

Understanding Heterogeneous Nucleation Mechanisms in Polyolefins

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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.

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