LITERATURE REVIEW

In real world applications, most polymers are used in the solid state. Several polymer processing techniques can be use to form an article with desired shape and size. In semi-crystalline polymers, the physical properties of polymeric solid part are influenced by polymer morphology (i.e., percent crystallinity, average crystalline size, and distribution of crystalline size). As this morphology is affected by operating conditions (e.g., temperature, pressure and shear stress) and additives (e.g., nucleating agent), the properties can be controlled to some degree by the processing conditions. Hence, it is important to quantitatively determine the final morphology of the polymeric materials.

Experimental Investigations

Numerous studies on crystallization kinetics and polymer morphology have been investigated using various experimental techniques (Schultz, 2001). Differential scanning calorimetry (DSC) can effectively provide the quantitative information of overall crystallization kinetics. The growth of spherulites can be experimentally observed by the polarized light microscope (PLM) and atomic force microscope (AFM) when cooling from the melt. The polarized light microscope (PLM) and atomic force microscope (AFM) can also provide the quantitative information on a nucleation rate and a growth rate, but only qualitative information on detailed morphology (i.e., average crystallite size and distribution of crystallite size). Therefore, the understanding of morphology-property relationship is largely qualitative (e.g., a polymer with a large crystallite size will be more brittle than a polymer with a small crystallite size). A more quantitative relationship is required, especially from polymer engineer's viewpoint, to better control physical properties of semi-crystalline polymers.

In the experiment, several phenomena occurred simultaneously; the simple mechanisms (e.g., growth rate, variation of growth rates, number of predetermined

nuclei, mode of nucleation, and rate of nucleation) can not be easily separated to examine how each parameter influence crystallization process. In this work, investigation will be performed computationally to help provide more quantitative insight on polymer morphology and also to help examine the effect of each crystallization parameter separately.

In the study of Supaphol (Supaphol *et al.*, 2000), the total concentration of the pre-determined nuclei, the average spherulites diameter and the linear growth rate as a function of crystallization temperature though syndiotactic polypropylene (s-PP) samples were observed using differential scanning calorimetry (DSC) under isothermal conditions at different crystallization temperatures ranging from 30°C to 95°C. Evidently, as the crystallization temperature increases, the total concentration of pre-determined nuclei and the linear growth rate decrease. The average spherulites diameters were found to be increased.

Furthermore, Sapphol (Supaphol *et al.*, 2001) performed an investigation on the overall kinetics of crystallization process under isothermal conditions from both melt and cold-crystallization process of s-PP using DSC. A non-linear multi-variable regression program was used to fit the experimental data obtained from the DSC according to Avrami and Malkin macrokinetic models. The crystallization kinetics parameters specific to each the model was obtained along with the best fits, it found that, for crystallization from the melt state, all of the crystallization rate parameters exhibit a double bell-shaped curve when plotted as a function of crystallization temperature. The two maximums observed at T_c of 30°C and 60°C. In contrast to the case of crystallization from the melt state, the plot of crystallization kinetics parameters for data obtained from the cold crystallization versus crystallization temperature exhibit the typical bell-shaped curve with the maximum at T_c of 58°C. Comparison of the crystallization rate parameters measured from both melt and cold crystallization process indicate that crystallization from the cold state proceed in much faster rate than from the melt state. The researches above are working in the area of polymer crystallization. The set of data with a complete material characterization, including a study of crystallization kinetics in various crystallization temperatures and detail description of the morphology of considered material were presented. This information obtained from these cited literatures have been used in the simulation program developed in this work to validate and investigate effect of crystallization temperature.

Computational Investigations

Recently, there have been a number of researchers studying the crystallization kinetics and polymer morphology in various thermal conditions using the approach. Leephakpreeda (Leephakpreeda, 2001) computational proposed mathematical model for crystallization of semi-crystalline polymer to predict the size of the crystallites under quiescent non-isothermal conditions. The model is based on the assumption that the fronts of the spherulites will grow normally outward with a growth rate given by the local temperature at that moment. The contour of the spherulite can be obtained by connecting the points on the interface for any given time. The results indicated that the cooling rate has a strongly effect on the kinetics of crystallization and the formation of the microstructure. As the cooling rate increases the highest rate of crystallization kinetics during the process occurs at a lower temperature, the numbers of the nuclei per unit area proportionally increase and the spherulites form a fine structure. If the cooling rate is slower, a few form and resulting spherulite become coarser. Therefore, this implies that the average of spherulite size can be influenced by the simultaneous interaction between nucleation and growth, which depend on the cooling conditions.

Raabe (Raabe, 2004) developed a new 3D cellular automaton model with a Monte Carlo simulation for prediction of spherulite growth phenomena in polymers at the mesoscopic scale. The cellular automaton is an algorithm that describes the spatial and temporal evolution of complex systems by applying local switching rules to the discrete cell in a cubic lattice. The cellular automaton approach presented in this work was formulated on the basis of the Hoffman-Lauritzen theory for spherulite growth in

semi-crystalline polymers. It is used to calculate the switching probability of each grid point as a function of its previous state and the state of the neighboring grid points. The actual decision about a switching event is made by evaluating the local switching probability using a Monte Carlo step. The state of non-crystallized cell belong to an amorphous region may change due to the expansion of a crystallizing neighbor spherulite which grows according to the local temperature, Gibbs free energy associated with that transformation, and interface properties. The use of experimental input data of polyethylene allows one to make predictions on a real time and space scale. The simulated spherulite growth kinetics is in good qualitative agreement with experimental data from the literature. For the final distribution of spherulite, it found that the conditions with a very small numbers of nuclei give a large average spherulite size and the conditions with a very large number of predetermined nuclei give a smaller average spherulite size.

Lamberti (Lamberti *et al.*, 2005) studied the light transmission through a crystallizing polymer using graphic simulations, consisting of sporadic and predeterminate nucleation and growth of spherulites in a square lattice. Interaction between a light beams crossing a sample of polymer has been described by a series of simple graphical rules, accounting for both absorption and scattering. When a light beam meets either an amorphous phase or spherulite it is partially absorbed; when a light beam meets an interface between the amorphous phase and a spherulite it is partially scattered. The effect of crystallization parameters (e.g., number of pre-determined nuclei, nucleation rate, and growth rate) on the crystallization kinetics, which are obtained by increasing the growth rate in presence both of constant number of pre-determined nuclei and constant nucleation rate, give rise to faster crystallization process. An increase in the number of pre-determined nuclei, which is obtained either by increasing the number of pre-determined nuclei, which is provide the number of pre-determined nuclei, which is obtained either by increasing the number of pre-determined nuclei, which is obtained either by increasing the number of pre-determined nuclei or by increasing the sporadic nucleation rate, causes faster crystallization process.

Previously proposed models help provide insights on the final morphology, but none investigates the morphological development in details. In this work, develop a Monte Carlo model for providing all detail information on polymer morphological development will be developed using the key crystallization parameters (e.g., a growth rate, a density of nuclei and crystallization temperature). This works will focus in great details on the effect of key crystallization parameters on morphological development during isothermal crystallization of polymer using our proposed model.