned composition fluctuations, leading to increased thermodynamic interactions between the major and minor components within the local volume around a copolymer chain, which therefore slows the diffusion of the copolymer. These simulation results expand on our group's previous copolymer dynamics simulations and agree with our experimental neutron reflectivity studies of P(S-*ran*-MMA) copolymer diffusion in a PMMA matrix.

Acknowledgements

This research is supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering.

CHAPTER 3 :
A STUDY OF THE EFFECTS OF BRANCHING ON POLYMER
COMBS USING A BFM MONTE CARLO SIMULATION

Abstract

In this work we have studied the effect of temperature, composition and branched architecture on the structure and dynamics of homopolymer and copolymer combs in blends with a linear homopolymer using a Monte Carlo bond fluctuation simulation. The copolymers studied in these simulations were arranged in branched combs where the backbone and the side-chains were different monomer species. The number and the molecular weight of the branches were varied to study the effects of branch packing densities on copolymer structure and motion. Additionally, the temperature of the simulation was varied to determine the effect of the balance of available thermal energy and the thermodynamic parameters between the two types of monomers on the various architectural configurations. The R_g of the combs and their constituent branches were measured to study the impact of these parameters on polymer comb structure and the center-of-mass diffusion for the combs

It was found that at low temperatures, enthalpic contributions dominate the equilibrium structure of the copolymer comb system while at high temperatures, entropic contributions begin to dominate the structure and dynamics of the homopolymer and copolymer combs. Additionally, the diffusion coefficient of the combs varied with copolymer molecular weight as Mw^{-2} , which differs significantly from the logarithmic power law dependence measured in H- and star polymers. This increase in speed is most likely due to the retraction of branches of the polymer comb towards the backbone, decreasing possible entanglements with

the linear matrix. This conformation limits the impact of entanglements between the branches of the polymer comb and the surrounding matrix on the comb's movement. These studies therefore provide insight to the thermodynamic forces at play in a homopolymer blend containing branched copolymers and allows for the tailoring of the connectivity and composition of branched copolymers to improve their design and performance.

Introduction

Recent progress in polymer synthesis has made the synthesis of branched polymers featuring an array of various branched architectures possible, ranging among combs, brushes, stars, and hyper-branched polymers.^{80–83,84–86} Incorporation of side-chains on to a polymer backbone creates a variation in chain conformation, which grants the polymer useful and interesting structural and dynamic properties. A common method to take advantage of the interesting properties of branched polymers is to blend them with linear polymers in which the branched polymers have been shown to selectively segregate to the surface. As a result of this behavior, branch polymers have become important tools for the delivery of surface modifiers to a given surface.^{1,2,4} The speed of this segregation process plays a crucial role in the effectiveness of a chosen branched copolymer as a surface modifier; the faster the branched polymer diffuses through the homopolymer matrix, the higher the probability it reaches this surface. The branched copolymer must be able to reach the targeted surface or interface within an appropriate time period, as defined by the processing conditions, in order to ensure surface modification.

Current theory does not completely describe the effects of branching on polymer dynamics. Experiments using branched polymers such as star and H-copolymers have determined that the motion of such branched polymers is dependent solely on the molecular weight of the branch⁸⁷ while experimental dynamic studies on neat grafted homopolymer combs reveal that the dynamics of

polymer combs are different from bottle brush polymers and linear polymers as well.⁸⁸ Recent neutron reflectivity experiments also suggest that the diffusion of hyper-branched polystyrene polymers in a matrix of linear polystyrene polymers is faster than expected.⁸⁹ These results demonstrate the gaps in the current understanding of the effect of branching on the structure and dynamics of polymer systems and illustrate the need for more work in order to bridge these gaps in knowledge regarding the effects of branching on polymer dynamic properties.

Additionally, the dynamics of branched polymer chains in multicomponent homopolymer/ copolymer systems are not well understood because the role of connectivity in the motion of such polymers is complex. The impact of connectivity has been studied in linear polymers previously by our group^{68–70} and others⁷¹, and the results of those studies indicate that interactions between constituent dissimilar monomers within the copolymer chain cause conformational changes in the polymer chain. These results, as well as recent work that examine the impact of polymer chain connectivity in partially miscible homopolymer blends^{63–65} and multi-block copolymers^{66,67} indicate that a significant driving force that controls the dynamics of individual chains in a polymer blend is the local concentration of segments around a given polymer chain. However, many of these studies only account for the connectivity of polymer segments in determining the local segment concentration, while neutron reflectivity experiments⁶⁸ indicate that the sequence distribution of the segments

within an individual copolymer chain also play a crucial role in defining the local concentration around a polymer. Simulation studies of homopolymer/copolymer systems have also shown that the thermodynamic interactions between strongly interacting monomer segments have a critical impact on the local structure of the copolymer and the composition of its local environment, and thus dynamics of the copolymer.

To this end, we present a coarse-grained Monte Carlo simulation to probe the role of both the thermodynamic potential between interacting monomer types within a copolymer comb and the packing and size of the branches of that comb on the dynamics of the copolymer comb in a blend with linear homopolymers. We detail two sets of experiments: one where the effect of the thermodynamic interactions between the branch and backbone is studied by varying the temperature of the simulation; and the other where the molecular weight of the branches along with their packing density on the comb backbone is varied at a constant temperature. The combined results of these two experiments yield insight into how thermodynamics affect the conformation of the copolymer comb and how this molecular assembly affects the overall dynamics of the copolymer comb within a homopolymer blend. Studying the combined effects of monomer interactions and the packing of the side-chain on copolymer comb structure and dynamics enables improved tailoring of copolymer combs to attain a desired set of required physical parameters that control local motion, which in turn will alter

the diffusive behavior within the blend enabling better transport of the comb to a preferred surface or interface.

Model and Simulations Details

The model used in this work as a basis for simulations is the Bond Fluctuation Model which successfully simulated dynamics in polymer blends in previous studies.^{53,72–75} In the three-dimensional version of the bond-fluctuation model⁵¹ each monomer represents a Kuhn segment and occupies eight sites on a simple cubic lattice. Monomers on a chain are connected with one another by bonds whose lengths vary in the range $2 \leq l \leq \sqrt{10}$. Only six possible bond classes are allowed: $[2,0,0]$, $[2,1,0]$, $[2,1,1]$, $[2,2,1]$, $[3,0,0]$, $[3,1,0]$, where $[]$ implies all permutations of the coordinates with either positive or negative signs. This restriction leads to 108 possible bond vectors and prevents chain kinking. As a result of these restraints, the bond fluctuation model incorporates some of the flexibility associated with an off-lattice model while maintaining the advantages of working on a lattice. Previous studies indicate that the model can effectively capture the dynamics of polymer melts as well as blends.⁶⁹

The modified model used in this study varies from the standard bond fluctuation model by allowing the monomer segments to overlap, but this overlap incurs a thermodynamic penalty. This model has been used to simulate finite excluded volumes effects in simulations of polymer melts on a lattice.^{56,57} To incorporate this into the model, an overlap penalty is assigned to the monomer segment attempting to move and varies depending on the degree of overlap.

Overlapping one corner of another monomer incurs a penalty of $\frac{\epsilon}{8}$ where ϵ is the penalty for complete overlap, which is not allowed. This penalty is added to the energy of the respective monomer during the calculation of the total change in energy used in the Metropolis sampling of that Monte Carlo step. A result of this condition is that the minimum bond length between monomers in the simulation is lowered to 1, a distance that corresponds to an overlap penalty of $\frac{\epsilon}{4}$.

The systems in each of the simulations in this study consist of 1728 polymer chains of chain length $N=32$ in a cubic lattice of 96 units in length, resulting in an average monomer density of $\rho=0.5$. Thermodynamic interactions between both monomers have been implemented by tagging each as type A or B. The thermodynamic interactions between monomers are represented by the pairwise interactions $\epsilon_{AA} = \epsilon_{BB} = -1$ and $\epsilon_{AB} = 1$. Non-bonded interactions were applied to pairs of monomers that have bond vectors of $[2,0,0]$, $[2,1,0]$ and $[2,1,1]$, which results in a $\sqrt{6}$ radius containing 54 possible neighboring lattice sites. The temperature in these simulations was defined as $T^* \stackrel{\text{def}}{=} \frac{k_B T}{\epsilon}$ and were carried out using a standard Metropolis algorithm. These parameters and conditions are consistent with previous studies of polymer melts using the bond fluctuation model.^{77,78}

In order to simulate branches that emerge from the backbone, random points along the $N=32$ backbone were selected as branch points and linear side chains were inserted from those points, such that the branch point is bound to three monomer units: its' two neighboring units in the backbone along with the

first unit in the branch. The final monomer unit of each branch is considered a terminal monomer similar to the terminal monomer units on the backbone. Using this protocol allows the measurement of the R_g of the branch from the branch point monomer unit to the terminal monomer unit at the end of the branch. After each of the branched chains was constructed, the backbone monomers were tagged as A and the monomer units in the branches were tagged as B, creating the branched copolymer comb. The initial simulation box configuration was then generated by filling the remaining space in the simulation box with type A homopolymer chains parallel to the z-axis, where all bond lengths were equal to 2 which is the minimum bond distance allowed using the unmodified bond fluctuation model, until the simulation box contained a ~10% loading of branched polymers and 50% monomer density.

Once all of the chains were placed in the simulation box and the monomer segments properly tagged, the simulation was carried out at reduced temperatures of $T^* = 2, 4, 6$, and 10 and the mean-squared center-of-mass, $\langle r_{cm}^2 \rangle$, and the radius of gyration, R_g , for each chain, as well as those of the branches, were recorded as the simulation was allowed to equilibrate. In the simulations where T^* was varied, the ratio of branch monomers to backbone monomers was held at a constant 1:1 ratio yielding a total branched polymer with 64 monomer units. Additionally, additional simulations were performed at $T^*=10$ where the number of branches per backbone in the copolymer was varied from 2 to 8 branches, while the branch lengths varied from 4 to 16 monomer units. These

branched copolymers therefore cover copolymer chain molecular weights that range from 40 to 96, encompassing branch lengths that range between 4 and 16. This, in turn, comprises a broad parameter space in branch chain size, copolymer chain length, number of branches and copolymer diffusion rate.

The computer programs were constructed from the ground up utilizing the object-oriented nature of the C++ programming language. The resulting source code was compiled using the GCC compiler for the Linux system environment based on an x86_64 architecture. The compiled binaries were run on a single quad-core Intel Xeon processor-based system at the University of Tennessee and on the ORNL Institution Cluster (OIC) at Oak Ridge National Laboratory until equilibrium was achieved. In these simulations, equilibrium is defined as the point in time where the homopolymer and copolymer chain motion was diffusive, $\langle r_{cm}^2 \rangle \sim t^1$, and the R_g of the homopolymer chains and copolymer backbones and branches converge to a constant value. System dynamics were quantified by calculating the diffusion coefficient D of the various polymers in the system as the $\lim_{t \rightarrow \infty} \frac{\langle r_{cm}^2 \rangle}{6t}$, where t is time defined in the number of Monte Carlo steps (MCS).

Results

Constant Backbone/Branch Ratio with Varying Temperature

The initial simulations in this work were conducted using copolymer combs with a constant 1:1 ratio of backbone monomer units and the total number of branched monomer units. As a result, the total molecular weight of the

copolymer comb remains 64 monomer units, however the size and number of the branches was varied. Figure 3.1 plots the R_g of the copolymer comb as a function of branch size; therefore the data points for branch size 4 in Figure 3.1 correspond to simulations where the copolymer combs consisted of a backbone composed of 32 monomer units and eight branches that were 4 monomer units in size. In this fashion, the number of branches and the size of the branches were varied such that the total number of branched monomer units was always equal to $N/2$ or 32.

Figure 3.1 displays the radius of gyration of the copolymer comb for each branch size as a function of reduced temperature, ranging from $T^*=2$ to $T^*=10$. These R_g values were calculated for the entire comb, and as such is slightly larger than 8 monomer units, which is the expected R_g for a 32 monomer unit linear homopolymer undergoing a random walk. The values in Figure 3.1 for each branch size seem to collapse towards the R_g value measured for a linear homopolymer in the simulation as temperature is decreased. As seen in the inset of Figure 3.1, this collapse is nearly linear with temperature for the combs with the smallest branch sizes, but the trend becomes less pronounced with the larger branch sizes. At a branch size of 16 monomer units, the R_g of the copolymer comb at temperatures higher than $T^*=2$ remain fairly constant, indicating that the thermodynamic interactions between the A backbone and B branches do not significantly impact the size of the combs at this higher temperature. To corroborate this interpretation, the R_g of the copolymer branches with respect to

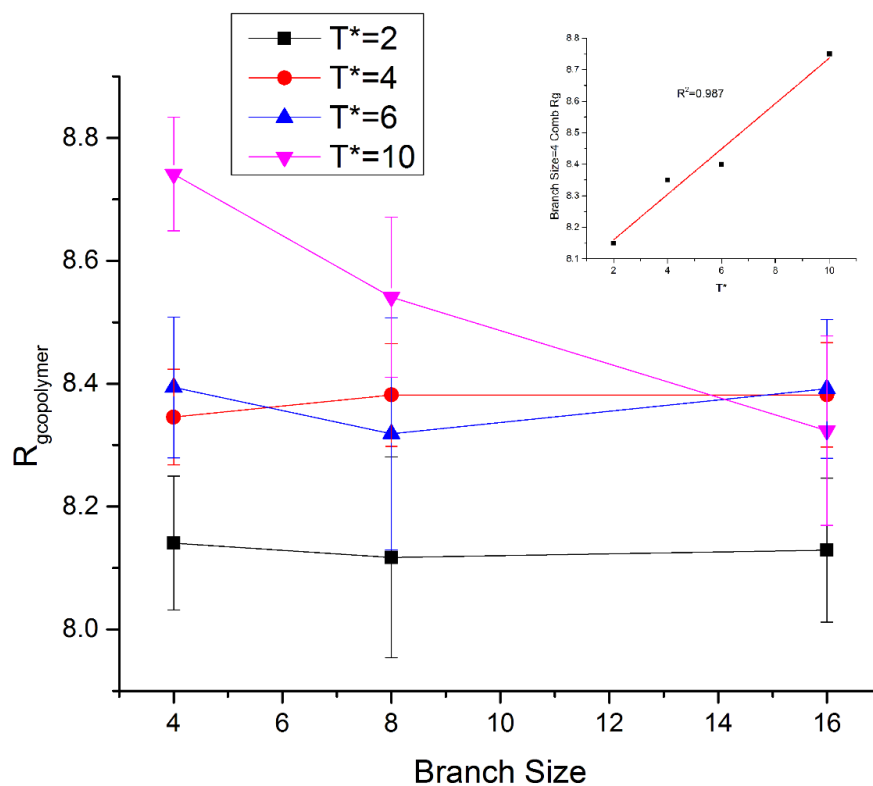


Figure 3.1: Radius of gyration of the branched copolymers for different temperatures at constant molecular weight. As T^* decreases, the copolymer chain starts to collapse in order to reduce thermodynamic interactions. Inset: Plot of R_g of combs with branch sizes equal to 4 vs reduced temperature.

branch molecular weight are presented in Figure 3.2. The R_g of the branches increase nearly linearly with branch size, however the values are smaller than the expected R_g of a free chain of similar molecular weight undergoing a random walk. This decrease from the R_g of identical linear chains suggests that the tethering of the *B* branch monomers to the backbone *A* monomers impacts the conformation of the side chain, due to the presence of the thermodynamic interaction between the monomers and is supported by the increased spread of R_g values at different temperatures for larger chains.

The center-of-mass diffusion coefficient for the copolymer combs in simulations with varying temperature is presented in Figure 3.3. There is not an obvious trend in diffusion with varying temperature at lower branch sizes, especially for the branch that is 8 monomers long. However, for the branches that are 16 monomer units in length, the diffusion coefficient decreases with reduced temperature, which is similar to the behavior of linear chains observed in our previous studies due to the decreased amount of available thermal energy. For $T^*=2$, the copolymer combs exhibit a near linear decrease of the diffusion rate with branch size, whereas the same-sized combs at higher temperatures plateau at a higher rate of diffusion. This effect correlates with the decrease in the branch R_g at larger branch sizes and higher temperatures as shown in Figure 3.2.

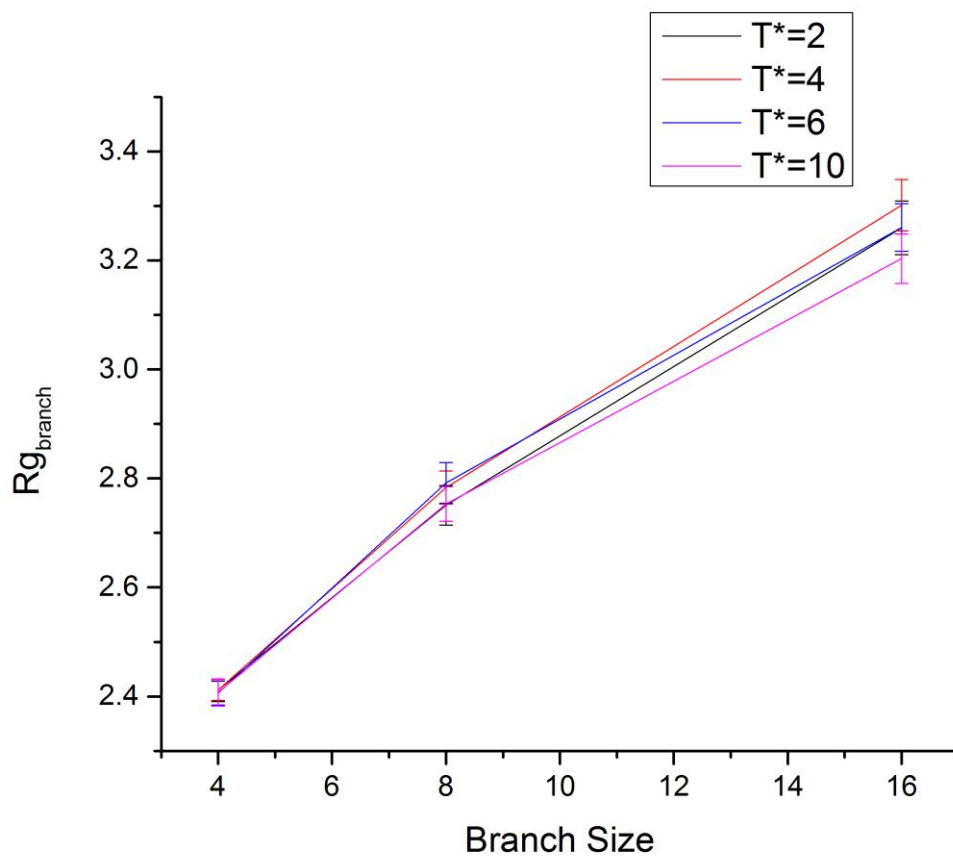


Figure 3.2: The average radius of gyration for individual branches on each comb from Figure 1 at various temperatures. There does not seem to be a prevalent trend with temperature.

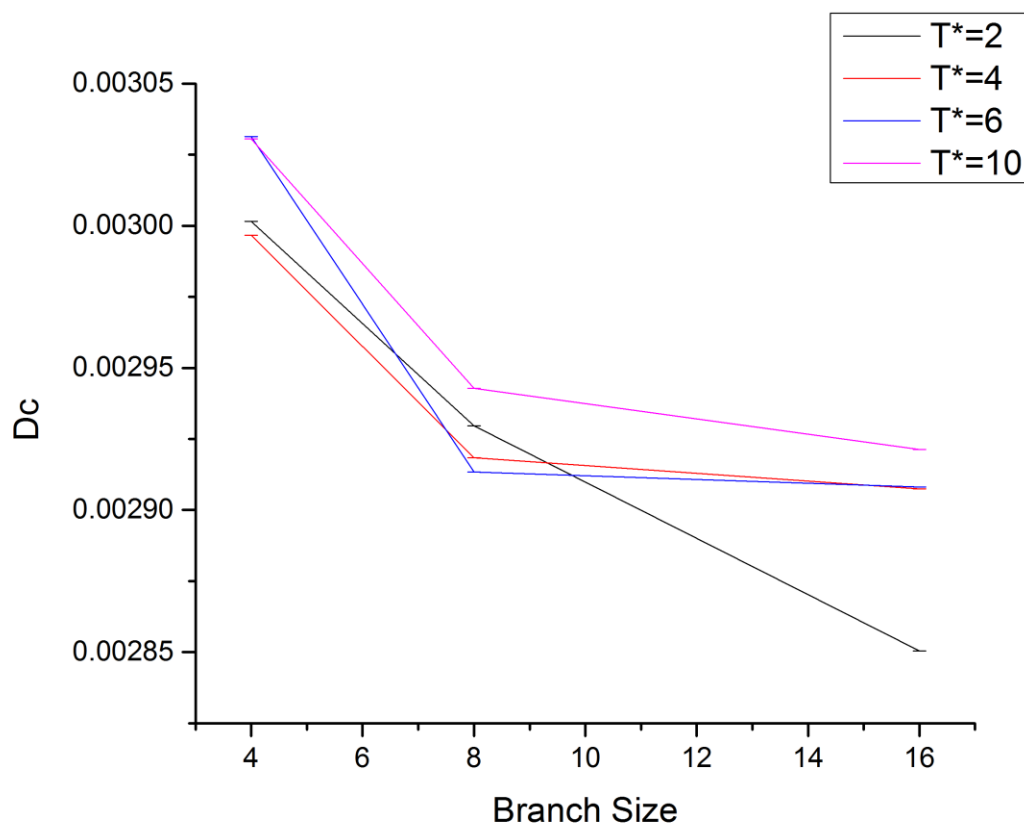


Figure 3.3: Diffusion coefficients for polymer combs in Figure 1 at different temperatures. The combs at $T^*=2$ exhibit a near linear dependency on branch size.

Variable Branch/Backbone Ratio at Constant Temperature

In the second set of simulations, the temperature was held constant at $T^*=10$ and the ratio of the *A* backbone monomer units to *B* branch monomer units was allowed to vary, resulting in a wide parameter space of branch size and the number of branches per backbone. This set of experiments included simulations of branched copolymer combs in a blend with linear homopolymers and a separate set of simulations containing homopolymer combs in a blend with linear homopolymers of the same monomer type. Figure 3.4 displays a log-log plot of the R_g of the branch in the copolymer comb as a function of branch molecular weight, which is similar to the data presented in Figure 3.2 for the variable temperature experiment. The circles represent the copolymer data; the black data points are the data for combs with only two branches, the blue denote the characteristics of the combs with four branches, and finally the red data points are the data for combs with eight branches. The data in Figure 3.4 demonstrate that at higher temperature, the sizes of the branches of the copolymer combs increase with molecular weight at a slower rate than expected for a free chain, data for which is represented by the dark blue stars. The slopes of the log-log plot of the branch R_g as a function of branch molecular weight for all of the branched combs tested in this experiment are below 0.3, indicating that the monomers within the branches for these combs aggregate into globular structures. Figure 3.5 shows a log-log plot of the total comb R_g as a function of the total comb molecular weight, where the triangles represent copolymer data, the circles represent homopolymer data, and colors correlate to the same

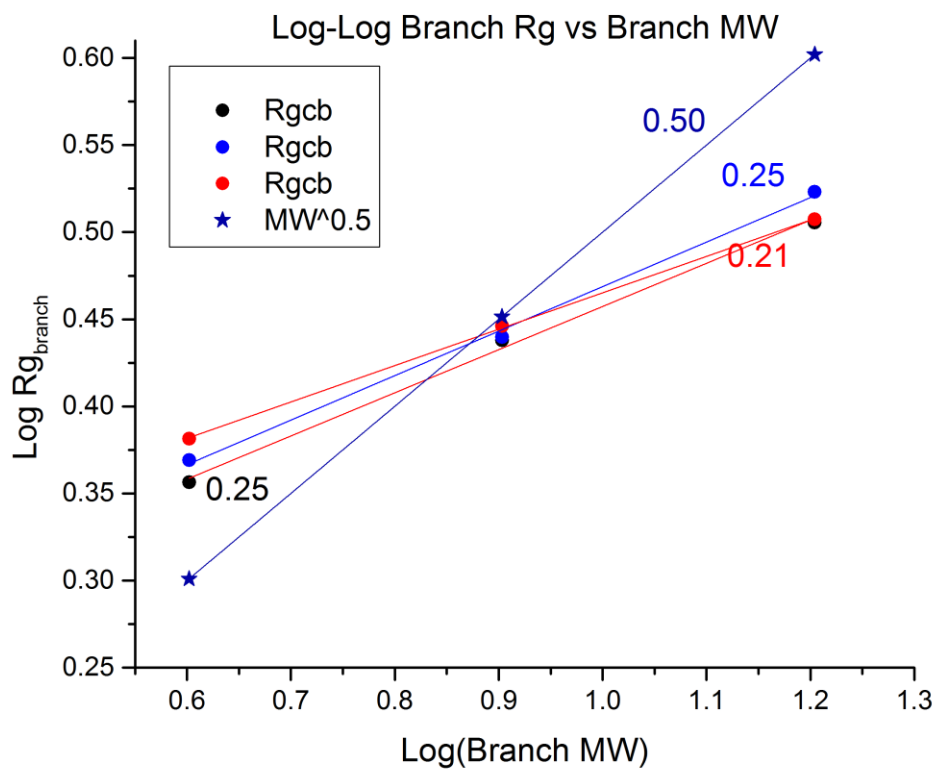


Figure 3.4: A log-log plot of the radius of gyration of individual branches in combs of different molecular weights.

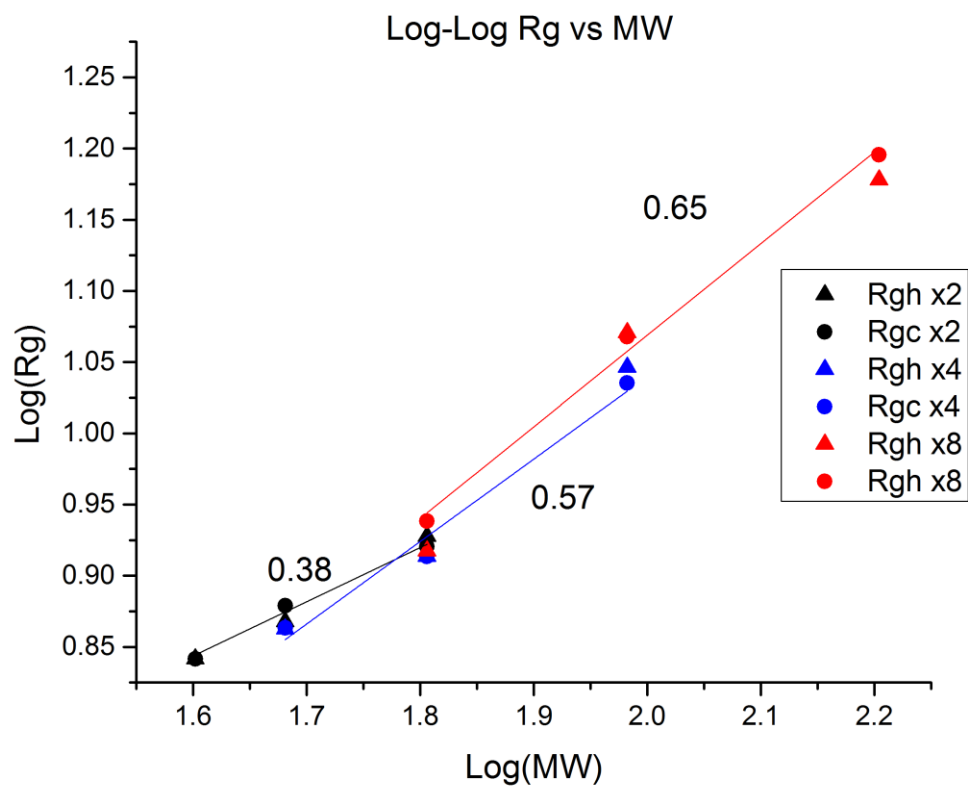


Figure 3.5: Log-log plot of the radius of gyration for the polymer combs described in figure 4. At lower branch density (the black colored data points), the chain is much more condensed.

molecular characteristics as in Figure 3.4. In Figure 3.5, there is little difference between the copolymer and homopolymer data and the slopes of these data indicate that the conformation of the total comb with two branches are more globular than combs with a greater number of branches packed onto the backbone, which are more Gaussian coil shaped.

The center-of-mass (COM) diffusion coefficients obtained from the constant temperature experiment are plotted as a function of copolymer molecular weight on a log-log scale in Figure 3.6. These log-log data are fit via linear regression to show that the diffusion of the copolymer and homopolymer combs vary similarly with molecular weight to the -2.0 power, indicating that COM diffusion of the polymer combs is dominated by the presence of the branches, but are not significantly impacted by the thermodynamic potential between monomers since there is no change in slope between the homopolymer and copolymer data sets. Additionally, the $D \sim M^{-2}$ dependence differs significantly from the logarithmic dependence of viscosity on branch molecular weight that has been experimentally determined for other branched polymer systems, such as star and H-polymers⁹⁰

Figure 3.7 presents the diffusion data of linear homopolymers as a function of molecular weight over a similar molecular weight range as the combs in Figure 3.6. These linear chains exhibit a -1.3 power-law dependence on molecular weight, slightly higher than the -1.0 dependence expected for unentangled polymer chains. A -1.0 power-law dependence of COM diffusion

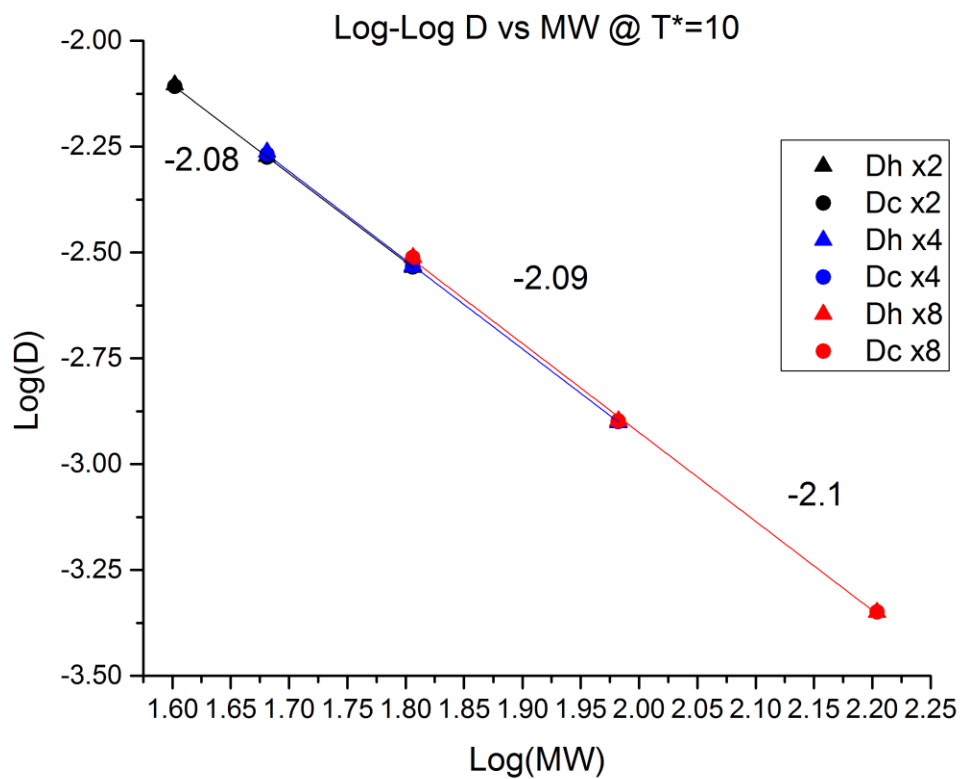


Figure 3.6: Log-log plot of the diffusion coefficient for the series of polymer combs from Figure 3. These combs feature a -2 power law dependence on molecular weight suggesting they are reptating.

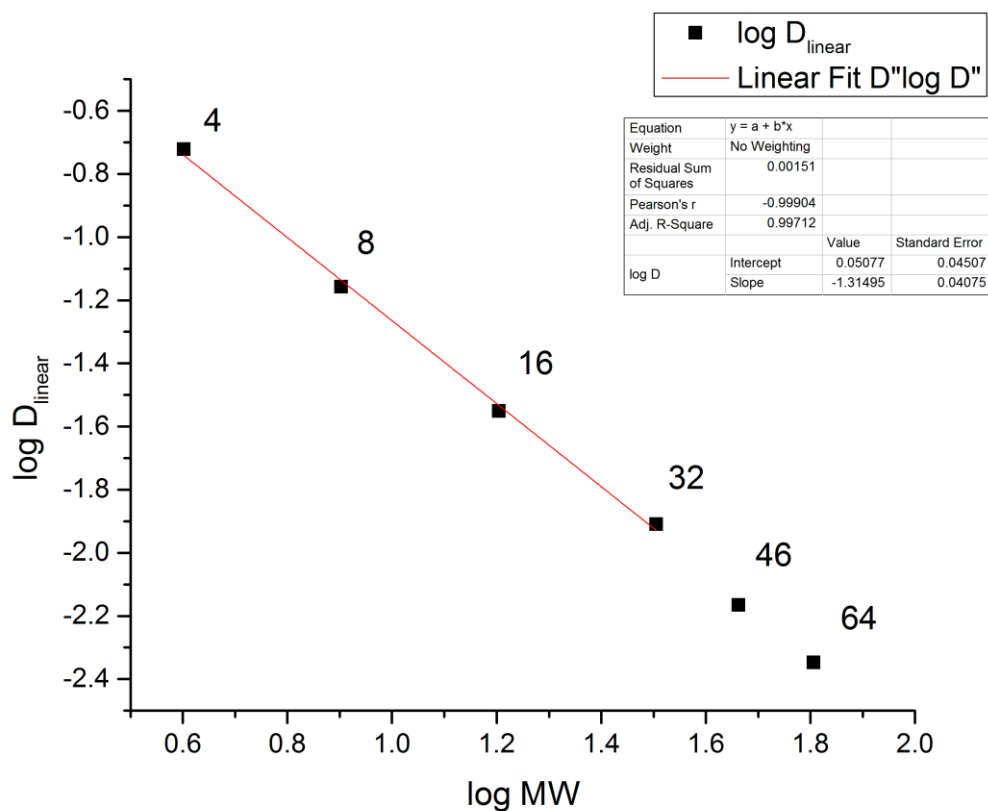


Figure 3.7: Log-log plot of the diffusion coefficients of the linear analogues of the combs in Figure 5. These combs exhibit a -1.3 power law dependence on molecular weight.

with molecular weight for polymer chains is indicative of Rouse like motion, where the polymer chains are not entangled with neighboring chains that restrict their motion. A power-law dependence of -2.0 is consistent with the diffusion of a polymer chain via reptation, which is a valid model for polymer chains that are entangled with the matrix polymers, significantly slowing their motion. Figure 3.8 displays diffusion data dependent on molecular weight similar to the data presented in Figure 3.6 and Figure 3.7, but for linear A homopolymer chains without the thermodynamic overlap penalty described in the Experimental section. These results show that these polymers exhibit the expected -1.0 power-law dependence of unentangled Rouse dynamics. This indicates that the ~ -0.3 discrepancy in slope in Figure 3.7 is due to the incorporation of excluded volume effects, and is in agreement with the deviations from ideality found in the literature.⁹¹

Discussion

Structure

The results of the Monte Carlo study of copolymer comb dynamics and structure shed light on how the thermodynamic landscape affects the structure and dynamics of branched copolymers in a homopolymer blend. The first system studied consists of copolymer combs that are composed of a backbone with 32 monomer units and have a varying number of branches with corresponding length such that the total number of branch monomers in a comb is 32. Simulations with constant copolymer composition and variable temperature

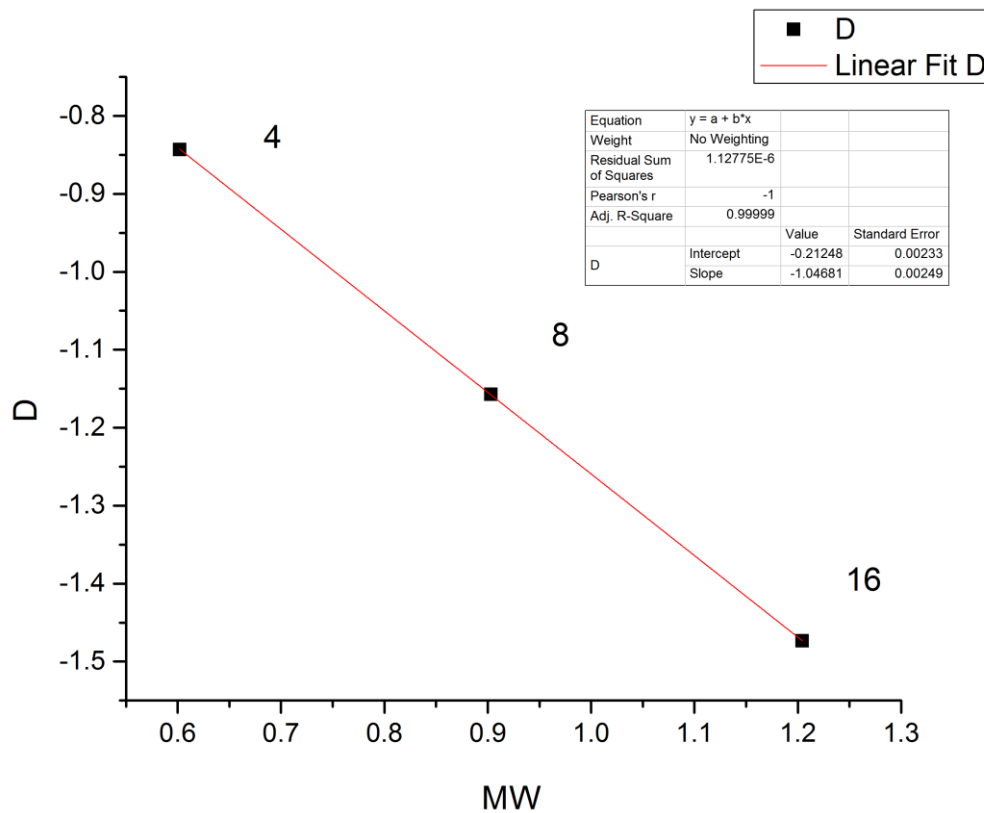


Figure 3.8: Diffusion coefficients for linear polymers with an infinite overlap penalty. These chains exhibit the expected -1 power law dependency on molecular weight for polymers below the entanglement length.

reveal the impact of available thermal energy on the dynamics and structure of the copolymer chains in the system. The structural results of these simulations, presented in Figure 3.1 and Figure 3.2 demonstrate that the impact of the thermodynamic repulsion between the *A* and *B* monomers increases with a decrease in temperature.

The radii of the gyration of the copolymer at $T^*=2$ does not change with branch length, indicating that $T^*\sim 2$ is where the *A-B* monomer thermodynamic interactions begin to dominate the conformation of the copolymer chain since the R_g of the comb is independent of branch size. This observation is in agreement with previous work using a similar system of linear copolymer chains, which found that at low temperatures the R_g of a copolymer collapses to a smaller size than the homopolymer analogue.⁶⁹ In our simulations, at temperatures near $T^*=2$, the interactions between the *A* and *B* monomers become too great to be overcome by the ambient thermal energy that is available in the system, and as a result the copolymer backbone collapses to minimize interactions between the branch *B* monomers and the *A* linear homopolymer matrix. At higher branch molecular weights and at lower temperatures, the branches extend further away from the backbone relative to the higher temperature results seen in Figure 3.2, and the separation between these two temperature groups increases with branch molecular weight. Inspecting the data that establish the R_g of the whole copolymer chain and the branches in Figure 3.1 and Figure 3.2 indicate that at low temperatures, regardless of the branch size, the comb backbone collapses in

order to minimize *A-B* branch-matrix interactions. This decreases the R_g of the total comb even at large branch sizes. As the temperature is increased, the ambient thermal energy available shields the *A-B* interactions between the backbone and the branches and therefore the R_g of the copolymer at higher temperatures becomes dominated by the entropic factors caused by the increase of the branch packing near the backbone. At $T^*=10$, the R_g of the copolymer combs with the largest branches converge to the same value as that of the combs at $T^*=4$ and 6 as a result of the decreased branch packing.

The R_g data presented in Figure 3.1 and Figure 3.2 demonstrate that the copolymer comb structure in the simulations of 1:1 backbone/branch ratio at different temperatures is the result of the thermodynamic balance between the enthalpic contributions that dominate at low temperatures and the entropic contribution arising from the conformation of the branch chains and the comb backbone. At higher branch packing densities, the number of conformations available for the backbone is reduced by the presence of the tethered side chains, which decreases the entropy of the system. In the variable chain/backbone molecular weight experiments, where the temperature was uniform for each simulation at $T^*=10$, there is an ample amount of thermal energy available in the copolymer comb's environment such that the thermodynamic interactions between dissimilar monomer types play less of a role in defining the conformation and dynamics of the branched polymer.

The most obvious trend in Figure 3.4, which plots the molecular weight dependence of the branch radius of gyration, is that while the R_g of the branch increases with the branch molecular weight, it increases at a much lower rate than is expected for a free chain in the melt. As in the simulation that monitored the structure and dynamics of copolymers with a constant ratio of backbone and branch monomers is 1:1 at $T^*=10$, there is sufficient thermal energy to overcome the repulsive interactions between the *A* and *B* monomers, which results in the *B* side chains to “tuck” in closer to the *A* backbone. The data in Figure 3.4 support this interpretation since the slope of the log-log plots is less than 0.3, indicating that the branches are forming globular structures near the backbone; a relationship that holds true for all of the densities of branches. These results suggest that at high temperatures, the increase of the entropic contribution of the chain packing is what drives the structure of the chains resulting in disordered aggregation of the *B* branches.

The results presented in Figure 3.5, which shows the molecular weight dependence of the radius of gyration of the entire branched polymer, illustrate the effect of the packing density of the branches on the R_g of the copolymer comb at high temperatures. At lower numbers of branches per chain, i.e. where only two side chains are present on the backbone, the comb becomes denser since the backbone is free to attain more compact conformations. Previous work has established that long-chain branched polymers with fewer branch-points are more compact than linear analogues of the same molecular weight.⁹² The

available flexibility of the backbone and relatively long branches increase the number of possible conformations in which the comb can arrange itself, increasing the entropy of the system, and allowing the copolymer combs with only two long branches to become a more disordered aggregate. At higher packing densities, i.e. comb copolymers with 4-8 branches per chain, the flexibility of the backbone is reduced due to the presence of the side chains. The increased number of side chains causes the copolymer comb to become more extended, such that it expands from a compact aggregate to a coiled shape that approaches Gaussian behavior. This trend in branch density and its effects on chain shape is similar to that found in polyethylene where the intrinsic viscosity of the long-branched polymer with fewer branch-points is lower than the linear analogue at identical molecular weight and branched chains with shorter chains and a higher number of branch-points.^{93,94}

Dynamics

The center-of-mass diffusion of the polymer combs within the Monte Carlo simulations presented in this work is affected by the monomeric interactions between the disparate *A* comb backbone and *B* branches in addition to an entropic contribution that results in the packing of the branches among the backbone of the comb. The results of the experiments at different temperatures in Figure 3.3 demonstrate how a change in temperature impacts the relative importance of these factors. At the low temperature $T^*=2$ where the enthalpic interactions between the *A* backbone monomers and the *B* branch monomers

dominate, the diffusion coefficient linearly decreases with branch size. This correlates with the structural result for this simulation in Figure 3.2 where the branch monomers extend from the backbone in an attempt to minimize the energy between the backbone and branch monomers. As the branch monomers extend away from the backbone, the probability of contact between *A* and *B* monomers decreases due to the decrease in monomer density away from the backbone, however the probability of entanglement with the surrounding matrix increases, anchoring the entire chain and retarding its' center-of-mass motion. At higher temperatures above $T^*=2$, the available thermal energy overcomes the repulsive interactions between the *A* and *B* monomers, where it becomes possible for the branches to contract, increasing branch-backbone contact and decreasing possible branch-matrix entanglements which can slow down the comb. These effects combine to enable the combs to move faster at higher temperatures, even those combs with larger molecular weight branches.

Collapse of the side chain branches is also evident in the results of the simulations with a variation in the composition of the comb copolymer, which also impacts the diffusion of these copolymers. In Figure 3.6, the molecular weight dependence of the diffusion coefficient shows a power law dependence of -2.0 for the copolymer combs, which is consistent with reptative motion. This compares to the -1.3 power law dependence of the linear homopolymer chains found in Figure 3.7. This is a surprising result since experimental viscosity measurements of star copolymers and H-polymers in homopolymer blends have

a non-linear power law dependence with molecular weight.⁹⁰ In addition, the -2 power law dependence of the diffusion coefficient on comb molecular weight seems to be independent of branch packing on the backbone. This is true, even though the R_g of the polymer combs at $T^*=10$ in Figure 3.5 indicate that the density of the packing of the branched copolymer changes from a globular aggregate to more like a Gaussian coil as the number of branched increases. Figure 3.8 serves to demonstrate that the -2 power law dependence observed in Figure 3.6 is not an artifact of the modified BFM used in this study since Figure 3.8 shows the -1.0 linear power law dependence expected for unentangled chains. As mentioned above, the difference in the value of the slope in Figure 3.7 and Figure 3.8 is the result of non-idealities due to the inclusion of excluded volume effects.

The conclusion that the molecular weight dependence of the diffusion is independent of branch packing, combined with the results of Figure 3.4, which suggest the comb branches are similar in shape regardless of molecular weight, indicate that the -2 power law dependence is not dependent on the shape of the copolymer comb at low temperature, which is dominated by the flexibility of the backbone. Instead, it seems the molecular weight dependence of the diffusion coefficient is due to the conformation of the comb's branches, which are condensed and globular near the backbone. This conformation likely limits the number of possible entanglements of the comb with the surrounding matrix. This decrease in entanglements, which slow diffusion, likely explains why branched

polymers containing a more extended backbone diffuse more quickly than branched polymer architectures containing no backbone such as star polymers, or a very flexible backbone, similar to H-polymers.

Conclusion

In this work we studied the effect of temperature, branch length and packing density, and monomer composition on the structure and dynamics of homopolymer and copolymer branched combs. It was found that at low temperatures, enthalpic contributions dominate the conformation of the branched copolymer comb system and therefore branches extend further away from the backbone, increasing the possibility of chain-slowng entanglements. At high temperatures, entropic contributions begin to dominate the structure of the homopolymer and copolymer combs, and the packing density of the branches on the comb backbone begin to play a more important role. Additionally, we determined that the branched combs diffuse faster at higher temperatures than expected, as compared to star and H-polymers, and this increase in speed is most likely due to the retraction of branches of the polymer comb towards the backbone, decreasing possible entanglements. The retraction of the branches has the effect of limiting the impact of entanglements between the branches of the polymer comb and the surrounding matrix on the comb's movement.

The dynamic and structural data of polymer combs generated in this work, in addition to the observation of minimal structural and dynamic changes between homopolymer and copolymer combs at high temperatures, provides

insight into the observed changes in diffusion behavior between homopolymer and copolymer combs and linear and other branched polymer architectures. By investigating the temperature dependence of the branched copolymer diffusion we have probed the balance of enthalpic and entropic factors in determining the branched polymers equilibrium conformation. These studies enable a better understanding of the forces at play in a homopolymer blend containing branched polymers and allows for the tailoring of the connectivity and composition of branched copolymers to improve the design and performance of materials that effectively drive the transport of surface active functionalities to surfaces and interfaces.

Acknowledgements

This research is supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering.

CHAPTER 4 :
INTRODUCTION TO 3D PRINTING WITH POLYMERIC
MATERIALS AND FUSED DEPOSITION MODELING

Extrusion Based Additive Manufacturing using Polymeric Materials via Fused Deposition Modeling

Recent advances in additive manufacturing (AM) have made rapid prototyping of functional models a reality by three-dimensional printing (3DP) highly spatially accurate and reasonably strong parts. In the past, parts produced via rapid prototyping have been used as illustrative aids and visual presentations, not necessarily as functional parts. Extrusion-based AM processes such as fused deposition modeling (FDM) produce highly accurate parts more quickly and cheaply when compared to previous prototyping methods. Parts are designed using computer-aided design (CAD) programs and are reduced to a series of two dimensional “slices” using open source software. This file is then fed to the printer, which then produces the individual slices of each sample to build up the final specimen, including such printing parameters as extrusion speed and bed temperatures. FDM uses cheap and widely available stock thermoplastic resin such as acrylonitrile-butadiene-styrene (ABS) copolymer and biodegradable polylactic acid (PLA), which is deposited from a heated nozzle suspended from a gantry system in a layer-by-layer fashion to construct three dimensional parts that are accurate down to fractions of a millimeter.

Fused Deposition Modeling

In FDM, a filament of polymeric thermoplastic material is pushed using an extrusion mother into a heated extruder nozzle. Using a gantry system, the

extruder nozzle is then directed across an XY plane to form a pattern of material, after which the nozzle is then lifted in the z direction at certain distance, and the pattern is repeated. The patterning of the layers is determined by computer software taking into account many factors including the part' shape, the z resolution of the extrusion motor, the desired density of thermoplastic in the interior of the part, and the desired width of the exterior walls of the part. The part is deposited in a layer-by-layer fashion until the part is completed, a process that enables the ability to reliably print reproducible parts featuring complex three dimensional geometries. In FDM, a filament of polymeric thermoplastic material is pushed using an extrusion motor into a heated extruder nozzle. Using a gantry system, the extruder nozzle is then directed across an XY plane to form a pattern of material; after each layer is deposited, the nozzle is then lifted in the z direction where the pattern of the next layer is deposited. The patterning of the layers is determined by computer software taking into account many factors including the part shape, the z resolution of the extrusion motor, the desired density of thermoplastic in the interior of the part, and the desired width of the exterior walls of the part. The part is deposited in a layer-by-layer fashion until the part is completed, a process that enables the reliable printing of reproducible parts featuring complex three dimensional geometries.

Materials Used in FDM

The feed materials used in fused deposition modeling are amorphous thermoplastics, the most common being acrylonitrile-butadiene-styrene

copolymer (ABS) and polylactic acid (PLA). These thermoplastics are chosen specifically for their low melting temperatures and flow properties resulting in high processibility.⁹⁵ PLA has two additional advantages in that it is a biodegradable thermoplastic polyester and that it is derived from renewable resources such as corn starch. As a result of these qualities, PLA is the second most consumed (by volume) bio-derived plastic in the world in 2010.⁹⁶ ABS is a commonly used elastomer in FDM because of its' relative strength compared to other thermoplastics and its low surface roughness of 12.5 μ m and part accuracy, which can reach ± 0.127 mm when printed.⁹⁷ While ABS is often selected for its strength, most thermoplastics, including ABS, 3D printing of these material often produce specimens that lack the isotropic mechanical properties that are needed to produce a fully functional replacement part using FDM.⁹⁸

New strategies utilizing material composites have been developed to overcome the strength limitation of thermoplastics used in FDM. Various carbon-based nanostructures have been used to reinforce the thermoplastic matrix including vapor-grown carbon fibers⁹⁸, carbon nanotubes^{99,100}, and high aspect ratio carbon fibers¹⁰¹. These materials have shown promise in increasing the bulk properties when blended with ABS, however when these composites are used with FDM they have resulting in low flexibilities¹⁰² and handleability¹⁰³ and usually further exacerbate the most prominent weakness of FDM which is the inter-layer strength between deposited filaments.

To create a more structurally robust material, chemical additives that exploit non-covalent interactions have been added to less commonly used elastomers including supramolecular networks of hydrogen bonding within maleated polyisoprene¹⁰⁴; ionic bonding in carboxylated nitrile-butadiene rubber (XNBR)¹⁰⁵; and complexes of ruthenium(II) and terpyridine-polyethylene glycol (PEG)^{106,107}, iron(II) with terpyridine end-capped poly(L-lactide) (PLA)¹⁰⁸, and copper(II) complexed with NBR^{109,110}. However, these materials tend to be susceptible to high temperatures and as such are not suitable candidates for use with FDM. Chemical additives utilizing covalent bonding have been used in conjunction with thermoplastics such as ABS, however by adding what essentially become chemical hardeners, the ABS loses its desired processability.¹¹¹ These results suggest that any strategy to improve the strength of inter-layer interfaces will have to be incorporated post-deposition during the printing of the model.

Overview of the FDM Process

Extruder Head/Hotend

The materials feedstock source pellets used in fused deposition modeling is first extruded into long spools of filament with a 1.75mm or 3.0mm diameter using a twin-screw extruder. Using a pair of pinch rollers the filament is then fed through a cooling barrel into a metal block heater surrounding a brass liquefier that is heated to a certain temperature (usually 210°C for ABS) that ensures that the thermoplastic filament melts within. The temperature of the liquefier is

controlled via the metal heating block and a thermistor embedded within it. Usually one of the pinch rollers is attached to the extrusion stepper motor that controls the rate that the filament is fed into the liquefier, and to better facilitate control of the extrusion speed, the pinch rollers are often tooled with grooves for a better grip on the filament. The force from the extrusion motor ensures that there is always a positive pressure on the liquefier that forces the molten thermoplastic out of the brass nozzle. More exotic FDM systems that are used on larger industrial scales directly use feed thermoplastic pellets into a screw-type extruder that is wrapped in a heated jacket ensuring that the pellets are molten.

Print Bed

The polymeric material is extruded from the heated nozzle onto a bed that is usually made from glass or metal that has been covered with kapton tape intended to prevent the material from bonding to the bed. However, depending on the size of the part being printed and the thermal environment around the part, uneven cooling rates can cause the part to shrink and pull up from the bed. Usually off-the-shelf extra hold hairspray or ABS slurry, which is composed of ABS dissolved in acetone, is used to ensure good adhesion to the bed surface during the printing process. In addition to kapton tape or ABS slurry, the bed surface is often heated to ensure an even distribution of heat that might prevent the part from warping during the print process. The thermal energy added from a

heated bed plays a further role in the development of necking between filaments in the part, which will be discussed in detail below.

Print Control

The extruder head containing the heated liquefier and nozzle, or hotend, is suspended via a gantry and is positioned in the X, Y, and Z directions using three stepper motors. These three motors work in conjunction to produce the desired pattern of material that is deposited on the print bed. The stepper motors are controlled by the 3D printers firmware, which receives commands and print positioning data from a computer that is attached to the printer. The computer software used is dependent on the model of 3D printer, but all of the software options offer the same features: communication with the printer; adjustment of various printing parameters such as extrusion speed, motor positioning and speed, print bed size and temperature, and hotend temperature; and print control including stopping, starting, and pausing the print process.

Generating Gcode

The patterning of material deposition in each layer of a printed part is determined from a set of spatial coordinates that are sent to the printer from the attached computer. A series of X,Y points representing each layer is sent to the printer and the stepper motors move the hotend from point to point while the extruder motor forces material through the hotend, creating the pattern of deposited filament in each layer. The set of coordinates representing each layer is called gcode and is generated by a “slicing” program that defines a three

dimensional part by a series of two dimensional “slices” or planes. The actual points that are used to create each slice are calculated by the slicing software and are based on many different parameters including: print speed, desired infill density in the interior of the part, surface spatial resolution of the part, filament bead diameter, and the part shape. The most commonly used slicing program is called Slic3r¹¹² which is available as open-source software and usually included in most commercial 3D printer software suites.

Strength of FDM Printed Parts

As previously mentioned, while FDM 3D printing can produce very spatially accurate parts, these parts do not possess the structural properties required for use in structural applications. The macroscopic strength properties of ABS FDM printed samples have been characterized based on different print orientations¹¹³ and other print parameters.^{114,115} Additionally there has been work suggesting that the reduced strength of FDM printed parts is caused by the presence of voids and lack of molecular orientation, causing inefficient interfilament bonding.¹¹⁶ The literature also reports work attempting to describe the role of physical inter- and intra-filament bonding in FDM printed models based on the viscous sintering of polymer spheres¹¹⁷ modified to include the effects of heat transfer¹¹⁸ and by extending this model from spherical particles to FDM filaments.¹¹⁹ Many of these models make questionably valid assumptions; namely that they assume a heterogeneous temperature distribution within a filament that is of infinite length and do not account for partial bonding between

filaments. While models based on the mechanism of sintering have been used to predict neck formation between adjacent deposited filaments with time, they have not been sufficiently accurate to effectively describe the process of inter-diffusion of heat and material exchange that occurs in the sample during FDM 3D printing.¹²⁰ The failure of these models demonstrates the need for an improved molecular understanding of the physical nature of the interface between filaments.

CHAPTER 5 : UNDERSTANDING AND IMPROVING THE QUALITY OF INTER-FILAMENT BONDING IN FDM 3-D PRINTING

Abstract

In this study, the effect of inter-filament heat transfer and material diffusion on inter-filament bonding in FDM 3D printed parts was examined. Work was performed to better understand and characterize the chemical nature of acrylonitrile-butadiene-styrene copolymer (ABS), the most common FDM filament material. The available thermal energy during the FDM print environment was determined quantitatively by tracking the temperature of the bottom most printed layer using a thermocouple attached to the print bed. The role of the thermal history as a result of the deposition process on the quality of inter-layer bonding in an FDM ABS part was measured using a T-peel test and an innovative sample design. Additionally, the interface between ABS filaments layers was improved using the chemical cross-linking agent 4,4'-diaminodiphenylmethane (DADPM), the effect of which was verified using additional T-peel test.

These studies have increased our understanding of the thermal history of a filament in the 3D printing process and on its impact on the inter-filament bonding during the fused deposition modeling print process. Furthermore, the chemical crosslinking developed demonstrates a possible method for physically linking layers in FDM printed parts, improving the bulk strength of the part. The insight provided in this work may aid in the development of techniques that can produce FDM parts that could be used as replacement parts in structural applications, or as completely standalone products. The resulting processes can

produce highly spatially accurate parts of complex geometries more quickly and cheaply than traditional assembly methods.

Introduction

Additive manufacturing has become a popular tool in prototyping in recent years because of its capability for rapidly producing geometrically complex prototypes using cost-effective stock material. Fused deposition modeling (FDM) 3D printing is a form of additive manufacturing that has recently become a popular technique for prototyping three dimensional models with complex geometries.¹²¹ Parts are designed using computer-aided design (CAD) programs and are reduced to a series of two dimensional “slices” using open source software. This file is then fed to the printer, which then produces the individual slices of each sample to build up the final specimen, including such printing parameters as extrusion speed and bed temperatures. FDM uses cheap and widely available stock thermoplastic resin such as acrylonitrile-butadiene-styrene (ABS) copolymer or biodegradable polylactic acid (PLA) that is deposited from a heated nozzle suspended from a gantry system in a layer-by-layer fashion to construct three dimensional parts that are accurate down to fractions of a millimeter. FDM printed parts exhibit strengths and weaknesses that are dependent not only on the process in which they were produced, but also on the physical and chemical properties of the thermoplastic used as printing stock. The primary weakness of FDM is that improperly chosen combinations of print parameters and stock materials can result in weak interfaces between adjacent filaments and parts that lack the structural integrity needed to act as fully functional structural products.⁹⁸ As a result of the complexity of the 3D printing

process, the chemical structure of the filament material, the structures and defects they form, and the available thermal energy during the print process all play an important role in the physical understanding of interface development between deposited filaments in the FDM process.

The thermoplastic filament used in FDM printing is only exposed to the heated extrusion head for a short amount of time, therefore the thermal energy present in a newly deposited layer dissipates rapidly. The transience of the semi-molten state of the newly deposited filament presents the primary limiting factor on the inter-diffusion of materials between adjacent filaments previously deposited.¹²⁰ The current models describing the physical understanding of this process is based on sintering between adjacent deposited filaments that allows for the exchange of heat and material between them. Sintering is traditionally described as the coalescence of two equally spherical droplets of a Newtonian fluid, however much work has been done to modify the existing sintering models to better describe the process of heat and material transfer between adjacent FDM deposited filaments.^{120,118} Many of these models make questionably valid assumptions; namely that they assume a heterogeneous temperature distribution within a filament that is of infinite length and do not account for partial bonding between filaments. These deficiencies render current models unreliable and as a result they are unable to accurately predict neck growth between adjacent filaments which is an important indicator of increased bonding as a function of extrusion temperature and time.^{119,122} The failure of these models highlights the

need for an improved molecular understanding of the physical nature of the interface between filaments. Given a better understanding how inter-filament bonds form and the relationship of interface formation to the thermal history of the deposition process, better deposition processes can be designed that can print stronger parts.

In addition to studying the FDM print process, methods to consistently improve sub-optimal interfaces between deposited filament layers and further increasing the tensile strength of printed parts by modifying the stock materials used in the printing process have been of interest of late. Additives such as reinforcing carbon fibers and chemical hardeners have been blended with stock material which thereby increases the integrity of the FDM printed part. However these techniques have resulted in a loss of flexibility¹⁰² and handleability¹⁰³ and do not sufficiently improve the inter-layer strength between adjacent filaments, which is the primary weakness of FDM. Work has been done to investigate improving FDM printed part strength by developing new filament materials utilizing chemical hardeners that incorporate both non-covalent and covalent bonding that promote crosslinking in individual filaments and between layers . Various forms of non-covalent bonding in elastomers have been studied that could find use in FDM including: supramolecular networks of hydrogen bonding within maleated polyisoprene¹⁰⁴; ionic bonding in carboxylated nitrile-butadiene rubber (XNBR)¹⁰⁵; and complexes of ruthenium(II) and terpyridine-polyethylene glycol (PEG)^{106,107}, iron(II) with terpyridine end-capped poly(L-lactide) (PLA)¹⁰⁸,

and copper(II) complexed with NBR^{109,110}. In the case of the NBR blend studies, the addition of the network of coordinating bonds significantly improved the tensile strength of the resulting material, however a common weakness of all of these non-covalent techniques is their relative susceptibility to high temperatures that are required for use with FDM materials. Covalent chemical bonds can resist the high temperatures often required in the processing of elastomers, such as NBR in blends with epoxies. Additionally, crosslinking these blends with diamines has also been proven to positively affect tensile strength.¹¹¹ Studies of these materials yield insight into methods to improve the inter-filament bonding strength between adjacent FDM deposited filaments using chemical means, however there has not been much work using these materials in the FDM print process.

The most common material that is used in FDM 3D printing is ABS, which has a number of methods for commercial synthesis. Consequentially, ABS can be synthesized as a graft copolymer, where styrene-acrylonitrile copolymer (SAN) is grafted to a polybutadiene (PB) backbone, or as a blend of SAN copolymer and PB homopolymer. Both of these forms of ABS are sold commercially and often a supplier does not reveal, or does not know, the method of synthesis or monomer ratios of styrene, acrylonitrile, and butadiene for a given batch of ABS purchased in bulk for use in 3D printing filament. These two types of ABS are chemically very similar to one another and as a result are very hard to characterize using one analytical method.¹²³ Also, it has recently become

popular to recycle ABS, creating the possibility for blends of ABS batches with different monomer ratios to be used as source material, further complicating the chemical make-up of a given ABS sample.¹²⁴ Therefore, in order to better understand how to improve the structural properties of FDM printed ABS parts, there is a need for better characterization of the sourced ABS used in the FDM deposition process.

Therefore, we have completed a series of experiments to address the needs outlined above that will address the deficiency in understanding the heat and material flow that occurs in the printing of FDM parts, the results of which will enable the design of methods to increase the bulk strength of ultimate 3d printed specimens. Below, we directly correlate the thermal history that results from the FDM deposition process to the mechanical properties of an FDM printed part. Additionally, we have also developed a novel technique to quantitatively characterize the impact of the incorporation of chemical cross-linkers on the interlayer interface. The goal of these experiments is to therefore study and improve inter-filament bonding between deposited layers of ABS filaments in 3D printed parts using fused deposition modeling such that they may eventually be used as fully functional replacement or stand-alone products in structural applications.

Experimental

Sample Production

The core of a FDM 3D printer is a “hotend” primarily comprised of a heated extrusion nozzle, which is suspended by a gantry system and moved using common positional stepper motors in three dimensions as depicted in the diagram in Figure 5.1. Thermoplastic is extruded from the heated nozzle in a layer-by-layer fashion in a pattern predetermined by a computer algorithm in a process called “slicing” where the software generates a series of two dimensional “slices” of the object that is to be printed. These slices contain a series of points in an XY plane to which the extruder nozzle moves while extruding thermoplastic. The pattern in which the thermoplastic is deposited is determined by the slicing program based on a wide array of parameters including the density of material in each layer known as the infill, the speed the positional motors move the extrusion nozzle, and the speed of the extrusion motor that determines the material flow rate. Once the printer has completed an entire slice, the series of XY points that represent the next layer are loaded and the extruder head is raised in the Z dimension based on the desired layer thickness and printer proceeds to extrude the next layer; this process continues until the part is completed.

The 3D printer used in these experiments was a Solidoodle 3 manufactured by Solidoodle Inc. It contains a heated aluminum bed that has an 8”x8” printable area. The stock Solidoodle hotend including the heating block, polyether ether ketone (PEEK) cooling barrel and extrusion nozzle were replaced with an E3D hotend obtained from Filastruder.com. This replacement hotend

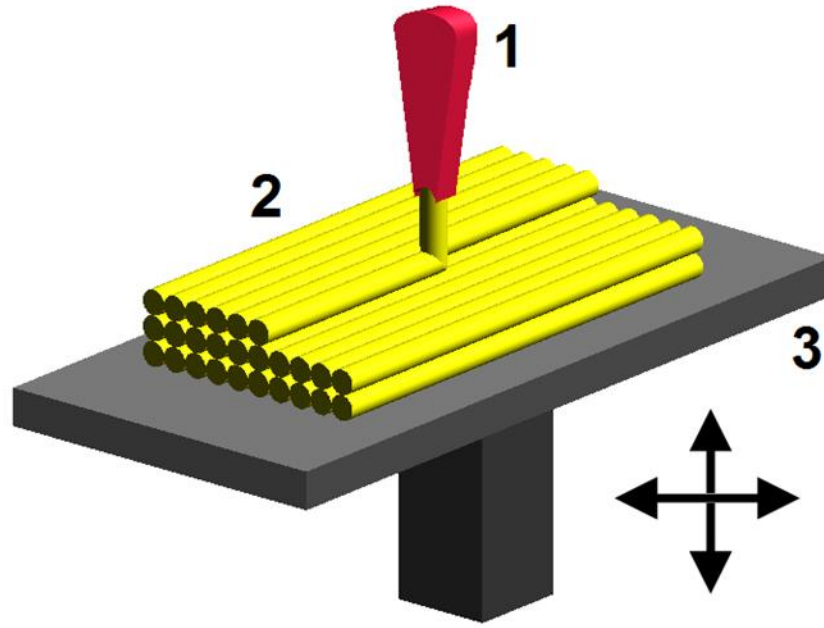


Figure 5.1: Diagram of a commercial desktop 3D printer.

uses an aluminum cooling barrel which can withstand extrusion temperatures up to 300°C and utilizes a brass nozzle with a smaller material reservoir along with an attached cooling fan to facilitate better filament throughput performance.

Thermoplastic Characterization

The thermoplastic used in this work was a commercially obtained acrylonitrile-butadiene-styrene copolymer filament produced by Solidoodle Inc. The molecular weight of the filament was determined using a Tosoh EcoSEC GPC system with an RI detector and tetrahydrofuran (THF) as the elution solvent. The glass transition temperature of the ABS filament was determined using a TA Instruments Q-1000 using a 20°C temperature ramp from -140-130°C. TGA was performed on two ABS samples, one sample of pre-extruded ABS and another cut from a post-extruded part. Additionally, the following materials were also examined by TGA for comparison purposes: two samples of styrene-acrylonitrile copolymer (SAN) one with a 29:71 styrene/acrylonitrile ratio and one with a 56.4:43.6 ratio donated by an industrial collaborator; and pure cis-polybutadiene (PB) and polyacrylonitrile (PAN) obtained from Scientific Polymer Products. Approximately two milligrams from each sample was weighed out and loaded into a TA Discovery TGA-MS. A six-step temperature program ranging from 40-600°C reported by Zamani et al. and outlined in Table 5.1 was performed that is intended to isolate the PB degradation, thus providing a basis to estimate the amount of PB in each sample.¹²³ The program quickly ramps up to 300°C at 50°C/min, followed by a 10°C/min temperature ramp to 365°C, at

Table 5.1: Temperature Program for the Degradation of Different Components in
ABS Samples

<u>Step</u>	<u>Initial Temperature (°C)</u>	<u>Final Temperature (°C)</u>	<u>Heating Rate (°C/min)</u>	<u>Holding Time (min)</u>
1	40	300	50	0
3	300	365	10	0
4	365	365	0	25
5	365	460	50	0
6	460	460	0	25
7	460	600	50	0

which point the temperature is held constant for 25 minutes. It is expected that SAN, but not PB, degrades at this temperature. Since the styrene and acrylonitrile portions of the ABS ternary system degrade at a lower temperature than the polybutadiene block, the remaining mass is ascribed to the PB. Next, the temperature is quickly ramped to 460°C and held there for 25 minutes, where it is expected that the PB degrades. Finally the temperature is ramped very quickly to 600°C in order to burn off any remaining organic residue. This process enables the qualitative estimation of the amount of PB in a sample of ABS.

Bed Temperature Profiles

The purpose of the first experiment performed in this project was to characterize the impact of the thermal history of the filament that results from the deposition process on the resulting inter-filament bonding in the printed part. The sample geometry that was used for this analysis was a rectangular prism with dimensions of 35 x 12.4 x 1.8mm, where the gcode for each sample was generated using the program Slic3r¹¹² and were printed on the above-mentioned modified Solidoodle 3 3D printer. Additional printing parameters include a 0.3mm z axis resolution with 100% rectilinear infill. An Omega thin foil type k thermocouple was fastened to the print bed such that it monitors the temperature of the bottom layer in each printed sample part. The voltage signal from this thermocouple was calibrated using deionized water at 0°C and 100°C and collected using a Keithley 196 system digital multimeter. The samples were then printed on top of the embedded thermocouple at three different bed

temperatures: 80, 100, and 120°C to monitor the thermal history of the printed samples over the course of the deposition and correlate this information to the variation in available thermal energy in a given print environment. It is important to note that the actual bed temperatures differ from those temperatures reported above, where the actual bed temperatures as measured with an IR thermometer were consistently ~20°C below the set-point values.

The samples were also printed in two orientations in an attempt to understand the effect of the sample orientation and the distance from the print bed on the thermal history and inter-filament diffusion between deposited filaments over the course of the printing process. The H orientation denotes where the rectangle lies flat on the print bed, i.e. the width of the rectangle is parallel to the print bed, such that the entire model is within 1.8mm of the bed surface. Similarly, the Z orientation prints the sample with the width of the rectangle perpendicular to the surface, rises 12.4mm off the bed surface and therefore only ~1/10th of the material deposited for the Z orientation is within 1.8mm of the bed surface. Depictions of both the H and Z orientation are shown in Figure 5.2. Using these configurations, the time evolution of the temperature of the first deposited layer was collected for each bed temperature for both the H and Z oriented samples. Subsequently, DMA experiments were performed on each H and Z sample printed at all three bed temperatures using a TA Instruments Q-800 DMA in dual cantilever mode for a single frequency at 10Hz following a temperature ramp of 10°C per minute from -100 to 150°C. This

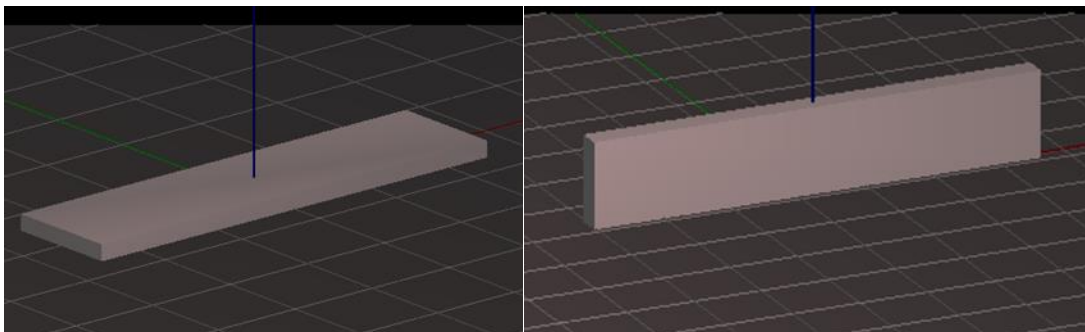


Figure 5.2: 3D rendering of H (left) and Z (right) 3D printed samples used in the bed temperature and DMA experiments mentioned above.

experiment measures the storage modulus of each sample printed at each bed temperature and in the H and Z orientations.

Interfacial Adhesion Measurements

To quantify the bonding between adjacent layers in a FDM printed part, a purpose-built 3D model depicted on the left side of Figure 5.3 was created using AutoCAD software to fabricate a sample that can be utilized in an ASTM D1876-95 T-peel experiment, where the width of the sample was 4mm. These samples were printed on a Solidoodle Workbench 3D printer with a bed temperature of 100 °C such that the length of the sample was in the x axis. In order to produce such samples, support material was included in the model using a column patterning with 2.5mm spacing as seen in the middle of Figure 5.3. For all samples, the bottom half of the samples was printed, including support materials.

At this point in the printing process, the printing was paused for 0, 30, 45, 60, or 180 minutes. These pause times were integrated into the printing process to evaluate the effect of layer cooling on interlayer strength in the printed part. This process is important, as such cooling might occur during a pause in production to correct print defects. In addition, the temperature of the upper surface of the bottom layer was measured with an IR thermometer, immediately before deposition of the top half the part, to monitor the extent of cooling that occurs during this pause. The strength of the interface was then determined using T-Peel tests that follow the ASTM D1876-95 standard.

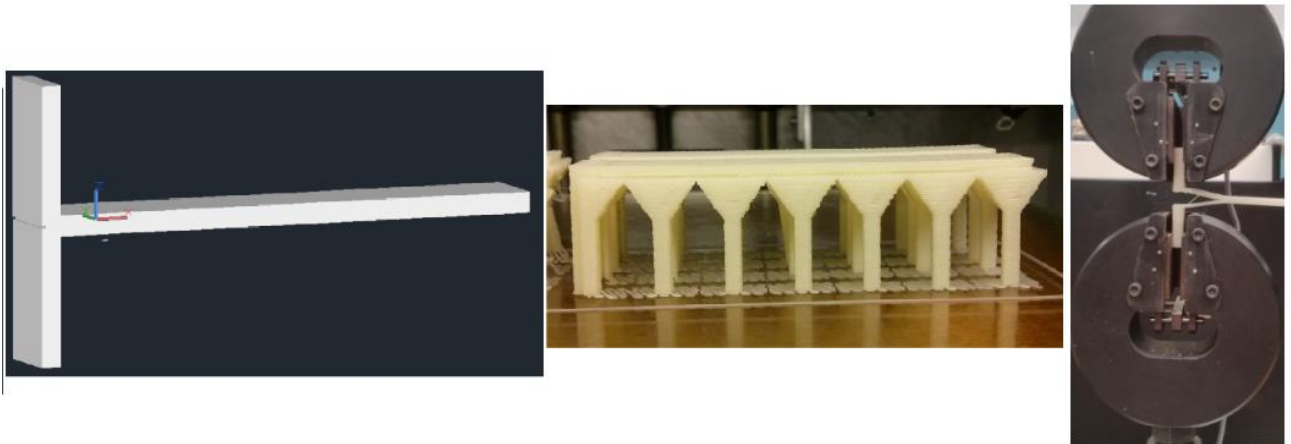


Figure 5.3: (Left) 3D diagram of t-peel sample that is sliced into gcode. (Middle) The bottom half of a t-peel sample including samples. (Right) T-peel sample being peeled.

In a second set of samples, identical samples were fabricated, except that after the pause time, chemical cross-linking agents were deposited on the exposed surface of the bottom half and the printer was allowed to resume printing the top half of the samples. These crosslinking agents were incorporated to improve the interlayer strength in the printed part by chemically bonding adjacent layers together. The impact of the presence of these crosslinking agents on the interlayer interface was then quantified by measuring the interfacial adhesion of the modified interface with the ASTM T-Peel test. The chemical cross-linking agents examined in our experiments were 4,4'-diaminodiphenylmethane (DADPM) obtained from Fischer Scientific and copper(II) sulfate pentahydrate obtained from Sigma-Aldrich, where the chemical structure of DADPM is displayed in Figure 5.4. The DADPM was dissolved in acetone to create a 10% by weight solution suitable for deposition onto printed parts. The copper sulfate hydrate was heated on a hot plate in order to drive off water, turning the powder from a deep blue color to a pale white. This dry CuSO₄ was then suspended in acetone at 10% by weight such that it could be deposited in a similar fashion as the DADPM.

The interfacial adhesion between the two layers was determined by a standard ASTM T-Peel test, as shown on the right side of Figure 5.3. This experiment was completed on a custom Universal Testing Machine with a 50 lbs. load cell at a rate of 0.069in/min, which resides at the Materials Demonstration Facility at the Oak Ridge National Laboratory. The force required to peel the

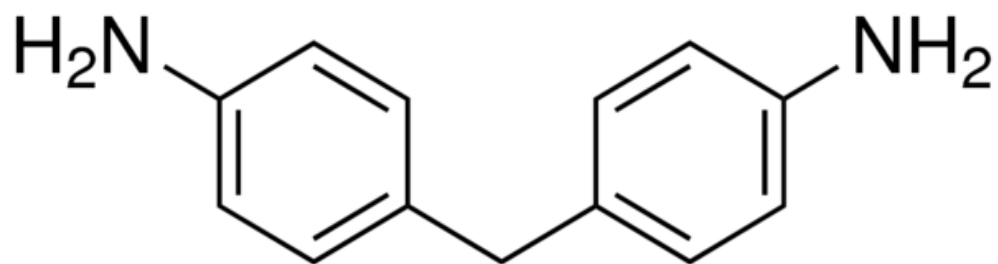


Figure 5.4: Chemical structure of 4,4'-diaminodiphenylmethane, the diamine used for covalent crosslinking in the interfacial adhesion experiments above

samples was collected using a custom virtual instrument environment developed using National Instruments LabVIEW. This force was then divided by the width of sample to quantify the interfacial adhesion G_a , the force required to separate adhered layers.

Results

Characterization of ABS

The ABS filament used in the following experiments was characterized using gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The GPC results show that the molecular weight of the ABS is 122KDa with a PDI of 2.36, based on polystyrene standards. DSC results show that the glass transition temperature of the glassy portion of the ABS filament is 105.09°C. Figure 5.5 contains TGA data for two ABS filament samples obtained from Solidoodle Inc. (ABS and New White), two ABS samples obtained from the Manufacturing Demonstration Facility at Oak Ridge National Lab (MDF and Post), pure PB and PAN samples mentioned in the Experimental, and two SAN samples of different composition (Sparkle and SAN). The TGA data presented in Figure 5.5 was obtained utilizing the temperature program in Table 5.1 designed to isolate the temperature region in which degradation of PB occurred, which is from ~350-450°C from the degradation of the SAN portion of the ABS. The percent of the sample that remains where there is a shoulder in the curve starting at ~350°C is proportional to the weight percent of the remaining PB after the styrene and acrylonitrile blocks have degraded.

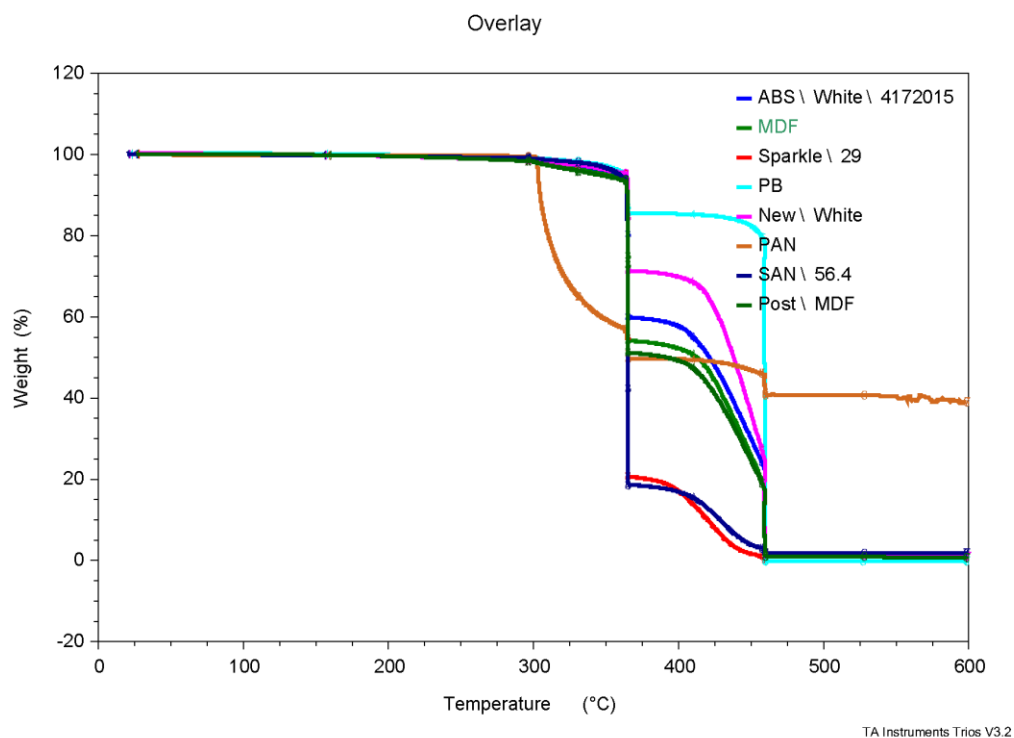


Figure 5.5: TGA data for both ABS samples used in this work (ABS White and New White), pre- and post-extrusion ABS samples from MDF (MDF and Post MDF), two SAN samples (Sparkle 29 and SAN 56.4), and pure PB and pure PAN samples.

According to the analysis in Figure 5.5, the pure PB sample contains the highest PB content and the ABS sample contain considerably less PB while the SAN samples contain the least. Even though this figure suggests that the PB content in these samples is near 50%, ongoing investigation in our lab suggests that PB is a minor component in ABS samples, therefore quantitative analysis using this form of analysis should be done with care.

Figure 5.6 isolates the results of this TGA experiment for the two ABS samples obtained from the Manufacturing Demonstration Facility on their Big Area Additive Manufacturing printer, comparing the degradation characteristics of the ABS samples from before and after the printing process. Comparison of the two curves shows that there is a difference in the weight loss at the 350°C anneal, indicating that the post-printing sample contains less PB, which is consistent with the degradation of the polybutadiene segments during the 3D printing process on the big area additive manufacturing printer at the MDF.

Bed Temperature Profiles

Figure 5.7 displays the temperature profiles of the first layer of the samples that are printed at three bed temperatures and two print orientations. For all of the experiments, the thermocouple was adhered to the print bed using Kapton tape so that the probe was approximately in the center of the printed rectangular sample. The profiles captured indicate that as each layer of new material is deposited by the extruder, the previously deposited layers are reheated. In the H orientation this reheating of the bottom layer occurs for at

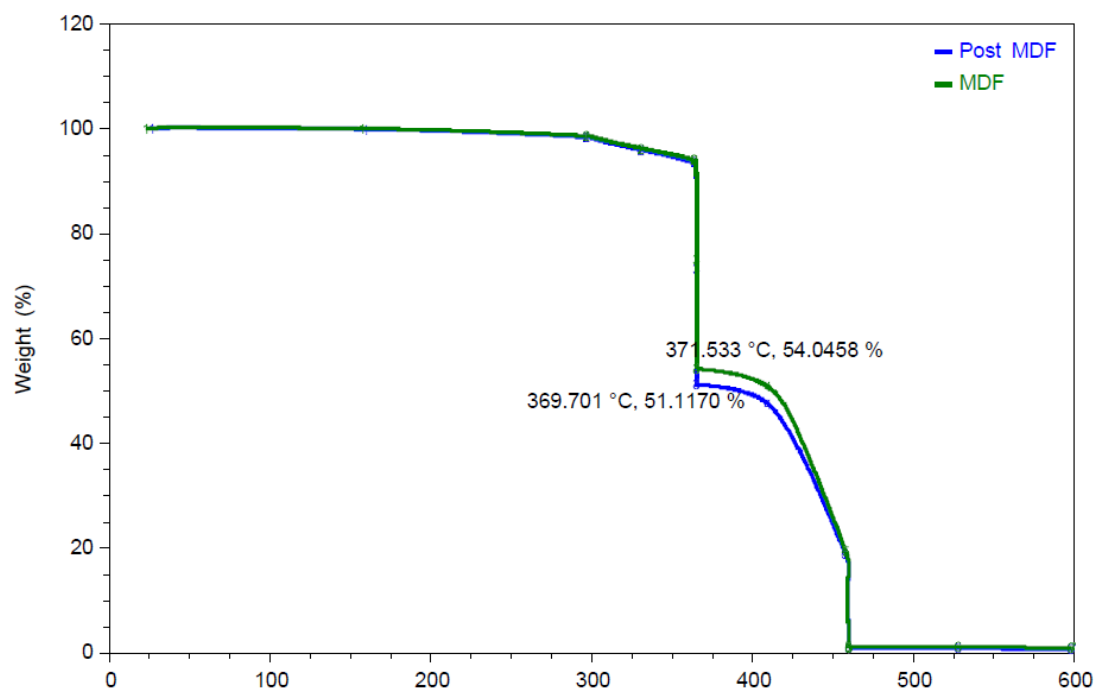


Figure 5.6: TGA data for pre-extruded ABS copolymer (green) and post-extruded printed ABS samples obtained from MDF at ORNL.

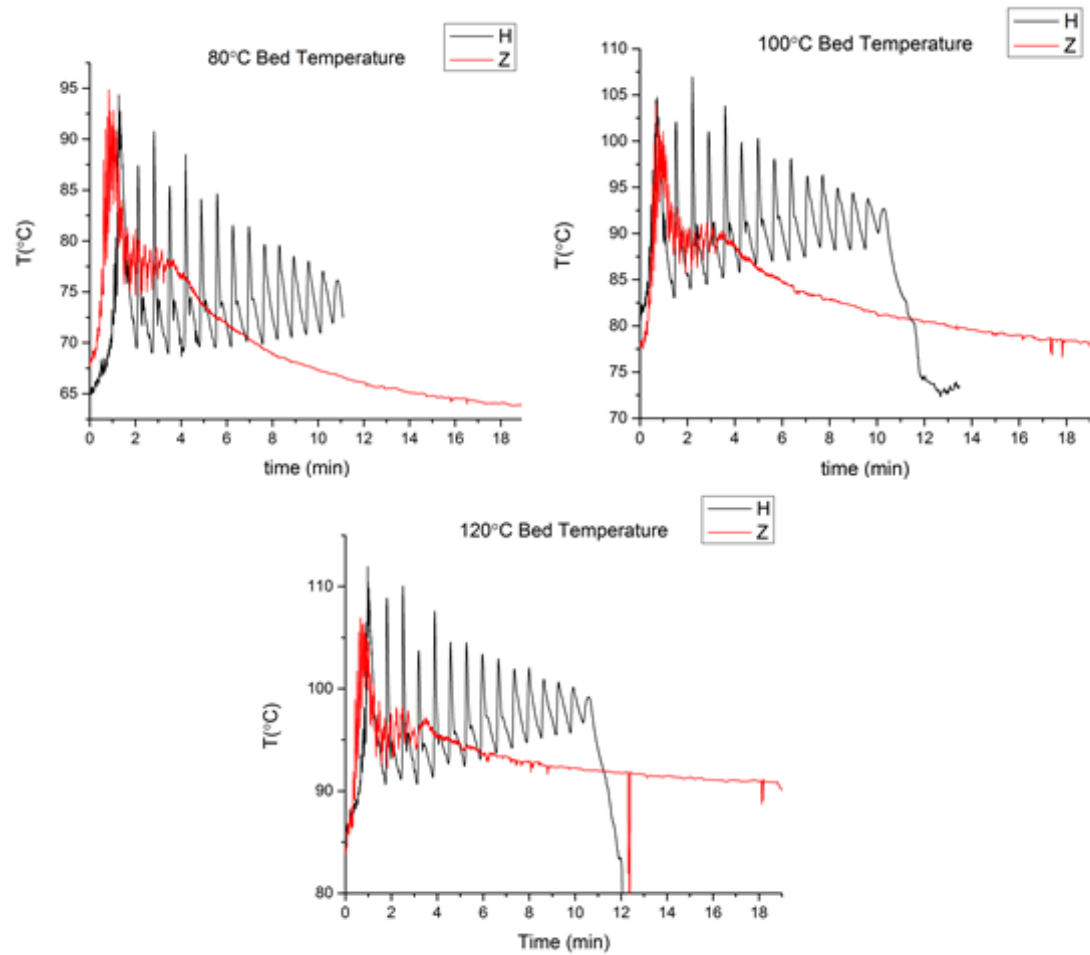


Figure 5.7: Bed temperature profiles for 80°C (top left), 100°C (top right), and 120°C (bottom).

least 13 layers. Moreover, in the case of the 100°C and 120°C bed temperatures, they are heated above the T_g of ABS for a significant portion of the print time. The reheating process is not as distinct in the Z print orientation, since the extruder moves away from the print bed at a faster rate, and corresponds to the low volume of each layer in this orientation. The H orientation samples exhibit a much more obvious trend as a result of the extruder spending more time depositing each layer closer to the thermocouple.

Dynamic Mechanical Analysis

The mechanical properties of the H orientation samples that are printed with a 100°C or 120°C bed temperature were then monitored in a single-frequency DMA experiment at 10Hz and 15 micron amplitude for a temperature ramp of 10 °C per minute from -100 to 150°C. The average of these data is presented in Figure 5.8 where the red line is the average for the 100°C bed temperature samples and the blue line is the average for the 120°C bed temperature samples. The 80°C bed temperature results were very inconsistent and are not presented. The data in Figure 5.8 demonstrate that the storage modulus of the samples increases with an increase in bed temperature from 100-120°C suggesting better inter-filament material transfer at higher bed temperatures.

Interfacial Adhesion Measurements

The interfacial adhesion measurements of the t-peel samples are presented in Figure 5.9 where the black squares represent data for t-peel

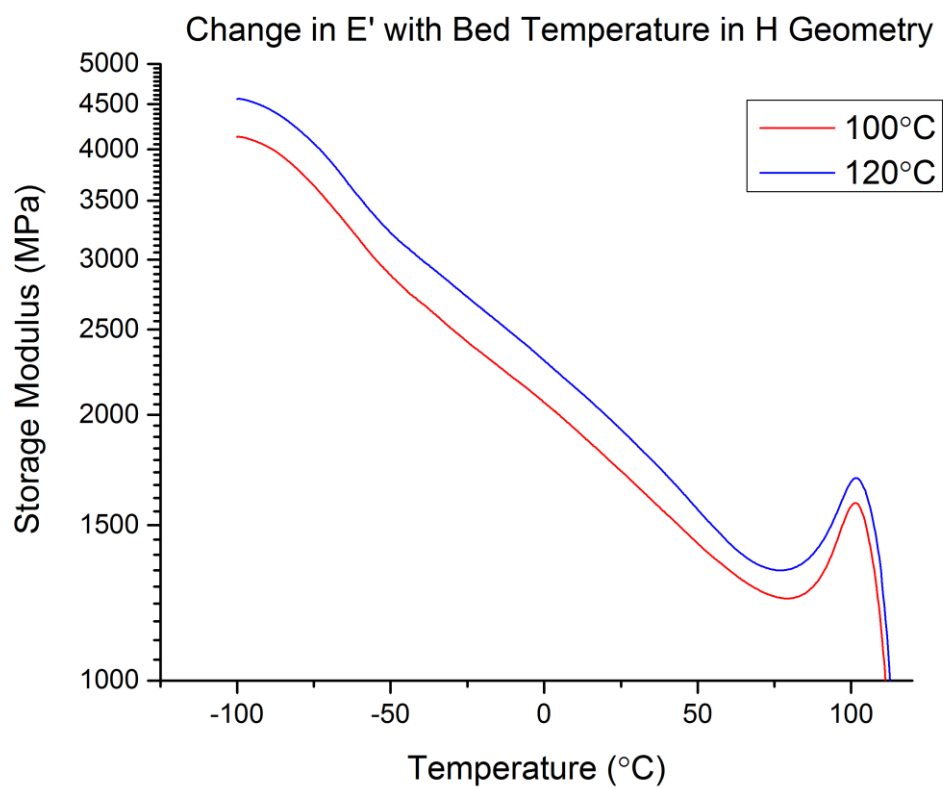


Figure 5.8: The storage modulus (E') as of samples printed in the H geometry at 100°C (red) and 120°C (blue).

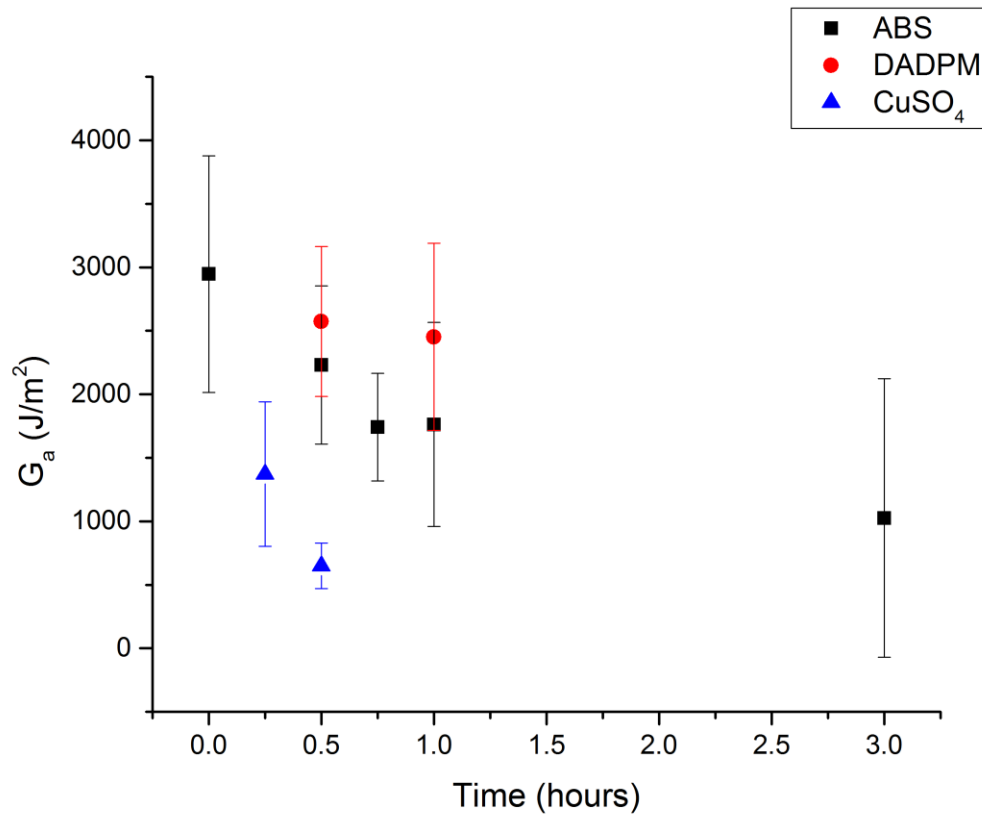


Figure 5.9: Interfacial adhesion (G_a) measured for the neat ABS printed samples (black square), samples treated with DADPM cross-linker (red circle), and samples treated with CuSO_4 cross-linker (blue triangle).

samples made from neat ABS, the red circles represent data for the t-peel samples treated with DADPM after a pause time, and the blue triangles are data for t-peel samples treated with a CuSO_4 suspension after a pause time. The data in Figure 5.9 result from peeling approximately 10 samples per wait period ranging from no lag time to 3 hours before the deposition of the next layer. The large error bars are similar in magnitude to those found in t-peel tests of polymer films and are the result of a set of 5-10 samples. These data do not include the samples where the crack that results from pulling the two sample halves apart started to deviate from the interface between the halves.²⁹ This deviation occurred in 25% of the measured data for the DADPM samples. In the data presented in Figure 5.9, there is a clear downward trend in surface adhesion as pause time increases. Additionally, Table 5.2 lists the temperature of the top layer of the bottom half of the t-peel sample just before the print process resumes after the listed pause time. The data in Table 5.2 illustrate the loss of thermal energy in the bottom half of the t-peel sample during the print pause.

In the neat ABS samples, where there was no cross-linker applied, interlayer bonding is a function of inter-filament diffusion that occurs upon deposition of the top layer, which is dramatically influenced by the available thermal energy. As the extruded bottom half of the t-peel cools, the amount of this thermal energy decreases, therefore decreasing the extent of inter-diffusion between the filaments, and limiting the bonding between the layers. However, the application of DADPM to the pre-deposited surface before the next layer is

Table 5.2: Temperature of the top layer of the bottom half of the printed t-peel part after print pause

<u>Pause Time</u> (minutes)	<u>Temperature After Pause Time</u> (°C)
0	52
30	46.8
60	33

applied results in increased interfacial adhesion suggesting that the applied DADPM forms covalent bonds between the layers, increasing the inter-filament bonding. Alternatively, the application of the suspended CuSO_4 in a similar fashion decreases this adhesion, indicating that the presence of the Cu_2SO_4 /acetone solution decreases inter-filament bonding.

Discussion

Correlating Inter-filament Bonding to Heat and Material Transfer

In FDM printed parts, the strength of the printed part is dependent on the bonding between the individual beads of filament deposited during the printing process. The primary mechanism for mechanical interlayer bonding involves material transfer between adjacent thermoplastic layers and requires that the printing environment achieve temperatures above the glass transition temperature of the extruded material that allow the molecular level inter-diffusion of the polymer chains to strengthen these interfaces. The principle sources of heat for a previously deposited filament are the heated extruder nozzle, the heated filament that is deposited neighboring the previously deposited filament, and the heated printing bed. The thermal energy contribution from the extruder nozzle and the neighboring filament to a previously deposited filament is transient in nature, while the heated bed provides a constant contribution of thermal energy. These heat sources, therefore, direct the inter-diffusion of polymer at the inter-filament interface by providing thermal energy to both the extruding filament and the already cooled material. The resulting availability of

thermal energy in such an environment therefore controls the inter-diffusion of polymer between adjacent extruded filaments, and must be more carefully characterized to develop methods to rationally improve the interfacial adhesion and the bulk strength of the ultimate printed part.

The three heat sources combine to give the temperature profiles that are presented in Figure 5.7. These temperature profiles exhibit an oscillation of the temperature, including spikes that are the result of the extruder head passing over the embedded thermocouple during the printing of each layer and the resulting heat transfer from the hot filament to the cool previously deposited filament. The height of these spikes decreases with each additional layer, and is dependent on not only the temperature of the extruder nozzle but also on the temperature of the heated bed on which the print occurs. When the print bed temperature is increased above 100°C, the addition of new material from the extruder nozzle heats the previously deposited material above the glass transition temperature of ABS (~105 °C). This cycle of heating and cooling results in thermal annealing of the printed part, where the thermal load is time-dependent but is sufficient to keep the previously deposited filaments above the T_g of ABS for extended periods of time, and encourages the inter-diffusion of polymer between adjacent extruded filaments. The extent of the resulting material transfer between the adjacent filaments in a layer is dependent on the distance of that layer from the bottom and the pattern in which that layer was deposited.

An example of the increase of inter-filament diffusion with increased time above the T_g of ABS is shown in Figure 5.10, which contains a photograph of the cross-section of a sample printed in the Z orientation as explained in the Experimental section. In Figure 5.10, the first layers of the model are on the bottom left and the upper layers are added in the top-right direction such that the black arrow in Figure 5.10 describes the axis of material deposition. In the Z configuration, the extrusion nozzle deposits material in a series of concentric rectangles and as a result, there is a characteristic gap along the center of the sample. In Figure 5.10, this gap is present starting near the bottom left corner of the image and extends at roughly a 45° angle to the top right. As the layers are deposited further from the bed the amount of the thermal energy available decreases, resulting in less necking and more clearly defined filament in the upper layers. Thus, the aggregate thermal energy that a given filament is exposed to will vary with the distance of the deposited layer from the heated bed. Moreover, this variation in thermal history means that, for a given set of print conditions, the lowest layers will have the most time above T_g , while those at the top of a sample will experience the least time above T_g .

This gradient nature of the thermal history of the part resulting from the deposition process drives the inter-filament diffusion process in the layers closer to the heated bed to occur more than it does in those that are farther from the surface. This effect is evident in the DMA data presented in Figure 5.8 where the increased storage modulus of the sample that is printed on a 120°C bed can be

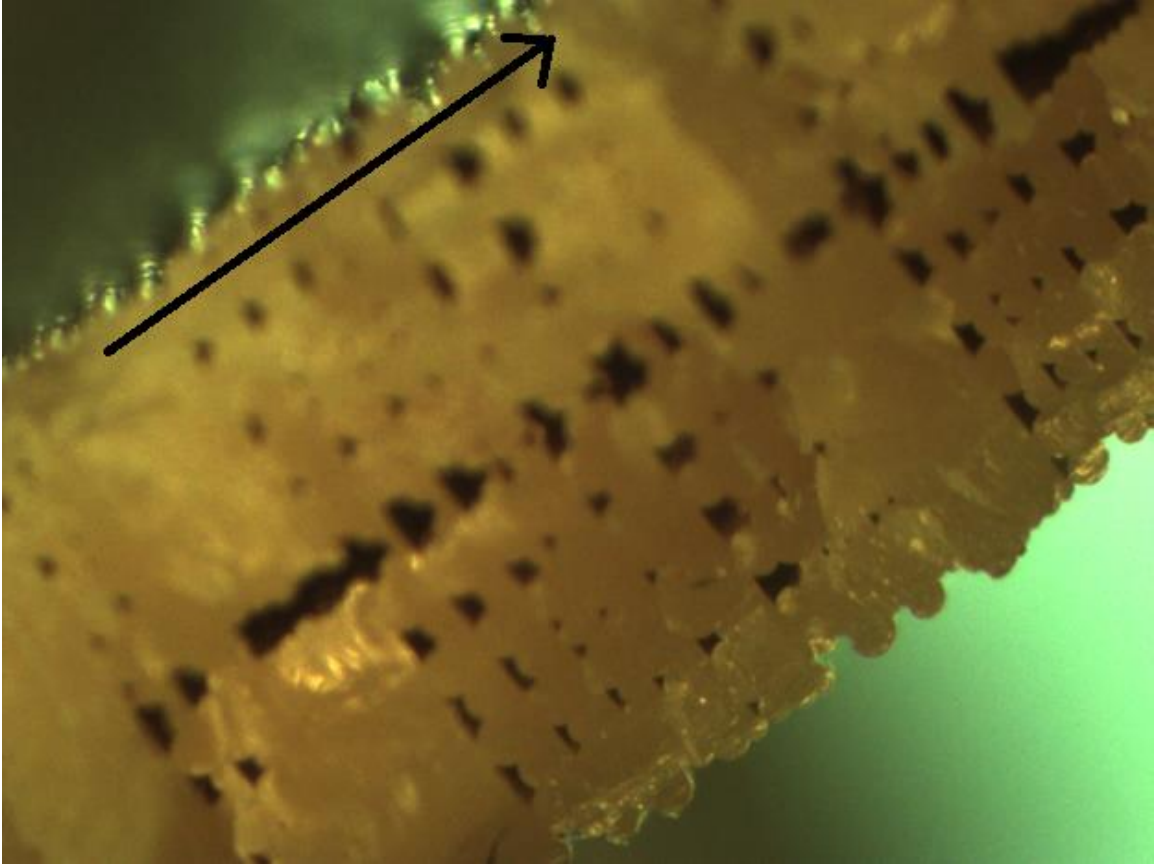


Figure 5.10: Cross-section of a Z orientation sample notice the gap in the middle decreases as more layers are deposited towards the top right in addition to more definitive filament. The black arrow points in the direction of material deposition.

correlated to the increased amount of time the filaments are above the T_g of ABS relative to the sample that is printed on a bed that is 100 °C. The increased time above T_g correlates directly to the amount of inter-filament diffusion. Thus, the sample that is printed on a bed that is 120°C is more robust and exhibits a higher storage modulus at all temperatures.

Currently, a theoretical model that describes the heat flow and resulting inter-diffusion between extruded filaments in FDM extrusion that is based on a lumped-capacity (LC) analysis of the cooling process has been developed.^{120,119} In the LC analysis, the deposition of a single bead of filament is simplified into a one-dimensional heat transfer model where the extruder nozzle moves at a constant rate. This heat transfer model makes the assumption that the temperature distribution across the cross-sectional area of the filament is uniform, that the filament length is infinite in the plane of deposition, and that the heat applied is constant. All three of these assumptions are violated for real-world 3D printing with a thermoplastic such as ABS. The thermal conductivity of common polymeric materials, including ABS, is notoriously low, resulting in their inability to dissipate heat which can lead to an uneven heat distribution in the YZ plane of the ABS filament.¹²⁵ The in-plane patterning of the filament during the 3D printing process guarantees that filaments lie adjacent to one another, ensuring that the filament does not approach infinite lengths along the coordinate of deposition and further restricting heat dissipation. The heat transfer that will occur between adjacent hot filaments is also ignored in these models. The

lumped LC model, therefore, ignores many parameters and processes that are inherent in the FDM technique.

There are also many experiments reporting successful analytical models that describe the sintering in polymers. One such model, based on Frenkel's model of sintering¹¹⁷, and proposed by Pokluda et. al.¹¹⁸ describes neck growth between two sintering particles and has been used to predict necking between adjacent deposited FDM filaments.¹²⁰ This approach was further expanded to account for cylindrical filaments, establishing a time-dependence for the necking between any two adjacent filaments within a singular part.¹²² Both of these techniques utilize the LC heat transfer method described above to predict the heat flow that controls the material exchange between filaments. This model also assumes the flow between filaments is Newtonian in nature, however molten polymers and even dilute polymer solutions are non-Newtonian.^{126,127}

The authors in the work cited above use these combined models to predict the average tensile strength of FDM printed samples using ASTM-D638. In Gurralla and Regalla's work¹²², the authors concluded that the model over-estimated the ultimate tensile load for both print configurations they investigated, while in Bellehumeur and Gu's work¹²⁰ the model consistently under-estimated the neck radius for adjacent sintering filaments. These results lead to the conclusion that combining the above models into a singular method fails to accurately describe the heat flow that occurs in real 3D printed samples, and therefore fails to predict the extent of inter-diffusion between adjacent layer in the

x and y plane. As a result, at this time there does not seem to be an accurate analytical framework for predicting the effect of heat and material transfer between layers on the inter-layer strength in a 3D printed part.

As a result of the deficiency of current theoretical models for heat and material transfer in FDM printed parts, we have focused on experimentally examining the adhesion between adjacent material layers that result from the heat and material transfer process. Using the ASTM T-Peel test, the effects of the thermal history of the printed part can be quantified by monitoring the interfacial adhesion between two thermally distinct layers. As described above, in these experiments the printing process was paused and the half-printed part was allowed to cool for a range of times, which vary from zero minutes to three hours. The data in Table 5.2 shows that the surface cools from 52 °C to 33 °C in the hour wait time. After the pause, the printing process of the T-Peel sample was finished. The interfacial adhesion strength of the interfaces between the cooled half and the newly deposited heated half was determined by the T-Peel test. The interfacial adhesion between the two layers describes the quality of the mechanical bonding as a result of the material transfer between the two layers, and thus there is a direct correlation between the temperature of the surface immediately prior to deposition and the interfacial strength of that interface.

This marked decrease in interfacial adhesion in samples with a long pause time therefore supports the concept that the thermal environment in which the part is printed and the part's resulting thermal history greatly influences the

quality of the interlayer bonding. This effect also correlates with the results of the DMA experiments above, where the amount of available thermal energy correlates to the storage modulus of the sample, indicating that understanding and controlling the thermal history of the deposited filament *during the deposition process* is crucial to rationally improving the amount of mechanical inter-filament bonding in the final part. This effect is even more evident in Figure 5.9 and Table 5.2, as the deposited filament is allowed to cool for an extended period of time. There seems to be a limit in the pause time near an hour where the heat provided by the heated nozzle during the extrusion of the next layer is insufficient to promote material transfer, producing weak interfaces. These data, therefore, further support the concept that adequate thermal energy must be available to the part being printed to allow polymer inter-diffusion between filaments and that even a few minutes delay in printing can have deleterious effects on the success of this process, decreasing the extent of interlayer bonding and therefore the bulk strength of the part. Furthermore, these data illustrate the need for a better physical model that describes the thermal history of a deposited filament in 3D printing, as well as a model to describe the inter-filament bonding in the FDM printing process that accounts for the transient thermal history of the deposited filaments during the deposition process.

Chemical Interlayer Bonding

The decrease in interfacial bonding between layers of neat ABS with pause time represents a real-world limit in the mechanical bonding via material

transfer driven by thermal energy between layers in FDM printed parts. An alternative to increase the bonding between the adjacent layers in an FDM part is to chemically bond together the filaments between layers using a chemical cross-linker. To test chemically bonding adjacent layers together as a method to increase interlayer bonding strength, two methods to chemically cross-link the ABS filaments were studied: the first using the transition metal Cu^{2+} to form coordinating bonds with the nitrile functional groups in the ABS copolymer; and the second by forming covalent bonds between components in ABS and the diamine 4,4'-diaminodiphenylmethane (DADPM) via an amidization reaction. Figure 5.9 contains the measured interfacial adhesion strengths of the interfaces that were strengthened with both of these chemical cross-linkers.

The red circle data points in Figure 5.9 show that the addition of the Cu^{2+} suspension to the interface between deposited layers did not increase the interlayer strength, but actually lowered the interfacial adhesion below that of the neat ABS samples. While the deposition temperatures that is approximately 210°C are high enough to initiate the formation of coordinating bonds, there was no evidence of Cu^{2+} to $-\text{CN}$ bond formation in the Cu^{2+} treated samples during the print processes studied in this work. This is most likely due to the availability of water molecules scavenged from the acetone solution, in addition to the water vapor in the air around the printer itself. The presence of this water allows the Cu^{2+} ions to encounter water molecules, where they form strong coordinating bonds effectively deactivating the Cu^{2+} for bonding to the ABS nitrile groups. The

decrease in interfacial adhesion resulting from this addition may be due to restructuring or cooling of the surface as a result of the presence/evaporation of solvent that further inhibits interlayer diffusion. Thus, the evaporation of the acetone solvent may be cooling the surface of the sample before deposition, reducing inter-filament material transfer and decreasing the interfacial adhesion between the two layers. As a result, it will be important to determine the role that solvent evaporation plays in the thermal environment of these samples during the deposition process in future studies.

The data showing the change in interfacial adhesion with addition of the DADPM diamine to the T-peel samples in Figure 5.9 indicates that the addition of the DADPM cross-linker improves the strength of the interlayer bond over that of the neat ABS for both the 30 minute and 1 hour pause times. The same solvent, acetone, was used for both the DADPM diamine and Cu^{2+} ions experiments, eliminating the possibility that this increase in interfacial adhesion is simply due to solvent welding. This improvement demonstrates the viability of applying a chemical cross-linker in solution to an ABS surface during the 3D printing process to provide a quantifiable increase in interfacial strength between adjacent layers that are consecutively printed.

As mentioned in the Results, a fault developed in a number of the t-peel DADPM-treated samples where the crack began to deviate from the interface between the bottom half of the t-peel sample and the top half. These data were not included in the calculation of the interfacial adhesion results in Figure 5.9, as

they do not reflect an accurate measurement of the energy required to separate the two halves of the t-peel sample at the interface between the two halves. However, since the fault deviates into other layers within the t-peel sample, this result suggests that the bond formed at the interface between the two halves may be actually stronger than the initial interface. If this is the case, then the data presented in Figure 5.9 reflect only the weakest interfacial bonding created via the DADPM, and explains why the measured adhesion in the DADPM samples never exceed the value measured for the neat ABS samples. Measuring the interfacial adhesion in the samples that deviate from the interface will be vital to confirm this result, however developing a strategy to measure the strength of these interfaces is non-trivial and will be the focus of the future work with these samples.

While the exact mechanism for the chemical crosslinking between ABS and DADPM is not well understood, it most likely occurs between reactive chemical functionalities, such as carboxyl groups, that result of the thermo-oxidative degradation of the polybutadiene (PB) monomers of the ABS copolymer. Thermal degradation of the butadiene in ABS copolymer has been shown to occur in temperatures as low as 70-90°C leading to the formation hydro-peroxides which then degrade into carbonyl and hydroxyl products.¹²⁸ This process requires access to oxygen and as a result will primarily occur at the surface of a particular molded ABS part. In study by Tiganis et. al. the increase of carboxyl and hydroxyl functionalities on the surface of ABS resins after thermal

aging was measured using FTIR¹²⁹; work by Arostegui et al. also used FTIR to qualitatively demonstrate the increase in these functionalities in recycled ABS samples that had been deposited, melted and then redeposited.¹²⁴ The samples in our studies were printed at 210°C, leading us to the conclusion that the same thermal degradation process is occurring on the surface of each deposited filament. It is therefore likely that the terminal amines of the DADPM react with the carboxyl groups on the surface of the filaments, creating covalent bonds between the surfaces of adjacent deposited filaments. This hypothesis is also supported by the weight loss between pre- and post-extruded ABS materials in the TGA data shown in Figure 5.6.

Conclusion

The anisotropy of samples fabricated by FDM is a crucial limitation in the use of this technology as a technique to fabricate structural components. The anisotropy is a primary result of poor interlayer adhesion during the fabrication process. In this work, we have addressed this problem by investigating the importance of available thermal energy during the print process that results from the transient thermal history for FDM printed parts and have demonstrated a method to correlate the part thermal history during the deposition process to the interlayer adhesion in 3D printed parts. Additionally, we have developed a technique to apply a chemical cross-linker during the print process and have provided evidence that the addition of this cross-linker can increase interfacial strength between deposited ABS copolymer filaments.

This knowledge becomes important in the scale up of the 3D printer process to a manufacturing technology. For instance, during the 3D printing process, the wait time between deposition of additional layers of material presents a complex problem that becomes more apparent in large scale additive manufacturing where there may be a significant time delay between the deposition of adjacent filaments and an even larger delay between layer deposition. In these cases, treating the surface of the previously deposited filaments with a chemical cross-linker can provide interlayer strength in the absence of sufficient inter-filament material transfer.

The results of these experiments increase our understanding of the thermal history of a filament in the 3D printing process and on its impact on the inter-filament bonding during the process of fused deposition modeling. Furthermore, the method for chemical crosslinking presented in this work demonstrates that it is possible to physically link layers in FDM printed parts. This understanding provides a foundation to design improved methods of deposition that encourage bonding between deposited filaments, biasing increase part strength, which is the primary weakness of FDM printed parts. If FDM printed parts can become more isotropically robust, they may be used as replacement parts in structural applications, or as completely standalone products. These parts could be produced more quickly and from cheaper stock materials than traditional assembly methods, leading to reduced cost and better product throughput.

CHAPTER 6 : CONCLUSIONS AND FUTURE WORK

Modeling Structure and Dynamics of Polymer Systems Using Monte Carlo Simulations

Modeling Dynamics of Copolymer Systems

The work completed in this dissertation has confirmed that copolymer connectivity, composition distribution and heterogeneity of the monomer friction factors in a copolymer/homopolymer blend impact concentration fluctuations within the copolymer local volume. These fluctuations effect the diffusion of the copolymer within the homopolymer matrix and can be quantified by measuring the effective chain friction factor of the copolymers, thereby measuring the diffusion of the copolymers throughout the homopolymer melt. Our results demonstrate that random copolymer diffusion does not have a linear power law dependence on the copolymer composition similar to block copolymers. Instead the diffusion of random copolymers is kinetically affected by the dominant motion of the faster monomer and thermodynamically affected by the concentration of the minority monomer component within a given monomer's local volume.

The final configuration of the polymer chains in the simulations presented here reveal that the effective local concentration of styrene is larger than what Lodge-McLeish theory predicts. Since the minority component has a monomeric friction coefficient that is three orders of magnitude lower than that of the majority component, the motion of the copolymer becomes kinetically driven. This process results in the development of local volumes that are richer in the minority component throughout the blend. As a result, the motion of the copolymer chain attenuated by the aforementioned composition fluctuations, leading to increased

thermodynamic interactions between the major and minor components within the local volume around a copolymer chain, which can slow the diffusion of the copolymer. The balance of the kinetically driven motion resulting from the quickness of the minority component and the thermodynamic interactions that can slow this motion is what determines the rate of motion for the copolymer chain. These simulation results expand on our group's previous copolymer dynamics simulations and agree with our experimental neutron reflectivity studies of P(S-*ran*-MMA) copolymer diffusion in a PMMA matrix.

The Effects of Branching on Polymer Combs

In this work, it was found that at low temperatures, enthalpic contributions resulting from backbone-branch monomer interactions dominate the conformation of the branched copolymer comb in the blend with a homopolymer matrix. As a result of these interactions, the branches extend further away from the backbone, increasing the probability of entanglements with the matrix surrounding the comb. At high temperatures, entropic contributions resulting from the packing of chains near comb backbone begin to dominate the structure of the homopolymer and copolymer combs. Additionally, the results show that the branched combs diffuse faster at higher temperatures than star and H-polymers. We determined that this increase in speed is most likely due to the retraction of branches of the polymer comb towards the backbone, decreasing possible entanglements.

The motion of the branches of the comb are a result of the thermodynamic balance in the environment around the branched comb, which impact the entanglements between the polymer comb and the surrounding matrix, regulating the diffusion of the comb. By investigating the temperature dependence of the branched copolymer diffusion, we have probed this balance of enthalpic and entropic factors. These studies have enabled a better understanding of these forces and allow for the tailoring of the connectivity and composition of branched copolymers to improve the design and performance of materials that effectively drive the transport of surface active functionalities to surfaces and interfaces.

Future Work

Future work using the Monte Carlo simulations detailed in this dissertation will include combining the two technique's described above into a single experiment. By combining the two simulation methods, an experiment could be performed that further investigates the role of excluded volume effects and monomer composition within a branched copolymer chain. Additional studies would include other branched polymer architectures into the system to study the effect branched connectivity has on the diffusion of branched compatibilizers such as star copolymers and combs. This work has demonstrated that utilizing thermodynamic interactions between copolymer components and a movement restriction accounting for difference in monomer mobility, Monte Carlo computer simulations provides insight into the fundamental driving forces that govern the

non-linear diffusive behavior of copolymers within a homopolymer matrix that are observed in experimental studies.

Inter-filament Bonding in FDM Printed Materials

In this work, we have addressed the problem of anisotropy of samples that are fabricated by fused deposition modeling (FDM) due to poor interlayer adhesion by investigating the importance of available thermal energy during the print process that results from the transient thermal history for FDM printed parts on the inter-filament adhesion. The results also demonstrate a method to correlate the thermal history of a 3D printed part during the deposition process to the interlayer adhesion. Additionally, we have developed a technique to apply a chemical cross-linker during the print process and have provided evidence that the addition of this cross-linker increases interfacial strength between deposited layers of ABS copolymer filaments.

The results of these experiments increase our understanding of the thermal history of a filament in the 3D printing process and on its impact on the inter-filament bonding during the process of fused deposition modeling. Furthermore, the method for chemical crosslinking presented in this work demonstrates that it is possible to chemically link layers in FDM printed parts. This understanding provides a foundation to design improved methods of deposition that encourage bonding between deposited filaments, biasing increase part strength, which is the primary weakness of FDM printed parts. If FDM printed

parts can become more isotropically robust, they may be used as replacement parts in structural applications, or as completely standalone products.

In the future we hope to better characterize the monomeric composition of ABS samples using solution and solid-state nuclear magnetic resonance spectroscopy (NMR) and Fourier-transform infrared spectroscopy (FTIR).

Additionally, it would be beneficial to study the surface of the ABS samples after deposition using FTIR to determine what chemical functionalities are present at the surface that might be available for chemical reactions. Finally, along with collaborators, we hope to develop a method for directly applying the chemical crosslinker to the surface of the ABS part in a layer-by-layer fashion during the deposition process. This process would enable the chemical crosslinker to be applied directly before the next layer of filament is deposited, leaving very little time for the solvent to evaporate or the crosslinker to degrade. These improvements and a better understanding of the chemical nature of the surface of FDM printed ABS samples would allow us to devise a superior method for increasing the inter-filament strength.

REFERENCES

- (1) Lee, J. S.; Quirk, R. P.; Foster, M. D. *Macromolecules* **2004**, 37 (26), 10199–10204.
- (2) Martter, T. D.; Foster, M. D.; Ohno, K.; Haddleton, D. M. *J. Polym. Sci. Part B: Polym. Phys.* **2002**, 40 (15), 1704–1708.
- (3) Gersappe, D.; Harm, P. K.; Irvine, D.; Balazs, A. C. *Macromolecules* **1994**, 27, 720–724.
- (4) Irvine, D. J.; Mayes, A. M.; Griffith, L. G. *Biomacromolecules* **2001**, 2 (2), 85–94.
- (5) Rigby, D.; Lin, J. L.; Roe, R. J. *Macromolecules* **1985**, 18 (11), 2269–2273.
- (6) Park, D. W.; Roe, R. J. *Macromolecules* **1991**, 24 (19), 5324–5329.
- (7) Boyd, R. H.; Phillips, P. J. *The Science of Polymer Molecules*; Cambridge University Press: New York, NY, 1996.
- (8) Hiemenz, P.; Lodge, T. *Polymer Chemistry*; CRC Press, 2007.
- (9) Gjaldbaek, J. C.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1950**, 72 (1), 609–611.
- (10) Kontogeorgis, G. *The Hansen Solubility Parameters (HSP) in Thermodynamic Models for Polymer Solutions*; CRC Press, 2007.
- (11) DeVoe, H. Adapted from Figure 11.4
http://chemwiki.ucdavis.edu/Textbook_Maps/Physical_Chemistry_Textbook_Maps/DeVoe's_Thermodynamics_and_Chemistry/11%3A_Reactions_and_Other_Chemical_Processes/11.1_Mixing_Processes
(accessed Jan 1, 2015).
- (12) Datta, S.; Lohse, D. *Polymeric Compatibilizers*; Hanser Gardner Publications, 1996.

- (13) Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley-Interscience, 2005.
- (14) Dadmun, M. *Macromolecules* **1996**, 29 (11), 3868–3874.
- (15) Pellegrini, N.; Sikka, M.; Satija, S.; Winey, K. I. *Macromolecules* **1997**, 30 (97), 6640–6644.
- (16) Strand, M. Adapted from LCST-UCST plot.svg
[https://en.wikipedia.org/wiki/Critical_point_\(thermodynamics\)](https://en.wikipedia.org/wiki/Critical_point_(thermodynamics)) (accessed Jan 1, 2015).
- (17) Ouhadi, T.; Fayt, R.; Jerome, R.; Teyssie, P. *Polym. Commun.* **1986**, 27 (7), 212–215.
- (18) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Society* **1989**, 22 (3), 1449–1453.
- (19) Heikens, D.; Barentsen, W. *Polymer*. **1977**, 18 (1), 69–72.
- (20) Fayt, R.; Jérôme, R.; Teyssié, P. *J. Polym. Sci. Polym. Phys. Ed.* **1981**, 19 (8), 1269–1272.
- (21) Creton, C.; Kramer, E. J.; Hui, C. Y.; Brown, H. R. *Macromolecules* **1992**, 25 (12), 3075–3088.
- (22) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, 23, 4780–4787.
- (23) Brown, H. R.; Deline, V. R.; Green, P. F. *Nature* **1989**, 341, 221–222.
- (24) Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* **1993**, 26, 4155–4163.
- (25) Dai, C.-A.; Jandt, K. D.; Iyengar, D. R.; Slack, N. L.; Dai, K. H.; Davidson, W. B.; Kramer, E. J.; Hui, C.-Y. *Macromolecules* **1997**, 30 (96), 549–560.

- (26) Char, K.; Brown, H. R.; Deline, V. R. *Macromolecules* **1993**, 26, 4164–4171.
- (27) Brown, H. R. *Macromolecules* **1989**, 22, 2859–2860.
- (28) Dadmun, M. D. *Macromolecules* **2000**, No. 1, 9122–9125.
- (29) Eastwood, E. a.; Dadmun, M. D. *Polymer*, **2002**, 43 (25), 6707–6717.
- (30) Noolandi, J. *Macromol. Theory Simulations* **1992**, 1 (5), 295–298.
- (31) Yeung, C.; Balazs, A. C.; Jasnow, D. *Macromolecules* **1992**, 25 (4), 1357–1360.
- (32) Lyatskaya, Y.; Gersappe, D.; Balazs, A. C. *Macromolecules* **1996**, 28, 6278–6283.
- (33) Lyatskaya, Y.; Balazs, A. C. *Macromolecules* **1996**, 29 (23), 7581–7587.
- (34) Dadmun, M.; Van Hook, A.; Noid, D.; Melnichenko, Y.; Sumpter, B. *Computational Studies, Nanotechnology, and Solution Thermodynamics of Polymer Systems*; Springer, 2001.
- (35) Dadmun, M. D. *Macromol. Theory Simulations* **2001**, 10 (9), 795–801.
- (36) Rouse, P. E. *J. Chem. Phys.* **1953**, 21 (7), 1272.
- (37) de Gennes, P. G. *J. Chem. Phys.* **1971**, 55 (2), 572.
- (38) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. II* **1978**, 74, 1789–1801.
- (39) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press, 1996.

- (40) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford Science Publications, 1986.
- (41) Wittmer, J. P.; Meyer, H. *Monte Carlo Simulation of Polymers : Coarse-Grained Models*; 2004; Vol. 23.
- (42) Frenkel, D.; Smit, B. *Understanding Molecular Simulation - –From Algorithms to Applications*, 2nd ed.; Academic Press: San Diego, CA, 2002.
- (43) Binder, K.; Heermann, D. W. *Monte Carlo Simulation in Statistical Physics*, 5th ed.; Springer: Berlin-Heidelberg, 2010.
- (44) Landau, D.; Binder, K. *A Guide to Monte Carlo Simulations in Statistical Physics*, 3rd ed.; Cambridge University Press: Cambridge, UK, 2009.
- (45) Montroll, E. W. *J. Chem. Phys.* **1950**, 18 (5), 734.
- (46) Robert, C.; Casella, G. *Monte Carlo Statistical Methods*; Springer, 2010.
- (47) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, 21 (6), 1087–1092.
- (48) Grest, G. S.; Kremer, K. *Phys. Rev. A* **1986**, 33 (5), 3628–3631.
- (49) Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1990**, 92 (8), 5057.
- (50) Hilhorst, H. J.; Deutch, J. M. *J. Chem. Phys.* **1975**, 63 (1975), 5153.
- (51) Carmesin, I.; Kremer, K. *Macromolecules* **1988**, 21 (9), 2819–2823.
- (52) Carmesin, I.; Kremer, K. *J. Phys.* **1990**, 51, 915.
- (53) Deutsch, H. P.; Binder, K. *J. Chem. Phys.* **1991**, 94 (3), 2294.

- (54) Lobe, B.; Baschnagel, J. *J. Chem. Phys.* **1994**, *101* (2), 1616.
- (55) Hansen, J. P.; McDonald, I. *Theory of Simple Liquids*; Academic Press, 1990.
- (56) Wittmer, J. P.; Cavallo, a.; Kreer, T.; Baschnagel, J.; Johner, a. *J. Chem. Phys.* **2009**, *131* (6), 064901.
- (57) Wittmer, J. P.; Schulmann, N.; Polińska, P.; Baschnagel, J. *J. Chem. Phys.* **2011**, *135* (18), 234901.
- (58) Wittmer, J. P.; Meyer, H.; Baschnagel, J.; Johner, a.; Obukhov, S.; Mattioni, L.; Müller, M.; Semenov, a. N. *Phys. Rev. Lett.* **2004**, *93* (14), 147801.
- (59) Wittmer, J.; Beckrich, P.; Johner, A.; Semenov, A. N.; Obukhov, S. P.; Meyer, H.; Baschnagel, J. *Eur. Lett.* **2007**, *77*, 56003.
- (60) Beckrich, P.; Johner, a.; Semenov, a. N.; Obukhov, S. P.; Benoît, H.; Wittmer, J. P. *Macromolecules* **2007**, *40* (10), 3805–3814.
- (61) Meyer, H.; Wittmer, J. P.; Kreer, T.; Beckrich, P.; Johner, A.; Farago, J.; Baschnagel, J. *Eur. Phys. J. E* **2008**, *26*, 25–33.
- (62) Wittmer, J. P.; Beckrich, P.; Meyer, H.; Cavallo, a.; Johner, a.; Baschnagel, J. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **2007**, *76* (1), 011803.
- (63) Lodge, T. P.; McLeish, T. C. B. *Macromolecules* **2000**, *33* (14), 5278–5284.
- (64) Kamath, S.; Colby, R. H.; Kumar, S. K.; Karatasos, K.; Floudas, G.; Fytas, G.; Roovers, J. E. L. *J. Chem. Phys.* **1999**, *111* (13), 6121.
- (65) Saxena, S.; Cizmeciyan, D.; Kornfield, J. a. *Solid State Nucl. Magn. Reson.* **1998**.

- (66) He, Y.; Lutz, T. R.; Ediger, M. D. *Macromolecules* **2003**, 36 (21), 8040–8048.
- (67) He, Y.; Lutz, T. R.; Ediger, M. D.; Lodge, T. P. *Macromolecules* **2003**, 36 (24), 9170–9175.
- (68) Kamath, S. Y.; Arlen, M. J.; Hamilton, W. A.; Dadmun, M. D. *Macromolecules* **2008**, 41 (9), 3339–3348.
- (69) Kamath, S. Y.; Dadmun, M. D. *Macromol. Theory Simulations* **2005**, 14 (8), 519–527.
- (70) Kamath, S. Y.; Dadmun, M. D. *J. Chem. Phys.* **2006**, 125 (9).
- (71) Milhaupt, J. M.; Lodge, T. P.; Smith, S. D.; Hamersky, M. W. *Macromolecules* **2001**, 34 (16), 5561–5570.
- (72) Paul, W.; Binder, K.; Heermann, D. W.; Kremer, K. *J. Chem. Phys.* **1991**, 95 (10), 7726.
- (73) Binder, K.; Baschnagel, J. *Physica A* **1994**, 204, 47–75.
- (74) Baschnagel, J.; Binder, K.; Wittmann, H. *J. Phys. Condens. Matter* **1993**, 5, 1597–1648.
- (75) Kamath, S.; Colby, R. H.; Kumar, S. K. *Macromolecules* **2003**, 36 (22), 8567–8573.
- (76) Binder, K.; Paul, W. *J. Polym. Sci. Part B Polym. Phys.* **1997**, 35, 1–31.
- (77) Müller, M.; Binder, K. *Macromolecules* **1995**, 28 (6), 1825–1834.
- (78) Muller, M. *Macromolecules* **1995**, 28, 6556–6564.
- (79) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, 66 (1939), 1594–1601.

- (80) Huckstadt, H.; Gopfert, A.; Abetz, V. *Macromol. Chem. Phys.* **2000**, *201*, 296–307.
- (81) Mah, S.; Hwang, H.; Shin, J. *J. Appl. Polym. Sci.* **1999**, *74*, 2637–2644.
- (82) Pitsikalis, M.; Sioula, S.; Pispas, S.; Hadjichristidis, N.; Cook, D. C.; Li, J.; Mays, J. W. *J. Polym. Sci. Part A Polym. Chem.* **1999**, *37* (23), 4337–4350.
- (83) Holley, D. W.; Ruppel, M.; Mays, J. W.; Urban, V. S.; Baskaran, D. *Polym. (United Kingdom)* **2014**, *55* (1), 58–65.
- (84) Hinestrosa, J. P.; Uhrig, D.; Pickel, D. L.; Mays, J. W.; Kilbey II, S. M. *Soft Matter* **2012**, *8* (39), 10061.
- (85) Fernyhough, C. M.; Young, R. N.; Poche, D.; Degroot, a. W.; Bosscher, F. *Macromolecules* **2001**, *34* (20), 7034–7041.
- (86) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33* (7), 759–785.
- (87) Lodge, T. *Phys. Rev. Lett.* **1999**, *83* (16), 3218–3221.
- (88) Lin, Y.; Zheng, J.; Yao, K.; Tan, H.; Zhang, G.; Gong, J.; Tang, T.; Xu, D. *Polymer (Guildf)*. **2015**, *59*, 252–259.
- (89) Imel, A. *Polymer Additives Effects on Structure and Dynamics*, 2015.
- (90) Fetters, L. J.; Andrea, D. K.; J, D. S. P.; Vitus, F. J. *Macromolecules* **1993**, *26*, 647–654.
- (91) Meyer, H.; Wittmer, J. P.; Kreer, T.; Beckrich, P.; Johner, a.; Farago, J.; Baschnagel, J. *Eur. Phys. J. E* **2008**, *26* (1-2), 25–33.
- (92) Drott, E. E.; Mendelson, R. A. *J. Polym. Sci. Part A-2* **1970**, *8*, 1361–1371.

- (93) Bovey, F. a; Schilling, F. C.; McCrackin, F. L.; Wagner, H. L. *Macromolecules* **1976**, 9 (1), 76–80.
- (94) Wagner, H. L.; McCrackin, F. L. *J. Appl. Polym. Sci.* **1977**, 21 (10), 2833–2845.
- (95) Blake, P.; Fodran, E.; Kock, M.; Menon, U.; Priedeman, B.; Sharp, S. In *Solid Freeform Fabrication Proceedings*; 1997.
- (96) Ceresana. *Market Study: Bioplastics*; 2011.
- (97) Cheah, C. M.; Chua, C. K.; Lee, C. W.; Feng, C.; Totong, K. *Int. J. Adv. Manuf. Technol.* **2005**, 25 (3-4), 308–320.
- (98) Shofner, M. L.; Lozano, K.; Rodríguez-Macías, F. J.; Barrera, E. V. *J. Appl. Polym. Sci.* **2003**, 89 (11), 3081–3090.
- (99) Mari, D.; Schaller, R. *Mater. Sci. Eng. A* **2009**, 521-522, 255–258.
- (100) Khare, R. a.; Bhattacharyya, A. R.; Panwar, A. S.; Bose, S.; Kulkarni, A. R. *Polym. Eng. Sci.* **2011**, 51 (9), 1891–1905.
- (101) Tekinalp, H. L.; Kunc, V.; Velez-garcia, G. M.; Duty, C. E.; Love, L. J.; Naskar, A. K.; Blue, C. a; Ozcan, S. *Compos. Sci. Technol.* **2014**, 105, 144–150.
- (102) Fu, S. Y.; Lauke, B.; Mäder, E.; Yue, C. Y.; Hu, X. *Compos. Part A Appl. Sci. Manuf.* **2000**, 31 (10), 1117–1125.
- (103) Zhong, W.; Li, F.; Zhang, Z.; Song, L.; Li, Z. *Mater. Sci. Eng. A* **2001**, 301 (2), 125–130.
- (104) Chino, K. *KGK Kautschuk Gummi Kunststoffe* **2006**, 59 (4), 158–162.
- (105) Ibarra, L.; Alzorriz, M. *J. Appl. Polym. Sci.* **2007**, 103 (3), 1894–1899.

- (106) Schubert, U. S.; Hofmeier, H. *Macromol. Rapid Commun.* **2002**, 23 (9), 561–566.
- (107) Hofmeier, H.; Schmatloch, S.; Wouters, D.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, 204 (18), 2197–2203.
- (108) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2001**, 22, 1358–1363.
- (109) He, H.; Fu, R.; Shen, Y.; Han, Y.; Song, X. *Compos. Sci. Technol.* **2007**, 67 (11-12), 2493–2499.
- (110) Yuan, X.; Shen, F.; Wu, G.; Wu, C. *Polym. Compos.* **2008**, 29 (3), 302–306.
- (111) Iijima, T.; Yoshioka, N.; Tomoi, M. *Eur. Polym. J.* **1992**, 28 (6), 573–581.
- (112) Ranellucci, A. Slic3r - G-code generator for 3D printers <http://slic3r.org/> (accessed Jul 27, 2015).
- (113) Bellini, A.; Güçeri, S. *Rapid Prototyp. J.* **2003**, 9 (4), 252–264.
- (114) Ahn, S.-H.; Montero, M.; Odell, D.; Roundy, S.; Wright, P. K. *Rapid Prototyp. J.* **2002**, 8 (4), 248–257.
- (115) Sood, A. K.; Equbal, A.; Toppo, V.; Ohdar, R. K.; Mahapatra, S. S. *CIRP J. Manuf. Sci. Technol.* **2012**, 5 (1), 48–54.
- (116) Rodríguez, J. F.; Thomas, J. P.; Renaud, J. E. *Rapid Prototyp. J.* **2001**, 7 (3), 148–158.
- (117) Ristić, M. M.; Milosević, S. D. *Sci. Sinter.* **2006**, 38 (1), 7–11.
- (118) Pokluda, O.; Bellehumeur, C. T.; Machopoulos, J. *AIChE J.* **1997**, 43 (12), 3253–3256.

- (119) Bellehumeur, C.; Li, L.; Sun, Q.; Gu, P. *J. Manuf. Process.* **2004**.
- (120) Sun, Q.; Rizvi, G. M.; Bellehumeur, C. T.; Gu, P. *Rapid Prototyp. J.* **2008**, *14* (2), 72–80.
- (121) Arivazhagan, A.; Masood, S. H. *Int. J. Eng. Res. Appl.* **2012**, *2* (3), 2009–2014.
- (122) Gurralla, P. K.; Regalla, S. P. *Virtual Phys. Prototyp.* **2014**, *9* (3), 141–149.
- (123) Zamani, A.; Abbasi, F.; Agah, A. M. *J. Appl. Polym. Sci.* **2009**, *114*, 1908–1913.
- (124) Arostegui, a.; Sarrionandia, M.; Aurrekoetxea, J.; Urrutibeascoa, I. *Polym. Degrad. Stab.* **2006**, *91* (11), 2768–2774.
- (125) Zhou, W.; Wang, C.; Ai, T.; Wu, K.; Zhao, F.; Gu, H. *Compos. Part A Appl. Sci. Manuf.* **2009**, *40* (6-7), 830–836.
- (126) Gaskins, F. H. *J. Rheol. (N. Y. N. Y.)* **1960**, *4* (1), 265.
- (127) Brodnyan, J. G. *J. Rheol. (N. Y. N. Y.)* **1961**, *5* (1), 205.
- (128) Shimada, J.; Kabuki, K. *J. Appl. Polym. Sci.* **1968**, *12*, 655–669.
- (129) Tiganis, B. E.; Burn, L. S.; Davis, P.; Hill, a. J. *Polym. Degrad. Stab.* **2002**, *76* (3), 425–434.

VITA

Edward Roy Duranty was born in Newport, RI on September 21st, 1984. As a young child he moved from Newport to Columbia, SC, and again moved in 3rd grade to Atlanta, GA where he spent the rest of his youth. After graduating from South Gwinnett High School in 2002, Eddy begin his undergraduate career at Georgia Southern University where he performed research in physical chemistry for Dr. James LoBue and graduated with a Bachelor of Science in Chemistry in 2006. In the summer of 2007, Eddy started his graduate studies in the Department of Chemistry at the University of Tennessee in Knoxville, TN where he eventually became the student of Dr. Mark Dadmun. In November of 2015, Eddy successfully defended his dissertation and graduated in December 2015 with a Ph.D. degree in Chemistry.