Understanding Heterogeneous Nucleation Mechanisms in Polyolefins

by

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Abstract

The family of polyolefins are among the most widely used semi-crystalline polymers in the modern world, with many of their desirable properties due to their microstructure formed during crystallization. While processing conditions have a large impact on crystallization, an additional tool is the use of additives called nucleating agents (NAs), that improve the rate at which small crystallites form and can even promote different crystal polymorphs over others. However, much of the current understanding of NAs is based on trial-and-error, with no predictive power. Experimental methods to study heterogeneous nucleation are often plagued with confounding factors that lead to uncertainty in the measured kinetics and thermodynamics of nucleation. Molecular simulations have recently showed promise to investigate the nano time- and length- scales associated with nucleation, but remain unverified with real materials. This thesis advances the way that heterogeneous nucleation is studied, using a two-pronged approach in studying potential NAs: in the laboratory, and with molecular dynamic simulations.

Two experimental methods were refined to accurately measure kinetic and thermodynamic parameters of polymer + NA pairings. In the first method, micro-droplets of high-density polyethylene were crystallized on single crystal substrates, allowing precise control of the NA – polymer interface. The second method is the current state of the art, and consisted of micro-droplets of high-density polyethylene containing nanoplatelet additives in an immiscible matrix. This method sacrifices some control of the nucleation interface in order to expand the number of testable NAs to virtually any material. Finally, a third experimental method based on a novel combination of the other two methods was introduced to independently validate results obtained by the state of the art method for the first time. Of broader significance, a thermodynamic efficiency metric was defined to allow comparison of NAs between different polymers in a more robust way than prior metrics.

Molecular dynamic simulations formed the second major tool in studying heterogeneous nucleation. The effects of three new NAs on the nucleation of an n-alkane were tested, paralleling the laboratory experiments of the most successful NAs. The same kinetic and thermodynamic parameters obtained in the laboratory with real materials were compared for the first time, demonstrating excellent qualitative agreement. Molecular mechanisms were also investigated, including epitaxy and strain in the alkane crystal that reduced lattice mismatch. The strength of interaction between the NA and the alkane was quantified in a new way, and found to be a key factor in determining nucleating efficiency.

The results of this thesis provide new insight into molecular mechanisms of nucleation, and the improved methods pave the way for high-throughput experiments and simulations to screen the nucleating efficiency of many materials. With this approach, novel NAs can be more rapidly discovered, and intelligent selection from a database of NAs will allow the production of next-generation materials with tailored crystal morphologies and improved macroscopic properties.

Thesis Supervisor: Gregory C. Rutledge
Title: Lammot du Pont Professor in Chemical Engineering
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Soli Deo Gloria.
Table of Contents

1. Introduction to Heterogeneous Nucleation of Polyolefins ................................................. 9
   a. Motivation ........................................................................................................................... 9
   b. Thermodynamics .............................................................................................................. 12
      i. Classical Nucleation Theory ...................................................................................... 12
      ii. Heterogeneous Nucleation ....................................................................................... 13
   c. Kinetics ............................................................................................................................ 15
   d. Experiments .................................................................................................................... 16
   e. Simulations ....................................................................................................................... 17
   f. Nucleating Agents and Mechanisms .............................................................................. 19
   g. Thesis Objectives ............................................................................................................ 20
   h. References ....................................................................................................................... 21

2. Heterogeneous Nucleation of Micro-droplets on Single Crystal Substrates ....................... 24
   a. Introduction ....................................................................................................................... 24
   b. Methods ............................................................................................................................ 27
      i. Materials ....................................................................................................................... 28
      ii. HDPE Preparation ....................................................................................................... 28
      iii. NA Substrate Preparation ......................................................................................... 29
      iv. Preparation of Samples for Crystallization Experiments ........................................... 30
      v. Thermal Procedures for Crystallization ..................................................................... 31
   c. Results ............................................................................................................................... 32
      i. Nonisothermal Crystallization ..................................................................................... 32
      ii. Isothermal Crystallization ......................................................................................... 33
   d. Discussion .......................................................................................................................... 35
      i. Difficulties with Other Materials ................................................................................. 35
      ii. Nonisothermal Analysis with Polymer Films ............................................................. 37
      iii. Practical Limitations and Summary of Results ......................................................... 40
   e. Conclusions ...................................................................................................................... 42
   f. References ......................................................................................................................... 42

3. Heterogeneous Nucleation of High-Density Polyethylene Crystals on Graphene within
   Microdomains ...................................................................................................................... 44
   a. Introduction ....................................................................................................................... 44
   b. Methods ............................................................................................................................ 47
      i. Materials ....................................................................................................................... 47
      ii. Crystal Growth Rate .................................................................................................... 47
      iii. Nucleation Rate .......................................................................................................... 47
         1. Domains in Immiscible Blends ................................................................................ 47
         2. Droplets on Substrate .............................................................................................. 48
      iv. Particle Size Distribution ............................................................................................ 49
   c. Results ............................................................................................................................... 50
      i. Crystal Growth Rate .................................................................................................... 50
      ii. Size of IB Domains ..................................................................................................... 51
      iii. Nucleation Rate .......................................................................................................... 56
         1. Domains in Immiscible Blends ................................................................................ 56
         2. Droplets on Substrate .............................................................................................. 60
      iv. Avrami Model ............................................................................................................. 61
      v. First Order Nucleation Model .................................................................................... 63
   d. Discussion .......................................................................................................................... 66
List of Figures
Figure 1.1. Annual global production of plastics
Figure 1.2. Annual global production of two common polyolefins
Figure 1.3. Depiction of crystalline and amorphous phases of semi-crystalline polymers
Figure 1.4. Homogeneous nucleation free energy barrier
Figure 1.5. Heterogeneous nucleation factor $f$
Figure 1.6. Heterogeneities present in polymer domains
Figure 1.7. Simulation of surface induced crystallization of C50 on crystalline polyethylene
Figure 2.1. Method of growing PHP crystals
Figure 2.2. Spraying configuration to disperse micron droplets of HDPE onto the NA substrate
Figure 2.3. Hot stage used during nucleation experiments
Figure 2.4. Constant cooling rate experiments for HDPE droplets
Figure 2.5. Induction times for HDPE droplets on PHP substrate
Figure 2.6. Induction times for HDPE droplets on GaAs substrate
Figure 2.7. Polarized microscopy of HDPE droplets on GaAs
Figure 2.8. AFM height images of HDPE droplets on GaAs
Figure 2.9. Example of the ranges over which the tested polymer nucleating agents were active in constant cooling rate experiments
Figure 3.1. Experimentally measured crystal growth rate plotted according to Lauritzen-Hoffman theory
Figure 3.2. Cross sectional SEM images from IB samples
Figure 3.3. Box-and-whisker plots of the particle size distributions of the diameters of HDPE+GNP domains in both IB and DoS samples, and for GNP
Figure 3.4. Polarized optical microscopy images of a DoS sample
Figure 3.5. Characterization of GNPs
Figure 3.6. Crystallization of IB samples in DSC experiments with constant cooling rates from the melt
Figure 3.7. Isothermal crystallization exotherms using an empty reference pan and using a reference pan containing polystyrene
Figure 3.8. Isothermal crystallization data for a representative IB sample
Figure 3.9. Relative crystallinity as a function of time for all IB isothermal crystallization experiments
Figure 3.10. Crystallized fraction as a function of time for DoS isothermal crystallization experiments
Figure 3.11. Representative fits of Avrami equations to the data for fractional crystallinity versus time
Figure 3.12. Avrami index as a function of crystallization temperature
Figure 3.13. Examples of first order nucleation model fit to the data for the evolution of the uncrystallized fraction of droplets
Figure 3.14. Nucleation rates as a function of temperature for all samples, according to classical nucleation theory
Figure 3.15. Fitted values of interfacial free energy difference and $J_0$
Figure 3.16. Interfacial contact area, $A$, scaled by the minimum calculated $A$ value
Figure 4.1. Structure of hexagonal boron nitride and transition metal dichalcogenides
Figure 4.2. Representative simulation box containing C50 bounded by substrate on two sides
Figure 4.3. Trajectories of crystal growth front from molecular simulations
Figure 4.4. Interfacial free energy difference, $\Delta \sigma$, calculated from critical nucleus sizes measured by molecular dynamics simulations.
Figure 4.5. Crystallization of samples at a constant cooling rate from the melt
Figure 4.6. Evolution of crystallinity at different $T_c$ for sample BN-0.5%
Figure 4.7. Avrami index $n$, obtained from fitting of the DSC data
Figure 4.8. Nucleation rates according to classical nucleation theory.
Figure 4.9. Fitted values of interfacial free energy difference, $\Delta \sigma$, nucleation efficiency, $E$, and nucleation prefactor, $J_0$
Figure 4.10. Comparison of force field parameters: two-body interaction strength, three-body interaction strength, and atomic spacing of NAs
Figure 4.11. Comparison of force field parameters: interaction strength between NAs and C50, and areal density of the energy of interaction between NAs and C50
Figure 4.12. Comparison of SW parameter values to parametric studies of GN-like NAs
Figure 4.13. Calculation of unit cell parameters from simulation
Figure 4.14. Lattice mismatches between NA and C50 crystals
Figure 4.15. Nucleation rates from experiments and simulations, relative to BN.
Figure 4.A.1. Stress, $\sigma$, due to deformation of BN nanoplatelets as a function of strain, $e$
Figure 4.S1. Evolution of crystallinity for experimental samples

Figure A.1. Feedback loop integrating Bayesian optimization with MD simulations
Figure A.2. Comparison of SW parameters
Figure A.3. Example of simulation boxes for C50 and C20
Figure A.4. Example crystal growth front trajectories from one simulation
Figure A.5. Induction times measured from simulations with C50 and realistic binary zincblende NAs
Figure A.6. Induction times measured from simulations with C20 and hypothetical zincblende NAs

List of Tables
Table 2.1: Nucleating ranges of polymer substrates
Table 2.2: Nucleation results on various substrates
Table 3.1: Characteristic sizes of polyethylene domains and GNPs
Table 3.2: Final Crystallinities of Each IB Sample
Table 4.1: Force Field Parameters for Non-Bonded Lennard-Jones Interaction Potential
Table 4.2: Force Field Parameters for Stillinger-Weber Interaction Potential
Table 4.3: Parameter Values for Nucleation Equations
Table 4.A1: Comparison of elastic constants determined experimentally with those reproduced through simulation using the combined SW-LJ force field
Table A.1: Force Field Parameters for Non-Bonded Lennard-Jones Interactions
1. Introduction to Heterogeneous Nucleation of Polyolefins

Motivation

Polymers are a continually growing industry, with annual global production surpassing 300 million metric tonnes in 2015 and steadily increasing (Fig. 1.1). The largest subgroup of polymers by production is polyolefins, making up 62% of polymers produced in 2013, and polyolefin production is still exponentially increasing, as shown in Fig. 1.2 for two common polyolefins: polyethylene and polypropylene. This increasing trend will likely be further bolstered by the discovery of shale gas from which polyolefins can be produced. As of 2017, $179 billion in shale gas projects were underway in the United States. With the increased supply and lowered costs of producing ethylene and propylene from shale gas, this trend in polyolefin production is likely to increase.

![Graph of annual global production of plastics](image)

Figure 1.1. Annual global production of plastics (data from ref. 1).
An important property of polyolefins is that they are semi-crystalline, consisting of amorphous portions sandwiched between crystalline lamella, as depicted in Fig. 1.3. In the crystalline lamella, polymer chains can fold with no amorphous segments between crystalline segments of that chain (fold), with some amorphous segments (loop), or so that the chain extends through the amorphous region and folds into a different lamella (tie molecule). The quantity and size of these features, existing at the nanoscale, are thought to be responsible for the unique bulk mechanical, thermal, and optical properties that are desired in polymers. This morphology is formed as a polymer melt cools and crystallizes. Thus, it is important to be able to control the process of crystallization to obtain desired properties by influencing these fine structural features.

Figure 1.2. Annual global production of two common polyolefins in thousands of tons: (a) polyethylene (b) polypropylene. Reproduced with permission.$^2$
Crystallization kinetics can be controlled with temperature and pressure, but also of great importance for polymer crystallization is the use and choice of nucleating agents (NAs). NAs affect the rate of crystallization and nucleation frequency to differing degrees, and they can also promote specific crystal polymorphs. Because of the great effect that NAs can have on forming the microstructure of the semicrystalline polymer, it is important to either choose an appropriate NA or develop a novel NA in order to obtain these desirable bulk properties.

Despite decades of research into NAs for polymers, the fundamental mechanisms are still unclear and remain an area of research. NAs have been historically developed by trial and error since there is no current method for predicting the effectiveness of a NA a priori. This strategy can be slow to develop novel NAs. This is evidenced by the first commercial NA for high density polyethylene (HDPE) only being produced since 2006, despite HDPE being one of the most common semi-crystalline polyolefins that has been used for decades. Therefore, insight into nucleation mechanisms would be of great importance to the polymer industry and to the users of polymer products.
Thermodynamics

Classical Nucleation Theory

Homogeneous nucleation is classically described as a competition between the favorable formation of a crystalline nucleus and the unfavorable formation of an interface between the amorphous melt and the crystal. This free energy for the formation of a spherical nucleus, $\Delta G$, is the sum of free energy contributions due to the energetically-unfavorable formation of a new interface, $\Delta G_i$, and the energetically-favorable formation of the crystalline phase, $\Delta G_p$, below the melting temperature, $T_m$, given by

$$\Delta G = \Delta G_s + \Delta G_f = 4\pi r^2 \sigma - \frac{4\pi r^3}{3} \Delta G_v,$$  \hspace{1cm} (1.1)$$

where $r$ is the radius of the nucleus, $\sigma$ is the interfacial free energy between melt and crystal, and $\Delta G_i$ is the free energy difference per unit volume between melt and crystal. $\Delta G_i$ is dependent on the degree of undercooling, where Eq. 1.2 describes small undercoolings, and Eq. 1.3 describes larger undercoolings:

$$\Delta G_v \approx \rho_n \Delta H_f \frac{\Delta T}{T_m},$$  \hspace{1cm} (1.2)$$

$$\Delta G_v \approx \rho_n \Delta H_f T \frac{\Delta T}{T_m^2}.$$  \hspace{1cm} (1.3)$$

$\rho_n$ is the molecular density of the crystal, $\Delta H_f$ is the heat of fusion, and $\Delta T = T_m - T$ is the degree of undercooling. By setting the derivative of the free energy with respect to the radius to zero, the critical radius (Eq. 1.4) and thus the critical free energy (Eq. 1.5) at this radius are given by:

$$r^* = \frac{2\sigma}{\Delta G_v},$$  \hspace{1cm} (1.4)$$

$$\Delta G^* = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_v)^2}.$$  \hspace{1cm} (1.5)$$
The free energy barrier, critical nucleus, and dependence on undercooling are shown below in Fig. 1.4. The free energy given here assumed a spherical nucleus, but other nucleus shapes are possible. Other common shapes that are considered are cylinders and rectangular prisms.

![Diagram](image)

Figure 1.4. Homogeneous nucleation free energy barrier (black curves) (a) highlighting the interplay between unfavorable surface free energy, $\Delta G_s$ (dashed blue curve), and favorable free energy of formation of the crystal phase, $\Delta G_f$ (dotted red curve); (b) free energy barrier dependence on undercooling ($\Delta T$). The critical nucleus size ($r^*$) and critical free energy barrier ($\Delta G^*$) are marked by the black dot at the maxima of the curves.

**Heterogeneous Nucleation**

Heterogeneous nucleation is an alternative method of nucleation that proceeds by an energetic pathway with a reduced energy barrier to forming a critical nucleus, such that

$$\Delta G^*_{\text{heterogeneous}} = f \cdot \Delta G^*_{\text{homogeneous}},$$

(1.6)

where $f$ is a factor between 0 and 1. Strongly active heterogeneities can greatly reduce the critical energy barrier and would have small values of $f$, approaching zero in the limit of a perfectly active heterogeneity. Weakly active heterogeneities do not reduce the critical energy barrier as much, having $f$ values approaching 1 for an inactive heterogeneity. Heterogeneities such as an interface with a substrate, contaminants, or additives can all be locations where this form of nucleation can occur. Additives that specifically promote nucleation or a particular crystallographic structure are called NAs and are the interest of this work.
The interaction between the polymer and NA can be captured using the contact angle, according to Young’s equation. Using this, an expression for \( f \) has been derived as \(^{12}\)

\[
f(m, x) = \frac{1}{2} \left( 1 + \left(\frac{1-x^2}{w} \right)^2 \right) + x^3 \left[ 2 - 3 \left(\frac{x^3}{w} \right) + \left(\frac{x^3}{w^2} \right)^2 \right] + 3mx^2 \left(\frac{x^3}{w} - 1 \right).
\]

\[\text{(1.7)}\]

\( x \) is the dimensionless radius of curvature of the substrate given by \( x = R/r^* \), where \( R \) is the radius of curvature of the substrate. \( m \) is the related to the contact angle, \( \theta \), as given by Young’s equation: \(^{13}\)

\[
m = \cos \theta = \frac{\sigma_{li} - \sigma_{ch}}{\sigma_{lc}},
\]

\[\text{(1.8)}\]

where \( \sigma_\theta \) is the interfacial free energy between phases \( i \) and \( j \), with \( l \) denoting the melt, \( h \) denoting the heterogeneity, and \( c \) denoting the crystal nucleus. \( w \) is defined as \( (1+x^2-2mx)^{1/2} \) to simplify Eq. 1.7. For a flat substrate, \( x \gg 1 \), and \( f \) reduces to \(^{14}\)

\[
f(m) = \frac{1}{4} (2 - 3m + m^3).
\]

\[\text{(1.9)}\]

The significance of \( m \) corresponds to the level of structural match and interaction between the heterogeneity and the melt. The dependence of \( f \) on \( m \) and \( x \) are shown in Fig. 1.5a, with the simplified dependence on \( m \) in the limit of a flat substrate \( (x \gg 1) \). As can be seen from Fig. 1.5b, small values of \( m \) correspond to weak NA while large values of \( m \) correspond to active heterogeneities. The dependence of \( m \) on lattice spacing is also depicted in Figure 1.5c, where certain lattice dimensions provide local maxima in \( m \) (inverted axis) and hence a lower nucleation barrier.
Figure 1.5. Heterogeneous nucleation factor $f$: (a) Dependence of $f$ on $m$ and $x$ (reproduced with permission).\textsuperscript{12} (b) $f$ as a function of $m$ for $x\gg 1$, corresponding to a flat heterogeneity relative to the crystal nucleus. (c) The dependence of $m$ on lattice spacing. An optimal spacing exists, but there are also local maxima at certain lattice mismatches (reproduced with permission).\textsuperscript{14}

**Kinetics**

The nucleation rate, $J$, is typically represented as an activated process,\textsuperscript{15} dependent on a free energy barrier to chain diffusion, $E_d$, and the critical free energy, $\Delta G^*$, described previously:

$$J = J_0 \exp \left[ -\frac{E_d + \Delta G^*}{k_B T} \right],$$

(1.10)

where $k_B$ is the Boltzmann constant, and $J_0$ is a temperature independent pre-factor related to the frequency of nucleation events. The time taken to form stable persistent nuclei is characterized by the induction time given by\textsuperscript{11}

$$\tau = \tau_{\text{mononuclear}}^* + \tau_{\text{polynuclear}}^* = \frac{1}{J} + \left( \frac{1 + 4\nu}{\nu} \right)^{1/v} \left( \frac{G_c}{\nu d} \right)^{1 + 4\nu/d},$$

(1.11)

where $J$ is the nucleation rate, $V$ is the volume of the system, $v$ is a growth exponent, $d$ is the dimensionality of the system, $\alpha_d$ is the detectable fraction of crystallized volume, $c_s$ is a shape factor, and $G_c$ is the crystal growth rate. The first term describes the time taken to form exactly one stable nucleus, while the second term describes systems where crystallization occurs through the appearance of multiple
stable nuclei. In practice, depending on the system volume, the mononuclear term dominates in small volumes, and the polynuclear dominates in large volumes. Therefore, one solution to reduce the influence of $\tau_{\text{polynuclear}}$ is to reduce the size of the crystallizable domain. If the domain size is small enough that the ratio of the nucleation rate relative to the growth rate is also small, only mononuclear nucleation will be observed, and the second term in Eq. 1.11 can be ignored.

**Experiments**

There are a few problems with studying nucleation experimentally. One problem is that the critical nucleus size is on the order of nanometers, but most experimental methods cannot detect a crystal until it has grown to be microns in size. Therefore, the experimentally measured induction time is not the true induction time as shown by:

$$\tau_{\text{observed}} = \tau^* + \tau' + \tau_g,$$

(1.12)

where $\tau^*$ is the true induction time, $\tau'$ is the lag time due to non-instantaneous equilibration of the polymer system generally proportional to the viscosity of the melt, and $\tau_g$ is the time the nucleus grew from the critical size (nanometers) to an experimentally observable size (microns). Another problem is any small amount of impurities such as dust can initiate nucleation, and thus cause the measured nucleation rate to be characteristic of the dust rather than the NA being tested. Additional problems are impingement of growth fronts from multiple nuclei and a buildup of the latent heat of fusion.

An experimental method which mitigates these problems relies on dividing the sample into many micron sized droplets. In this way, crystal growth is limited, and since nucleation is generally much slower than growth, $\tau_g$ is negligible. The effect of impurities can be greatly reduced if the number of droplets outnumbers impurities, such that some droplets will contain no impurities, as diagramed in Fig. 1.6. By using small droplets, only one nucleation event per droplet is observed, and effects of slow thermal equilibration is minimized. Additionally, an ensemble of droplets can be studied in each experiment to
get a statistical average of the stochastic behavior of nucleation. This method was pioneered by Vonnegut using droplets of tin, and was later used to study alkanes and HDPE droplets suspended in solution.

Figure 1.6. Heterogeneities (black circles) present in polymer domains (boxes) (a) large domains where all domains have heterogeneities and would nucleate heterogeneously (b) small domain sizes where some domains do not have heterogeneities and could nucleate homogeneously or nucleate at the surface of the substrate.

This method was further adapted by Massa et al. by spincoating a thin polyethylene oxide (PEO) layer which dewetted into micron sized droplets upon heating from a polystyrene substrate. PEO crystals are optically birefringent, while the amorphous melt is not. Therefore, the appearance of birefringence can be used to detect when a droplet has crystallized. This same method was also used study bulk, surface, and edge nucleation in PEO and surface nucleation in PE. A more detailed summary of their analyses can be found in Chapter 2.

Simulations

HDPE chains can be modeled in a simplified way by treating each CH\textsubscript{2} repeat group as single unit strung together on a chain, known as a united atom model. By choosing an appropriate force field, the behavior of HDPE can still be accurately modeled in a more computationally efficient manner. One force field that has been used extensively to model polyethylene crystallization phenomena is the Paul, Yoon, and Smith (PYS) force field, as modified by Waheed et al. This force field is capable of capturing the enthalpy of fusion and melting temperature of n-alkane rotator phases, but due to the use of united atoms, this force field does not show the rotator phase transition to orthorhombic for PE or to monoclinic for n-alkanes.
Regarding heterogeneous nucleation, Bourque et al. captured the nucleation and growth of crystalline layers of n-pentacostane (C50) on a HDPE crystal.\textsuperscript{26} C50 is an oligomer of polyethylene that is below the entanglement molecular weight, and serves as a model analogue to HDPE with faster chain dynamics; however, due to the small size of the nucleus, nucleation mechanisms observed with C50 should be analogous to PE. Structurally, C50 was shown to nucleate and grow as an isotropic circular nucleus rather than extended chains. Kinetically, the surface nucleation rate reached a steady value after four crystalline layers, and the surface nucleation rate was temperature independent.\textsuperscript{26} Snapshots of the growth front progressing through the amorphous melt are shown below in Fig. 1.7.

Figure 1.7. Simulation of surface induced crystallization of C50 on crystalline polyethylene. (a) simulation box with crystalline polyethylene in blue and amorphous C50 in grey (b)-(e) propagation of crystal front into the amorphous melt. (f) detailed snapshot of layered growth (note periodic boundaries) and a growing nucleus in layer 5. Reprinted with permission.\textsuperscript{26} Copyright 2016 American Chemical Society.

The families of tetrahedrally coordinated crystals and graphene-like crystals were also studied as NAs for C50.\textsuperscript{27,28} Both silicon and graphene can be modeled with the same relatively simple force field (Stillinger-Weber).\textsuperscript{29} By changing three parameters in the force field relating to atomic spacing, and bond and angle rigidities, many hypothetical variants on these two materials could be explored in a genomic-like testing of NAs. From this parametric study, key parameters were identified that influenced the nucleation rate of C50 (interaction strength between C50 and the NA, rigidity and atomic spacing of the
Mechanistically, both epitaxy and adhesion strength were found to be important factors.27,28

**Nucleating Agents and Mechanisms**

Heuristics that are common to effective NAs have been developed, such as insolubility in the polymer melt, a melting temperature greater than the polymer, a crystalline structure, and polar and nonpolar components to maintain solubility while allowing a degree of wettability.30 Both inorganic and organic additives have been reported;9 a few examples are calcium carbonate,31 silicon dioxide,32 graphite,33 ultra-high-molecular-weight-PE,34 benzoic acid compounds,30,35 carbon nanotubes,36,37 and montmorillonite clay.38 The different crystallographic planes of a NA or surface treatment of the NA can show differences in nucleating ability, thus expanding the list of NAs even more. Altering the surfaces of NAs through acid treatment or the use of a coupling agent are known to affect nucleating ability, sometimes even destroying the nucleating ability of the NA.39 Collective analysis of these different NAs and surfaces could be used to study competing mechanisms.

One commonly proposed mechanism is epitaxy, where there is a match between the crystal lattice of the NA and the polymer crystal.40–43 It is theorized that the NA lattice encourages polymer chains to align into crystalline order. A modification of this theory allows for surface roughness to promote polymer chain alignment, and is called “soft” epitaxy or grapho-epitaxy, as opposed to the “hard” epitaxy of crystal lattice matching.44–46 Soft epitaxy could be demonstrated by amorphous substrates that have a local periodic roughness or by surfaces that are structured at the nanometer scale. Epitaxy could also occur for polyolefins with side groups if the side groups can interact with and align with the NA.41 Other theories propose chemical interactions between the NA and polymer, such as reactive interactions between the NA and the polymer that results in polymer chain fragmentation. The resulting ionic end groups are theorized to associate into a nucleus from which crystallization can proceed.47 In total, the competing effects of lattice matching, interfacial energy, and chemical composition of the NA all likely play a role in nucleating effectiveness. Therefore, a more complete methodology for studying these
mechanisms would greatly improve the understanding and predictive capabilities of heterogeneous nucleation theory.

Thesis Objectives

The goal of this thesis was to improve the understanding of the nucleation mechanisms of NAs in polyolefins. This encompassed a two-pronged approach in studying materials as NAs: in the laboratory, and with MD simulations. Experimental tools for investigating NAs were developed and improved to more accurately characterize the nucleating ability of several substances, avoiding the many limitations that have plagued prior experimental methods. Prior simulation methods were extended to model realistic materials that were studied experimentally. Combined, these two tools were used to validate observations and theories from each method, and thus form a more complete picture of heterogeneous nucleation. This work helps pave the way for simulations and experiments to be used to study nucleation as part of the Materials Genome Initiative, where NAs could be rapidly screened and characterized to aid in the development of novel NAs in the future.

Therefore, the specific aims to improve the understanding of the nucleation mechanisms of NA in polyolefins are as follows:

1. Prepare NA surfaces considering crystallographic plane, interfacial energy with PE, surface roughness, and surface treatment
2. Observe nucleation of HDPE on each NA
3. Characterize nucleation mechanisms
4. Observe nucleation with simulations
5. Modify simulations to improve predictive capability
6. Develop heuristics within families of NA

The remainder of this thesis details the effort made in addressing these aims. Chapter 2 describes the initial experimental method that was used to study heterogeneous nucleation of PE, including the
significant challenges and limitations of this method. Chapter 3 provides two alternative methods that successfully measured nucleation rates experimentally, and allowed the extraction of thermodynamic efficiencies over a range of crystallization temperatures. Chapter 4 describes MD simulations that were used to predict the nucleation rates and efficiencies of 3 real materials, as well as provide insight into molecular mechanisms; the experimental method of chapter 3 was then used to verify the trends in kinetics and thermodynamic parameters that were observed in silico. Finally, Chapter 5 contains the major conclusions from these results and recommendations for future work.

References


2. Heterogeneous Nucleation of Micro-droplets on Single Crystal Substrates

Introduction

Crystallization of semicrystalline polymers is often modeled as an activated process, consisting of two components: formation of a critically-sized crystal nucleus from the melt phase (i.e. nucleation), and subsequent post-critical crystal growth. It is difficult to measure the nucleation process experimentally due to the nanometer-sized critical nucleus. This often leads to inferences about nucleation being drawn from measurements of bulk properties, such as the heat released by crystallization or the appearance of a signal unique to the crystalline phase (e.g. optical birefringence or crystalline peaks in Raman spectroscopy or x-ray scattering). However, depending on the relative rates between nucleation and growth, the bulk properties that are measured may change at a rate that is controlled by growth, by nucleation, or by some mixture of the two.¹

Both the crystallization temperature and the size of the crystallizable sample influence this balance of rates. In order to measure just the nucleation rate, the crystallization temperature can often be chosen such that nucleation is the rate-limiting step. The size of the sample can also be reduced so that crystal growth after nucleation is restricted. This increases the proportion of the signal coming from measurable bulk properties that corresponds to nucleation, rather than growth. The practical limitation here is that the sample needs to be large enough so that the signal from the change in bulk property is detectable.

A final consideration is the effects of impurities that could serve as nucleation sites. Residual catalyst from polymerization, additives such as antioxidants or viscosity modifiers, or even dust can all provide sites for heterogeneous nucleation to occur.²,³ When measuring homogeneous nucleation or testing the heterogeneous nucleation effects of individual additives (i.e. a nucleating agent, NA), these competing sites on impurities could interfere with accurate measurements of nucleation rates.
Droplet methods greatly reduce the issues of growth and impurities, as first demonstrated by Vonnegut, and later by Turnbull et al. By reducing the size of the crystallizable domain to the micro-scale, growth after nucleation is limited. By breaking up the polymer melt into more droplets than there are impurities, impurities are segregated into a subset of the population of droplets, leaving a fraction of droplets impurity-free. Additionally, observing many droplets in a single experiment allows for ensemble averaging of the stochastic nucleation process.

The droplet method was further advanced by Massa et al. Atactic polystyrene (PS) was spincoated onto a substrate, and then a thin film of polyethylene oxide (PEO) was spincoated on top. Upon heating the sample above the melting temperature of PS and annealing for 24 hours, the unfavorable interactions between PS and PEO caused the PEO to dewet from the PS surface and form micron sized droplets in the shape of spherical caps. Upon cooling from the melt, the crystallization of each droplet was detected by the appearance of crystalline birefringence, observable as a bright droplet when the sample is examined under crossed polarized lenses. It was observed that once a droplet nucleated, the crystal grew to fill the entire droplet instantaneously in the experimental timescale. This is evidence that nucleation rates were being measured, rather than crystal growth rates. Homogeneous nucleation for a subset of the droplet population was observed and verified in several ways, through: correlation plots of crystallization temperature, scaling analysis on the relationship between induction time for nucleation and droplet radius, and ellipsometry on droplets that were an order of magnitude smaller (as small as 100 nm in diameter). The results were also consistent with homogeneous nucleation studies in diblock PEO-polybutadiene copolymers.

Carvalho and Dalnoki-Veress further refined this methodology using isotactic PS (iPS) as a substrate. iPS can crystallize, and this allowed the researchers to change the surface texture using different thermal histories. By rapidly quenching iPS films from the melt, a smooth amorphous substrate could be formed. Alternatively, other iPS films were crystallized at two different temperatures, resulting in different growth rates of crystal spherulites that led to two different levels of surface roughness. Upon the addition of PEO
droplets to these three different substrates using the above methodology, different types of nucleation of PEO was observed. The same scaling analysis that had been validated earlier with atactic PS substrates was applied, and PEO was found to nucleate homogeneously upon amorphous iPS substrates. However, for the two crystalline iPS substrates that were prepared at different temperatures, heterogeneous nucleation of PEO was observed to occur at the interface with the substrate (iPS substrate with intermediate roughness) and at the three-phase contact line (iPS substrate with roughest surface). The location of these nucleation events were also confirmed with atomic force microscopy. Homogeneous and surface-induced nucleation events were observed to have lamella radiating out of the interior of the droplet, while samples that nucleated at the three-phase contact line exhibited lamella radiating from the edge of PEO droplets.

The final iteration of this methodology was applied to study the nucleation of high-density polyethylene (HDPE) on atactic PS substrates. Following the same principle of forming micro-droplets via dewetting, HDPE droplets were shown to nucleate at the interface with the substrate. Although termed “homogeneous nucleation” based on a correlation analysis of repeated non-isothermal crystallization experiments, it would be logical to conclude that these were actually heterogeneously nucleated events. While active heterogeneities have a low activation energy barrier that could result in measurable correlation, the interface with PS has a more significant barrier, requiring much deeper undercoolings for nucleation to occur. This would lead to more stochastically distributed results.

A notable addition to the experimental procedure for studying HDPE nucleation was a purification step. HDPE was dissolved in dicholorobenzene, and then filtered through a 0.2 μm filter to reduce impurities prior to spincoating the HDPE onto the PS substrate. This was necessary to observe nucleation that was occurring due to the substrate rather than any impurities present in the HDPE droplets. HDPE readily nucleates on almost anything, so achieving high levels of purity is critical, even when using the micro-droplet method to create a fraction of impurity-free droplets. However, depending on the vendor for PE, filtration may not remove enough impurities. Filtration could be problematic for impurities that melt
below the filtration temperature as these would not be separated. An alternative method is extraction of the impurities using a solvent or combination of solvents at temperatures where the impurities dissolve but the polymer does not. A classic method using this idea is Soxhlet extraction whereby a hot solvent from a reservoir is continuously passed over a polymer sample in a thimble, and the hot solvent with dissolved impurities is allowed to pass back into the reservoir for recycle. An ASTM standard for additive extraction from polyolefins discusses the use of Soxhlet extraction, but this standard also discusses extraction using ultrasonication. Nielson compared these methods and found Soxhlet extraction to be far more time intensive and less effective than ultrasonication, requiring over a day while ultrasonication required 1 hour. The best combination of solvents was found to be a 75:25 mixture of dichloromethane:cyclohexane to extract a range of polar and nonpolar impurities.

This experimental method using microdroplets is a promising strategy to study heterogeneous nucleation. Although heterogeneous nucleation of HDPE by a PS was an unintended result of Carvalho and Dalnoki-Veress, it demonstrates the possibility of studying the heterogeneous nucleation effects of other materials. Substrates can be formed out of a NA of interest, and the same methodology can be applied. The remainder of this chapter discusses these efforts and highlights some notable limitations with this experimental method.

**Methods**

The methods presented here derive from the droplet experiments of the Dalnoki-Veress group, where PS was the substrate that was used as a NA for PE. This method has been adapted to allow testing of a variety of other materials as NAs. Because the materials tested here have favorable interactions with PE, the dewetting process could not be relied upon to form micro-droplets as done by Carvalho and Dalnoki-Veress. Instead, micro-crystals of HDPE were suspended in solution and sprayed onto substrates. The overall procedure started with purifying PE, preparing a suspension of HDPE micro-droplets, preparing the NA as a substrate, creating the PE-NA sample, and testing the sample with temperature controlled polarized optical microscopy.
Materials

All materials were obtained from Millipore-Sigma, unless noted otherwise. High-density polyethylene with a melt flow index of 12g/10min (190 °C, 2.16 kg load) and an as-received density of 0.952 g/mL was used. The atatic polystyrene had a Mw = 192 kDa. Nucleating agents that were obtained in powder form were: potassium hydrogen phthalate (PHP), benzoic acid, anthracene, sodium benzoate, potassium benzoate, D-sorbitol, and the following polymers: polymethylmethacrylate (PMMA), polyethylmethacrylate (PEMA), polycaprolactone (PCL), polysulfone (PSU), polyvinylpyrrolidone (PVP), ethyl cellulose (EC), polyacrylonitrile (PAN), and polyvinylalcohol (PVA). Nucleating agents that were obtained as a substrate or film were: gallium arsenide (GaAs, obtained from University Wafer Inc., [100] facet), monolayer graphene mounted on silicon or copper, pyrolytic graphite (obtained from Electron Microscopy Sciences), and polytetrafluoroethylene (PTFE, obtained from Goodfellow Cambridge Ltd. as a film). Nucleating agents that were obtained as large cleavable crystals were: sodium chloride (NaCl, obtained from Ted Pella Inc. as 10 x 10 x 10 mm single crystals), calcite (CaCO3, obtained from Ward's Science), and graphite (obtained from Ward’s Science). Finally, graphene oxide was obtained as an aqueous suspension of graphene oxide platelets (obtained from Graphenea Inc. as a 0.05% graphene oxide water dispersion with > 95% monolayer content).

HDPE Preparation

Purification was a two part process. In the first part, HDPE was dissolved in boiling dimethyl sulfoxide and toluene (1:1) for 4 h, recrystallized and filtered from solution, washed with toluene, and dried. The second step followed an ASTM standard for removing impurities from polyolefins:13,14 HDPE was sonicating in dichloromethane and cyclohexane (3:1) for 2 h, filtered, washed with toluene, and dried.

A suspension of micron-sized crystals of purified HDPE was prepared in a toluene solution via a self-seeding procedure.15 0.02-0.03 g HDPE was dissolved in 10 mL boiling toluene for 30 minutes, quenched to 80 °C for 5 minutes to allow the HDPE to crystallize, heated until the crystals just appear to
melt, and then quenched to 85 °C for final crystallization. This resulted in a distribution of HDPE crystal sizes, with diameters in the range of 1-10 μm.

*NA Substrate Preparation*

NA substrates were prepared by a variety of methods, depending on the material. Some substrates were available as wafers (GaAs, monolayer graphene mounted on Si or Cu substrate, pyrolytic graphite, PTFE) requiring only a rinse with acetone to remove dust. All polymer substrates (excluding PTFE) were dissolved in solvent and spincoated onto a glass slide (PS-toluene, PMMA-toluene, PEMA-toluene, PCL-toluene, PSU-dimethylsulfoxide, PVP-water, ethyl cellulose-dichloromethane, PAN-dimethylformamide, PVA-water). Some substrates were available as large single crystals and were cleaved along a chosen crystallographic facet to produce a smooth surface for interfacing with HDPE (NaCl, CaCO₃, graphite). Graphene oxide was prepared by drying a droplet of the aqueous suspension on a glass slide. Finally, the last group of NA required growing at least millimeter sized single crystals from a powder, followed by cleaving (PHP, benzoic acid, anthracene, sodium benzoate, potassium benzoate, D-sorbitol).

Of particular importance for the results below, PHP fell into this last category. Single crystals were grown by sonicking PHP in water (1.2 g/10 mL), and placing the uncovered vial into a covered dish containing isopropyl alcohol (anti-solvent), such that the vial was exposed to anti-solvent vapors (Fig. 2.1). The anti-solvent vapors encouraged the formation of plate-like PHP crystals at the surface of the aqueous solution which then grew into larger crystals, up to 1 cm in size, with the (010) crystallographic plane growing as the dominant surface.¹⁶
Figure 2.1. Method of growing PHP crystals. An open vial of PHP dissolved in water was placed in a closed system containing isopropyl alcohol. Vaporized isopropyl alcohol served as an anti-solvent at the surface of the aqueous solution where PHP crystals form.

**Preparation of Samples for Crystallization Experiments**

Samples were prepared for nucleation testing by sonicating the PE-toluene solution for 10 minutes to break up any agglomerates of HDPE micro-crystals. Immediately following sonication, the HDPE-toluene solution was sprayed onto a freshly prepared substrate with an airbrush, using the experimental setup shown in Fig. 2.2. Density of HDPE crystals on the substrate surface was controlled by the air pressure into the brush, liquid flowrate, and duration of spraying. After spraying, samples were examined under polarized microscopy to confirm that there was a balance in the density of droplets such that droplets did not impinge on each other but were not too sparsely positioned (at least 50 droplets per 500 μm x 500 μm viewing window). To remove residual toluene but avoid any oxidative degradation of HDPE molecules, the samples were heated to 160 °C under an inert nitrogen atmosphere.¹⁷

![Spraying configuration to disperse micron droplets of HDPE onto the NA substrate. The spincoater was used to prepare polymer substrates prior to spraying with the HDPE-toluene suspension.](image-url)

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¹⁷
**Thermal Procedures for Crystallization**

To test the nucleating ability of a material, the sample was heated under nitrogen in a temperature controlled hot stage (Linkam LTS350 Hot Stage, Linkam TMS 94 Controller) to 160 °C for 5 minutes (Fig. 2.3). This was approximately 20 °C above the equilibrium melting temperature of HDPE and was found to be long enough to erase any possible melt memory (confirmed by the absence of rapid crystallization near 130 °C, which was observed for shorter equilibration times at 160 °C or for lower temperatures). The sample then followed one of two thermal procedures: constant rate cooling (1-4 °C/min) to 70 °C to identify temperatures where the substrate becomes an active nucleating agent, or a quench to a predetermined crystallization temperature (T_c) followed by an isothermal period of 30 minutes or until crystallization ceased. Droplets were observed with microscopy (Zeiss Axioplan 2) with snapshots taken every 10 seconds (Zeiss AxioCam MRc). A droplet was determined to have crystallized by the appearance of birefringence under crossed polarizers. For the isothermal experiments, there was some thermal lag in the entire sample reaching T_c, especially when the substrate was formed out of polymer films that were thermally insulating. An artifact of the experiment existed where the hot stage thermally expanded and shifted the sample slightly as temperatures change, noticeable under magnification. The moment when the top of the substrate interfacing with HDPE droplets reaches T_c was determined by tracking the movement of droplets until they were stationary. Any droplets that crystallized before this point were not considered to have nucleated at T_c and were removed from further analysis.
Figure 2.3. Hot stage used during nucleation experiments. The temperature is controllable to within 0.1 °C and is placed under the microscope between crossed polarizers.

Images were analyzed in ImageJ.\textsuperscript{18} For samples that had a clear distinction between HDPE crystals and the substrate, a simple greyscale threshold was manually set to identify droplets that reached a critical brightness. For samples with a less clear distinction, a variety of methods were used to varying degrees of success: thresholding RGB images with the hue of the background removed (HSB color system), using binary differences between subsequent images to detect changes, using binary differences with the initial image to detect net changes, and using binary divide with both subsequent and initial images. The first method was found to generally be the most accurate as binary differences and divides often led to many noisy artifacts and false identification of droplet nucleation.

Results

*Nonisothermal Crystallization*

Materials have varying degrees of effectiveness as NAs for PE, and thus induce nucleation at different temperatures during cooling at a specified rate. Peaks in the number of crystallized droplets in constant cooling rate experiments were used to determine the temperature where the NA becomes very active. Fig. 2.4 demonstrates two examples of materials that became active at different temperatures, with $T_c = 85$ °C for PS and $T_c = 116$ °C for PHP. Note, as nucleation is an activated process, nucleation could occur on these materials at higher/lower temperatures, but these led to either very slow/rapid nucleation that is infeasible to measure with the experimental setup described here. Therefore, temperatures slightly above (~1 °C) the peak in crystallized droplets were chosen for convenience. Another feature of these data is the presence of impurities in HDPE that could cause nucleation. This can be seen in the PS data above 90 °C and in PHP above 120 °C. The purification procedure described in the methods was very important in removing many of these impurities, but the remaining impurities could add noise to the data when examining materials that become active NAs at similar temperatures.
Figure 2.4. Constant cooling rate experiments for HDPE droplets on (a) PS and (b) PHP.

**Isothermal Crystallization**

Isothermal experiments were next used to measure the nucleation rate at the specific $T_c$ identified from nonisothermal experiments. The induction time is the time for a nucleus to form and is a function of the nucleation rate, $J$, and size of the droplet, $R$, given by Eq. 2.3 above.

$$\tau = (JR^n)^{-1}$$

(2.1)

The variable $n$ is an important parameter that describes how the induction time scales with the size of the droplet. $n = 3$ is characteristic of nucleation in the bulk of the droplet. In the case of these experiments, this would indicate nucleation from impurities in the HDPE melt. More generally, homogeneous nucleation also would exhibit $n = 3$, but this only occurs at appreciable rates at very low temperatures ($<70$ °C for PE). $n = 2$ is characteristic of nucleation occurring at a surface. For these experiments, surface-induced nucleation can occur at two interfaces: at the interface with the substrate, and at the interface with nitrogen. The latter interface with the atmosphere is unlikely to decrease the nucleation barrier, and can be discarded as a possibility. Finally, $n = 1$ is characteristic of nucleation at the three phase contact line. This is expected to occur if polymer molecules are constrained in some way along this contact line, either from wetting or dewetting processes that deform the polymer droplets. This is considered an artifact of the experimental method and is not a desirable type of heterogeneous nucleation for the analysis.
presented here. Therefore, in order to confirm that the material being tested was actually causing surface-induced heterogeneous nucleation, a value of $n = 2$ needed to be demonstrated.

Since each droplet undergoes an independent nucleation event with induction times being exponentially distributed, maximum likelihood estimation (MLE)\(^{(10)}\) was used to calculate the most likely value of $n$ and nucleation rate, $J$, that corresponded to the experimentally observed induction times. The probability that a droplet nucleated is the inverse of the induction time. The likelihood function, $L$, is given by Eq. 2.2.

$$L(J, n, t, r) = \prod_{i=1}^{N} J r_i^n \exp[-t_i J r_i^n]$$  

(2.2)

$t$ and $r$ are vectors of the induction times and radii of all the droplets, and $N$ is the total number of droplets that nucleated at $T_c$. The most likely values of $n$ and $J$ were found by maximizing the log of $L$. This analysis applied to droplets nucleating on PHP data at 116 °C is shown in Fig. 2.5, and gave a value of $n = 1.92 \pm 0.15$, demonstrating surface-induced nucleation.

![Graph showing induction times for HDPE droplets on PHP substrate.](image)

Figure 2.5. Induction times for HDPE droplets on PHP substrate. MLE was used to determine the value of the scaling parameter, $n$, and the model (Eq. 2.1) using this value is shown by the red line. $n = 1.92 \pm 0.15$, confirming a surface-induced mechanism.
Discussion

Difficulties with Other Materials

While this method was successful for confirming heterogeneous nucleation on a PHP substrate, many other materials that were tested did not yield such results. Table 2.2 at the end of this section summarizes the complications with these materials. A few examples are discussed here to highlight important results and shortcomings of the methods.

GaAs is a tetrahedrally coordinated crystal and was of interest as it belongs to a class of materials simulated by Bourque. GaAs wafers were tested with the above method, but resulted in a value of \( n = 0.89 \) (Fig. 2.6). This suggests that nucleation may be occurring at the contact line of the droplets which is an undesired artifact of the experimental method. However, there was considerable spread in the data which weakens the significance of such a claim. The primary difficulty with this material was a drop in the brightness of HDPE crystal birefringence from a freshly sprayed substrate, compared with the same sample after HDPE had been melted and recrystallized, exemplified in Fig. 2.7. This made detecting when droplets crystallized difficult, and led to only the largest droplets being detected (note difference in radii plotted in Fig. 2.5 vs Fig. 2.6). This had an important impact on the scaling analysis as the largest droplets were more likely to have impurities that may nucleate at different rates as compared to the GaAs substrate.
Figure 2.6. Induction times for HDPE droplets on GaAs substrate at 110 °C. MLE was used to determine $n = 0.89 \pm 0.28$ (red line), suggesting that nucleation may be occurring at the three phase contact line.

![Image](image1.png)

Figure 2.7. Polarized microscopy of HDPE droplets on GaAs at room temperature (a) before melting (b) after melting. Note the spreading of droplets and the noticeable drop in birefringence.

One hypothesis was that HDPE was wetting the substrate due to favorable interactions, and HDPE droplets were thinning out while melted. This resulted in a shorter optical path to refract light when the droplets recrystallized and thus a weaker birefringent signal. Atomic force microscopy (AFM) was used to examine several droplets on this substrate. Fig. 2.8 shows two droplets that have lateral dimensions on the micron scale, large enough to be visible with microscopy and typical of the sizes of droplets presented in the data above. However, the height of these droplets were on the order of tens of nanometers, far too thin for a strong birefringent signal to be detected with polarized optical microscopy. These droplets were originally sprayed onto this surface with shapes roughly spherical, providing an optical path on the order of microns, and were thus detectable (Fig. 2.7a), but after melting and recrystallization, they spread on the surface with thicknesses of only tens of nanometers (Fig. 2.7b).
Figure 2.8. AFM height images of HDPE droplets on GaAs at room temperature. Approximate droplet dimensions (a) lateral 3 μm x 2 μm, height 50 nm (b) lateral 1 μm x 0.5 μm, height 15 nm.

Raman microscopy was briefly examined as an alternative method to detect HDPE crystals, but was discarded as the spectra were no more sensitive than polarized microscopy, and droplets needed to be examined individually for several seconds to obtain a spectrum as opposed to tens to hundreds of droplets being examined in an instant with polarized microscopy.

Nonisothermal Analysis with Polymer Films

Due to these issues with detecting birefringence, materials that HDPE would be unlikely to wet were also investigated. These were polymer films, namely polymethylmethacrylate (PMMA), polyethylmethacrylate (PEMA), polycaprolactone (PCL), polysulfone (PSU), polyvinylpyrrolidone (PVP), ethyl cellulose (EC), polyacrylonitrile (PAN), and polyvinylalcohol (PVA). When these materials were examined in constant cooling rate experiments, it was found that rather than demonstrating a peak in nucleation at a particular temperature (when the material becomes active as a nucleating agent), there was a broad range of up to 30 °C where nucleation was occurring. This is exemplified in Fig. 2.9: HDPE crystallizes on the EC substrate between 110 °C and 90 °C, and HDPE crystallizes on the PMMA substrate between 120 °C and 90 °C. Such a broad range of T_c’s suggests the presence of impurities in the PE. However, since the same solution of HDPE was sprayed onto PMMA, any nucleation above 110 °C should be attributed to the PMMA surface. The ranges for all the polymer substrates tested are shown in
Table 2.1, and may be due to the variety of sites available for heterogeneous nucleation in an amorphous polymer film.

![Graph showing fraction crystallized vs temperature for PMMA and Ethyl Cellulose.](image)

Figure 2.9. Example of the ranges over which the tested polymer nucleating agents were active in constant cooling rate experiments.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Nucleating Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>120 – 95</td>
</tr>
<tr>
<td>PEMA</td>
<td>120 – 100</td>
</tr>
<tr>
<td>PCL</td>
<td>122 – 98</td>
</tr>
<tr>
<td>PSU</td>
<td>125 – 110</td>
</tr>
<tr>
<td>PVP</td>
<td>124 – 110</td>
</tr>
<tr>
<td>EC</td>
<td>110 – 90</td>
</tr>
<tr>
<td>PAN</td>
<td>123 – 110</td>
</tr>
<tr>
<td>PVA</td>
<td>122 – 103</td>
</tr>
</tbody>
</table>
Because there was no temperature where a large population of droplets crystallized, meaningful results could not be gathered by the standard isothermal experiments. A nonisothermal model has been proposed by Cormia et al.\textsuperscript{6} This model compares experiments with two different constant cooling rates, and it provides a way to estimate a value for \( n \) and the nucleation rate over a small range in temperature. Therefore, nonisothermal experiments provide an alternative strategy to identify temperature ranges where a surface induced mechanism could be occurring. The evolution of the fraction of crystallized droplets, \( N_r \), over time is given by

\[
1 - N_r = \sum_{\text{droplets}} \exp \left( -r^n K_0 \exp \left( -\frac{\Delta G^*}{k_B T} \right) t \right). \tag{2.3}
\]

\( K_0 \) is a constant related to the concentration of nucleation sites (temperature insensitive) and the transport resistance to chain reptation (assumed here to be constant over the temperature range for crystallization). \( \Delta G^* \) is the critical nucleation barrier, \( k_B \) is the Boltzmann’s constant, and \( T \) is the temperature. The critical nucleation barrier was calculated as a function of temperature numerically by comparing experiments with different cooling rates:

\[
\ln \frac{r_2}{r_1} = \frac{2\Delta G^* \Delta T_d}{k_B T \Delta T_{av}}. \tag{2.4}
\]

\( r_1 \) and \( r_2 \) are the cooling rates in two separate experiments. \( T = (T_1 + T_2)/2 \), where \( T_1 \) is a temperature from the experiment using \( r_1 \), and \( T_2 \) is the corresponding temperature from the experiment using \( r_2 \) for the same \( N_f \) (i.e. \( N_f(T_1)_{\text{rate 1}} = N_f(T_2)_{\text{rate 2}} \)). \( T_m \) is the equilibrium melting temperature, \( \Delta T_{av} = T_m - T \), and \( \Delta T_d = T_2 - T_1.\textsuperscript{22} 
\) The temperature dependence of the critical nucleation barrier was described by

\[
\Delta G^* = \frac{A}{(T \Delta T)^2}. \tag{2.5}
\]

\( A \) is a collection of constants (fitted parameter), and \( \Delta T \) is the undercooling from the equilibrium melting temperature. Since \( A \) should be constant, the temperature range over which the fitted value of \( A \) was
constant was likely a region where a single nucleation mechanism was occurring (competing mechanisms would have different nucleation barriers). Finally, $n$ and $J$ in Eq. 2.3 can be fit.

For the four substrates examined (EC, PCL, PSU, and PVP) only EC ($n=2.05$) and PVP ($n=1.52$) exhibited $n$ values consistent with heterogeneous nucleation. With temperature ranges of nucleation activity identified, the standard analysis using isothermal crystallization could be used to determine nucleation rates.

**Practical Limitations and Summary of Results**

Finally, several substrates could not be tested due to an incompatibility with the experimental method. Examples include materials that melted within the temperature ranges of the experiment (70 °C – 160 °C) (e.g. benzoic acid), birefringent materials that could not be oriented to extinction (e.g. PTFE film), and materials where growth of millimeter sized crystals was unsuccessful (e.g. benzoates). These limitations are detailed in Table 2.2.
Table 2.2. Nucleation results on various substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Scaling (n)</th>
<th>Active Range (°C)</th>
<th>Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>2.07 ± 0.21</td>
<td>85</td>
<td>Difficulty purifying HDPE to the extent that a sizeable fraction of droplets were pure enough to remain un-nucleated until the PS substrate became active near 85 °C.</td>
</tr>
<tr>
<td>PHP</td>
<td>1.92 ± 0.15</td>
<td>116</td>
<td>Uniaxially birefringent, but could be oriented to extinguish PHP birefringence to allow detection of HDPE birefringence</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.52</td>
<td>111</td>
<td>Wetting of HDPE on substrate lead to weakly birefringent HDPE crystals</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.88 ± 0.28</td>
<td>110</td>
<td>Wetting of HDPE on substrate lead to weakly birefringent HDPE crystals</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>-</td>
<td>-</td>
<td>Crystals grew in needles (difficult substrate preparation). T_m = 122 °C, and even rapid heating then cooling to melt HDPE resulted in the substrate completely melting</td>
</tr>
<tr>
<td>CaCO_3</td>
<td>-</td>
<td>-</td>
<td>Biaxially birefringent (no orientation yielded extinction under crossed polars)</td>
</tr>
<tr>
<td>PTFE</td>
<td>-</td>
<td>-</td>
<td>Birefringent in all orientations</td>
</tr>
<tr>
<td>Dried solution of graphene oxide</td>
<td>0.98 ± 0.14</td>
<td>120</td>
<td>Not a single crystal so surface roughness could have an effect</td>
</tr>
<tr>
<td>Graphene single sheet on Si/Cu</td>
<td>-</td>
<td>-</td>
<td>When heated, graphene sheet degraded due to a difference in thermal expansion with the Si or Cu substrates the graphene sheet was mounted on</td>
</tr>
<tr>
<td>Graphite</td>
<td>-</td>
<td>-</td>
<td>Cleaved poorly giving a rough surface that was also reflective</td>
</tr>
<tr>
<td>Pyrolytic graphite</td>
<td>-</td>
<td>-</td>
<td>While there was some background reflections, HDPE droplets appeared to thin to the point where their birefringence was undetectable</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-</td>
<td>-</td>
<td>Sublimed during HDPE melting, obscured hot stage window</td>
</tr>
<tr>
<td>Sodium/potassium benzoate</td>
<td>-</td>
<td>-</td>
<td>Unsuccessful in growing millimeter sized single crystals using water/ethanol (solvent/anti-solvent) strategy</td>
</tr>
<tr>
<td>D-Sorbitol</td>
<td>-</td>
<td>-</td>
<td>Melting temperature too low (T_m = 94 °C)</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>2.05</td>
<td>110 - 90</td>
<td>Analyzed with nonisothermal model. Surface nucleation unconfirmed with standard isothermal analysis</td>
</tr>
<tr>
<td>PVP</td>
<td>1.52</td>
<td>124 - 110</td>
<td>Analyzed with nonisothermal model. Presence of impurities likely competing with surface nucleation, resulting in noise in trends drawn from the data</td>
</tr>
<tr>
<td>Other polymer substrates</td>
<td>&gt;2.5</td>
<td>See Table 1</td>
<td>No peak in constant cooling experiments. Nonisothermal analysis yielded scalings consistent with impurities</td>
</tr>
</tbody>
</table>
Conclusions

Surface induced nucleation was demonstrated on two surfaces, PS and PHP. However, there have been difficulties in confirming a surface-induced heterogeneous nucleation mechanism on many substrates that have been suggested in the literature to be good nucleating agents for polyethylene. Only the smallest droplets (diameters < 5 µm) do not have impurities which could compete as nucleation sites with the substrate being studied. However, many of the substrates have favorable interactions with polyethylene (which is in part why they are good nucleating agents), leading to small polyethylene droplets spreading on the substrate. Unfortunately, any significant amount of thinning of these small droplets make their crystallization undetectable by the optical method employed. Therefore, only the population of larger droplets could be detected, and this population is more likely to have impurities. Because impurities nucleate polyethylene over the same temperature range as the substrates, this competition could not be avoided. This is believed to be the main reason why surface induced nucleation has not been confirmed on many of these substrates. Therefore, the experimental methodology needs to be modified to improve contrast and detectability of HDPE crystals.

References


3. Heterogeneous Nucleation of High-Density Polyethylene Crystals on Graphene within Microdomains


Introduction

The organization of a semicrystalline polymer into crystalline and noncrystalline domains, or its microstructure, has a large effect on the mechanical,1–5 thermal,6 electrical,7,8 and optical 9–13 properties of the polymer. This microstructure depends on many factors, one of which is the kinetics of crystallization. In most cases, polymers crystallize through the processes of nucleation and growth, by which small stable crystalline clusters, called nuclei, form first, and these nuclei subsequently grow by accretion of polymer from the surrounding melt or solution. The kinetics of nucleation and growth can be manipulated by changes in temperature, pressure, flow-induced melt structure, or the introduction of nucleating agents (NA), which alter the rate of nucleus formation,14 or may promote the formation of one crystal polymorph over another.15,16 NAs can be crystalline powders of small molecules 17–20 or other polymers.21–24 Self-nucleation occurs on crystalline residuals from an incompletely melted polymer.25–29 NAs thus provide a mechanism by which to tailor macroscopic properties for a desired application.30 However, determining the “effectiveness” of a NA is still largely a matter of empiricism.20

The study of nucleation, and NAs, is complicated when nucleation and growth occur concurrently, as is often the case when new nuclei are forming at the same time as old nuclei are growing. Thus, a crystallization rate obtained from the measurement of a bulk kinetic property, such as the rate of release of enthalpy of crystallization, is usually influenced by both nucleation and growth. Nucleation rates are even more difficult to measure for highly effective NAs, which cause nucleation to occur so rapidly that it is often considered to be “instantaneous” relative to subsequent crystal growth.
To study nucleation alone, Vonnegut introduced the droplet method, wherein the extent of crystal growth that is allowed following a nucleation event is limited by the size of the droplet.\textsuperscript{31} By limiting the size of droplets so that the time to nucleate is much longer than the time for a nucleated crystal to grow to the full extent of the droplet, observations like the rate of release of crystallization enthalpy is determined by nucleation. For polymers, it is important that droplets are large enough so that the polymer chains themselves can behave as in an unconfined melt,\textsuperscript{32–35} yet small enough to ensure that nucleation rate is dominant. Confinement on the order of hundreds of nanometers to a few micrometers in diameter have been shown to satisfy these requirements.\textsuperscript{34}

For polymers, a variation of the droplet method involves melt-blending two immiscible polymers, such that the crystallizable polymer is the minor component of the two-phase mixture and dispersed within microdomains. Rasmussen and Loper used this type of sample for nucleation measurements with differential scanning calorimetry (DSC).\textsuperscript{36} Santana and Müller subsequently extended this approach to the study of homogeneous nucleation of isotactic polypropylene (iPP) blended with polystyrene (PS).\textsuperscript{37} More recently, heterogeneous nucleation of iPP blended with additives,\textsuperscript{27} high-density polyethylene (HDPE) at the interface with iPP,\textsuperscript{24} and self-nucleation of HDPE\textsuperscript{29} have been investigated using microdomains in an immiscible matrix. In addition to measuring nucleation rates, the mechanisms of epitaxy (with a crystalline matrix) and graphoepitaxy due to roughness of the interface with the surrounding amorphous or crystalline matrix have been observed in these two-phase mixtures.\textsuperscript{38} A comprehensive review of this methodology was presented very recently by Fenni et al.\textsuperscript{38} One advantage of this methodology is the ability to quantify nucleation rates at multiple temperatures. Using the temperature dependence of nucleation rate and applying classical nucleation theory, the critical free energy barrier to nucleation can be calculated. This energy is a useful metric for quantifying the effectiveness of a NA.

The phenomenon of dewetting of a crystallizable polymeric melt or solution upon a substrate offers another strategy to form microdomains or droplets. In this method, a thin film of crystallizable polymer is
first spin-coated as melt or solution on top of a second material (substrate) and rapidly cooled or the solvent evaporated. Upon heating above $T_m$, the crystallizable polymer de-wets from the substrate and coalesces into droplets. Since this method produces droplets at a much lower number density relative to melt-blended samples, DSC is generally too insensitive to measure crystallization of these droplets. Instead, polarized optical microscopy (POM) can be used to track crystallization within these droplets. This methodology has been used to study nucleation of polyethylene oxide on PS $^{39-42}$ and HDPE on PS.$^{43}$ A significant advantage of this methodology is that the crystallization of individual droplets can be observed directly, and the induction time correlated with the size of the crystallizing droplet. Nucleation on lines, at interfaces or within the volumes of droplets can be distinguished by their different scalings with droplet radius.$^{42}$

Graphene has been widely studied as a nanofiller for HDPE. HDPE-GNP composites have improved mechanical,$^{4,44}$ electrical,$^{44,45}$ thermal,$^{44-46}$ and gas barrier properties$^{44}$ relative to neat HDPE. GNP has also been shown to increase the rate of crystallization of HDPE, attributed to enhanced nucleation.$^{4,46,47}$ However, these studies are limited to bulk crystallization, and only report increased crystallization temperatures, reduced crystallization half times (or the time to reach 20% relative crystallinity in the case of Bourque et al.$^4$), and fitted Avrami constants. A noteworthy exception is the work of Tarani et al.$^{47}$ who also report apparent activation energies calculated by the Friedman method. While useful in quantifying enhanced nucleation, these apparent activation energies are not intrinsic values for the HDPE+GNP system, as they depend on GNP loading.

In this paper, we examine the heterogeneous nucleation of HDPE on GNPs within microdomains using two different methods: DSC of immiscible blends of HDPE+GNP dispersed in PS matrices, and POM of HDPE+GNP droplets on a PS substrate. The nucleating efficiency of a powdered additive in HDPE as measured by these methods is reported for the first time. Estimates of the magnitude of the interfacial free energy difference (a key component of the critical free energy barrier to nucleation) are obtained and compared.
Methods

Materials
All materials were obtained commercially from Millipore Sigma. The polyethylene was a high-density resin with a melt flow index of 12 g/10 min at 190 °C and 2.16 kg load, with a density of 0.952 g/mL as-received. The polystyrene was atactic with $M_w = 192$ kDa. Graphene was obtained as a powder with a nominal particle size of 5 μm.

Crystal Growth Rate
To measure the linear crystal growth rate of this HDPE, a small amount of HDPE was melted between two glass slides and pressed to form a thin film. The sample was placed in a hot stage (Linkam LTS350 Hot Stage, Linkam TMS 94 Controller), covered with a heat shield containing a small hole for observation to minimize thermal gradients across the sample, purged with nitrogen for 10 minutes to provide an inert atmosphere to limit polyethylene degradation at elevated temperatures, and melted for 5 minutes before being quenched to the desired crystallization temperature. Isothermal crystal growth was measured between 118 and 124 °C, at 1 °C increments. The linear growth rate was obtained from the rate of change of spherulite radii as a function of time using polarized optical microscopy (POM, Zeiss Axioplan 2), with snapshots taken every 10 seconds (Zeiss AxioCam MRc).

Nucleation Rate

Domains in Immiscible Blends
For this method, the experimental design of Santana and Müller and Wang et al. was used. An immiscible blend of micron-sized domains of polyethylene and graphene nanoplatelets (HDPE+GNP) in a polystyrene (PS) matrix was prepared by first melt-blending graphene at various weight fractions (5, 2, and 0.5 wt%) with HDPE in a twin blade blender (Brabender ATR Plasticorder with 3-piece mixer) for 10 minutes at 180 °C and 100 rpm. This blend of HDPE+GNP was then mixed at 15 wt%, in PS for 30 minutes at 180 °C and 100 rpm. The PS/HDPE+GNP sample was hot pressed (Carver Model C) at 115 °C (above the glass transition temperature of PS, but below the melting temperature of HDPE) to a
thickness of roughly 1 mm. A 3 mm disc was punched out for DSC analysis. We refer to this method as Immiscible Blending (IB).

Thermal characterization was performed using DSC (TA Instruments DSC 2500). A reference pan containing PS of similar mass to each sample was used to reduce the effects of the endothermic hook observed upon quenching from the melt to the crystallization temperature.48 Between each experiment, the sample was melted at 180 °C for 2 minutes. The sample was then either cooled at a fixed rate (10 °C/min) for nonisothermal crystallization or quenched and held at a fixed temperature (121, 122, 123, 124 °C) for isothermal crystallization. Crystallization was analyzed by tracking the exothermic heat flow of the sample.

Droplets on Substrate
For this method, the experimental design of Carvalho and Dalnoki-Veress43 was followed, with some modification. Rather than spin-coating HDPE onto the desired substrate, HDPE microcrystals containing nucleating agents were sprayed from solution onto the PS substrate. This method has several advantages. First, it is widely applicable to a variety of substrates, not just those for which HDPE de-wets. Second, it avoids the long equilibration times in an oven at elevated temperatures required to ensure that HDPE de-wets from the substrate into micro-droplets. Third, the HDPE and nucleating agents are less likely to become separated due to retraction of the three-phase contact line on the substrate, which can result in deposition of the nucleating agents on the substrate outside of the polymer droplets. We refer to this method as Droplets on Substrate (DoS).

First, microcrystals of HDPE containing GNP were formed in toluene via a self-seeding process. HDPE (0.1 wt%) and GNP (0.01 wt%) were sonicated in toluene for 15 minutes to break up the GNP from its aggregated state as received. Then, the HDPE was crystallized in solution by self-seeding, as follows: first, the solution was heated to the boiling point of toluene (110.6 °C) for 10 minutes to dissolve the HDPE; second, the HDPE was crystallized onto suspended GNP by cooling to 80 °C; third, the resulting dispersion was reheated until the HDPE crystals were almost completely re-dissolved, as confirmed
visually; fourth, the solution was cooled once again to 25 °C for the self-seeded crystallization. The crystals formed during the first two steps are generally too large for the DoS method. The self-seeding step leads to HDPE+GNP particles that are smaller and more uniform in size. This solution containing HDPE microcrystals was then sprayed with an airbrush onto a spin-coated PS substrate to create the DoS sample that was used for thermal experiments. Residual toluene was removed by heating the DoS sample under an inert atmosphere.

A fully formed DoS sample was thermally characterized using a hot stage (Linkam LTS350 Hot Stage, Linkam TMS 94 Controller) in combination with POM (Zeiss Axioplan 2, Zeiss AxioCam MRe). The sample was covered by a heat shield, and the hot stage was purged with nitrogen for 10 minutes then sealed. The hot stage was heated to 160 °C for 5 minutes to completely melt the HDPE. The sample was then quenched and held at the desired temperature for isothermal crystallization, with snapshots taken every 10 seconds. Crystallization was analyzed by tracking the time when molten droplets, which appear dark when viewed through crossed polarizers, turn bright due to the formation of birefringent crystals.

Compared to the large number (millions) of nucleation events that occur in a single IB experiment, a significantly smaller number of nucleation events (100 to 200) were observed per experiment by DoS; for this reason, all DoS experiments were performed in triplicate, and the results added together.

**Particle Size Distributions**

The morphologies of IB samples were examined with scanning electron microscopy (SEM, SEC Co. SNE-4500M Plus). Particle size distributions (PSD) for each sample were measured from cross-sections of hot-pressed material from DSC sample preparation. Samples were cooled in liquid nitrogen for ten minutes and then fractured in five places to obtain cross-sections. These fractured cross-sections were sputter coated with gold and viewed at 1000x magnification with SEM under vacuum with an accelerating voltage of 30 kV.
The PSD of GNPs were measured with SEM. First, dilute suspensions of GNP in toluene (0.01 wt%) were sonicated for 15 minutes. Then, this suspension was drop-coated onto an SEM stage and heated on a hot plate at 50 °C to evaporate the solvent. Samples were viewed at 200x and 1000x magnification.

Particle sizes for all samples were counted using Fiji. HDPE domains and GNP in microscopy images were approximated as ellipsoids. Effective diameters were calculated as the diameter of a sphere of equivalent volume for IB and DoS samples, and the diameter of a circle of equivalent area for GNPs.

**Results**

**Crystal Growth Rate**

According to Lauritzen-Hoffman theory,\(^5\) the crystal growth rate can be described by

\[
\log G = \log G_0 - \frac{U^*}{R(T_c - T_\infty)} - \frac{K_g}{T_c \Delta T f},
\]

where \(G_0\) in the first term is the growth rate pre-factor, which is assumed to be relatively insensitive to temperature. The second term describes the transport resistance, where \(U^*\) is the activation energy for diffusion across the interface between the crystal and melt phases, \(R\) is the universal gas constant, \(T_c\) is the crystallization temperature, and \(T_\infty\) is the temperature at which all viscous motion stops. The third term describes secondary nucleation, where \(K_g\) is the secondary nucleation constant, \(\Delta T = T_m^0 - T\) is the degree of undercooling below the equilibrium melting temperature \((T_m^0)\), and \(f\) is a correction, given by

\[
f = \frac{2T_c^*}{T_c + T_m^0}.
\]

Values for material specific parameters were obtained from the literature: \(U^*\), \(T_\infty\), and \(T_m^0\) are 6276 J/mol,\(^5\) 160 K,\(^5\) and 416 K,\(^5\) respectively. The crystal growth rate, \(\log G\), is plotted versus the inverse of \(\Delta T f\) in Fig. 3.1. The experimental data follow Lauritzen-Hoffman theory reasonably well and are consistent with prior reports for HDPE in this temperature range.\(^5\)}
Figure 3.1. Experimentally measured crystal growth rate (filled circles) plotted according to Lauritzen-Hoffman theory (dotted line).

Size Distributions of IB Domains

Representative cross-sections of the IB samples prepared by freeze-fracturing are shown in Fig. 3.2. The small ellipsoidal shaped domains in each image are HDPE+GNP. The edges of many steps are also visible where the sample did not fracture smoothly. PSDs were formed from five images for each sample, with population sizes of roughly 1000 droplets per sample. The HDPE domain sizes were well-described by lognormal distributions; the results are shown in Fig. 3.3. Number and volume averaged diameters are provided in Table 3.1. With the melt blending procedure used here, HDPE+GNP domain sizes were reproducible, and no dependence of droplet size on GNP loading was observed.
Figure 3.2. Cross sectional SEM images from IB samples (% refers to GNP wt% in HDPE): (a) IB-5%-1, (b) IB-5%-2, (c) IB-2%, and (d) IB-0.5%. In each image, the white arrows highlight HDPE+GNP domains, and the dashed rectangles highlight jagged fracture planes.
Table 3.1. Characteristic sizes of polyethylene domains and GNP. \( d_n \) and \( d_v \) are the number and volume averaged diameters, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d_n ) [( \mu m )]</th>
<th>( d_v ) [( \mu m )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IB-5%-1</td>
<td>0.84</td>
<td>1.43</td>
</tr>
<tr>
<td>IB-5%-2</td>
<td>1.13</td>
<td>2.09</td>
</tr>
<tr>
<td>IB-2%</td>
<td>0.91</td>
<td>1.62</td>
</tr>
<tr>
<td>IB-0.5%</td>
<td>1.21</td>
<td>2.26</td>
</tr>
<tr>
<td>DoS</td>
<td>3.13</td>
<td>-</td>
</tr>
<tr>
<td>GNP</td>
<td>4.48</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.3. Box-and-whisker plots of the particle size distributions of the diameters (d) of HDPE+GNP domains in both IB and DoS samples, and for GNP on its own. For each sample, the boxes indicate the 25th, 50th, and 75th percentiles; bars extending from the boxes indicate the range of the data excluding outliers; o’s indicate outliers; x’s indicate means.
Size Distributions of DoS Droplets

Optical images of a DoS sample are shown in Fig. 3.4. Under crossed polars, crystallized HDPE droplets appear bright, while molten droplets appear dark. Figure 4a shows the sample at room temperature, while Figure 4b shows the same sample during crystallization, after only a fraction of the droplets has nucleated and crystallized. The PSD and the number averaged diameter of the DoS sample is included in Fig 3.3 and Table 3.1. Since nucleation events for DoS samples were determined visually, the number average rather than volume average particle diameter was used. The average droplet sizes were three times larger in DoS samples than IB samples.

![Image of optical microscopy images](image.png)

**Figure 3.4.** Polarized optical microscopy images of a DoS sample: (a) at room temperature, (b) part of the way through the crystallization procedure.

Size Distribution of Graphene Nanoplatelets

SEM images of drop-coated GNPs are shown in Fig. 3.5. Aggregations of GNPs are noticeable in these images; we believe such aggregates formed while the suspension dried. Aggregates that could not be visually separated into distinct, individual platelets were not measured. To image a large number of platelets, two magnifications were used. The PSD of as-received GNPs is shown in Fig. 3.3. Statistical
measures of this PSD are included in Table 3.1. Of note, only 12% of the GNP$s have diameters smaller than 1 μm in the as-received sample, which was subjected only to sonication before imaging; the majority of GNP$s are larger than the HDPE domain sizes in the IB samples. Nevertheless, the DSC results clearly indicate the presence of GNP$s within the HDPE domains (vide infra). It is also possible that the melt blending procedure used for IB samples alters the GNP PSD by fracturing larger platelets into smaller ones. GNP$s do not experience such mechanical attrition during preparation of DoS samples; however, those droplets are larger, so that a larger fraction of the GNP population fits inside the HDPE domains of the DoS sample. For these reasons, the loadings of GNP$s within HDPE microdomains of all samples are likely to be smaller than the nominal values.

![SEM image of GNP after sonication and drop coating on a sample holder (a) 200x magnification (b) 1000x magnification.](image)

**Figure 3.5. Characterization of GNP$s.** SEM image of GNP$s after sonication in solvent and drop coating on a sample holder (a) 200x magnification (b) 1000x magnification. For purposes of determining PSD, both magnifications were used. Since the image viewed at 1000x covers only 1/25th the area of the image at 200x, the relative frequency of data at the higher magnification was weighted by this factor before combining with the data at the lower magnification.
Nucleation Rate

Domains in Immiscible Blends
To determine the temperature range where GNPs nucleate HDPE, samples were cooled from the melt at 10 °C/min. The DSC exotherms are shown in Fig. 3.6. Also included in Fig. 3.6 is the exotherm from a sample of PS/HDPE without GNPs. The sample without GNPs shows no crystallization until approximately 80 °C, which can be traced to heterogeneous nucleation at the interface between the HDPE and PS phases, consistent with reports in the literature for other PS/HDPE systems.29,43 By contrast, samples containing GNP exhibit a strong exothermic peak near 120 °C, also consistent with prior reports for HDPE+GNP systems.44,45 The volume fraction of droplets containing GNPs was calculated by integrating the two crystallization peaks and expressing as a fraction of the total enthalpy. In samples containing nominally 2 to 5 wt% GNP, > 95% of domains nucleated on GNPs, while in samples containing nominally 0.5 wt% GNP, this fraction dropped to 83%.

![Graph](image1)

![Graph](image2)

Figure 3.6. Crystallization of IB samples in DSC experiments with constant cooling rates from the melt. (a) DSC thermograms of all IB samples compared to a sample containing no GNP. (b) Volume fraction of PE droplets in the graphene-nucleated peak for each IB sample.
From the thermograms shown in Fig. 3.6, four temperatures were chosen for isothermal crystallization experiments (121 to 124 °C, in 1 °C increments). These temperatures were chosen to target the leading edge of the crystallization peaks in Fig. 3.6a, where a nucleation limited process is most likely to occur. This nucleation-limited assumption is confirmed in the Discussion below.

At the lower temperatures (121 and 122 °C), HDPE+GNP nucleated so quickly that the presence of an endothermic hook during the quench to T_c masked the onset of crystallization unless care was taken to use a reference pan containing PS similar in thermal mass to the sample itself. A comparison between an empty reference pan and one containing PS is shown in Fig. 3.7; a small overshoot is still present due to a close but still imperfect matching of the thermal masses of reference and sample pans. Fig. 3.8 shows the resulting isothermal crystallization exotherms for a representative sample (IB-5%) at each temperature. Also included in this figure is the temperature evolution of each sample during crystallization. Even at the deepest undercooling, the temperature was already within 0.6 °C of T_c at the start of crystallization. The final crystallinities achieved during isothermal crystallization experiments were calculated by integrating the area under the curves and normalizing by the specific enthalpy of fusion $\Delta h_f = 280 \text{ J/cm}^3$, using a density of 1.003 g/cm$^3$ for the polyethylene crystal.$^{51,53,54,56}$ These values are reported in Table 3.2. The final crystallinities decrease with decreasing GNP loading, as expected, and with increasing T_c, which we attribute to the difficulty in growing larger nuclei at higher T_c.
Figure 3.7. Isothermal crystallization exotherms using an empty reference pan (dashed black line) and using a reference pan containing polystyrene (solid grey). The black arrow indicates the presence of an endothermic hook that masks the initial onset of crystallization at short times when using an empty reference pan.

Table 3.2. Final Crystallinities of Each IB Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>121 °C</td>
</tr>
<tr>
<td>IB-5%-1</td>
<td>24</td>
</tr>
<tr>
<td>IB-5%-2</td>
<td>24</td>
</tr>
<tr>
<td>IB-2%</td>
<td>27</td>
</tr>
<tr>
<td>IB-0.5%</td>
<td>13</td>
</tr>
</tbody>
</table>

The relative crystallinity by mass, \(w_c\), was calculated as a function of time using

\[
w_c = \frac{\Delta h(t)}{\Delta h_{total}},
\]

(3.3)

where \(\Delta h(t)\) is the specific enthalpy released as a function of time, and \(\Delta h_{total}\) is total specific enthalpy released by the end of the experiment. These enthalpies were calculated by integrating the heat flow curves measured by DSC in Fig. 3.8. The relative crystallinity by volume was calculated by\(^{57}\)
\[ X = \frac{w_c}{w_c + \frac{\rho_c}{\rho_a} (1 - w_c)} \]  

(3.4)

where \( \rho_c \) is the density of a perfect HDPE crystal (1.003 g/cm\(^3\)) and \( \rho_a \) is the density of amorphous HDPE at 25 \(^\circ\)C (0.850 g/cm\(^3\)). \(^{58}\) Fig. 3.9 shows the evolution of relative crystallinities for the IB samples at each of the nominal GNP loadings. The curves are roughly sigmoidal in shape, and the rate of crystallization decreases with increasing temperature for each sample, as expected.

Figure 3.8. Isothermal crystallization data for a representative IB sample (IB-5\%), at (a) 121 \(^\circ\)C, (b) 122 \(^\circ\)C, (c) 123 \(^\circ\)C, (d) 124 \(^\circ\)C. Heat flow is shown in solid black (left axis), while the temperature profile is shown in grey (right axis).
Figure 3.9. Relative crystallinity as a function of time for all IB isothermal crystallization experiments, (a) IB-5%-1, (b) IB-5%-2, (c) IB-2%, (d) IB-0.5%.

**Droplets on Substrate**

Three DoS samples were crystallized isothermally at each of the four temperatures employed for the IB samples. Relative crystallinity as a function of time was calculated as the number fraction of droplets crystallized with respect to the total number of droplets that crystallized at that temperature. The evolution of relative crystallinity is shown in Fig. 3.10. While small droplets nucleated and turned bright instantaneously to the eye, crystallites in larger droplets at higher temperatures sometimes grew in size over two successive images. In such instances, the time at which light transmission was first detected in the droplet was taken as the induction time.
Figure 3.10. Crystallized fraction as a function of time for DoS isothermal crystallization experiments at each crystallization temperature. Data were combined from three experiments (~500 droplets).

**Avrami Model**

The Avrami equation can be written as

$$\log(-\log(1 - X)) = \log K + n \log(t - t_0)$$

where $t_0$ is the induction time prior to the onset of crystallization, $K$ is the crystallization rate, and $n$ is the Avrami index, often presented as

$$n = n_G + n_N$$

where $n_G$ is the dimensionality of growth, and $n_N$ takes values based on the type of nucleation, with 0 corresponding to instantaneous nucleation, 1 corresponding to sporadic nucleation, and 0.5 corresponding to diffusion-limited nucleation. Non-integer values of $n_N$ are often reported and explained as nucleation that has both sporadic and instantaneous contributions.\(^{57}\)

The parameters in the Avrami equation were obtained by fitting Equation 5 to data for fractional crystallinity versus time, $X(t)$, for low crystallinitities, $X = 0.03$ to 0.2, where the assumptions underlying
the Avrami equation are most accurate. The effects of secondary crystallization processes, such as isothermal thickening, which can be significant for HDPE, are thus minimized. A representative case showing the quality of fit is provided in Fig. 3.11. The fitted values for the Avrami index, n, for each sample are shown in Fig. 3.12. Within the recommended region of low conversion, IB samples generally exhibit n values between 1.5 and 2, while the averaged DoS sample has n values between 0.5 and 1. An n value near 1 is consistent with a nucleation-limited process. The larger n values exhibited by IB samples suggest that these samples may not be entirely nucleation-limited, despite the small sizes of the HDPE domains (c.f. Fig. 3.3). This observation is considered further in the Discussion section.

a.  

![Graph a](image1)

b.  

![Graph b](image2)

Figure 3.11. Representative fits of Avrami equations to the data (123 °C) for fractional crystallinity versus time: (a) IB-5%-1 and (b) DoS. Solid black lines denote experimental data, while dotted grey lines denote the Avrami model fit to 3-20% conversion.
Figure 3.12. Avrami index as a function of crystallization temperature for the several IB and DoS conditions studied in this work.

**First Order Nucleation Model**

For a nucleation-limited process, the uncrystallized fraction of HDPE domains for both sample types should evolve in time according to

\[ \log(1 - X) = -J(t - t_0) \],

(3.7)

where \( X \) is the crystallized fraction of domains and \( J \) is the nucleation rate. From classical nucleation theory,\(^{51,60}\) the nucleation rate for heterogeneous nucleation is

\[ \log(J) = \log(J_0) - \frac{U^*}{R(T_c - T_\infty)} - \frac{16\sigma\Delta \sigma T_m^0}{kT_c(\Delta T \Delta h_f)^2} \],

(3.8)

where \( J_0 \) is a constant pre-factor that is related to the frequency of nucleation events. \( J_0 \) is relatively insensitive to temperature but is a function of the interfacial contact area between HDPE and GNP. Parameters in the second term are the same as those defined with Equation 1. The third term describes the thermodynamic driving force for crystallization, where \( \sigma \) and \( \sigma_c \) are the interfacial (crystal/melt) free energies for the lateral and stem end surfaces of the HDPE crystal, \( T_m^0 \) is the equilibrium melting
temperature for the perfect HDPE crystal, \( k \) is the Boltzmann constant, and \( \Delta h_f \) is the enthalpy of fusion per unit volume. As previously mentioned, \( \Delta h_f \) has been widely accepted to be 280 J/cm\(^3\).\(^{51,53,54,56}\) Several values have been reported for \( \sigma_\sigma \) and \( \sigma \), depending upon the equilibrium melting temperature that is used. Values of 1380 erg\(^2\)/cm\(^4\) and 9.6 erg/cm\(^2\) have been reported for \( \sigma_\sigma \) and \( \sigma \), respectively, using an equilibrium melting temperature of 416 K.\(^{53,54}\) These values have been chosen to allow easy comparison to nucleation results reported for HDPE+polypropylene immiscible blends that also used these values.\(^{24}\) For comparison, using a higher equilibrium melting temperature of 418.7 K, \( \sigma_\sigma \) and \( \sigma \) have been reported to be 1062 erg\(^2\)/cm\(^4\) and 11.8 erg/cm\(^2\), respectively.\(^{56}\)

\( \Delta \sigma \) is the interfacial free energy difference \( (\sigma_{\text{substrate-crystal}} + \sigma_{\text{crystal-melt}} - \sigma_{\text{substrate-melt}}) \) that characterizes a specific polymer-NA pair. It is of particular importance for quantifying the effectiveness of a NA: a lower value of \( \Delta \sigma \) corresponds to a lower free energy barrier to nucleation, and hence the NA is more effective for that polymer. Alternatively, \( \Delta \sigma \) can be non-dimensionalized by the equivalent quantity for homogeneous nucleation, \( \sigma \), yielding a value for the “inefficiency” of the NA between 0 (perfect heterogeneous nucleation) and 1 (homogeneous nucleation); we thus define the thermodynamic efficiency, \( E = 1 - \Delta \sigma / \sigma \).

Fig. 3.13 shows the comparison of the best-fit first order nucleation model to the experimental data for the four temperatures in both the IB and DoS experiments. Here also, 3-20 % conversion was used to fit the nucleation model in the IB case.\(^{24,27,57}\) This region was changed to 5-40% for the DoS experiment to reduce the effects of statistical noise due to the limited number of data points in the DoS experiment. For all samples, the same trend of increasing crystallization rate (steeper slope) with decreasing temperature is observed. It is clear that there is curvature in the experimental data for IB samples at higher temperature, consistent with the Avrami indices in Fig. 3.12. In contrast, the DoS data is linear in this region.

From Equation 7, the slope of the model line on a semi-logarithmic plot provides an estimate of the nucleation rate between HDPE and GNP. The nucleation rate as a function of the thermal driving force is
plotted in Fig. 3.14. The nucleation rate is related to \( \Delta \sigma \) and \( J_0 \) by Equation 8. \( \Delta \sigma \) is proportional to the slope of the best fit line through this data.

The calculated values for \( \Delta \sigma \) and \( J_0 \) are shown in Fig. 3.15. The IB and DoS experiments exhibit excellent agreement for \( \Delta \sigma \). Averaging \( \Delta \sigma \) over the several GNP loadings gives \( \Delta \sigma = 0.83 \pm 0.18 \) erg/cm\(^2\), or an inefficiency of \( \Delta \sigma/\sigma = 0.087 \) (thermodynamic efficiency \( E = 0.913 \)). The value of \( \Delta \sigma \) would nearly double to 1.55 erg/cm\(^2\) and \( \Delta \sigma/\sigma \) would increase by 50\% using values associated with the higher \( T_m^0 \), for a thermodynamic efficiency \( E \) of 0.869. On the other hand, \( J_0 \) is roughly constant across samples. These results are discussed further in the Discussion section.

Figure 3.13. Examples of first order nucleation model fit to the data for the evolution of the uncrystallized fraction of droplets: (a) IB (solid lines indicate experimental data, dotted lines indicate model), and (b) DoS (points indicate experimental data, lines indicate model).
Figure 3.14. Nucleation rates as a function of temperature for all samples, according to classical nucleation theory.

Figure 3.15. Fitted values of (a) interfacial free energy difference ($\Delta \sigma$) and (b) $J_0$. Error bars denote the 95% confidence interval for the parameter from linear regression. The averaged value for interfacial free energy difference is $\Delta \sigma = 0.83 \pm 0.18$ erg/cm$^2$ (95% confidence interval).

**Discussion**

**Confirmation of Nucleation-Limited Process**

One of the purposes of the droplet method is to create a condition under which crystallization is nucleation-limited. For a crystallization process to be truly nucleation-limited, the induction time to observe a nucleation event ($t_{\text{nucel}} = 1/J$) must be significantly longer than the time for that crystal nucleus to grow to impingement on the edges of the droplet ($t_{\text{grow}} = (d_r/2)/G$). The ratio of $t_{\text{grow}} / t_{\text{nucel}}$ has been named
the “Turnbull number”\textsuperscript{38} and serves as an indicator for whether the crystallization process in an IB sample is growth-dominated (Turnbull number \(\sim 1\)) or nucleation-dominated (Turnbull number \(<< 1\)). From the highest nucleation rates reported in Fig. 3.14 (DoS) and the crystal growth rates of Fig. 3.1, the Turnbull number varies from \(6 \times 10^{-4}\), for a 1 \(\mu\)m domain to \(3 \times 10^{-3}\) for a 5 \(\mu\)m domain. Thus, for the range of domains and droplet sizes employed in this work, the induction time for nucleation is at least an order of magnitude larger than the time for subsequent growth. This is consistent with a nucleation-limited process.

Fenni et al. have discussed the significance of the Avrami index in IB samples in conjunction with the Turnbull number.\textsuperscript{38} In self-nucleated iPP+PS IB samples, the Avrami index was indicative of a change from nucleation-controlled crystallization (\(n = 0.75\) to \(1.5\), Turnbull number \(<< 1\)) to growth-controlled crystallization (\(n = 2\) to \(3.5\), Turnbull number \(\sim 1\)), depending upon the self-nucleation temperature that was chosen. For the present HDPE+GNP IB samples, despite very low Turnbull numbers, Avrami indices between 1.5 and 2 were calculated. Cheng et al.\textsuperscript{46} also found Avrami indices decreased from 2.5 for neat HDPE to between 1.6 and 2.1 upon adding reduced graphene oxide (RGO) to HDPE. They attributed these values to the formation of many nuclei at the HDPE/RGO interface. These nuclei impinge upon each other at a very early stage in crystallization, forming a quasi-2D layer of spherulites, and thus changing the overall dimensionality of growth. However, we observed nucleation rates that were much slower than growth. Finally, in contrast to the IB samples, the Avrami index for the DoS sample was roughly 1, as expected for nucleation-controlled crystallization. Despite this difference, the same interfacial free energy difference, \(\Delta \sigma\), was obtained from both methods, which would be inconsistent with IB samples demonstrating a growth-controlled crystallization process. The origin of the Avrami index \(n > 1\) in Fig. 3.12 must be found elsewhere.

\textbf{Interfacial Free Energy Difference}

From Fig. 3.15, there is excellent agreement in the value of \(\Delta \sigma\) from sample to sample and from one method to the other. Few values of \(\Delta \sigma\) for HDPE heterogeneously nucleated on various substrates have
been reported in the literature. Ishida and Bussi investigated heterogeneous nucleation on ultrahigh modulus HDPE fibers.\textsuperscript{53} Carmeli et al. used IB experiments to measure heterogeneous nucleation of HDPE at the interface with a semicrystalline iPP matrix.\textsuperscript{24} A comparison is made in Table 3.3. For both the PE fiber and iPP, lower values of $\Delta \sigma$ were measured than our value for HDPE+GNP. This is reasonable, as both of these NAs are more similar to HDPE chemically than graphene. In fact, it is remarkable that the reported value of $\Delta \sigma$ for HDPE+iPP is smaller than that for HDPE+PE fiber. In any case, graphene has a very low barrier to nucleation. Also shown in Table 3.3 is a selection of data for other polymer-NA systems, highlighting the lowest values of $\Delta \sigma$ for the NAs that were reported in each case, many of which have lower thermodynamic efficiency values than the HDPE+GNP system in this work. For example, Wang et al. found that several common NAs for iPP yielded $\Delta \sigma/\sigma$ values roughly 2–4 times the value of GNP in this work, yet were sufficient to act as NAs.\textsuperscript{27} Thus, we conclude that graphene is a good nucleating agent for HDPE, a conclusion that has been reported elsewhere based on crystallization half-times, shifts in crystallization temperature, or other indirect methods.\textsuperscript{4,46,47}
Table 3.3. Values of $\Delta \sigma$ for Various Polymer+NA Combinations, and Comparison of their Efficiencies

<table>
<thead>
<tr>
<th>Polymer + Nucleant</th>
<th>$\Delta \sigma$ [erg/cm$^2$]</th>
<th>Thermodynamic Efficiency $E = 1 - \Delta \sigma / \sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE + GNP (this work)</td>
<td>0.826 ± 0.175</td>
<td>0.913</td>
</tr>
<tr>
<td>HDPE + PE fiber 53</td>
<td>0.3</td>
<td>0.969</td>
</tr>
<tr>
<td>HDPE + iPP 24</td>
<td>0.184 - 0.189</td>
<td>0.981 - 0.98</td>
</tr>
<tr>
<td>iPP (α) + (4,6-di-tert-butylphenyl)phosphate 27</td>
<td>4.2</td>
<td>0.635 ($\sigma$ from 61)</td>
</tr>
<tr>
<td>iPP (β) + quinacridone quinone 27</td>
<td>2</td>
<td>0.826 ($\sigma$ from 61)</td>
</tr>
<tr>
<td>Polycaprolactone + PE fiber 62</td>
<td>0.15</td>
<td>0.978 ($\sigma$ from 63)</td>
</tr>
<tr>
<td>Polycaprolactone + impurities 63</td>
<td>1.53</td>
<td>0.775 ($\sigma$ from 63)</td>
</tr>
<tr>
<td>Polybutene-1 + iPP 64</td>
<td>2.04</td>
<td>0.717 ($\sigma$ from 65)</td>
</tr>
<tr>
<td>Polybutene-1 + Polybutene fiber 66</td>
<td>0.31</td>
<td>0.957 ($\sigma$ from 65)</td>
</tr>
<tr>
<td>Poly(butylene succinate) + impurities 63</td>
<td>1.97</td>
<td>0.841 ($\sigma$ from 63)</td>
</tr>
</tbody>
</table>

Effect of Graphene Concentration

The nucleation rates (in events/s) in Fig. 3.14 and Eq. 3.7 do not account explicitly for the interfacial area between HDPE and GNP in each case. However, the inherent nucleation rate (in events/cm$^2$/s) should be independent of GNP loading. By scaling the values for $J_0$ relative to that for the smallest GNP loading (IB-0.5%), we can obtain an estimate of the relative interfacial area between GNP and HDPE, for comparison across all samples. Fig. 3.14 suggests that $J_0$ should be proportional to GNP loading, yet this correlation is not visible in Fig. 3.15b. Because the logarithm of $J_0$ appears in Eq. 3.8, small errors in $\Delta \sigma$ between samples lead to large errors in $J_0$. Thus, for this calculation, the averaged value of $\Delta \sigma$ was used to recalculate $J_0$ for all the samples so that a more consistent comparison could be made. The scaled interfacial areas for each sample are shown in Fig. 3.16 (where IB-0.5% = 1). The scaled areas for the IB-5% samples are 2.3, despite nominally an order of magnitude increase in loading; the scaled area for IB-2% is 1.6, for a nominal increase in loading by a factor of 4. Since the domain sizes are insensitive to loading, the likely explanation is an increase in the number of GNP per domain for the nominally higher
loadings. The lack of a linear relationship between nominal GNP loading and interfacial area is consistent with increased aggregation of the GNPs or exclusion of the larger GNPs from the HDPE domains. In addition, Bartczak et al. have reported the migration of impurities from the minor phase to the major phase in blends of iPP dispersed in PS;\textsuperscript{67} this mechanism has also been noted by Fenni et al as a possible consequence of the melt blending procedure.\textsuperscript{38} Given the similar nature of aromatic groups in graphene and polystyrene, it is another possibility here. In contrast, the scaled interfacial area for the DoS sample is 5.6; this result seems to support either the exclusion or migration hypothesis.

![Graph of interfacial contact area](image)

Figure 3.16. Interfacial contact area, A, scaled by the minimum calculated A value (IB-0.5\%).

**Conclusions**

Droplet methods are an effective way to study stochastic processes like nucleation within a single experiment. Herein, two strategies to measure heterogeneous nucleation in microdomains of HDPE were implemented, the first strategy involving blending of HDPE+GNP within an immiscible polystyrene matrix to create isolated domains (IB), and the second involving spraying of HDPE+GNP dispersions in toluene onto a PS substrate (DoS). To the best of our knowledge, this is the first time heterogeneous nucleation of HDPE by a powdered additive has been quantified using these two methods. In both cases, the effect of GNP on HDPE nucleation was evidenced by an increase in the temperature of crystallization by 40 °C relative to HDPE without GNPs. To study nucleation at isothermal crystallization temperatures,
IB samples were characterized by DSC, and DoS samples by POM. For DSC, reducing the endothermic hook during quenching was critical to measuring nucleation in fast-crystallizing HDPE.

Nucleation rates were calculated for both methods, and the effectiveness of GNP as a nucleating agent for HDPE, as characterized by the difference in interfacial energies, $\Delta \sigma$, was quantified. Excellent agreement between the two methods in the determination of this quantity was found. Finally, the magnitude of $\Delta \sigma$ for HDPE nucleating on GNP was compared to other nucleants for HDPE that have been recently published in the literature. The $\Delta \sigma$ measured in this work for GNP was only slightly larger than for HDPE nucleating at iPP interfaces and at the interface with an HDPE fiber, both of which are nearly ideal nucleants for HDPE. This indicates that GNP is a very effective nucleating agent for HDPE. The thermodynamic efficiency of heterogeneous nucleation, $E$, allows comparison across other polymer-NA systems. The high value calculated here indicates that GNP is an efficient nucleating agent for HDPE when compared to different heterogeneously nucleated polymers.

References


(48) Thomas, L. C. Interpreting Unexpected Events and Transitions in DSC Results. *TA Instruments TA039*.


4. Heterogeneous Nucleation of High-Density Polyethylene Crystals on Binary Hexagonal Nanoplatelets

**Introduction**

In polymers, the kinetics of crystallization is largely responsible for the characteristic semi-crystalline morphology, which in turn imparts many favorable properties to these materials.\(^1\) These kinetics are typically dependent upon the cooling rate and/or temperature at which the polymer is processed, which in turn affect the relative rates of crystal nucleation and crystal growth as well as the number and size of crystallites in a representative volume. Importantly, the nucleation rate and number density of crystal nuclei also depend on the presence of certain foreign impurities or proprietary additives that act as nucleating agents (NAs). Such nucleating agents facilitate the formation of stable polymer crystal nuclei, a process known as heterogeneous nucleation. By stabilizing the formation of small crystal nuclei, NAs reduce the kinetic barrier to nucleation and can increase the rate of nucleation by orders of magnitude compared to homogeneous nucleation.\(^2\)

What constitutes an effective NA, however, is still largely a matter of empiricism.\(^3\) Continuum theories adapted from the nucleation of bubbles and droplets invoke contact angle phenomena based on differences in interfacial energies. On the other hand, molecular theories typically emphasize the roles of epitaxy and grapho-epitaxy. Epitaxy involves the matching of crystal lattice dimensions between the NA and the polymer to maximize favorable interactions,\(^4\)\(^-\)\(^7\) while in grapho-epitaxy, topological features like surface roughness or edges stabilize crystalline fragments of polymer chains through increased numbers of interactions.\(^8\)\(^-\)\(^10\) Recent molecular simulations have shown that not only the commensuration of interactions between polymer crystal and NA are important,\(^11\)\(^,\)\(^12\) but also the surface compliance of the polymer crystal or NA can play a role, allowing the accommodation of mismatches in epitaxy through small crystallographic strain.\(^11\)\(^-\)\(^13\)
Molecular simulations are an excellent tool for investigating polymer nucleation. Simulations allow for the direct observation (in silico) of events that occur on nanoscopic spatiotemporal scales. Epitaxy and crystallographic strain to improve epitaxy can be measured and correlated to the values of force field parameters that are used to describe different materials. For example, Bourque et al. examined heterogeneous nucleation of polyethylene oligomers on monatomic tetrahedrally coordinated (“diamond-like”) and hexagonal lattice (“graphene-like”) materials in precisely this way.\textsuperscript{11,12} Using different values for the 3-body bond angle, both types of materials were modeled using the relatively simple Stillinger-Weber (SW) force field, originally developed for silicon.\textsuperscript{14} The three key parameters in the force field are $\varepsilon$, $\lambda$, and $\sigma$, which control the lattice rigidity and atomic spacing of the simulated NA. Despite the simplicity of the SW force field, realistic material behavior can be reproduced by tuning these parameters.\textsuperscript{14–17} In the work of Bourque et al, these parameters were scanned over ranges of up to $\pm40\%$ relative to certain reference materials (diamond and graphene, respectively), to simulate 150 different materials, some of which were real but many of which were purely hypothetical.\textsuperscript{11,12} From these parametric scans, useful heuristics were extracted and recommendation for further improvements were made.

In particular, among the graphene-like, platelet materials, Bourque et al. predicted that hexagonal boron nitride (hBN) would be an even better NA for high-density polyethylene (HDPE) than graphene (GN),\textsuperscript{12} which is itself well-known to be an excellent NA for PE.\textsuperscript{18–21} Often seen as an alternative to GN, hBN has excellent thermal and oxidative stability\textsuperscript{22} and has been shown to improve the mechanical,\textsuperscript{23,24} thermal,\textsuperscript{23–26} gas barrier,\textsuperscript{27} and electrical properties\textsuperscript{28} of hBN-HDPE nanocomposites over those of the base polymer. Similar improvements have been noted for other polymers as well.\textsuperscript{29–33} Only recently, however, has hBN received attention as a crystallization modifier.\textsuperscript{34,35} Ayoob et al. observed a significant change in the morphology, crystallinity, and crystallization temperature of HDPE when crystallized in the presence of BN, but no epitaxial mechanism was suggested.\textsuperscript{28} Epitaxy has been experimentally observed
with HDPE and reduced graphene oxide. Because there is a close structural similarity between GN and hBN, epitaxy is also likely to be present in hBN-HDPE nanocomposites.

Hexagonal boron nitride has been studied with molecular simulations using a variety of force fields, and also as a nanocomposite with PE. Reactive force fields are generally the most accurate, but also the most computationally expensive. The SW potential presents a computationally simple model that makes long nucleation simulations feasible.

In addition to GN and hBN, two materials that are closely related to the hexagonal lattice but have non-planar bond angles are the transition metal dichalcogenides (TMDs), molybdenum disulfide (MoS$_2$) and tungsten disulfide (WS$_2$). In each monolayer of these TMDs, the transition metal atoms are sandwiched between two layers of sulfur atoms. These structures are contrasted with hBN in Fig. 4.1. Like hBN, TMDs are of interest as additives. Improvements in mechanical, thermal, and electrical properties have been noted for nanocomposites containing MoS$_2$ and WS$_2$, with the potential for novel applications arising from polymer nanocomposites with self-healing and electrical storage capabilities, antibacterial properties, and biodegradability and biocompatibility. Finally, SW parameterizations have already been developed for TMDs and have been used to model nanoplatelets undergoing mechanical processes.
Figure 4.1. Structure of hexagonal boron nitride (a-b) and transition metal dichalcogenides (c-d). (a) and (c) are side views of a single monolayer, and (b) and (d) are top-down views. $a_{BN}$ and $a_{TMD}$ are the unit cell parameters for the crystal lattice, and $d_{ZZ}$ and $d_{AC}$ are the distances between parallel “zigzag” and “armchair” lattice structures, which are present in both types of materials.

Experimentally, the method of immiscible blending (IB) has been found to be particularly powerful for the study of heterogeneous nucleation in polymers. This method is a variation of the original droplet nucleation experiments of Vonnegut. In the IB method, a crystallizable polymer is melt-blended as the minority component with a second, immiscible polymer, resulting in millions of micron-sized domains that serve as independent vessels for the study of nucleation phenomena. The domains are small enough that their complete crystallization is nearly instantaneous once nucleation occurs, but nucleation/crystallization within each domain is completely independent of that in any other domain. The result is an ensemble of nucleation events that result in an exothermic heat flow that can be detected by differential scanning calorimetry (DSC). When an additive is pre-mixed with the crystallizable polymer prior to melt-blending, heterogeneous nucleation can occur. Heterogeneous nucleation of isotactic polypropylene (iPP) in the presence of various additives and melt-blended with polystyrene has been reported. Heterogeneous nucleation has been reported for HDPE melt-blended with both iPP and
polystyrene, as well as when pre-mixed with certain pigments and GN as additives. This method is robust and can be extended easily to other additives, as well as other crystallizable polymers.

In this work, we study the heterogeneous nucleation of semicrystalline HDPE on hBN, MoS₂ and WS₂ both computationally by molecular simulation and experimentally by the method of immiscible blending and DSC. Experimentally, nucleation rates are calculated over a range of crystallization temperatures and NA loading, and the thermodynamic nucleation efficiency for each material is quantified. Computationally, the nucleation rate for each NA is measured, and the effects of epitaxy, lattice rigidity of the NA, and NA – polymer interaction strength are examined. Finally, a comparison between these two methods is made.

**Methods**

**Materials**

All materials were obtained from Millipore-Sigma. High-density polyethylene with a melt flow index of 12g/10min (190 °C, 2.16 kg load) and an as-received density of 0.952 g/mL was used. The majority component for immiscible blending was atactic polystyrene (PS) with a Mₙ = 192 kDa. Hexagonal boron nitride (hBN) nanoplatelets were obtained as a powder with a nominal particle diameter of 137 nm. MoS₂ and WS₂ nanoplatelets were also received in powder form, both with nominal particle diameters of 90 nm.

**Nucleation Rate**

**Molecular Simulation**

n-Pentacontane (C50) is an oligomer of polyethylene and was used as a model for HDPE in molecular simulations of heterogeneous nucleation. C50 was modeled as a chain of united atoms (UA), with each UA representing a CH₂ or CH₃ group. The force field developed by Paul, Yoon, and Smith (PYS) and subsequently modified by Waheed et al. was used for C50. This force field has been shown to reproduce the melting temperature and enthalpy of fusion of n-alkanes, including the melting
temperature of C50. This modified PYS force field was also used previously in studies of the heterogeneous nucleation of C50 on polyethylene, diamond-like and GN-like materials.

For NAs, the Stillinger-Weber (SW) force field was used. The overall potential for the SW force field is given by

\[ E_{SW} = \sum_{i<j} \phi_2(r_{ij}) + \sum_{i \neq j} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}), \]  

where \( i, j, \) and \( k \) index distinct atoms, \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( \theta_{ijk} \) is the bond angle formed by atoms \( i, j, \) and \( k \), and \( \phi_2 \) and \( \phi_3 \) are the two- and three-body interactions, given by

\[ \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{SW,ijk} \varepsilon_{SW,ijk} \cos \theta_{ijk} - \cos \theta_{0,ijk} \] \[ \times \exp \left( \frac{\gamma_{ij}\sigma_{SW,ij}}{r_{ij} - a_{ij}\sigma_{SW,ij}} \right) \exp \left( \frac{\gamma_{ik}\sigma_{SW,ik}}{r_{ik} - a_{ik}\sigma_{SW,ik}} \right). \]  

The parameters that are most relevant to this study are the strength of the two-body interaction (\( \varepsilon_{SW} \)), the strength of the three-body interaction (\( \lambda_{SW} \)), and the atomic spacing (\( \sigma_{SW} \)). In order to compare to previous work with GN-like materials, a new parameterization for hBN was optimized empirically, keeping many of the parameters in the SW potential constant, and only varying \( \varepsilon_{SW}, \lambda_{SW}, \) and \( \sigma_{SW} \). Bourque and Rutledge parameterized the SW force field for GN by optimizing parameter values in order to reproduce experimental elastic constants with molecular simulations. A similar method was followed here for hBN. Details are provided in the Appendix. Due to the complex structure of TMDs relative to planar hBN, a new parameterization for TMDs was not made (see below). Instead, SW parameterizations for single layer TMDs were obtained from the literature. Parameters for MoS\(_2\) were adjusted to reproduce experimental phonon dispersion curves; subsequent calculations of the Young’s modulus were in reasonable agreement with experimental values.
WS₂ to reproduce phonon dispersion curves obtained from ab initio calculations,⁷² and also resulted in simulated values of the Young’s modulus that were in agreement with ab initio calculations.⁷³,⁷⁴ For both of these force fields, the pair_style sw/mod in LAMMPS was used to compute three-body contributions to the force field over proper angle types, as described by Jiang.⁵² For this modification, \( \cos \theta_{ijk} - \cos \theta_{0,ijk} \) in \( \phi_3 \) is defined as \( \delta \), and is scaled by a switching factor \( f_c \), given by

\[
f_c(\delta) = \begin{cases} 
1, & |\delta| < \delta_1 \\
\frac{1}{2} + \frac{1}{2} \cos \left( \frac{\pi}{2} \frac{|\delta| - \delta_1}{\delta_2 - \delta_1} \right), & \delta_1 < |\delta| < \delta_2 \\
0, & |\delta| > \delta_2 
\end{cases}
\]  

where \( \delta_1 = 0.25 \) and \( \delta_2 = 0.35 \) for TMDs. This modification reduces the number of atom types needed to uniquely define all bond angles in TMDs from twelve atom types per sheet to only two atom types per sheet.⁵³

Multi-layered 2D materials were constructed so that NA thickness was larger than the cutoff distance of C50-C50 intermolecular interactions. The interaction between sheets was modeled using a Lennard-Jones (LJ) potential, as was done previously to model multi-layered sheets of GN,¹⁷ given by

\[
E_{LJ} = 4\varepsilon_{LJ} \left[ \left( \frac{\sigma_{LJ}}{r} \right)^{12} - \left( \frac{\sigma_{LJ}}{r} \right)^{6} \right], \quad r < r_{cutoff,LJ}
\]  

(4.5)

Note that \( \sigma_{LJ} \) and \( \varepsilon_{LJ} \) are distinct from \( \sigma_{SW} \) and \( \varepsilon_{SW} \). This potential was applied to both boron and nitrogen atoms in hBN and was optimized empirically as described in the Appendix. However, to avoid extensive modification of the force field for TMDs, the inter-sheet LJ potential was applied only between the metal atoms in TMDs, which is sufficient to maintain the experimentally observed inter-sheet spacing between the midpoints of each sheet. This was done for the sake of simplicity; additional potentials between sulfur atoms would have increased the number of parameters and were not necessary to maintain the correct distance. \( \sigma_{LJ} \) was set to reproduce the experimentally observed inter-sheet spacing, \( d = 2^{1/6} \).
\( \sigma_{\text{LJ}} \).\(^\text{75,76}\) The strength of the inter-sheet interactions, \( \varepsilon_{\text{LJ}} \), is small compared to that controlling the stiffness of the 2D platelet, and small variations in the inter-sheet distance are expected to have little influence on the interface between C50 and the NA substrate, so approximate values were taken from GN\(^\text{17}\) and applied to MoS\(_2\) and WS\(_2\), while the value for hBN was obtained by the force field fitting procedure in the Appendix.

Intermolecular interactions between C50 and the substrates were also modeled with LJ interactions, following Eq. 4.5. LJ parameter values for each substrate atom type were obtained from the Universal force field (UFF),\(^\text{77}\) and Lorentz-Berthelot mixing rules were applied. The same cutoff distance was used for all LJ interactions between UAs in C50 and between UAs and substrate atoms. Tables 4.1 and 4.2 contain the values of all relevant force field parameters.

**Table 4.1. Force Field Parameters for Non-Bonded Lennard-Jones Interaction Potential**

<table>
<thead>
<tr>
<th></th>
<th>C50(^\text{ (a)})</th>
<th>hBN (inter-sheet)</th>
<th>MoS(_2) (inter-sheet)</th>
<th>WS(_2) (inter-sheet)</th>
<th>B(^\text{ (d)})</th>
<th>N(^\text{ (d)})</th>
<th>Mo(^\text{ (d)})</th>
<th>W(^\text{ (d)})</th>
<th>S(^\text{ (d)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{\text{LJ}} ) [Å]</td>
<td>4.01</td>
<td>2.97(^\text{ (b)})</td>
<td>5.48(^\text{ (c)})</td>
<td>5.51(^\text{ (c)})</td>
<td>4.083</td>
<td>3.66</td>
<td>3.052</td>
<td>3.069</td>
<td>4.035</td>
</tr>
<tr>
<td>( \varepsilon_{\text{LJ}} ) [kcal/mol]</td>
<td>0.112</td>
<td>0.1873</td>
<td>0.0955(^\text{ (e)})</td>
<td>0.0955(^\text{ (e)})</td>
<td>0.18</td>
<td>0.069</td>
<td>0.056</td>
<td>0.067</td>
<td>0.274</td>
</tr>
</tbody>
</table>

\( r_{\text{cutoff, LJ}} = 10.025 \text{ Å} \) (a) ref. 66; (b) ref. 75; (c) ref. 76; (d) ref. 77; (e) ref. 17.
Table 4.2. Force Field Parameters for Stillinger-Weber Interaction Potential

<table>
<thead>
<tr>
<th></th>
<th>B-N-B and N-B-N</th>
<th>Mo-S-S (^{(a)})</th>
<th>S-Mo-Mo (^{(a)})</th>
<th>W-S-S (^{(a)})</th>
<th>S-W-W (^{(a)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_{SW})</td>
<td>27.36</td>
<td>67.88</td>
<td>62.45</td>
<td>37.69</td>
<td>33.55</td>
</tr>
<tr>
<td>(\sigma_{SW}) [Å]</td>
<td>1.28</td>
<td>1.252</td>
<td></td>
<td>0.889</td>
<td></td>
</tr>
<tr>
<td>(\varepsilon_{SW}) [kcal/mol]</td>
<td>68.63</td>
<td>23</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>5.8341</td>
<td>6.918</td>
<td>5.664</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.6022</td>
<td>7.223</td>
<td>24.525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p, q</td>
<td>4, 0</td>
<td>4, 0</td>
<td>4, 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\gamma, a)</td>
<td>1.2, 1.8</td>
<td>1, 2.523</td>
<td>1, 3.558</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\theta_0) [°]</td>
<td>120</td>
<td>81.78</td>
<td>81.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) ref. 53, where bond angle interactions have been re-defined to reproduce TMD bond angles.

Sheets of each NA were built using crystal files from the Springer Materials database.\(^{78-80}\) Lateral substrate dimensions were approximately 6.4 x 6.4 nm\(^2\), chosen to be longer than fully extended C50 chains, so that chains would not impinge upon their periodic image when crystallized, but not so large that multiple nuclei could form and frustrate crystal growth, previously noted in a few cases for GN.\(^{12}\) The number of sheets for each NA material was chosen to be thicker than the cutoff distance for C50 interactions: 4 sheets for hBN, 2 sheets for both MoS\(_2\) and WS\(_2\). Three hundred crystalline C50 chains were placed on top of the NA substrates. Periodic boundary conditions were used in all three directions, so that the C50 domain was bounded on either side in the z-direction by the NA substrate. A representative example of the simulation box is shown in Fig. 4.2.
Figure 4.2. Representative simulation box containing C50 (black atoms) bounded by substrate on two sides (blue and white atoms). The simulation box is periodic in all directions.

Simulations were performed in LAMMPS. All simulations were performed in the NPT ensemble at 1 atm, maintained by a Nosé-Hoover thermostat and barostat (damping frequencies: $\omega_T = 1/100 \Delta t$, $\omega_P = 1/1000 \Delta t$, $\Delta t = 3$ fs). The simulation box was periodic in all dimensions, and each dimension was varied independently. Forces were integrated with a rRESPA multi-timescale integrator, with an inner time step of 1.5 fs for bond length, bond angle, and bond dihedral interactions, and an outer time step of 3 fs for LJ and SW interactions.

The equilibrium melting temperature $T_m$ for C50 using the PYS force field is 370°C. Each C50+NA system was first equilibrated at 500 K for 20 ns. A simulation of 10 ns was sufficient to completely melt the starting crystalline configuration for C50, and configurations were saved every 1 ns subsequently, resulting in 10 independent melt configurations for each C50+NA system, based on an estimated Rouse time $\tau_R < 1$ns). Crystallization simulations were then run by quenching each melt configuration to $T_c = 360$ K, for an undercooling $(1-T_c/T_m)$ of 2.7%.

To quantify crystallization, the crystalline growth front was monitored as a function of time, following the methods of Bourque et al. Specifically, UAs were determined to be crystalline or amorphous using the local $p_2$ order parameter given by
\[ p_2(t) = \frac{1}{2} \left( 3 \left( \cos^2 \theta_{ij} \right) - 1 \right), \]

(4.6)

where \( \theta_{ij} \) is the angle between the vectors spanning the midpoints of the bonds to either side of the \( i \)th and \( j \)th atoms, and the average was taken over all UAs within a cutoff distance of \( 2.5 \sigma_{i,j} \) from the \( i \)th UA; UAs with \( p_2 > 0.4 \) were marked as crystalline. The C50 domain was sliced into 0.4 nm thick layers normal to the direction of growth, starting at the interface with the NA substrate and moving outwards into the C50 domain. Layers of this thickness correspond to the thickness of molecular layers within the C50 crystal.\(^8\)

The crystallinity within each layer, \( X(z) \), was calculated as the number of crystalline atoms divided by the total number of atoms within the layer. The location of the crystal growth front, \( D \), was calculated using a Gibbs dividing surface:

\[ \Delta X_{c,int} = \int_{-\infty}^{\infty} [H(z - D) - X(z)]dz = 0, \]

(4.7)

where \( H(z - D) \) is the Heaviside function.

**Experiment**

Following the methods of Santana and Müller,\(^8\) a mixture of HDPE and NA was melt-blended with PS using a twin blade blender (Brabender ATR Plasticorder with 3-piece mixer) under the same conditions as reported previously.\(^2\) Specifically, each NA was mixed with HDPE at three loadings (0.5, 2, 5 wt\%) at 180 °C and 100 rpm for 10 minutes. This mixture (PE+NA) was then melt-blended at 15 wt\% HDPE with PS at 180 °C and 100 rpm for 30 minutes. This final blend (PS/PE+NA) was hot pressed (Carver Model C) at 115 °C (which is above the glass transition temperature, \( T_g \), of PS but below the melting temperature, \( T_m \), of PE) into a sheet roughly 1 mm thick. A 3 mm diameter disc was punched out for thermal analysis with DSC. Each sample was prepared in duplicate.

Samples were analyzed by DSC (TA Instruments DSC 2500) using two procedures: nonisothermal crystallization at constant cooling rate (10 °C/min) from the melt (equilibrated for 2 minutes at 180 °C)
and isothermal crystallization at discrete crystallization temperatures (T_c = 121.5-124 °C at 0.5 °C increments) following a rapid quench from the melt (30 °C/min). A PS sample of similar thermal mass to the test sample was used as the reference in all experiments to reduce the effect of an endothermic hook upon rapid quenching to T_c, as noted elsewhere. The exothermic heat flow of the sample was used to quantify crystallization.

**Results**

**Simulated Nucleation**

Fig. 4.3(a) – (c) shows trajectories of the crystal growth front, D, for each NA, averaged over all replicates. After a short period of slow rearrangement leading to organization of C50 chain segments near the interface (below the dotted line), a stable crystallite forms and subsequently grows at a steady rate. The linear growth regime was extrapolated backwards to z = 0 nm to identify an induction time for nucleation, τ, as shown by the dashed lines in Fig. 4.3(a) – (c). The induction time for each NA is shown in Fig. 4.3d, with the corresponding nucleation rate (1/τ) being shown on the right ordinate axis. The interfacial area between C50 and substrate was the same, ~ 41 nm², for all of the nucleation simulations. From this data, the nucleation rate is highest for hBN (τ = 6.3 ± 0.8 ns), followed by MoS₂ (τ = 14.1 ± 1.6 ns), and lowest for WS₂ (τ = 19.2 ± 1.3 ns).
Figure 4.3. Trajectories of crystal growth front (D) from molecular simulations, averaged over 10
independent starting configurations (2 growth front trajectories per configuration): (a) hBN, (b) MoS$_2$, (c)
WS$_2$; (d) induction times (left ordinate axis) and nucleation rates (right ordinate axis) calculated from
these trajectories (error bars denote one standard deviation). (a – c) Averages (solid lines) are taken over
20 growth front trajectories, and the grey region in each plot denotes one standard deviation from the
average. The dashed lines denote the fit to the linear growth regime, and the dotted lines denote the lower
and upper bounds for fitting of the linear growth regime. The lower bound is limited by subcritical
fluctuations, while the upper bound is limited by impingement with the growth front propagating from the
opposing interface in the simulation. The induction time, $\tau$, is found at the intersection of the fitted line
and the time axis.

Thermodynamically, the interfacial free energy difference, $\Delta \sigma$, is responsible for the decreased free
energy barrier to heterogeneous nucleation relative to homogeneous nucleation. This parameter is of
particular significance for comparing the effectiveness of different NAs, and has been used to define the thermodynamic efficiency of a polymer + NA pair,\textsuperscript{21}

\[
E = 1 - \frac{\Delta\sigma}{\sigma},
\]

(4.8)

where $\sigma$ is analogous to $\Delta\sigma$ for homogeneous nucleation. In this definition, the best NAs yield efficiency values near 1.

From classical nucleation theory,\textsuperscript{83} a nucleus in the shape of a rectangular prism has a free energy, $\Delta G$, given by

\[
\Delta G = -abl\Delta g_v + al\Delta\sigma + 2bl\sigma + 2ab\sigma_e,
\]

(4.9)

where $a$ is the width of the nucleus, $l$ is the length of deposited chain stems, $b$ is the height of the nucleus, $\sigma$ and $\sigma_e$ are the interfacial free energies for the lateral and stem end surfaces of the C50 crystal in contact with the melt, and $\Delta g_v$ is the bulk free energy given by $\Delta g_v = \Delta h_r \Delta T / T_m^0$. $\Delta\sigma$ is more specifically defined as $\sigma_{\text{NA-crystal}} + \sigma_{\text{crystal-melt}} - \sigma_{\text{NA-melt}}$ and is unique to each polymer + NA pair.

Setting derivatives of $\Delta G$ with respect to each dimensional variable to 0 gives the dimensions of the critical nucleus,

\[
b^* = \frac{2\Delta\sigma}{\Delta g_v}, \quad A^* = a^* l^* = \frac{16\sigma_e}{(\Delta g_v)^2},
\]

(4.10)

where $A^*$ is the area of the critical nucleus. $A^*$ can be estimated by the area of the first layer of crystalline C50 UAs at the induction time and should be independent of substrate, according to Eq. 4.10 where $A^*$ is not a function of $\Delta\sigma$. $b^*$ was calculated as the height of a prism of equivalent volume to the actual nucleus observed in simulation (i.e. $b^* = V'/A^*$, where $V'$ is the volume of the critical nucleus). By estimating $b^*$ in this way, $\Delta\sigma$ can be calculated from Eq. 4.10; the results are shown in Fig. 4.4. By this analysis, MoS\textsubscript{2} is the most efficient (lowest $\Delta\sigma$) NA, followed by hBN and WS\textsubscript{2}, which are approximately equivalent.
Figure 4.4. Interfacial free energy difference, $\Delta \sigma$, calculated from critical nucleus sizes measured by molecular dynamics simulations. Data were averaged over 20 trajectories, and error bars denote one standard deviation.

**Experimental Nucleation**

The temperature range of interest for crystallization of HDPE in the presence of NAs was determined using nonisothermal crystallization experiments. The exotherms from DSC are shown in Fig. 4.5. Crystallization was observed to occur around 120 °C for all samples containing NAs. We have previously shown that samples produced using these methods with no added NAs exhibit crystallization peaks near 80 °C, consistent with prior work in the literature.\(^{21,61,84}\) The upward shift of the peak by 40 °C can be attributed to the presence of NAs. Crystallization in this temperature range is also consistent with other crystallization experiments reported for PE+BN and PE+MoS\(_2\) nanocomposites.\(^{28,44}\)

The presence of two high temperature peaks between 110 and 120 °C is noticeable in the DSC traces for almost all of the samples; this behavior was also observed in similar experiments with HDPE micro-domains nucleated in the presence of GN nanoplatelets.\(^{21}\) The lower temperature peak is more prominent in samples with lower loadings of NAs, while the higher temperature peak becomes more prominent as
loading is increased. The more effective nucleation process beginning above 120 °C was selected for in- depth analysis using isothermal crystallization experiments.

Figure 4.5. Crystallization of samples at a constant cooling rate from the melt. Data are organized by NA: hBN (blue), MoS2 (orange), WS2 (green). Percentages after NA type indicate the loading of NA in the sample. Curves have been vertically shifted to allow for comparison.

Isothermal crystallization experiments were run at six crystallization temperatures (Tc). The lower bound of Tc is limited by the onset of rapid crystallization before the sample can be fully cooled to Tc. The upper bound of Tc is limited by crystallization that is too slow to register with the DSC instrument used, without resorting to more exotic methods (e.g. isothermal step crystallization).59,60 The evolution of crystallinity as a function of time is shown in Fig. 4.6 for BN-0.5%, while the data for the remainder of samples are shown in Fig 4.5S1 of the Supplemental Information. Crystallinity was calculated as the cumulative heat flow, Δh(t), scaled by the total enthalpy of crystallization, given by

\[ \chi = \frac{\Delta h(t)}{\int_0^\infty \Delta h(t) \, dt} \]  

(4.11)
Figure 4.6. Evolution of crystallinity at different $T_c$ for sample hBN-0.5%. Each curve is the average of two replicates, and the error bars denote the high and low values of the replicates at evenly spaced intervals.

Avrami Model

The evolution of crystallinity was first analyzed using the Avrami equation:

$$\log(-\log(1 - X)) = \log K + n \log(t - t_0)$$

(4.12)

where $t_0$ is the induction time prior to the onset of crystallization, $K$ is the overall crystallization rate, and $n$ is the Avrami index, consisting of two components, $n = n_G + n_N$. $n_G$ is the dimensionality of growth, and $n_N$ is the dimensionality of nucleation. $n_G$ typically takes values between 0 (no growth) and 3 (growth in 3 independent directions). $n_N$ is often found to be a number between 0 (instantaneous nucleation) and 1 (sporadic nucleation), with 0.5 corresponding to a special case of diffusion-limited nucleation. Non-integer values of $n_N$ are often explained as having a combination of both sporadic and instantaneous nucleation.\(^85\)
Eq. 4.12 was fit to the data for crystallinity versus time in Fig. 4.6 and Fig. 4.S1 for conversions between 0.03 and 0.20. Secondary crystallization effects are insignificant in this region, allowing the most accurate characterization of primary crystallization processes.\cite{86} The fitted Avrami indices $n$ for all samples are shown in Fig. 4.7. Avrami indices between 1 and 2 are observed, with no apparent dependence on $T_c$. While a nucleation-limited process would be expected to exhibit an Avrami index near 1,\cite{58} similar indices of 1 to 2 were reported for experiments with HDPE microdomains nucleated in the presence of GN nanoplatelets.\cite{21}

![Avrami Index](image)

Figure 4.7. Avrami index $n$, obtained from fitting of the DSC data for crystallization vs time to the Avrami equation, Eq. 4.12, in the range $0.03 < X < 0.20$. Data was averaged over both replicates and all $T_c$ for each NA loading. Error bars denote one standard deviation.

**First Order Nucleation Model**

For a nucleation-limited process, the Avrami equation can be approximated as
\[ \log(1 - X) = -f(t - t_0) , \] (4.13)

where \( J \) is the nucleation rate. According to classical nucleation theory,\textsuperscript{83,87} the nucleation rate is a function of \( T_c \), given by

\[ \log(J) = \log(J_0) - \frac{U^*}{R(T_c - T_\infty)} - \frac{16\sigma\sigma_c\Delta\sigma T_m^0}{kT_c(\Delta T\Delta h_f f)^2} , \] (4.14)

where \( J_0 \) is a constant related to the number of potential nucleation sites and is relatively temperature insensitive. In the second term, \( U^* \) is the activation energy for polymer chain reptation in the melt, \( R \) is the universal gas constant, and \( T_c \) is the temperature at which all reptation stops, approximately 30 K below \( T_e \).\textsuperscript{88} In the third term, \( T_m^0 \) is the equilibrium melting temperature for PE, \( k \) is the Boltzmann constant, \( \Delta T = T_m^0 - T_c \) is the degree of undercooling below \( T_m^0 \), and \( \Delta h_f \) is the enthalpy of fusion. \( f \) is a correction factor to account for the temperature dependence of \( \Delta h_f \) at large \( \Delta T \),\textsuperscript{89} given by

\[ f = \frac{2T_c}{T_c + T_m^0} . \] (4.15)

Values reported in the literature for parameters in these equations are shown in Table 4.3.

<table>
<thead>
<tr>
<th>( U^* ) [J/mol]</th>
<th>( T_\infty ) [K]</th>
<th>( T_m^0 ) [K]</th>
<th>( \sigma\sigma_c ) [erg/cm(^4)]</th>
<th>( \sigma ) [erg/cm(^2)]</th>
<th>( \Delta h_f ) [J/cm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6276 (^{(a)})</td>
<td>160 (^{(b)})</td>
<td>416 (^{(b)-(c)})</td>
<td>1380 (^{(b)-(c)})</td>
<td>9.6 (^{(b)})</td>
<td>280 (^{(b)-(c)})</td>
</tr>
</tbody>
</table>

(a) ref. 90; (b) ref. 91; (c) ref. 92; (d) ref. 87; (e) ref. 93.

The nucleation rate as a function of the thermal driving force, as described by Eq. 4.14, is plotted in Fig. 4.8 for all samples. For all NA types, trends observed are in line with expectation: increasing NA loading
increases the nucleation rate, while increasing the temperature decreases the nucleation rate. Comparing between NA types, hBN exhibits the highest nucleation rates, while the nucleation rates for MoS$_2$ and WS$_2$ are roughly the same.

![Graph](image)

Figure 4.8. Nucleation rates according to classical nucleation theory. Symbols denote the average of two replicates at each NA loading, and error bars denote the high and low values; in most cases, the difference is smaller than the size of the symbol itself.

According to nucleation theory, the slope of the line through each of the sets of data in Fig. 4.8 is directly related to $\Delta \sigma$. Because the size of the critical nucleus cannot be measured with the experimental methods here, this analysis provides an alternative to Eq. 4.10 to calculate $\Delta \sigma$. Values for $\Delta \sigma$ and $J_0$ from linear regression on this data are shown in Fig. 4.9. For each NA type, the calculated values for $\Delta \sigma$ agree very well between 2-5% loading, with a small deviation at the lowest loading; averaging over 2-5% loadings,
the $\Delta \sigma$ values are as follows: hBN: $0.943 \pm 0.102$ erg/cm$^2$ ($E = 0.902$), MoS$_2$: $0.811 \pm 0.096$ erg/cm$^2$ ($E = 0.916$), WS$_2$: $0.944 \pm 0.118$ erg/cm$^2$ ($E = 0.902$); for 0.5% loading, the efficiencies are slightly lower: $E_{\text{BN}} = 0.895$, $E_{\text{MoS}_2} = 0.904$, $E_{\text{WS}_2} = 0.901$. Comparing between NA types, MoS$_2$ has the lowest value for $\Delta \sigma$ and thus the highest nucleation efficiency (i.e. lowest barrier to nucleation); however, the difference between NA types is not large enough to be statistically significant. Comparing $J_0$ across NA types, BN $>$ WS$_2$ $>$ MoS$_2$, without any clear trend as a function of NA loading. These results are examined further in the Discussion section.

Figure 4.9. Fitted values of interfacial free energy difference, $\Delta \sigma$ (left axis), and nucleation efficiency, $E$ (right axis, reversed axis); (b) nucleation prefactor, $J_0$. Error bars denote one standard deviation.

**Discussion**

**Simulated Nucleation**

**Effects of Force Field Parameters**

In their simulations of heterogeneous nucleation of C50 on GN-like materials, Bourque and Rutledge found an induction time of $14 \pm 2$ ns for C50+GN for a 50 nm$^2$ substrate.$^{12}$ Compared to the results above, and scaling the induction time for GN on a slightly larger substrate, we find that $\tau_{\text{BN}} < \tau_{\text{MoS}_2} < \tau_{\text{GN}} < \tau_{\text{WS}_2}$. Bourque and Rutledge also identified correlations between induction time and SW force field parameters: $\varepsilon_{\text{SW}}, \lambda_{\text{SW}},$ and $\sigma_{\text{SW}}$. $\varepsilon_{\text{SW}}$ and $\lambda_{\text{SW}}$ describe two- and three- body interaction strengths,
respectively, and $\sigma_{SW}$ describes atomic spacing. Varying these three SW parameters was sufficient to vary uniquely the rigidity of the NA substrate and the degree of epitaxial match to the C50 crystal structure, as all the other parameters in the SW force field were unchanged. However, in the parameterization for TMDs used in this work, other SW parameters were changed in addition to $\varepsilon_{SW}$, $\lambda_{SW}$, and $\sigma_{SW}$. Therefore, to better quantify two- and three-body interaction strengths and atomic spacing between different NAs, parameter combinations that appear in Eq. 4.2 and 4.3 are used here. Specifically, $(A_{SW} \varepsilon_{SW})$ is the prefactor in Eq. 4.2 for two-body interactions, $(\lambda_{SW} \varepsilon_{SW})$ is the prefactor in Eq. 4.3 for three-body interactions, and $(\sigma_{SW} a_{SW})$ is the atomic spacing that appears in the final term of Eq. 4.2.

These alternative definitions are used to compare NAs relative to GN in Fig. 4.10. Relative values are given as $x^* = x_{NA} / x_{GN}$, where $x$ is one of the foregoing force field parameter combinations. In both two- and three-body interactions, the same trend is observed, with GN being the most rigid substrate, followed by hBN, MoS$_2$, and WS$_2$ being the softest. hBN has a similar atomic spacing relative to GN, while both TMDs have larger spacings between atoms in the substrate. According to general trends noted by Bourque and Rutledge, weaker two- and three-body interactions result in increased lattice flexibility that better accommodates mismatches in epitaxy between the NA and C50; however, if these interaction are too weak, the two- and three-body interactions hinder crystallization because thermal fluctuations in the NA substrate become too strong. This compromise is reflected by the simulation results in this work, with a reduced induction time for hBN relative to GN (attributed to flexibility accommodating lattice mismatch) as predicted by Bourque and Rutledge, but a similar or slightly larger induction time for TMDs (attributed to poorer lattice matching and excessively strong thermal fluctuations).
Figure 4.10. Comparison of force field parameters, (a) two-body interaction strength for NAs ($A_{SW} \varepsilon_{SW}$), (b) three-body interaction strength for NAs ($\lambda_{SW} \varepsilon_{SW}$) where three-body interactions for TMDs are defined as in ref. 53, (c) atomic spacing of NAs ($\sigma_{SW} a_{SW}$). Values for each are scaled relative to GN, e.g. ($A_{SW} \varepsilon_{SW}$)$^* = (A_{SW,NA} \varepsilon_{SW,NA}) / (A_{SW,GN} \varepsilon_{SW,GN})$; $A_{SW,GN} = 5.8341$, $\varepsilon_{SW,GN} = 125.42$ kcal/mol, $\lambda_{SW,GN} = 40$, $\sigma_{SW,GN} = 1.28$ Å, $a_{SW,GN} = 1.8$.$^{17}$

A fourth parameter that was examined in the parametric sweep of Bourque and Rutledge was $\varepsilon_{AD}$. $\varepsilon_{AD}$ quantifies the strength of the intermolecular interactions between C50 and the NA using LJ interactions, calculated by $\varepsilon_{AD,X} = (\varepsilon_{L1,C50} \varepsilon_{L1,X})^{0.5}$, where X is an atom in the NA. The combined interaction strength for the NA, $\varepsilon_{AD}$, was averaged over the atoms in the NA according to atomic ratios. A comparison is made in Fig. 4.11a, where we find that $\varepsilon_{AD,GN} < \varepsilon_{AD,BN} < \varepsilon_{AD,MoS2} \sim \varepsilon_{AD,WS2}$. 

98
However, this comparison oversimplifies the energetic landscape between C50 and the NA substrates. The density of atoms is far greater in each hBN sheet as compared with the two TMD sheets due to the smaller atomic spacing in hBN (Fig. 4.10c). Additionally, two hBN sheets are within the LJ cutoff distance of the first layer of C50, while only a single TMD sheet is within this cutoff distance, due to the thicker structure of TMD sheets and the larger distance between sheets (c.f. $\sigma_{\text{LJ}}$ in Table 4.1 for inter-sheet interactions set by experimental inter-sheet spacing). Therefore, the total interaction potential between all NA atoms and C50 UAs, $\Phi_{AD}$, at the distance of the first crystalline layer of C50 was calculated by

$$\Phi_{AD} = \sum_k E_{LJ,k} \bigg|_{r=R_k^c} ,$$

where $E_{LJ,k}$ is the LJ potential given by Eq. 4.5 between the $k$th NA atom and C50, evaluated at the distance between that atom and the first crystalline layer of C50 UAs, $R_k$. $E_{LJ,k}$ is only evaluated for $R_k < r_{\text{cutoff,LJ}}$. This total potential strength was scaled by the interfacial area to obtain an areal density of the energy of interaction between the NA and C50 in the first crystalline layer. The results are shown in Fig. 4.11b, where a stark difference is observed between hBN and the TMDs: hBN > GN > MoS$_2$ ~ WS$_2$. Bourque and Rutledge found that increasing $\epsilon_{AD}$ reduced induction time, with no observed optimum.$^{12}$ This negative correlation is consistent with the induction times observed for the NAs here, where hBN exhibits the strongest NA-C50 interactions and the shortest induction time, while WS$_2$ has the weakest NA-C50 interactions and the longest induction time.
Figure 4.11. Comparison of force field parameters, (a) interaction strength between NA and C50 ($\varepsilon_{AD}$), and (b) areal density of the energy of interaction ($\Phi_{AD}/A$) between NA and C50 at the distance of the first crystalline layer of C50. Values for each are scaled relative to GN, e.g. $\varepsilon_{AD}^* = (\varepsilon_{AD,NA}) / (\varepsilon_{AD,GN})$. In (a), $\varepsilon_{AD}$ are averaged over the atoms in the NA according their atomic ratios, e.g. $\varepsilon_{AD,MoS2} = (\varepsilon_{AD,Mo} + 2\varepsilon_{AD,S}) / 3$. The values for $\varepsilon_{AD}$ and $(\Phi_{AD}/A)^*$ for GN are 0.1034 kcal/mol, and -2.566 kcal/(mol nm$^2$), respectively.

While all three of these NAs have SW parameters that are outside the bounds of the parametric sweeps of ref. $^{12}$, a few inferences can be made based on extrapolated trends from those results. For comparison here, the alternative definitions using combined parameters for atomic spacing and two-body interaction strengths are used as surrogates for $\sigma_{SW}^*$ and $\varepsilon_{SW}^*$ from ref. $^{12}$, respectively. For all three NAs, $\varepsilon_{AD}^* \approx 1.2$ (Fig. 2a in ref. 12) so the induction times of these NAs are compared to those results in Fig. 4.12. While all three NAs fall outside the range of parameter values in ref. 12, some trends can be extrapolated. $^{12}$ For TMDs, these NAs are outside of the convex minimum that was observed in the parametric sweep centered at $\varepsilon_{SW}^* = 0.33$, with an extrapolated $\tau_{TMD} \geq 20$ ns$^{12}$. In contrast, for hBN, $^{12}$ low induction times were observed for $\sigma_{SW}^* = 1$ across the range of values tested for $\varepsilon_{SW}^*$, with an extrapolated $\tau \sim 9$ ns$^{12}$. While based on extrapolation beyond the available data, these extrapolations are in rough quantitative agreement with the induction times calculated for the three NAs tested here.
Figure 4.12. Comparison of SW parameter values for hBN (blue X), MoS2 (orange X), and WS2 (green X) to parametric studies of GN-like NAs with $\varepsilon_{AD}^* = 1.2$ (ref. 12, Fig. 2a). Colored plot reproduced with permission.\textsuperscript{12}

\textit{Epitaxy}

Unlike the case for the experimental measurements, epitaxy is easily quantified by simulation. Hexagonal unit cells have been reported for these NAs, with the following lattice parameters: $a_{BN} = 2.50$ Å,\textsuperscript{78} $a_{MoS2} = 3.16$ Å,\textsuperscript{79} and $a_{WS2} = 3.15$ Å\textsuperscript{80} (c.f. Fig. 4.1). For C50, crystals always form in layers that are spaced about 4 Å apart, which corresponds well to the distance ($a_{C50}/2$) between layers of chains in the pseudo-orthorhombic unit cell of C50 when simulated using the PYS model; thus, the inter-chain spacing within the first layer that is relevant for epitaxy is the unit cell length $b_{C50,PYS} = 4.9$ Å.\textsuperscript{11,12}

Unit cell parameters were measured in simulations using the radial distribution function for NAs (between interfacial B-B atoms in hBN, and between interfacial S-S atoms in TMDs, Fig. 4.13a), and by averaging the distance between the longest C50 stem and its neighbors in a crystal cluster, $b_{C50,obs}$ (Fig. 4.13b). Within simulations, deviations from these reported values were observed for C50, with strain from the equilibrium unit cell being calculated as $\varepsilon_{strain} = (b_{C50,obs} - b_{C50,PYS}) / b_{C50,PYS} \times 100\%$. These strains are
shown in Fig. 4.13c for C50 and NAs, where differing amounts of strain to the C50 unit cell were observed for each C50+NA system, but only minor deviations from the reported values for a_{NA} were observed. For all three NAs, C50 crystallized with a smaller b_{C50} lattice parameter than the equilibrium value from the PYS force field; C50+hBN exhibited the largest strain (\( \varepsilon_{\text{strain}} = -8\% \)), followed by C50+MoS2 and C50+WS2 (\( \varepsilon_{\text{strain}} = -7\% \)).

Figure 4.13. Calculation of unit cell parameters from simulation. (a) The radial distribution function for each NA, averaged over the final 10 timesteps, where a_{NA} is calculated as the first peak in \( g(r) \). (b) Example calculation of b_{C50} from inter-chain distance between the longest crystalline stem and its neighbors in the crystal for a single MD trajectory (blue). The induction time, \( \tau \) (dotted red line) and the average for b_{C50} for \( t > \tau \) (dashed black line) are also shown. Strain, \( \varepsilon_{\text{strain}} \), calculated as deviation of unit cell parameters measured in simulation from the reported values for C50 (PYS, dark grey) and NA (experimental, light grey) crystals.
For these hexagonal NAs, there are two significant crystallographic spacings: the first is that between parallel “zigzag” (ZZ) directions, and the second is that between parallel “armchair” (AC) directions, as shown in Fig. 4.1. The spacing between parallel ZZ segments, $d_{ZZ}$, is given by $0.866 a_{NA}$, while the spacing between parallel AC segments, $d_{AC}$, is given by $a_{NA}$. Epitaxial mismatches are quantified as a percentage using

$$
\Delta = \frac{m_{C50} b_{C50} - m_{NA} d_{NA}}{m_{NA} d_{NA}} \times 100\%
$$

(4.17)

where $d_{NA}$ can be either $d_{ZZ}$ or $d_{AC}$ for a NA.\textsuperscript{5,94,95} Because the unit cells of the NAs are significantly smaller than the inter-chain spacing of C50, supercells of the NAs exhibit the best epitaxial matching with C50. $m_{C50}$ and $m_{NA}$ in Eq. 4.17 are integers corresponding to the number of unit cells required in the supercells to get the best epitaxial matches (smallest $\Delta$) between the crystal lattices of C50 and the NA.

In Fig. 4.14a, the nominal values for $\Delta$ for two supercell combinations ($2d_{NA} : d_{C50}$, and $3d_{NA} : 2d_{C50}$) are shown, calculated by using $b_{C50,VS}$ and the literature values for $a_{NA}$. The range of acceptable epitaxial mismatch is generally considered to be $|\Delta| \leq 15\%$, demarcated by the dashed black lines in Fig. 4.14. For hBN, a 2:1 supercell combination produces the best epitaxial match, while a 3:2 supercell combination is best for both TMDs.

Based on the epitaxial matching predicted from literature values, the AC direction should be favored for all NAs; however, in simulation, neither orientation is strongly favored over the other. The lattice mismatch based on the strained crystals observed in simulation, $\Delta_{\text{strained}}$, is shown in Fig. 4.14b, where the amount of lattice mismatch becomes more balanced between ZZ and AC. Given the nearly equal probability for a crystal to nucleate in the ZZ vs AC directions, satisfying the heuristic of $|\Delta_{\text{strained}}| \leq 15\%$ appears sufficient to yield an epitaxial benefit to nucleation for these NAs. Additionally, even though the lowest $\Delta_{\text{strained}}$ was present for both TMDs, hBN demonstrated lower induction times. In a study of
heterogeneous nucleation of small organic molecules, Chadwick et al. found that matching of surface functionalities between crystalline substrates and acetaminophen was more important in reducing induction time than improved epitaxial matching.\textsuperscript{96} This balance in importance between epitaxy and chemical interactions was also noted by Olmsted and Ward with other small organic crystals.\textsuperscript{97} A similar situation could be occurring here with C50. Therefore, the existence of small epitaxial mismatch between C50 and these NAs allow for fast nucleation, but this metric alone does not allow us to predict which NA would perform best. The other influences such as NA lattice rigidity and the chemical interaction between NA and C50 discussed above are also important.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_14.png}
\caption{Lattice mismatches between NA and C50 crystals: (a) \(\Delta\), the epitaxial mismatch using literature values for \(a_{\text{NA}}\) (experimental) and \(b_{\text{C50,PyS}}\), and (b) \(\Delta_{\text{strained}}\), lattice mismatch using strained unit cells observed in simulation. Lattice matching along the zigzag (ZZ) direction are shown in red, while blue corresponds to the armchair (AC) direction. A 2:1 supercell (2\(d_{\text{NA}} : d_{\text{C50}}\)) is shown for hBN, while a 3:2 supercell (3\(d_{\text{NA}} : 2d_{\text{C50}}\)) is shown for TMDs.}
\end{figure}

\textit{Crystallization at Lower \(T_c\)}

In experiments, \(\Delta\sigma\) was calculated according to Eq. 4.14, where the nucleation rate had been measured at several values of \(T_c\). For simulations, however, upon decreasing \(T_c\) from 360 K to 350 K, rapid nucleation of two or three stable nuclei at each interface was often observed, due to the stronger driving
force for nucleation. Competition between multiple clusters was previously observed in molecular simulations with C50 and GN-like materials at 360 K,\textsuperscript{12} as well as in some of the simulations discussed above (also 360 K). However, in these cases, secondary clusters were short lived, and the induction times calculated from the dominant cluster were not statistically different from simulations where only a single nuclei formed. The persistence of multiple nuclei at lower temperatures here was much longer-lived, and was inconsistent over 10 simulations. Sometimes nuclei resolved into one dominant nucleus rapidly, but often this resolution was delayed in other simulations by up to 20 ns, which was beyond the induction times observed at higher $T_c$ where nucleation is expected to be slower. From this data, an adequate estimation of the induction time at temperatures below 360 K could not be made with the methods of our analysis.

The symmetry of the hexagonal NA surfaces encourages nucleation in six epitaxial directions (three-fold symmetries in both the armchair and zigzag directions). C50 is too short to crystallize with folds, and the lateral dimensions of the substrate are roughly equal to the length of a C50 chain. The rapid formation of multiple stable nuclei with different orientations in this confined area frustrates the formation of a single crystal orientation, and persists for timescales longer than the induction time. As a result, subsequent crystal growth further into the melt was slowed. This phenomenon would also be expected to occur at 360 K for larger substrates, where there is room for a large stable secondary nucleus to form. However, we specifically designed the substrates with these particular dimensions to avoid this complication. This works for 360 K because the area of the critical nucleus is close to the area of the substrate; however at 350 K, the critical nucleus is much smaller, so there is enough room on the substrate for two large nuclei to form. Larger simulations could possibly resolve this issue.

**Experimental Nucleation**

For a nucleation-limited crystallization process, the Avrami index should be near 1, and the Turnbull number, $t_{\text{grow}} / t_{\text{nucl}}$, should be much less than 1.\textsuperscript{58} Here, $t_{\text{nucl}}$ is the characteristic time to nucleate a
crystallite within a micro-domain, \( t_{\text{nucl}} = 1 / J \), and \( t_{\text{grow}} \) is the characteristic time for the resulting crystallite to grow to fill the microdomain, \( t_{\text{grow}} = d / (2G) \), where \( d \) is the nominal size of the NA (c.f. Materials section) and \( G \) is the crystal growth rate of the HDPE resin used in this work.\(^{21}\) As was the case for similar experiments with GN as the NA,\(^{21}\) Avrami indices \( 1 < n < 2 \) were observed for all NAs in this work. However, the Turnbull numbers for these samples range from \( 10^{-5} – 10^{-4} \). This calculation implies that the crystallization process is indeed nucleation-limited. A nucleation-limited nature of the process was confirmed qualitatively using polarized optical microscopy, where induction times on the order of seconds to minutes were observed, but growth appeared instantaneous to the eye (\(<\!< 1 \text{ second})\).\(^{21}\)

Another interesting feature in the DSC data (Fig. 4.5) is the presence of two crystallization peaks observed during non-isothermal crystallization experiments, characterized by a transition in prevalence from a high-temperature peak at the two higher NA loadings (2% and 5%) to a second peak 2-3 °C lower at the lower NA loading (0.5%). The role of other impurities serving as nucleating agents can be eliminated as a possible mechanism because all NAs were received at 99% purity, as confirmed by manufacturer’s certificate of analysis; additionally, the presence of any impurities should always be in the same proportion to the NA, so there should be no difference as NA concentration is decreased. We hypothesize that this bimodal crystallization behavior is a consequence of NA aggregation: as the loading increases, the potential for contact between and aggregation of NA platelets in the samples increases. Lack of perfect register between the particles in such aggregates would lead to edges that promote a grapho-epitaxial nucleation mechanism and crystallization at a higher temperature. In samples with lower NA loadings, this level of aggregation may not be realized in many of the micro-domains, consistent with their having a much smaller high temperature peak; instead, nucleation on the planar surfaces of individual platelets is the predominant mechanism leading to crystallization at a slightly lower temperature. Further evidence for aggregation of NA particles is given by the lack of trends in \( J_0 \) as a function of NA loading (Fig. 4.9b). \( J_0 \) should be positively correlated with NA loading, but this is only weakly observed with WS\(_2\), and not observed for both BN and MoS\(_2\).
This difference in mechanism also may explain the difference in thermodynamic nucleation efficiency, $E$, that is observed between the higher NA loadings (2%, 5%) and the lower NA loading (0.5%). For 2% and 5% loading, the thermodynamic efficiency could be higher due to the grapho-epitaxial mechanism for heterogeneous nucleation, while the thermodynamic efficiency for 0.5% loading could be lower due to a significant percentage of the sample nucleating by a different mechanism, such as the conventional epitaxy that was observed in simulations. Interestingly, WS$_2$ did not exhibit lower $E$ at 0.5% loading than at 2% and 5% loadings, but still shows the two-peak behavior during non-isothermal crystallization.

Compared to other NAs for PE, the NAs studied here perform well ($E = 0.902$ to $0.916$). Using the same HDPE resin with GN nanoplatelets serving as the NA, a comparable value of $E = 0.913$ was reported previously. These values for thermodynamic nucleation efficiency are relatively high, indicating these materials are all effective as NAs for HDPE when compared to many other polymer/NA pairs that have been published in the literature.

**Comparison between Simulations and Experiments**

The nucleation rates observed experimentally are orders of magnitude slower than those calculated *in silico*. This is likely due to the fact that C50 is below the entanglement molecular weight for HDPE and thus has significantly faster dynamics. Nevertheless, qualitatively similar trends should be observed between simulations and experiments. The relative nucleation rates normalized by that previously reported for GN provide a useful comparison, as shown in Fig. 4.15. While agreement in relative nucleation rates is not quantitative, the same qualitative trend of $J_{BN} > J_{MoS2} \geq J_{WS2}$ is observed for both experiments and simulations.
Figure 4.15. Nucleation rates from experiments and simulations, relative to BN. Experimental nucleation rates were calculated as $J_{NA}/J_{BN}$ averaged over all $T_c$.

A comparison can also be made between $\Delta\sigma$ values that were calculated from experiments and those that were estimated from simulations using critical nucleus sizes. The values for $\Delta\sigma$ from simulation are approximately double the values calculated from experiments (Figs. 4.6 and 4.8). The difference could be due to the onset of a grapho-epitaxial mechanism hypothesized to occur in the experiments, whereas flat substrates were used for simulation, or from the limited data that was used to estimate $\Delta\sigma$. While the estimates from simulation are fairly noisy, the same qualitative trend that was observed with experiments is also demonstrated in the simulations: $\Delta\sigma_{\text{MoS}_2} < \Delta\sigma_{\text{BN}} \sim \Delta\sigma_{\text{WS}_2}$. This result provides a measure of confidence in the simulations and their ability to predict accurately the relative nucleation rates and interfacial energies in the real materials.

Despite MoS$_2$ having the smallest critical free energy barrier to nucleation ($\Delta G^* \sim \Delta\sigma$), hBN demonstrates the highest nucleation rates, observed both in experiments and simulations. The kinetic prefactor ($J_0$ in Eq. 4.14, Fig. 4.9b) is related to the concentration of nucleation sites. hBN has a smaller crystal unit cell than both TMDs, providing more sites for nucleation to occur per unit area, as reflected by the larger experimental value of $J_0$. The more dense layer structure of hBN is also suggestive of a higher interaction strength between the polymer and the hBN substrate, which correlates with faster nucleation rates. Since
the free energy barriers are very low and roughly the same across the three NAs, the concentration of nucleation sites and resulting stronger interactions are the significant factors that result in $J_{hBN} > J_{MoS2} \sim J_{WS2}$.

**Conclusions**

The use of molecular dynamics simulations to predict heterogeneous nucleation rates for high-density polyethylene with hexagonal 2D nucleating agents was directly tested against experimental measurements. Despite the simplicity of the force field used, excellent agreement in relative nucleation rates and relative values of the interfacial free energy difference, $\Delta \sigma$, is found, with hBN exhibiting the highest nucleation rate in both simulations and experiments. Simulations provide a detailed view into the mechanisms of heterogeneous nucleation. Strain in the oligomer crystal was found to reduce lattice mismatch, resulting in an increased probability of observing nucleation along either the zigzag or armchair directions of the substrates. Predictions from prior results with GN-like nucleating agents were validated, with a higher nucleating efficiency found for hBN. This improvement in NA performance is attributed to a softer crystal that accommodates small amounts of lattice mismatch without excessive thermal disorder. The strength of interaction between the nucleating agent and the oligomer was found to be a key factor in determining nucleating efficiency, with stronger interactions positively correlating with nucleation rate. With this validation of the predictive capabilities of molecular simulations for polymer nucleation, simulations can be used with higher confidence to examine many other nucleating agents or to design novel nucleating agents.

**Appendix – hBN Force Field Parameterization**

**Method**

The method employed by Bourque and Rutledge to optimize SW and LJ force field parameters to replicate experimental elastic constants was followed here. Specifically, the inter-sheet interaction strength, $\varepsilon_{LJ}$, the intra-sheet two-body interaction strength, $\varepsilon_{SW}$, and the intra-sheet three-body interaction
strength, $\lambda_{SW}$ were optimized. The inter-sheet distance, $\sigma_{LJ}$, and the intra-sheet bond length, $\sigma_{SW}$, were set by the experimental values ($d_{\text{inter-sheet}} = 3.33 \, \text{Å}$, $d_{\text{bond}} = 1.45 \, \text{Å}$, $\sigma = d/2^{1/6}$), and the bond angle, $\theta_0$, was fixed at 120° to replicate the symmetry of the hBN lattice. All other parameters in the SW force field were set at the values used previously for both GN and silicene.

hBN was built as 6 x 6 x 2 repeats of the unit cell structure (4 layers), and periodic boundary conditions were applied to approximate the real NA material. The a- and c-axes of the unit cell were aligned with the Cartesian x- and z-axes, respectively, of the simulation box. The same combination of the SW force field for intra-sheet interactions and LJ for inter-sheet interactions described in the main text was used.

Simulations were performed in LAMMPS. BN was equilibrated from its initial configuration in the NPT ensemble (300 K, 1 atm), maintained by a Nosé-Hoover thermostat and barostat (damping frequencies: $\omega_T = 1/100\Delta t$, $\omega_P = 1/1000\Delta t$, $\Delta t = 2$ fs). The simulation box was periodic in all dimensions, and each dimension could vary side lengths independently. A Verlet time step integrator with a time step of 2 fs was used to integrate the forces.

After equilibration, the simulation box was deformed along the x-, y-, or z- dimension at a constant engineering strain rate ($10^7 \, \text{s}^{-1}$), while the undeformed dimensions were held fixed. Temperature was held constant (300 K) by the thermostat, with velocity contributions due to deformation removed using the “remap x” command. The stress as a function of strain was used to calculate elastic constants over the linear regime at low deformation (0 – 5%). A linear model was fit to the simulated elastic constants, and a new set of parameter values was proposed to reduce the error between simulated elastic constants and their experimental values. This process was iterated several times until simulations reproduced the experimental values. Three independent simulations using the final parameter set were used to characterize the variance.
Results

The stress response as a function of strain for the final parameter set is shown in Fig. 4.A1. The elastic constants were estimated from the slope of the linear regime from 0 – 5% strain. As noted for GN,\textsuperscript{17} armchair and zigzag directions are also present in hBN, and lead to some anisotropy between \( C_{11} \) and \( C_{22} \), and between \( C_{12} \) and \( C_{21} \). Therefore, averaged values were used for comparison to experimental values. A comparison of experimental vs. simulated elastic constants is made in Table 4.A1.

![Figure 4.A1. Stress, \( \sigma \), due to deformation of hBN nanoplatelets as a function of strain, \( e \). (a) Deformation along the x-axis (left axis) and the y-axis (right axis). (b) Deformation along the z-axis.](image)

Table 4.A1. Comparison of elastic constants determined experimentally with those reproduced through simulation using the combined SW-LJ force field

<table>
<thead>
<tr>
<th></th>
<th>Experimental [GPa]</th>
<th>Simulation [GPa]</th>
</tr>
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<tbody>
<tr>
<td>( C_{11} )</td>
<td>750 ( ^{(a)-(c)} )</td>
<td>756 ± 2.5</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>150 ( ^{(a)-(c)} )</td>
<td>150 ± 0.7</td>
</tr>
<tr>
<td>( C_{33} )</td>
<td>32 ± 3 ( ^{(d)} )</td>
<td>31.2 ± 1.1</td>
</tr>
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</table>

(a) ref. 100; (b) ref. 101; (c) ref. 102; (d) ref. 103.

* original values from ref. 100, obtained from refs. 101,102.
Figure 4.S1. Evolution of crystallinity. The curves denote the averages of two replicates, and the error bars denote the high and low values of the replicates at evenly dispersed intervals. (a) hBN-2%, (b) hBN-5%, (c) MoS₂-0.5%, (d) MoS₂-2%, (e) MoS₂-5%, (f) WS₂-0.5%, (g) WS₂-2%, (h) WS₂-5%.
113

References

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5. Conclusions and Recommendations

Significance

This thesis demonstrates an advancement in the way that heterogeneous nucleation is studied in high-density polyethylene (HDPE). A combined approach using both droplet experiments in the laboratory and molecular dynamics (MD) simulations created a more complete view of the nucleation process. In this two pronged approach, heterogeneous nucleation kinetics and thermodynamics were quantified in a robust way.

Experimentally, kinetic and thermodynamic parameters of polymer + nucleating agent (NA) pairings, previously untested with the methods detailed in this thesis, were characterized in the laboratory. After fine-tuning these methods to more accurately capture nucleation kinetics, a new method was also introduced as a novel combination of two other methods reported in the literature. This new method was used to corroborate results obtained by the state of the art method, independently validating the state of the art method for the first time. With MD simulation, three new pairings of n-alkane + NA were tested, paralleling the laboratory experiments. The same kinetic and thermodynamic parameters obtained in the laboratory with real materials were compared for the first time, demonstrating excellent qualitative agreement. In addition to closing this loop between experiments and simulations, a thermodynamic efficiency metric was also defined to allow comparison of NAs between different polymers in a more robust way than prior metrics.

The combined use of simulations and experiments has now been demonstrated to be a successful approach for studying heterogeneous nucleation of PE. This could form the basis for characterizing a wide range of materials in a high-throughput study of heterogeneous NAs for polymers, in line with the Materials Genome Initiative. With this approach, novel NAs can be more rapidly discovered, and intelligent selection from a database of NAs will allow the production of next-generation materials with tailored crystal morphologies and improved macroscopic properties.
Specific Outcomes

The first major outcome of this thesis was the development of three experimental methodologies to study heterogeneous nucleation of HDPE using a variety of NAs, and the second was the first validation of MD predictions of nucleation rates and thermodynamic parameters, which also improved the understanding of molecular mechanisms of heterogeneous nucleation.

Improved Experimental Methods

The first method advanced a pre-existing sample design originally consisting of HDPE micro-droplets upon a polystyrene (PS) substrate. Rather than relying upon substrates that had very poor interactions with HDPE to induce dewetting and thus the formation of micro-droplets, a new procedure was created to study a wide range of materials, including very effective NAs. NAs were carefully prepared as a substrate in the form of a centimeter sized single crystal or a film, isolating a single crystallographic facet to serve as a NA for PE. A suspension of prepared HDPE microcrystals in toluene was sprayed upon this substrate, forming “Droplet on a Substrate” (DoS) sample. Recrystallization from the melt was tracked with polarized optical microscopy. While largely unsuccessful for most NAs that were tested, surface induced nucleation was demonstrated on another substrate (potassium hydrogen phthalate). The issues that limit the applicability of DoS on many substrates were identified: droplets thinning to the point of undetectable birefringence due to wetting, large concentrations of impurities such that only the smallest 1-3 micron droplets were impurity-free, birefringence/reflections from the substrates masking HDPE birefringence, and difficulty in obtaining large enough substrate crystals for testing. These limitations remain unrecognized in the literature for what appears to be such a promising methodology for nucleation research.

The second experimental methodology was also an improvement of prior work. NAs were blended with PE, and then this mixture was melt-blended as the minor component with PS, forming microdroplets of PE+NA in an immiscible PS matrix, named an “Immiscible Blend” (IB). In this thesis, this method was used to study heterogeneous nucleation of powdered additives in HDPE for the first time. This method
should be widely applicable to virtually any NA, unlike DoS, as long as the size of the NA can be reduced to the sub-micron range and is thermally stable over the experimental conditions (room temperature – 180 °C). A major complication in studying HDPE nucleation is the rapid nucleation rates that are usually present, especially for very effective NAs like those studied in Chapters 3-4. A major improvement in this thesis was in the way data was collected from differential scanning calorimetry, allowing for the characterization of the early stages of crystallization where nucleation dominates. This was crucial to obtaining accurate measurements of nucleation rates. Specifically, two-dimensional nanoplatelets were chosen as NAs: graphene, boron nitride, molybdenum disulfide, and tungsten disulfide. The selection of these materials ensured that only a single crystallographic facet was in contact with PE, even when blended with bulk HDPE in the initial preparation of samples. The increased thermal control and larger number of nucleation events per experiment was a significant improvement over the original DoS methodology. This allowed the measurement of heterogeneous nucleation rates over a range of isothermal crystallization temperatures, and thus the calculation of the thermodynamic quantity for interfacial free energy difference, $\Delta\sigma$, was achievable. $\Delta\sigma$ is unique to each polymer + NA pair, and is independent of many other factors that can skew interpretations of nucleation research, such as NA loading and level of dispersion of the NA in the polymer (both which affect nucleation rate). This parameter is also key to calculate a thermodynamic efficiency of a NA, defined in this thesis as the reduction in the free energy barrier relative to homogeneous nucleation. This definition allows for a more robust comparison across polymers for the performance of NAs than previous definitions of efficiency. Such a comparison was made between nine different polymer + NA pairs that have $\Delta\sigma$ values reported in the literature and four of the NAs tested in this thesis. The NAs studied in this thesis performed above a 90 % efficiency, among the best NA that have been characterized in this way. Acceptance and use of this efficiency metric by other researchers is recommended, and would allow for a simple but accurate comparison between polymers and NAs.
The third experimental methodology was a novel combination of the other two methodologies mentioned above. The original DoS methodology was modified to include the crystallization of HDPE microcrystals in the presence of powdered NAs in solution, prior to spraying onto a PS substrate. This sample design is also a two-dimensional version of the IB samples, where PS (matrix in the case of IB, substrate in the case of DoS) serves to keep PE+NA in microdroplet form. The modified DoS methodology was applied as a proof of concept with graphene, and was directly compared against results obtained from IB samples. DoS relies upon polarized optical microscopy to detect nucleation in a more direct way (appearance of crystalline birefringence), while IB indirectly detects nucleation using differential scanning calorimetry (exothermic release of the heat of crystallization). Independent measurements of nucleation rates and $\Delta\sigma$ from both methodologies were used as corroborating evidence to validate the IB methodology that is gaining popularity as a method to study heterogeneous nucleation in polymers, but which had never been validated by alternative methods before.

**Validation of MD Predictions and Deeper Insight into Molecular Mechanisms**

In addition to the experimental methods, the second major outcome was the enhanced insight into heterogeneous nucleation gained from MD simulations. This tool was used to study the nucleation of an oligomer of HDPE in the presence of three of the NAs that were studied experimentally. To accomplish this, a new force field parameterization was developed for boron nitride. Nucleation rates were measured, and $\Delta\sigma$ was estimated from simulations using a direct observation of the critical nucleus size. These results were compared to experimental measurements, and good agreement in relative rates and $\Delta\sigma$’s were found, validating the MD predictions. Additionally, mechanisms such as epitaxy, NA lattice rigidity, and strength of interaction between the NA were examined. While only small amounts of strain were present in the NA crystal lattice, larger strain was observed in the crystallographic lattice of the oligomer; this resulted in a balance of lattice mismatch between the oligomer and the zigzag and armchair directions of the NA crystals, causing nucleation to occur with equal probabilities in both orientations. From earlier parameter sweeps with graphene-like NAs, a compromise was hypothesized to occur with NA lattice
rigidity, where some flexibility could increase the nucleation rate, but large amounts of flexibility would result in excessive thermal disorder that hindered nucleation. While this hypothesis could be applied to boron nitride (some flexibility and fast nucleation) and the disulfides (too much flexibility from excessive thermal disorder), the very low strains observed in the NA crystals do not support this. However, the level of flexibility may be better represented by the magnitude of kinetic fluctuations about an equilibrium lattice spacing, rather than the value of the equilibrium lattice spacing itself; finer time stepping could be used to better sample these fluctuations and test if large fluctuations in the disulfides hinders nucleation relative to boron nitride. The strength of interaction was compared between NAs in a more robust way, and was a significant indicator of nucleation efficiency. The effects of crystallization temperature were also briefly investigated for the first time using this particular methodology. Multiple nuclei formed at disparate orientations and frustrated subsequent crystal growth into the melt. Because the oligomer crystallizes without chain folding, this requires a nucleus to spread laterally until it is appreciably close to the chain length in size before steady-state crystal growth can occur; this is easily satisfied at higher crystallization temperatures as the critical nucleus size is approximately the length of a chain and any smaller embryos quickly melt away, but at lower temperatures smaller embryos can be super-critical nuclei themselves and are much more resistant to melting away. Finally, boron nitride was found to be a more efficient NA than graphene, validating earlier predictions using hypothetical graphene-like NAs. This increases the confidence in the results of the parametric studies, which provided trends across two entire classes of NAs.

**Recommendations**

With the development of these tools demonstrated in a few select cases, it is recommended that these methods be applied in a larger scale study of NAs for HDPE. A high throughput study, implementing both experiments and simulations, would greatly expand the data from which mechanistic insight could be gathered, and the IB and modified DoS methods of this thesis are excellent candidates for this. While sample preparation of IB samples is a little tedious, the millions of nucleation events that are measured
per experiment provide excellent sampling of the induction time distribution. Additionally, the level of thermal control is far greater than with a hot stage on a microscope. However, the modified DoS method also has merit for potential high-throughput studies. Smaller amounts of both HDPE and NAs are needed for each study (thousand-fold reduction), and samples can be made more rapidly. However, only tens to hundreds of nucleation events are measured per experiment, resulting in poorer sampling of the distribution of induction times. The trade-off between these two experiments may depend on the polymer + NA pair(s) for study. Potential NAs that are suggested for further experimental research are in the family of tetrahedrally coordinated crystals, such as diamond-like (e.g. diamond and germanium) and zineblende (e.g. ZnS, GaAs, SiC) crystals. Unary diamond-like NAs have been studied with MD simulations, and experimental results with both unary diamond-like and zineblende NAs could be used to continue the process of validating MD simulation predictions. Other NAs that have been suggested in the literature but whose nucleating efficiencies have not been precisely characterized are also recommended for study to continue building the library of thermodynamic nucleating efficiencies, for example: benzoate, carbonate, and sulfate salts, minerals such as talc or vermiculite, and nanoclays (see Seven et al., 2016).

Other semicrystalline polymers are also recommended for study, particularly with experiments where the switch to a different polymer would minimally change these experimental methods. For example, HDPE was chosen for computational simplicity relative to other polyolefins; however, the design space for NAs for isotactic polypropylene (iPP) is perhaps larger due to the presence of different crystalline polymorphs, and may be of greater commercial interest as iPP crystallizes far slower and benefits more from the influences of NAs. Therefore, high-throughput experiments with other semicrystalline polymers would be a natural extension of this work. As computational performance continues to increase with new technology, obtaining meaningful nucleation rates with MD simulations for other polymers such as iPP may become an achievable reality, and could be used to further supplement the results of these high-throughput studies.
The original DoS method was limited due to the very high affinity for HDPE to nucleate upon any impurities that were present in commercial grade HDPE resins. While purification reduced this issue, only the smallest droplets at the limit of experimental detection were found to nucleate without the influence of impurities. This limited the number of suitable NAs to materials that HDPE did not wet upon to avoid excessive thinning, but these unfavorable interactions are not expected to be typical of the most efficient NAs. This methodology may still hold promise for other polymers that are commercially available as a resin with less impurities, allowing the use of larger droplets that are impurity-free and which do not thin to the extent that crystalline birefringence is no longer detectable. Other polymers may also exhibit a more significant difference in nucleation efficiency between NAs and impurities than was observed with PE. Larger, more easily detected droplets could be used; even if they contain impurities, nucleation would be dominated by the NA substrate. For choosing NAs, because large crystal substrates (on the order of centimeters in diameter) are needed for the original DoS method, minerals (e.g. talc or vermiculite) or large single crystals that are commercially produced (e.g. alkali halides, calcium carbonate) that have been mentioned as possible NAs in the literature are recommended as top candidates for the original DoS methodology.

Additional experimental tools are recommended to develop deeper understanding of nucleation, such as temperature-controlled contact angle measurements and small-angle X-ray scattering (SAXS). Temperature-controlled contact angle measurements could be used to quantify interactions between melted polymers and various NA substrates at temperatures relevant to crystallization. This information could help quantify the energetic interactions between the NA and polymer, separate from epitaxy, and may correlate to nucleating efficiency. SAXS could be used to quantify the level of aggregation of NA particles in IB samples after the NA has been mixed with HDPE, but before melt blending with PS to avoid complications in interpreting the competing signals of NA particle size and HDPE micro-domains. The level of aggregation of NAs in IB samples was not quantified in this thesis, but may account for important contributions to the nucleation rate (the prefactor, $J_0$, in the equation that describes how
nucleation rate is a function of temperature). Additionally, grapho-epitaxy due to aggregation of NAs was hypothesized to be the nucleation mechanism in IB samples with high NA loading in this thesis, while conventional epitaxy was proposed for the samples with the lowest NA loading. Quantifying the level of aggregation of NAs would be significant evidence for or against this hypothesis.

MD simulations are also recommended for further development. While a method to estimate \( \Delta \sigma \) was introduced in this thesis, examining the effects of crystallization temperature on nucleation rate would more closely parallel experimental calculations for \( \Delta \sigma \), and would be a novel for MD simulations of heterogeneous nucleation. For selections of new NAs, in order to parallel experimental studies, force fields beyond Stillinger-Weber may be required to accurately model many of the NAs recommended above. Development of a parametric study with a different force field would greatly expand the predictive power of MD simulations on larger classes of materials.

Further investigation into circumstances where multiple nuclei form in simulations is also recommended. The formation of multiple stable nuclei was observed in simulations for hexagonal lattice NAs (i.e. graphene-like), where multiple orientations with the same lattice spacing exist (three-fold degeneracy), as well as two different spacings (zigzag and armchair) that are often both within the range of acceptable lattice mismatch for epitaxy; however, this was never observed in tetrahedrally coordinated NAs (i.e. diamond-like), where only two orthogonal directions exist and are often so distinct from each other in lattice spacing that only one direction is favored for epitaxy. Multiple nuclei can be observed by decreasing the crystallization temperature for hexagonal NAs, and may occur even for tetrahedral NAs at high undercoolings; multiple nuclei can also be observed by using larger substrate lateral dimensions.

Heterogeneous nucleation in the laboratory with very effective NAs (e.g. graphene, BN, MoS\(_2\), WS\(_2\)) that have spatial dimensions much larger than the critical nucleus size likely crystallize from densely packed nuclei, as observed in this thesis for simulations at low \( T_c \) where the critical nucleus size was appreciably smaller than the lateral dimensions of the NA that were simulated. Better predictions of nucleation rates and thermodynamic parameters are expected if this mechanism is considered, and new insights from
observing crystallization from densely packed nuclei may be obtained that better reflect the actual nucleation processes with these NAs.

A final recommendation is the implementation of an optimization algorithm to more efficiently search for optimal NAs. Prior parametric studies of NAs were searched by hand. Binary zincblende materials are the logical next material class to investigate, where the optimization problem is more complex. In order to solve this problem, a Bayesian optimization algorithm has been created to select parameters to be tested by MD simulations, in order to more efficiently search the parameter space. A sensitivity analysis examining the effects of force field parameters on the induction time has been completed using MD simulations (see Appendix). This initial data can then be fed to the Bayesian optimization algorithm to complete the loop between optimizer and simulations; however this process has not been fully implemented yet. Closing and automating this loop would allow for rapid identification of the most efficient NA agent among this class of materials.
A. Appendix A – Molecular Dynamic Simulations of Binary Zincblende Nucleating Agents for Alkanes

Introduction

The search for nucleating agents (NAs) for polymers has long been based on trial and error. More systematic studies over two classes of materials, tetrahedrally coordinated (diamond-like) and hexagonal lattice (graphene-like) materials were pioneered by Bourque et al. The Stillinger-Weber (SW) force field, originally developed for silicon and commonly used to model semiconductor crystals, was used to model both silicon and graphene. By varying four parameters in this force field (σSW: bond length, εSW: two-body interaction strength, λSW: three-body interaction strength, εAD: NA-polymer interaction strength), 60 diamond-like and 90 graphene-like hypothetical materials were tested as NAs for an oligomer of polyethylene.

A natural progression of this methodology would be to study binary tetrahedrally coordinated materials, belonging to the zincblende (ZB) crystal family. In these materials, the optimum is not yet known, and the dimensionality of the problem is doubled, significantly increasing the complexity of the optimization problem. This motivates the need for algorithms that could search the parameter space more efficiently than a factorial experimental design for parameter screening.

Bayesian optimization (BO) is a promising method to optimize systems that are expensive to evaluate, with the goal of minimizing the number of function evaluations (i.e. simulations to measure an induction time) required to reach the optimum. BO searches the parameter space by balancing function evaluations between improving the accuracy of previously explored regions and exploring new regions of parameter space. In addition to the computational expense for obtaining an induction time for a given set of parameters, induction times are often described by wide distributions, and thus are inherently noisy. Recent developments have improved the way that BO can handle noisy measurements. By using a
noise-augmented acquisition function and batched sampling, the accuracy and robustness against noise were improved. This augmented BO algorithm was tested using the unary tetrahedrally coordinated and hexagonal lattice materials as case studies, where the optimum had previously been found and many function evaluations had already been made. BO was shown to effectively reduce the number of function evaluations needed to find the optimum.

The process of integrating BO with MD simulations is proposed in Fig. A.1. BO will be used to recommend SW force field parameters to be tested, and NAs using these parameter values will be simulated using MD. Induction times will be measured from MD and sent back to BO to be used in selecting the next parameter set. As found by Diwale et al., \(^4\) batched sampling improves the performance of BO. Therefore, BO will propose several parameter sets per iteration, and MD simulations using these parameter sets will be run in parallel.

![Feedback loop integrating Bayesian optimization with MD simulations](image)

Figure A.1. Feedback loop integrating Bayesian optimization with MD simulations

To start this process, initial measurements of induction times are needed to be input into the BO algorithm. Comparing optimal parameters from unary diamond cubic materials \(^1\) to parameters for ZB materials, four realistic crystals are near optimal for some of the parameters: cadmium sulfide (CdS), cadmium selenide (CdSe), zinc sulfide (ZnS), and zinc selenide (ZnSe). For each of these NAs, there are two main three-body interactions of interest: X-Y-X and Y-X-Y, where X is the metallic atom (Cd or Zn) and Y is the non-metal/metalloid (S or Se). For each of these ZB materials, one of its three-body
interactions was very similar to the optimum found for three-body interactions in the unary diamond cubic materials, while the other was significantly different. These materials will form the starting point for investigating binary ZB NAs.

Methods

n-pentacontane (C50) and n-eicosane (C20) were used as model approximations for HDPE in nucleation simulations for nucleation simulations. These alkanes were coarse-grained as united atoms, with each bead representing a CH$_2$ or CH$_3$ group. The Paul, Yoon, and Smith (PYS),$^5$ modified by Waheed et al.$^6,7$ was used to model these alkanes. The modified PYS force field reproduces the melting temperature and enthalpy of fusion of n-alkanes,$^8$ and has also been used previously to study the heterogeneous nucleation of C50,$^{1,2,9}$ and the homogeneous nucleation of C20.$^{10}$

Parameterization of ZnS, ZnSe, CdS, and CdSe in the SW force field have been reported by Zhou et al.$^{11}$ where parameters were optimized to accurately reproduce phase transformations, crystal structures, and experimental cohesive energies, lattice constants, and bulk moduli. Intermolecular interactions between the alkanes and the substrates were modeled with LJ interactions. Parameter values were obtained from the Universal force field (UFF)$^{12}$ for the substrates, and Lorentz-Berthelot mixing rules were applied. The same cutoff distance as LJ alkane-alkane intermolecular interactions was used. Table A.1 contains LJ parameter values for these materials, and the values for SW parameters can be found in Zhou et al.$^{11}$ In particular, the values for three key parameters are compared in Fig. A.2.

<table>
<thead>
<tr>
<th></th>
<th>Alkane (C50 and C20) (a)</th>
<th>Cd (b)</th>
<th>Zn (b)</th>
<th>S (b)</th>
<th>Se (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ$_{LJ}$ [Å]</td>
<td>4.01</td>
<td>2.848</td>
<td>2.763</td>
<td>4.035</td>
<td>4.205</td>
</tr>
<tr>
<td>ε$_{LJ}$ [kcal/mol]</td>
<td>0.112</td>
<td>0.228</td>
<td>0.124</td>
<td>0.274</td>
<td>0.291</td>
</tr>
</tbody>
</table>

$r_{\text{cutoff}} = 10.025$ Å; (a) ref. 5-7; (b) ref. 12.
NA crystals were built in the Avogadro software\textsuperscript{13} using crystal files from the Crystallography Open Database,\textsuperscript{14-17} oriented so that the (110) crystal facet was in contact with the alkane phase. Lateral dimensions were set to be longer than fully crystallized alkane chains to avoid impingement with periodic images (C50: \( \sim 7.5 \times 6.1 \text{ nm}^2 \), C20: \( \sim 4.2 \times 4.8 \text{ nm}^2 \)). The thickness of the substrates were larger than the cutoff distance of alkane interactions (\( \sim 1.2 \text{ nm} \)). 300 crystalline alkane chains were added on top of each of the NA substrates. Periodic boundary conditions were used so that the alkane domain was bounded on either side by the NA substrate. Simulation boxes for C50 and C20 are shown in Fig. A.3.
Figure A.3. Example of simulation boxes for (a) C50 and (b) C20. Alkane chains are shown in blue, metallic substrate atoms in grey, and nonmetallic substrate atoms in yellow.

Simulations were performed in LAMMPS.\textsuperscript{18} All simulations were in the NPT ensemble at 1 atm, maintained by a Nosé-Hoover thermostat and barostat (damping frequencies: $\omega_T = 1/100\Delta t$, $\omega_p = 1/1000\Delta t$, $\Delta t = 5$ fs). The simulation box was periodic in all dimensions, and each dimension could vary side lengths independently. Forces were integrated with a rRESPA multi-timescale integrator, with an inner time step of 2.5 fs for bond length, bond angle, and bond dihedral interactions, and an outer time step of 5 fs for LJ and SW interactions.

Each alkane-NA system was first equilibrated above the melting temperature (C50: 370 K,\textsuperscript{9} C20: 310 K \textsuperscript{10}) at 550 K for 20 ns. The first 10 ns fully amorphized the alkane chains,\textsuperscript{9} with configurations saved every subsequent 1 ns. Crystallization simulations were run by quenching each equilibrated melt configuration to the crystallization temperature (C50: 360 K, C20: 300 K).

Crystallization of individual united atoms was determined by the local $p_2$ order parameter,

$$p_2(t) = \frac{1}{2} \left( 3\cos^2 \theta_{ij} - 1 \right),$$

(A.1)
where $\theta_q$ is the angle between the vectors spanning the midpoints of the bonds to either side of the $i$th and
$j$th atoms, and the average was taken within a cutoff distance of $2.5\sigma_{ij}$; united atoms with $p_2 > 0.4$ were
marked as crystalline. The alkane domain was sliced into 0.4 nm thick layers parallel to the substrate-
alkane interface, starting at this interface and moving outwards into the alkane domain. Layers of this
thickness correspond to the thickness of layers in the C50 crystal. The crystallinity within each layer,
$X(z)$, was calculated as the number of crystalline atoms divided by the total number of atoms within the
layer. The crystal growth front, $D$, was calculated as a Gibbs dividing surface:

$$
\Delta X_{c,\text{int}} = \int_{-\infty}^{\infty} [H(z-D) - X(z)] dz = 0 ,
$$

(A.2)

where $H(z-D)$ is the Heaviside function.

Preliminary Results

$n$-Pentacontane

Based on previous work, C50 was chosen as the first model molecule for polyethylene. The growth front
was calculated using Eq. A.2, and an example trajectory is shown in Fig. A.4. Despite two NA-alkane
interfaces available as nucleating sites, only one nucleation event was observed in this example. This
trajectory has two key regions of growth: initial fluctuations before a critical nucleus is formed, followed
by steady state growth. Following the methods of Bourque et al., extrapolating this linear growth region
to the abscissa gives an estimate of the induction time for nucleation.
Figure A.4. Example crystal growth front trajectories from one simulation. A nucleation event was observed at one interface (interface 1, dark grey curve), but not at the other (interface 2, light grey curve). After subcritical fluctuations (below the dotted red line), the linear steady state growth regime is reached (dashed black line), and the induction time is found at the intersection with the abscissa.

However, when simulating the nucleation of C50 in contact with these NAs, very slow nucleation kinetics were observed (induction times on the order of 150 to >800 ns), drastically slower than the 4 – 90 ns observed with diamond cubic NAs [3]. This result is shown in Fig. A.5, where the hashed bars denote no observed nucleation within the simulated time. One possible explanation is that only one of the three-body interactions for each of these NAs were near the optimum for unary diamond-like materials, while the other three-body interaction was not.
Figure A.5. Induction times measured from simulations with C50 and realistic binary zincblende NAs (four simulations each). Hashed bars indicate simulations where no nucleation event was observed within the duration of the simulation.

**n-Eicosane**

Longer simulations using C50 could be studied to obtain better estimates of induction times for these NAs. From a practical perspective, the Bayesian Optimization scheme should first be tested using systems with much shorter induction times so that the computational cost of induction time sampling is small. To do this, a shorter alkane with more rapid dynamics, C20, was chosen. This change is expected to significantly reduce induction times.

From nucleation simulations with C50, ZnS proved to be the best of the four NAs that were tested. Defining ZnS as the base case, a small parameter sweep was conducted, where NA parameter values were perturbed ± 20% from the values for ZnS. Simulations for each parameter set was repeated four times with different starting configurations. Because the simulation box is composed of C20 molecules sandwiched between two NA surfaces, up to two nucleation events were possible for each simulation. However, the growth rate of C20 crystals is much faster than its nucleation rate. Therefore, in practice, most simulations resulted in only a single nucleation event, since propagation of the resulting crystal spanned the entire simulation box from one C20-NA interface to the other before nucleation could occur at the opposing interface.
The average calculated induction times, \( \tau \), are shown in Fig. A.6 for 31 hypothetical NAs. In five cases, rather than acting as NAs, the substrates melted, indicating parameter sets that did not produce stable crystalline substrates, and thus were not useful as NAs. However, as predicted, due to the faster dynamics of C20, a drastic decrease in the induction time was found (15x increase in the nucleation rate), as well as an additional increase of 7.5x in the computation performance (ns simulated / day). These data can be used as the starting point for the Bayesian optimization algorithm in the future, and the significant improvement in the computational cost of running simulations is an important step in making the optimization – simulation feedback loop feasible in a reasonable timeframe.

![Graphs showing induction times](image)

Figure A.6. Induction times measured from simulations with C20 and hypothetical zincblende NAs perturbed ± 20% from ZnS for each atom in the binary material, (a) \( \sigma_{SW} \), (b) \( \epsilon_{AD} \), (c) combined effects of \( \sigma_{SW} \) and \( \epsilon_{AD} \), and (d) \( \lambda_{SW} \).

For each parameter, the values are referenced to the value for ZnS (e.g. \( x^* = x_{NA} / x_{ZnS} \)), and subscript 1 denotes the metallic atom, while subscript 2 denotes the non-metallic atom. In (a) and (c), \( \tau = 0 \) indicates that the substrate melted.
References


