



## CHAPTER III

### THEORETICAL BACKGROUND

#### 3.1 Quiescent Crystallization

Isothermal bulk crystallization kinetics of semicrystalline polymers is usually studied by following a crystallization exothermic trace in a DSC. This can be carried out based on the assumption that the evolution of crystallinity is linearly proportional to the evolution of heat released during the course of crystallization. Based on this notion, the relative crystallinity as a function of time  $\theta(t)$  can be obtained according to the following equation: (Supaphol, 2001)

$$\theta(t) = \frac{\int_0^t \left( \frac{dH_c}{dt} \right) dt}{\int_0^{\infty} \left( \frac{dH_c}{dt} \right) dt} \in [0, 1] \quad (3.1)$$

where  $t$  and  $t = \infty$  are the elapsed time during the course of crystallization and at the end of crystallization process, respectively, and  $dH_c$  is the enthalpy of crystallization released during and infinitesimal time interval  $dt$ .

In order to quantitatively describe the macroscopic evolution of crystallinity during primarily crystallization under quiescent isothermal conditions, a number of macrokinetic models have been proposed over the past sixty years: they are, for examples, the so called the Avrami, the Tobin, the Malkin, and the Urbanovici-Segal models (Supaphol, 2001). In Avrami model, the relative crystallinity as a function of time  $\theta(t)$  is related to the crystallization time  $t$  according to the equation:

$$\theta(t) = 1 - \exp\left[-(K_a t)^{n_a}\right] \in [0, 1] \quad (3.2)$$

where  $K_a$  and  $n_a$  are the Avrami crystallization rate constant and the Avrami exponent, respectively. Usually, the Avrami rate constant  $K_a$  is written in the form of the composite Avrami rate constant  $k_a$  (i.e.  $k_a = K_a^{n_a}$ ). It was shown that  $k_a$  (the dimension of which is given in  $(\text{time})^{-n}$ ) is not only a function of temperature, but also a function of the Avrami exponent  $n_a$ . As a result, use of  $K_a$  should be more preferable than use of  $k_a$  due partly to the facts that it is dependent of the Avrami exponent  $n_a$  and its dimension is given in  $(\text{time})^{-1}$ . It should be noted that both  $K_a$

and  $n_a$  are constants specific to a given crystalline morphology and type of nucleation for a particular crystallization condition and that based on the original assumptions of the theory, the value of the Avrami exponent  $n_a$  should be an integer ranging from 1 to 4.

Aiming at improving the Avrami equation in describing the experimental data at the later stages of crystallization, Tobin proposed a different expression to describe the kinetics of phase transformation by taking the growth impingement into account. The original theory was written in the form of a nonlinear Volterra integral equation, of which the zero order solution is given by:

$$\theta(t) = \frac{(K_t t)^{n_t}}{1 + (K_t t)^{n_t}} \in [0,1] \quad (3.3)$$

where  $K_t$  is the Tobin rate constant, and  $n_t$  the Tobin exponent. Based on this proposition, the Tobin exponent needs not be integral, and it is mainly governed by different types of nucleation and growth mechanisms. It should be noted that, according to the original applications, the Tobin rate constant is written in the form of the composite Tobin rate constant  $k_t$  (i.e.  $k_t = K_t^{n_t}$ ), which is not only a function of time, but also a function of the Tobin exponent  $n_t$  (similar to the case of  $k_a$  mentioned previously). As a result, use of  $K_t$  should be more preferable than use of  $k_t$  due partly to the facts that it is independent of the Tobin exponent  $n_t$  and its dimension is given in  $(\text{time})^{-1}$ .

Derived based on a postulation that the overall crystallization rate equals the summation of the rate at which the degree of crystallinity varies with the emergence of primary nuclei and the rate of variation in the degree of crystallinity varies with crystal growth rate, we arrived at a totally different kinetic equation:

$$\theta(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)} \in [0,1] \quad (3.4)$$

where  $C_0$  is the Malkin exponent which relates directly to the ratio of the crystal growth rate  $G$  to the primary nucleation rate  $I$  (i.e.  $C_0 \propto G/I$ ), and  $C_1$  is the Malkin crystallization rate constant which relates directly to overall crystallization (i.e.  $C_1 = aG + bI$ , where  $a$  and  $b$  are specific constants). It should be noted that the dimension of the Malkin rate constant is given in  $(\text{time})^{-1}$ .

Recently, Urbanovici and Segal model proposed a new macrokinetic equation, which is essentially 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 written as:

$$\theta(t) = 1 - \left[ 1 + (r-1)(K_{us}t^{n_{us}}) \right]^{1/(1-r)} \in [0, 1] \quad (3.5)$$

where  $K_{us}$  and  $n_{us}$  are the Urbanovici-Segal crystallization rate constant and the Urbanovici-Segal exponent, respectively.  $r$  is the parameter satisfying the condition  $r > 0$ . At the condition where  $r \rightarrow 1$ , the Urbanovici-Segal model becomes identical to the Avrami model. This simply means that parameter  $r$  merely the factor determining the degree of deviation of the Urbanovici-Segal model from the Avrami model. It is worth noting that both  $K_{us}$  and  $n_{us}$  have similar physical meanings to the Avrami kinetics parameters (i.e.  $K_a$  and  $n_a$ ), and the dimension of  $K_{us}$  is also in (time)<sup>-1</sup>.

Actually, the Avrami model has been widely used to describe polymer crystallization kinetics under isothermal condition in the form

$$\theta(t) = 1 - \exp(-k_a t^{n_a}) \quad (3.6)$$

Equation (3.6) does not consider the induction time  $t_0$  for the crystallization process in polymers. An empirical relationship between induction time and crystallization temperature is generally used in the form (Guo and Narh, 2002)

$$t_i = t_m (T_m^0 - T_c)^{-\alpha} \quad (3.7)$$

where  $t_m$  (K <sup>$\alpha$</sup> ) and  $\alpha$  are material constants,  $T_m^0$  is the equilibrium melting temperature,  $T_c$  is the crystallization temperature, and  $t_i$  is the induction time at temperature  $T_c$ .

For non-isothermal conditions, on the basis of isokinetic conditions and the assumption that the number of activated nuclei is constant. Nakamura developed the following equation from the Avrami theory (Guo and Narh, 2002):

$$\theta(t) = 1 - \exp \left[ - \left( \int_0^t K(T) dt \right)^{n_a} \right] \quad (3.8)$$

where  $K(T)$  is the non-isothermal crystallization rate constant. Its relationship to the Avrami isothermal crystallization rate constant  $k$  can be expressed in the form

$$K(T) = [k(T)]^{1/n_b} = \ln(2)^{1/n_b} \left[ \frac{1}{t_{0.5}} \right] \quad (3.9)$$

where  $t_{0.5}$  is the crystallization half-time and  $t_{0.5}^{-1}$  is the overall rate of isothermal quiescent-state crystallization.

In LH secondary nucleation theory (Supaphol 2000), the linear growth rate  $G$  of a crystalline aggregate (e.g. spherulite or axialite) for each regime is independent on the degree of undercooling, and is defined by the following equation:

$$G = G_0 \exp\left(-\frac{U^*}{R(T_c - T_\infty)} - \frac{K_g}{T_c(\Delta T)f}\right) \quad (3.10)$$

where  $G_0$  is a pre-exponential term which is not strongly dependent on temperature,  $U^*$  is the activation energy for the transportation of segments of molecules across the melt/solid surface boundary and is usually given by a universal value of 1500 cal mol<sup>-1</sup>,  $T_c$  is the crystallization temperature,  $T_\infty$  is the temperature where the molecular motion ceases (i.e.  $T_\infty = T_g - 30$ ),  $R$  is the universal gas constant,  $\Delta T$  is the degree of undercooling (i.e.  $\Delta T = T_m^\circ - 30$ ), and  $f$  is a factor used to correct for the temperature dependence of the heat of fusion (i.e.  $f = 2T_c/(T_c + T_m^\circ)$ ) and  $K_g$  is the nucleation exponent, and is defined as:

$$K_g = \frac{\xi b_0 \sigma \sigma_e T_m^\circ}{k \Delta H_f^\circ} \quad (3.11)$$

where  $\xi$  equals 2 for regime II and 4 for regimes I and III,  $b_0$  denotes the crystal layer thickness along the growth direction,  $\sigma$  and  $\sigma_e$  are the lateral and fold surface free energy, respectively,  $T_m^\circ$  is the equilibrium melting temperature,  $k$  is the boltzmann's constant, and  $\Delta H_f^\circ$  is the equilibrium heat of fusion.

Referring to Equation (3.10), the first exponential term,  $\exp(U^*/R(T_c - T_\infty))$ , corresponds to the diffusion of polymer molecules or segment of them from the equilibrium melt onto the growth face. The second exponential term,  $\exp(-K_g/(T_c(\Delta T)f))$ , relates to the formation of the critical nucleus on the growth face.

Intuitively, from the competing contributions of the transport and nucleation terms, one expects that there should be a maximum in growth rate data at a temperature somewhere between the glass transition temperature and the equilibrium melting temperature. Indeed, maximum in the growth rate data as a function of crystallization temperature are usually observed at  $(0.7-0.9)T_m^\circ$ .

As mentioned earlier, in each regime the linear growth rate  $G$  relates directly to the secondary nucleation rate  $i$ :  $G \propto i^n$ , where  $n$  equals 1 in regime I and III, and 0.5 in regime II. Since the second exponential term in Equation (3.9) correspond directly to the secondary nucleation rate, observation of the relationship between  $G$  and  $I$  can be determined by rearranging the logarithmic product of Equation (3.9), which results in the equations:

$$\log G + \frac{U^*}{2.303R(T_c - T_\infty)} = \log G_0 - \frac{K_g}{2.303T_c(\Delta T)f} \quad (3.12)$$

In practice, the test of regime can be done through the plot of  $\log G + U^*/2.303R(T_c - T_\infty)$  versus  $1/2.303T_c(\Delta T)f$ . This type of plot factors out the contribution of the transport term to the growth rate, and the slope equals the negative value of the nucleation exponent (i.e., slope =  $-K_g$ ). According to Equation (3.11), regime I to II transition is evident when a downward change in slope is observed, whereas it is an upward change in slope that is observed in the transition from regime II to III.

It is well accepted that the bulk crystallization rate parameters (e.g.  $t_{0.5}^{-1}$ ,  $K_a$ ,  $K_t$ ,  $C_1$ , and  $K_{us}$ ) relate in one way or another, to the primary nucleation rate  $I$  and/or the subsequent crystal growth rate  $G$  (Supaphol, 2000), the temperature-dependence of the bulk rate parameters can accordingly be quantified and described. Even though the temperature-dependence of the parameters  $I$  and  $G$  are known to have a different temperature-dependence, the bulk crystallization rate parameters have often been taken to have a similar temperature dependence to that of the subsequent crystal growth rate  $G$  (written in the context of the original Lauritzen and Hoffmann secondary nucleation theory (LH theory) (Supaphol, 2000)), which can expressed as:

$$\psi(T) = \psi_0 \exp\left(-\frac{A}{R(T_c - (T_o - C))} - \frac{B}{T_c(\Delta T)f}\right) \quad (3.13)$$

where  $\psi(T)$  and  $\psi_0$  are the respective crystallization rate parameters (i.e.  $t_{0.5}^{-1}$ ) and the respective pre-exponential parameter (i.e.  $(t_{0.5}^{-1})_0$ ), related to the activation energy characterizing the molecular diffusion across the melt/crystal interface, while  $B$  is a parameter related to the secondary nucleation.  $T_g$  is glass transition temperature,  $C$  is the parameter which determines the temperature where the cessation of long range molecular motion is expected (i.e.  $T_g - C$ ) and is often taken to be either ca. 30 K or 50 K below the glass transition temperature,  $R$  is the universal gas constant,  $\Delta T$  is the degree of undercooling (i.e.  $\Delta T = T_m^\circ - T_c$ ), and finally  $f$  is the factor used to correct for the temperature dependence of the heat of fusion (i.e.  $2T_c / (T_c + T_m^\circ)$ ).

By assigning the universal values to  $U^*$  and  $T_g$  as suggested by Hoffmann et al. (Guo and Narh, 2002) there are only two unknown parameters:  $(t_{0.5}^{-1})_0$  and  $K_g$ , which have to be determined experimentally. The non-linear regression method was used to fit the experimental data to Eq.(3.13).

Chan and Isayev (1994) have carried out similar experimental studies using PET as a model material. By fitting Eq. (3.6) with their experimental data, the following constants were obtained:  $t_m = 4.68 \times 10^{12} \text{ K}^a \text{ s}$  and  $a = 6.40$ .

The non-isothermal crystallization process can be considered as a combination of finite steps of isothermal crystallization process. Thus, the non-isothermal crystallization process can be predicted by using parameters from the isothermal crystallization kinetics.

### 3.2 Shear induced Crystallization

All plastic processing operations involve the application of heat and stress, resulting in deformation of the polymer melt, especially at high shear rates. Because of the unique, long chain nature of polymer molecules, deformation of the melt resulted in molecular orientations. This orientation process when acting during crystallization may or may not affect the rate of crystallization and the morphology of the final product (Guo and Narh, 2002)

At the melting temperature, the free energy of the crystals equals the free energy of the melt so that the melting temperature may be written as

$$T_m^\circ = \frac{\Delta H_f}{\Delta S_f} = \frac{H_m - H_c}{S_m - S_c} \quad (3.14)$$

where  $\Delta H_f$  is the heat of fusion,  $\Delta S_f$  is the entropy of fusion,  $H_m$  and  $H_c$  are the enthalpies of the melt and crystalline phases, respectively, and  $S_m$  and  $S_c$  are the entropies of the melt and crystalline phases, respectively.

A polymer melt at rest consists of coiled and entangled molecules, which assume the most random set of conformations that maximize their entropy. The application of shear stress to the melt sample should be resulted in chain orientation of the polymer molecular chains. It is known that an oriented polymer molecule has fewer possible conformations than that of a coiled one and, therefore, has a lower entropy. For an oriented melt, the decrease in entropy may be considered to increase the melting temperature and the degree of undercooling. This idea was first proposed by Flory (Guo and Narh, 2002) and was applied to the thermodynamics of a cross-linked system subjected to a tensile force by considering a model of axially oriented crystalline regions coexisting with an amorphous zone.

By assuming that the free energy of the crystalline phase is independent of the applied strain, and that the deformation energy follows Hooke's law. Haas and Maxwell (Guo and Narh, 2002) arrived at the following expression for the increased melting point for a stressed polymer melt:

$$T_m = \frac{T_m^\circ}{\Delta H_f} \left[ \frac{\tau^2}{2G} \right] + T_m^\circ \quad (3.15)$$

where  $T_m$  is the melting temperature under shear stress,  $G$  is the elastic shear modulus of the polymer, and  $\tau$  is the elastic shear stress.

The first term on the right side of Eq. (3.14) can be thought of as the increase in melting temperature that is,

$$T_{\text{shift}} = \frac{T_m^\circ}{\Delta H_f} \left[ \frac{\tau^2}{2G} \right] \quad (3.16)$$

Equation (3.16) is based on the assumption that shear modulus is independent of the applied shear stress. However, the relationship between the shear modulus and shear stress is very complicated. Therefore, the melting temperature shift may not necessarily follow Equation (3.16).

At low shear stress, the polymer molecules do not receive enough energy for their chains to extend. Hence, there is usually a critical stress or shear rate associated with the coil-stretch transition for the orientational of the molecular chains. The effect of shear stress on the crystallization process becomes prominent only when the stress exceeds a critical value (Patel and Spruiell, 1991). However, in the extremely high stress range, when the molecules are fully extended, any further increase in shear stress will not cause further orientation of polymer molecules. The effect of stress on the crystallization process in the high stress range should thus tend to a constant value. Based on these analyzed, a phenomenological relationship between the equilibrium melting temperature shift and the shear stress  $\tau$ , in the form

$$T_{\text{shift}} = C_1 e^{\frac{C_2}{\tau}} \quad (3.17)$$

where  $C_1$  and  $C_2$  are material constants that can be determined directly from the experimental data.

If it is assumed that the effect of stress on the kinetics of crystallization is only by increasing the melting temperature, i.e. by increasing the degree of undercooling, then by replacing  $T_m^\circ$  in Eq. (3.12) with  $T_m$

$$T_m = T_m^\circ + T_{\text{shift}} \quad (3.18)$$

and therefore

$$f = \frac{2T}{T + T_m} \quad (3.19)$$

We can arrive at a simplified stress-induced crystallization model. The effect of shear stress on the induction time can also be obtained by replacing the equilibrium melting temperature in Eq. (3.7) with  $T_m$ :

$$t_i(T, \tau) = t_m (T_m - T)^{-a} \quad (3.20)$$

Since it is very difficult to follow the stress-induced crystallization process experimentally, efforts to investigate the effect of stress on the kinetics of crystallization have been scarce. By assuming that shear stress affects only the melting temperature of the polymer, the parameters needed to be determined in the stress-induced crystallization kinetics model are kept to a minimum. Consequently, it is possible to model stress-induced crystallization with available experimental methods.



A rotational viscometer is a common device used to study flow-induced crystallization in polymers. In the rotational viscometer with cone and plate geometry, constant shear gradient is applied to the melt at constant temperatures by the relative rotation of two plates. A sudden rise in the shear stress or viscosity with time was interpreted as the onset of crystallization. Rearranging Eq. (3.20)

$$T_m = T_c + \left[ \frac{t_m}{t_i} \right]^{1/a} \quad (3.21)$$

So the final result, the equilibrium melting temperature shift  $T_{\text{shift}}$  can be readily expressed as

$$T_{\text{shift}} = T_m - T_m^\circ = T_c + \left[ \frac{t_m}{t_i} \right]^{1/a} - T_m^\circ \quad (3.22)$$

Taking into account the effects of temperature lag between the sample and the differential scanning calorimetry (DSC) furnace and non-isothermal induction times which are obtained from isothermal induction times, Chan and Isayev (1994) analyzed the non-isothermal crystallization data for poly(ethylene terephthalate) (PET) over a range of cooling rates from 2 to 40°C/min using the differential form of the Nakamura equation.

$$\frac{d\theta}{dt} = nK(T)(1-\theta) [-\ln(1-\theta)]^{(n-1)/n} \quad (3.23)$$

$$K(T) = k(T)^{1/n} = (\ln 2)^{1/n} (1/t_{0.5}) \quad (3.24)$$

$$(1/t_{0.5}) = (1/t_{0.5})_0 \exp\left(\frac{-U^*}{R(T_c - T_\infty)}\right) \exp\left(\frac{-K_g}{T_c \Delta T f}\right) \quad (3.25)$$

where  $T_c$  is the crystallization temperature;  $t_{0.5}$  the time taken for half of the crystallization develop;  $(1/t_{0.5})_0$ , a pre-exponential factor that include all terms independent of temperature;  $R$ , the universal gas constant;  $\Delta T = T_m^\circ - T_c$ , degree of undercooling;  $T_m^\circ$ , the equilibrium melting temperature;  $f = 2T/(T + T_m^\circ)$ , a correction factor accounting for the reduction in the latent heat of fusion as the temperature is decreased;  $T_\infty = T_g - 30$  K, the temperature below which transport ceases;  $T_g$ , the glass transition temperature;  $U^*$ , the activation energy for segmental jump rate in polymer; and  $K_g$ , the nucleation exponent.

They calculated the relative crystallinity developed during non-isothermal crystallization under various constant cooling and heating rates with and without the inclusion of induction time. The results with the incorporation of induction time show generally good agreement between the experimental data and the model predictions.

Patel and Spruiell (1991) presented an analysis of available method of dealing with polymer crystallization for process modeling. Problems encountered in using isothermal data to predict non-isothermal results are discussed and illustrated using non-isothermal experimental data for nylon 6 collected over a range of cooling rates from 2 to 40°Cmin<sup>-1</sup>. It was concluded that none of available models is entirely satisfactory in predicting non-isothermal based on isothermal data. These authors used a non-linear regression method to fit their non-isothermal crystallization data using a simplified differential Nakamura model. By letting  $Y = \ln(1/(1-\theta))$ , the non-isothermal crystallization rate equation was written as follows:

$$\frac{dY}{dt} = nK(T)(Y)^{(n-1)/n} \quad (3.26)$$

$$K(T) = k(T)^{1/n} = C_1 \exp\left[\frac{-U^*}{R(T_c - T_\infty)}\right] \exp\left[\frac{-C_2}{T_c \Delta T f}\right] \quad (3.27)$$

$$C_1 = (\ln 2)^{1/n} (1/t_{0.5})_0 \quad (3.28)$$

where  $C_1$  and  $C_2$  are the parameters of the crystallization rate equation. Keeping  $n = 2$  ( $n$  is Avrami exponent), the non-isothermal data was fitted with various pairs of values of  $C_1$  and  $C_2$  (parameters of the model). For constant values of  $C_2$ , the data for each cooling rate was fitted individually to obtain the  $C_1$  value. Different values for  $C_1$  were obtained for different cooling rate. Using the average value of  $C_1$ , predictions according to the simplified differential Nakamura model were found to match the experimental data