CHAPTER II
LITERATURE SURVEY

2.1 Polymer Crystallization

The study of bulk crystallization behavior is important for understanding polymer processing steps and controlling final resulting physical properties and morphologies in semi-crystalline and crystalline polymers. Crystallization process of semi-crystalline polymers can be divided into primary and secondary crystallization. In primary crystallization; there is a primary nucleation and following crystal growth which is the development of crystalline lamellae and forming three-dimensional superstructure. If the crystallization time becomes very long, other types of crystallization (secondary) like crystal perfection and thickening happen to give the ultimate absolute crystallinity.

Nucleation mechanism plays an important role in crystallization either from solutions or melts. Nucleation mechanisms are divided into primary and secondary nucleation. Primary nucleation is the origination of crystalline phase from melt or solution. Secondary nucleation is a surface nucleation on an existing growth plane which causes further growth of the activated nucleus.

In order to understand crystallinity and be able to describe and predict its macroscopic evaluation, some theoretical and empirical mathematical models have been proposed. According to the scope of the kinetics studies, the models are divided into macroscopic and microscopic crystallization models.

2.2 Macroscopic Crystallization Kinetics

2.2.1 Isothermal Macroscopic Crystallization kinetics

In studying isothermal bulk crystallization kinetics of a semi-crystalline polymer, the crystallization exothermic in a DSC is used. It can be assumed that the evolution of crystallinity depends linearly on the evolution of heat

released during crystallization. Therefore, the relative crystallinity as a function of time θ (t) is derived by the following equation (Supaphol, 2001)

$$\theta(t) = \frac{\int_0^t \left[\frac{dHc}{dt}\right] dt}{\int_0^\infty \left[\frac{dHc}{dt}\right] dt}, \quad (1)$$

The limits of integration show the elapsed time during crystallization and at the end of the crystallization process. dH_c is the enthalpy of crystallization released during infinitesimal time interval dt.

There are various macrokinetic models which have been proposed to describe the macroscopic evolution of crystallinity during primarily crystallization under isothermal condition. Some of them are as follows:

The most common model used to describe the overall isothermal crystallization kinetics is the Avrami macrokinetic model that describes steady-state isothermal phase transformation:

$$\theta(t) = 1 - \exp[-k_a t^{n_a}] \quad (2)$$

In this equation, θ is the relative crystallinity as a function of time, k_a is the Avrami crystallization rate constant and n_a is the Avrami exponent of time. k_a and n_a are constant typical of a given crystalline morphology and nucleation at a particular crystallization condition. The amount of n_a is between 1-4. It is also possible to describe the non-isothermal crystallization behavior of a semi-crystalline polymer as well.

Avrami model is just suitable for describing the early stages of crystallization so it can not explain about complications which arise from the growth size impingement and secondary crystallization.

Another theory which was proposed by Tobin is able to explain about phase transformation kinetics with growth site impingement. According to this model, the relative crystallinity function of time θ (t) can be explained in the following:

$$\theta(t) = \frac{(K_t)^{n_t}}{1 + (K_t t)^{n_t}}, \quad (3)$$

K_t and n_t are the Tobin crystallization rate constants and the Tobin exponent n_t is governed by different types of nucleation and growth mechanism.

Malkin macrokinetic model based on the concept that crystallization is an autocatalytic process and the overall crystallization rate equals the summation of the rate at which the degree of crystallinity varies as a result of the primary nuclei and crystal growth. The crystal growth is proportional to the existing crystal surface, while the crystal surface is assumed to be a linear function of crystallinity. In isothermal condition, we have the following equation:

$$\theta(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)}, \quad (4)$$

where θ is the relative crystallinity as a function of time, C_0 relates directly to the ratio of the linear growth rate, G to the nucleation rate, I(C_0 α G/I)and C_1 relates directly to the overall crystallization rate (C_1= a.I+b.G, where a and b are constants). It must be considered that C_0 and C_1 are temperature-dependant constants.

Urbanovici and Segal proposed a new macrokinetic equation, which can be defined as a generalization of the Avrami model. In this proposition, the relation between the relative crystallinity as a function of time $\theta(t)$ and the crystallization time t is:

$$\theta(t) = 1 - [1 + (r-1)(K_{us}t)^{n_{us}}]^{1/(1-r)} \in [0,1] \quad (5)$$

where K_{us} and n_{us} are the Urbanovici-Segal crystallization rate constant, and the Ubranovici-Segal exponent, respectively. r is the parameter which satisfies the condition of r>0. At the condition where $r \to 1$, this model becomes identical to Avrami model. On the other hand, r is the factor which merely determines the deviation from the Avrami model. In addition, the Urbanovici-segal kinetics parameters have similar meanings tc the Avrami kinetic parameters.

2.2.2 Nonisothermal Crystallization Kinetics

In the study of non-isothermal crystallization using DSC, the energy released during the crystallization is a function of temperature rather than time like

isothermal crystallization. The relative crystallinity as a function of temperature θ (t) can be formulated as:

$$\theta(t) = \frac{\int_{T_0}^{T} (dHc/dT)dT}{\Delta Hc}, \quad (6)$$

where T_0 and T represent the onset and an arbitrary temperature, respectively, dH_c is the enthalpy of crystallization released during as infinitesimal temperature range, dT and dH_c is the overall enthalpy of crystallization for a specific cooling condition.
In DSC experiment, it is assumed that the temperature lag between sample and furnace is minimal, the relation between the crystallinity time t and sample temperature T can be formulated as $t= (T_0-T)/\phi$. T_0 is an arbitrary reference melt temperature and ϕ is cooling rate.

The Avrami theory was extended by Ozawa to describe non-isothermal crystallization case by assuming the sample will be cooled from the molten state bye a constant rate, so the time variable in Avrami model replaced by a cooling rate and the relative crystallinity is explained as follows:

$$\theta(T) = 1-\exp(-k_0/\phi^{n_0}), \quad (7)$$

K_0 and n_0 are the Ozawa crystallization rate constant and Ozawa exponent. They are similar to Avrami constants. By plotting ln [ln(1-θ(T)] versus lnθ (T) for a constant temperature, the Ozawa kinetics parameters can be derived from the y-intercept and the slope.

Another important model was developed by Ziabicki which describes polymer crystallization and phase transformation bye a first order kinetic equation:

$$\frac{d\theta(t)}{dt} = K_z(T)\,[1-\theta(t)], \quad (8)$$

where $K_z(T)$ is a temperature dependant crystallization rate function. In nonisothermal case, θ (t) and K_z (T) are dependant on the cooling rate used and may vary. Kinetics shows not only the changes in temperature as a function of time, but also changes of variables such as pressure and stress as a function of time. This model also emphasizes the effect of athermal and transient on the overall

crystallization. Ziabicki showed that the crystallization rate function K_z (T) and be described by a Gaussian function:

$$K_z(T) = K_{z,\max} \exp[-4\ln(2(T_c - T_{\max})^2 / D^2], \quad (9)$$

where T_{max} is the temperature that the crystallization rate has the maximum amount, $K_{z,max}$ is the crystallization rate at T_{max}, and D is the width at half height of the crystallization rate function. If we integrate equation 1 over the whole crystallization range ($T_g<T<T^0_m$), another important index is derived:

$$G_z = \int_{Tg}^{Tom} Kz(t)dT \approx 1.064\, K_{z,\max} D, \quad (10)$$

G_z is the parameter which describes the ability of semicrystalline polymers to crystallize when they are cooled at a unit cooling or heating rate.

In nonisothermal cases, equation 2 can be just applied when K_z (T) is replaced with a temperature derivative of θ (T) which used for each cooling or rate studied. So we will have:

$$G_{z,\phi} = \int_{Tg}^{T_m^0} (d\theta / dT)\phi dT \approx 1.064\, (d\theta/dT)_{\phi,\max} D_\phi, \quad (11)$$

Where $(d\theta/dT)_{\theta,max}$ and D_ϕ are the maximum crystallization rate and the width at half-height of $(d\theta/dT)_\theta$ function. $G_{z,q}$ is the kinetic crystallizability index for an arbitrary θ. G_z can be derived by the normalization of $G_{z,\theta}$ with θ.

One of the most common models is derived by Nakamura et al (1972). They generalized the Avrami macrokinetic model by adopting the isokinetic approximation and assumed that the final crystallinity is independent of the cooling process. The equation comes as the following:

$$\theta(t) = 1 - \exp\left[-\left(\int_0^t K(T)dt\right)^{na}\right], \quad (12)$$

where $K_n(T)$ is the Nakamura rate function that relates to the Avrami rate function $K_a(T)$ and also the crystallization half-time $t_{0.5}^{-1}$:

$$K(T)=[k(T)]^{1/na}=\ln(2)^{1/na}\left[\frac{1}{t_{0.5}}\right], \quad (13)$$

If we assume that temperature is an independent variable, then:

$$\theta\ (T,\phi) = 1 - \exp\left[-\left(\frac{1}{\phi}\int_{T0}^{T} K_n(T)dT\right)^{na}\right], \qquad (14)$$

Where ϕ is the constant cooling rate and T_0 is an arbitrary initial temperature. This equation can be used to predict the evolution of crystallinity as a function of temperature. Also, it can be used to estimate the Avrami kinetics parameters by directly fitting the non-isothermal crystallization measurement to the equation using nonlinear regression method.

2.3 Theories of Microscopic Kinetics Crystallization

In order to understand the whole process of crystallization, the concept of both nucleation and the subsequent crystal growth must be understood.

In the part of completion of the layer by the molecular thickness, there are three practical cases named regime I, II, or III. In regime I, the rate of completion of the layer is so high that the nucleation rate of a new stem cannot occur before the first layer. In regime II, the formation rate of nuclei on the substrate is comparable to the spreading rate of the lateral growing step; and finally in regime III the rate of deposition of the secondary nucleus is high so that nuclei are formed on partly grown strips.

Generally, the growth rate of three regimes can be shown by:

$$G = G_0 \exp\left[-\frac{U^*}{R(T_c - T_\infty)} - \frac{K_g}{T_c(\Delta T)f}\right], \qquad (15)$$

where G_0 is a pre-exponential term which is not dependant on temperature, U* is the activation energy or the transportation of segments across the melt/solid surface boundary and usually has the amount of 1500 cal mol^{-1}, Tc is the crystallization temperature and T_∞ is the temperature on which the molecular motion stops (i.e., $T_\infty = T_g - 30$), R is the universal gas constant and ΔT is the degree of undercooling (i.e., $\Delta t = T^\circ_m - T_c$) and f is a factor used to correct the temperature dependence of the heat of fusion which is near to unity at high temperature (i.e., $f = 2T_c/(T_c + T^\circ_m)$ and Kg is the nucleation exponent which defined as :

$$K_g = \frac{\xi b_0 \sigma \sigma_e T_m^{\ 0}}{k \Delta H_f^0}, \tag{16}$$

where ξ is 2 for regime 2 and 4 is for regime I and III. In equation 3, the exponential term exp [-U*/R (T_c-T_∞)] is related to the diffusion of polymer molecules or segments from the equilibrium melt on to the growth face. The second part, exp (-k_g/T_c (ΔT) f), is related to the formation of the critical nucleus on the growth face and relates to the secondary nucleation.

In each regime the linear growth rate G relates to the secondary nuclcation rate i (G α i^n) , n equals to I in regime I and III and 0.5 in regime II.

To investigate the relationship between G and i, we have the equation:

$$\log G + \frac{U^*}{2.303R(T_c - T_\infty)} = \log G_0 - \frac{Kg}{2.303T_c(\Delta T)f}, \tag{17}$$

From this equation, the regimes can be identified by the plot of log G+U*/2.303R (Tc-T∞) versus 1/2.303Tc (ΔT) f. The slope of the plot equals -K_g and the G_0 of each regime can be calculated from the y-interception of each regime on the plot. Transition in regime I to II is understood when a downward change in slope is observed and an upward change shows the transition from regime II to III.

The factor K_g is very important because it contains the variable ζ which reflects the regime behavior. K_g can be derived by the following equation:

$$K_g = \frac{\xi b_0 \sigma \sigma_e T_m^0}{k \Delta h_f^0} \tag{18}$$

ζ equals 2 for regime II and 4 for regime I and III, b_0 is the crystal layer thickness, σ and σ_e are the lateral and fold surface energy, respectively. T_m^o is the equilibrium melting temperature, k is the Boltzman's constant and Δh_f^o is the equilibrium heat of fusion per unit volume (i.e., $\Delta h_f^o = \Delta H_f^o \times \rho_c$).

The lateral surface energy may be estimate based on the modified Thomas-Stavely equation:

$$\sigma = \alpha \Delta h_f^o \sqrt{a_o b_o} \tag{19}$$

where a_0 and b_0 are the molecular width and molecular layer thickness respectively. Generally, the Thomas-Stavely constant α is usually assumed to be ≈0.1.However,

the α value is not at all universal and strongly dependant on the chemical structure of polymer.

The average work of chain folding $\bar{q}$ has been found to be one parameter most closely correlated with molecular structure, and probably the most important contribution to its relative magnitude is thought to be the inherent stiffness of the chain itself. The average work of chain folding $\bar{q}$ which is defined as:

$$\bar{q} = 2a_0 b_0 \sigma_e \tag{20}$$

2.4 Melting Point Depression

This phenomenon is found when we have a thermodynamic mixing of a crystalline polymer and an amorphous polymer. The depression of melting temperature depends strongly on the composition and cooling rate and this is related to the ability of migration of the segments and the change in the composition. Nishi (1975) proposed an equation to determine the melting point depression for two polymer system:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{RV_{2u}}{\Delta H_{2u} V_{1u}}\right)\chi_{12}(1-v_2)^2 \tag{21}$$

where T^0_m is the equilibrium melting temperature, V_u is the molar volume of the repeating units, χ_{12} is the polymer-polymer interaction parameter, R is the gas constant, and T is the absolute temperature. v_2 is the volume fraction of polymer. In this equation, χ_{12} plays an important role on the melting behavior of the polymer system. We can realize the melting point depression just when χ_{12} is negative. If we assume that $\chi_{12} = BV_{1u}/RT$, we have:

$$\frac{1}{V_1}\left[\frac{1}{T_m} - \frac{1}{T_m^0}\right] = -\frac{BV_{2u}}{\Delta H_{2u}}\frac{V1}{T_m} \tag{22}$$

From the plot of (1/V1) ((1/Tm)-($1/T^0_m$) versus V_1/T_m, the value of χ_{12} can be derived.

2.5 Determination of the Equilibrium Melting Temperature

According to the theory which belongs to Hoffman-Weeks, the equilibrium melting temperature $T_m^{\ o}$ of a semicrystalline polymer can be derived by a linear extrapolation of the observed T_m-T_c data to the line T_m=T_c according to the following equation, the linear Hoffman-Weeks extrapolation (LHW):

$$T_m = \frac{T_c}{2\beta} + T_m^{\ o}\,[1 - \frac{1}{2\beta}] \tag{23}$$

Where β is the thickening ratio which indicates the ration of the thickness of the mature crystal l_c to that of the initial one l_c^*; β is supposed to be greater than or equal to one. The factor 2 shows that the thickness of the crystals undergoing melting is approximately two times more than the initial thickness.

Although some non-linearity in the observed T_m-T_c data can be explained over a wide range of the temperature, Marand et al [] offers a new procedure to determine the $T_m^{\ o}$ value of a semi-crystalline polymer which the observed T_m data was taken from samples crystallized at different temperatures and the same priori lamellar thickening coefficient. This new mathematical derivation states a relationship between the observed melting temperature and the corresponding crystallization temperature. This equation is called the non-linear Hoffman-weeks extrapolation (NLHW) which comes as following:

$$\frac{T^o{}_m}{T_m^o - T_m} = \beta^m \frac{\sigma_e^1}{\sigma_e^{GT}}\left[\frac{T_m^o}{T_m^o - T_c} + \frac{D_2 \Delta H_f^o}{2\sigma_e^1}\right] \tag{24}$$

or in a simple form :

$$M = \beta^m \frac{\sigma_e^1}{\sigma_e^{GT}}[X + a] \tag{25}$$

Where β^m is the thickening coefficient, σ_e^{GT} is the fold surface free energy associated with nuclei of the critical size including the extra lateral surface energy due to fold protrusion and the mixing entropy associated with stems of different lengths (σ_e^{GT} is the basal interfacial energy as appeared in the Gibbs-Thomson

equation), σ_e^1 is the interfacial energy associated with basal plane of the mature crystallite, and D_2 is a constant. Most of the cases, it can be assumed that $\sigma_e^1 \approx \sigma_e^{GT}$.

2.6 Blending

Polymer blends are one of the most interesting issues in polymer field. This is a way to obtain new important properties with no need to synthesis any new one which has proven to be too expensive for various applications. The final properties of polymer blends not only depend on the property of each polymer constituent but also completely depend on the composition and percentage, amount of compatibility and also crystallinity and morphology in crystalline polymers.

In crystallization of blends of two crystallizable components, a homogeneous melt is interesting due to different aspects such as thermodynamic, phase transforming kinetics and resulting crystallinity and structure.

Binary polymer blends are classified into amorphous/amorphous, crystalline/amorphous and crystalline/crystalline systems, based mainly on the crystallizability of the components. When at least one of them is crystallizable, there is a liquid-solid phase separation which makes a wide variety of morphological patterns. Due to the miscibility of the components and their ability to crystallize, there are a variety of supermolecular or phase morphologies. Recently, there are a lot of attentions to polymer blends containing semi-crystalline polymers.

In melt-miscible crystalline/amorphous or crystalline/crystalline blends, crystallization is accompanied by segregation of the amorphous diluents which competes with co-crystallization. Therefore, these blends tend to form several phase structures that vary with the miscibility of the components. In crystalline-amorphous polymer blends, the amorphous polymer chains could be present in interlamellar or intrafibrillar, interfibrillar or intraspherulitic, or interspherulitic regions or some combination between them. When we have crystalline-crystalline polymer blends, separation of two polymers makes further variation in the microstructure obtained. They can coexist in a lamellae (co crystallization) or lamella. This separate lamella can coexist in a fibril or form separate fibrils and consequently fibrils can coexist in a

spherulite or form separate spherulite. The morphological structure is characterized by the distance over which the diluents are segregated and the diluents can expelled into interlamellar, interfibrillar or interspherulitic regions. Different morphology and scales can lead to different properties. In this case, if the two components are crystallizable individually at two different crystallization temperatures (T_c, two-step crystallization), the low T_c component (LTC, T_c^2) can dwell in the interfibrillar and interspherulitic regions of the high T_c component (HTC, T_c^1). The morphology of the resulting blends depends very much on the crystallization kinetics of the two constituents, the mobility, and the composition of the blends. At a critical temperature ($T_c^1=T_c^2$), a strange phenomenon of interpenetrating spherulitic crystallization occurs in which the spherulite of one component can grow inside those of the other.

In the crystallization of blends of two crystallizable components, having a homogenous melt is interesting due to thermodynamic issued, phase transformation kinetics and the resulting crystalline and molecular structure. For thermodynamic reason, the mixed crystallization of polymers is rare. In eutectic crystallization, both components crystallize simultaneously under isothermal conditions and a finely dispersed structure of the crystals of the blend components will be derived. This kind of crystallization is rare because the melting point depression of blends is very small. In step crystallization, the crystallization happens in two stages in which the crystallization behavior and morphology of one component affected by the other. It must be considered that the exact composition in the crystalline phase has not been determined because of the phase segregation that occurs, and the composition may changes depending on the blend composition and crystallization condition.A lot has been done on PHB blends to achieve desired properties and crystallization mechanisms.

2.7 Related Research Works

Recently there have been various publications dedicated to the studies on PHAs with regards to their crystallization, blending and thermal degradation behavior.

Blumm et al (1995) investigated the miscibility, crystallization and characterization of PHB/PLLA. They understood that just low molecular weight PLLA could be miscible in the melt over the whole composition range. They found two types of spherulites which formed during crystallization. In some blends, spherulites of the opposite type interpenetrated when the growth front met with the lamellae when one type of spherulites continued to grow in the interlamellar regions of the other type of the spherulites.

El-Shafaee et al (2001) studied the miscibility, crystallization and morphology of PHB/cellulose acetate butyrate (CAB) blends. They noticed that this blend shows miscibility in all composition range. CAB also decreases the growth rate of PHB spherulites and the nucleation factor. The morphology also changed with CAB presence and the amorphous interlamellar thickness increases with increasing CAB content.

Yoshie et al (2001) studied the cocrystallization and phase segregation of PHB/PHB-HV. They studied the phase structure and spherulite growth of this miscible system and they understood that the extent of phase segregation increases with increasing the amount of PHB-HV. When the amount of HV is low, the system shows complete cocrystallization. By increasing the amount of HV or the crystallization temperature, the PHB-HV content in cocrystallized phase decreased

Chen at al (2002) studied nonisothermal crystallization and melting behavior of PHB/maleated PHB and they showed that, because of the MA group, the crystallization of PHB is hindered. There is different crystallization mechanism which cause by recrystallization during the heating process.

Qiu et al (2003) studied miscibility and crystallization behavior of a biodegradable semicrystalline polyesters, PHB/poly(butylenes succinate).They found out that PHB is immiscible with PBSU .The crystallizatio□

upon quenching from the melt to room temperature, very complicated morphology occurred by the crystallization and segregation of the system simultaneously. They also studied crystallization kinetics and derived growth rate and overall crystallization rate.

Chiu et al (2005) studied PHB/PVA and claimed that this type of blends thickened the PHB crystals. By increasing PVA composition, the segregation is improved. The morphological structure is characterized by interfibrillar segregation. The crystal growth rate played a key role in controlling the segregation of PVA