



CHAPTER II

LITERATURE REVIEW

The crystallization of polymers can be broadly classified into three categories, which are (1) *crystallization during polymerization*, (2) *crystallization induced by orientation*, and (3) *crystallization under quiescent condition*. Only the third one, which is the crystallization with no external forces acting to the system during the crystallization process, was interested in this research work.

Furthermore, it should be noted that the crystallization of polymers can be subcategorized into (a) *crystallization from polymer solution*, (b) *crystallization from polymer melt*, and (c) *crystallization from polymer glassy state*. The second and the third types could be often called as “*melt-crystallization*” and “*cold-crystallization*”, respectively.

To understand the crystallization behavior of polymers, there are some basic concepts and theories to be reviewed, which are *morphology*, *thermodynamics* and *kinetics theory* of polymer crystallization.

2.1 The Morphology of Semi-Crystalline Polymers

In 1930, based on the X-ray diffraction results showed that in both natural and synthetic polymers presented certain crystalline feature. The Bragg reflection patterns also showed the broader peak than those obtained from non-polymeric low molecular weight substances. Hermann *et al.* (1930) proposed the model called “*fringed-micelle*” model based on these observations as shown in Figure 2.1(a). According to the model, some parts of polymer segments align themselves together to form bundled crystalline regions which surrounded by the amorphous regions. However, this model was unable to explain the optical properties of polymer spherulites and their small angle X-ray scattering pattern.

Several years later, the electron diffraction results on cast films of gutta-percha was reported by Storcks (1938). He observed that the total length of the chains was much greater than the thickness of the films and led him to first propose a

chain-folded structure to explain the experimental result. Individually Fischer, Till, and Keller in 1957, reported the growth of the single crystals of linear polyethylene from dilute solution which is in the form of thin platelets of ca. 10 nm thickness. Due to the electron diffraction experiments, the molecules are believed to align themselves normal to the lamellar platelets and it was suggested that the molecules have to fold back and forth on themselves. The “*folded-chain lamellar model*” was then proposed due to these observations as shown in Figure 2.1(b).

The observation of the semi-crystalline polymer morphology through the polarized light optical microscope made an evidence of large crystalline superstructure called “*spherulites*” which is commonly found for many polymer crystallized from a concentrated solution or a polymer melt. Microscopically, spherulites consist of ribbon-like lamellae that grow out radially from the center as shown in Figure 2.1(c).

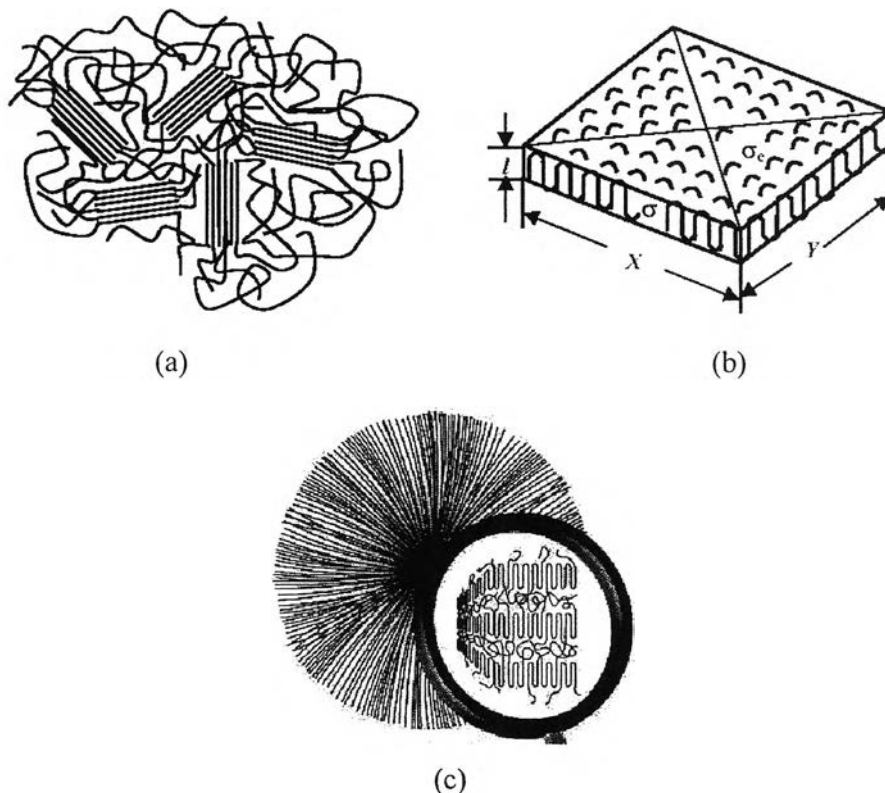


Figure 2.1 The proposed polymer crystal morphologies (a) “fringed-micelle model” (b) “folded-chain lamellar model” and (c) “spherulitic morphology”.

2.2 Polymer Crystallization Kinetics

It is now well understood that the crystallization of polymer occurs via the nucleation mechanism which are divided into “primary nucleation” and “secondary nucleation”. The primary nucleation is the formation of an initial small amount of crystalline materials (nuclei) which can be categorized into two types depending upon the origin of the nuclei. If there are some existing nuclei which may be a foreign particle or any second phase that initiate the crystallization, then the primary nucleation is termed “*heterogeneous nucleation*”. If no second phase existing in the system and the nuclei forms spontaneously due to the supercooling, then it is referred as “*homogeneous nucleation*”. Wunderlich *et al.*(1976) have further advocated the subdivision of the classification by incorporating the third category called “*self-nucleation*” which is due to the preexisting or residual nuclei that survived the initial melt condition (or dissolution condition). The secondary nucleation is the subsequent crystal growth to continue the crystallization process on the growth surface by induction of more and more polymer molecules.

After the primary crystallization, the increase in crystallinity with slower rate is an evidence of the secondary crystallization which has been observed in many cases. The possibility of the secondary crystallization may be attributed to lamellar thickening process.

2.3 Kinetics Models

Avrami model (Avrami, 1939; Avrami, 1940; Avrami, 1941) is the most common approach for describing the kinetics of phase transition. In order to describe the overall isothermal crystallization kinetics of a semi-crystalline polymer, the Avrami equation is expressed as

$$\theta(t) = 1 - \exp[-(K_A t)^n], \quad (2.1)$$

where $\theta(t)$ is the relative crystallinity function of time, K_A is the Avrami rate constant, and n_A is the Avrami exponent. Usually, K_A is written in the form of a composite Avrami rate constant k_a (i.e. $k_a = K_A^{n_A}$). The mathematical background of Avrami equation is based on “the famous raindrop problem” solved by Poisson in 1837. The phase transition is considered to be similar to the waves expanding due to randomly falling raindrops. According to the derivation of the Avrami equation, it could be referred that K_A is dependent on the shape of the growing crystalline entities and the amount and type of nucleation. The exponent n_A is dependent upon the nucleation type and growth geometry but not the amount of nucleation. Despite its popularity, the Avrami model has been argued to be appropriate for describing only the early stages of the crystallization process. The complications arise due to the effects of growth site impingement and secondary crystallization process, which occur in the later stages of the crystallization process.

The relative crystallinity function of time $\theta(t)$ is, by definition, the ratio of the crystallinity value attained up to an arbitrary crystallization time to the total apparent crystallinity value attained over the crystallization period. Since crystallization is an exothermic process, it is assumed that the crystallinity value is linearly proportional to the enthalpy released during the crystallization process. This notions allows for the $\theta(t)$ function to be determined from the ratio of the integral of the enthalpy of crystallization over an arbitrary crystallization period to the integral of the enthalpy of crystallization over the overall crystallization period, i.e.

$$\theta(t) = \frac{\int_0^t (dH_c/dt') dt'}{\Delta H_c}, \quad (2.2)$$

where dH_c is the instantaneous enthalpy of crystallization released at an arbitrary crystallization time and ΔH_c is the enthalpy of crystallization released over the course of crystallization period.

Malkin *et al* (1984) proposed a macrokinetic equation 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 the primary nuclei and the rate of variation in the degree of crystallinity varies with the crystal growth rate. Mathematically, they arrived at an equation of the form:

$$\theta(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)}, \quad (2.3)$$

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 rate constant which relates directly to overall crystallization rate (i.e. $C_1 = aG + bI$, where a and b are specific constants). It should be noted that the units of C_1 are given as an inverse of time.

Urbanovici and Segal (1990) modified the Avrami model and proposed a new kinetic equation in the following form:

$$\theta(t) = 1 - \left[1 + (r - 1)(K_{US} t)^{n_{US}} \right]^{1/(1-r)}, \quad (2.4)$$

where K_{US} and n_{US} are the Urbanovici-Segal rate constant and the Urbanovici-Segal exponent, respectively, and r is a parameter which satisfies the condition $r > 0$. When the value of r approaches 1, the Urbanovici-Segal equation becomes identical to the Avrami equation. This simply means that the parameter r is merely a factor determining the degree of deviation of the Urbanovici-Segal model from the Avrami model. It is noted that the Urbanovici-Segal kinetic parameters (i.e. K_{US} and n_{US}) have a similar physical meaning to the Avrami kinetic parameters (i.e. K_A and n_A) and the units of K_{US} are, again, given as an inverse of time.

Based on the mathematical derivation of Evans (1945), Ozawa (1967) extended the Avrami theory to be able to describe the non-isothermal crystallization data without the use of x-scale transformation. Mathematically, the relative crystallinity function $\theta(T)$ can be represented as a function of cooling rate as

$$\theta(T) = 1 - \exp\left(-\frac{k_o}{\phi^{n_o}}\right), \quad (2.5)$$

where k_o and n_o are Ozawa crystallization rate constant and Ozawa exponent respectively. It should be noted that the Ozawa kinetic parameters (i.e. k_o and n_o) hold similar physical meaning as those of the Avrami ones.

Instead of describing the crystallization process with complicated mathematical models, Ziabicki (1967) proposed that the kinetics of polymeric phase transformation can be described by a first-order kinetic equation of the form

$$\frac{d\theta(t)}{dt} = K(T)[1 - \theta(t)], \quad (2.6)$$

where $\theta(t)$ is the relative crystallinity as a function of time and $K(T)$ is a temperature-dependent crystallization rate function. In the case of non-isothermal crystallization, functions $K(T)$ and $\theta(t)$ vary and are dependent on the cooling rate used.

For a given cooling condition, Ziabicki showed that the crystallization rate function $K(T)$ can be described by a Gaussian function of the following form

$$K(T) = K_{\max} \exp\left[-4 \ln 2 \frac{(T_c - T_{\max})^2}{D^2}\right], \quad (2.7)$$

where T_{\max} is the temperature where the crystallization rate is the maximum, K_{\max} is the crystallization rate at the T_{\max} and D is the half-width of the crystallization rate-temperature function. With use of the isokinetic approximation, integration of equation (2.7) over the whole crystallizable range of temperature ($T_g < T < T_m^0$) leads to an important characteristic value for the crystallizability G , which is defined as

$$G_z = \int_{T_g}^{T_m^0} K(T) dT \approx 1.064 K_{\max} D. \quad (2.8)$$

In the case of non-isothermal crystallization studies using DSC where cooling rate is a variable, equation (2.8) can be applied when the crystallization rate

function $K(T)$ is replaced with a derivation function of the relative crystallinity $\dot{\theta}_\phi(T)$ specific for each cooling rate studied (i.e., crystallization rate function at different cooling rate). Therefore, equation (2.9) is rewritten to be

$$G_\phi = \int_{T_e}^{T_m^0} \dot{\theta}_\phi(T) dT \approx 1.064 \dot{\theta}_{\max,\phi} D_\phi, \quad (2.10)$$

where $\dot{\theta}_{\max,\phi}$ and D_ϕ are the maximum crystallization rate and the half-width of the derivative relative crystallinity as a function of temperature $\dot{\theta}_\phi(T)$. According to equation (2.10), G_ϕ is the kinetic crystallizability at an arbitrary cooling rate (ϕ). The kinetic crystallizability at *unit cooling rate* G_Z can therefore be obtained by normalization G_ϕ with ϕ (i.e., $G_Z = G_\phi/\phi$).

2.4 Thermodynamics Consideration of Polymer crystallization

2.4.1 Gibbs-Thomson Equation

From the schematic drawing of a lamellar structure of polymer crystalline shown in Figure 2.1(b), the Gibbs free energy of crystal forming at any temperature, T , with finite crystal size can be written as

$$\Delta G_{crystal}(T) = 2XY\sigma_e + 2l(X + Y)\sigma - lXY\Delta G_f^\infty(T) \quad (2.11)$$

where X and Y represent the dimensions of the basal crystal plane, l is the lamellar thickness, σ and σ_e are lateral and fold surface free energy respectively, and ΔG_f^∞ is the free energy of fusion per unit volume for a perfect crystal with infinite dimension which can be expressed as

$$\Delta G_f^\infty(T) = \Delta H_f^\infty(T) - T\Delta S_f^\infty(T) \quad (2.12)$$

where $\Delta H_f^\infty(T)$ and $\Delta S_f^\infty(T)$ are the enthalpy and entropy changes upon the fusion at temperature T . At equilibrium melting temperature, T_m^0 , the melt is in equilibrium with the perfect crystal of infinite size, thus $\Delta G_f^\infty(T_m^0) = 0$. Then the equation (2.12) gives

$$\Delta S_f^\infty(T_m^0) = \frac{\Delta H_f^\infty(T_m^0)}{T_m^0} \quad (2.13)$$

By assuming no thickening, X and $Y \gg l$, and $\sigma \ll \sigma_e$, the equation (11) at $T = T_m$ can be rewritten as

$$\Delta G_f^\infty(T_m) = 2\sigma_e/l \quad (2.14)$$

From equation (2.12) at any melting temperature, T_m

$$\Delta G_f^\infty(T_m) = \Delta H_f^\infty(T_m) - T_m \Delta S_f^\infty(T_m) \neq 0 \quad (2.15)$$

Assuming $\Delta H_f^\infty(T_m) = \Delta H_f^\infty(T_m^0)$ and $\Delta S_f^\infty(T_m) = \Delta S_f^\infty(T_m^0)$, and combining equation (2.13), (2.14) and (2.15) together, thus

$$T_m = T_m^0 \left[1 - \frac{2\sigma_e}{l \Delta H_f^\infty(T_m^0)} \right] \quad (2.16)$$

The well-known ‘‘Gibbs-Thomson’’ equation can be obtained as written in equation (2.16) which correlates the melting temperature and the thickness of a given lamellar crystal.

2.4.2 Lauritzen-Hoffman Secondary Nucleation Theory

The secondary nucleation theory for linear flexible macromolecules which are crystallized from the melt into chain-folded lamellae was introduced by

Lauritzen and Hoffman (Lauritzen and Hoffman, 1960; Hoffman and Lauritzen, 1961; Lauritzen and Hoffman, 1973) and continuously developed and revised in many publications (Hoffman et al., 1976; Hoffman, 1982; Hoffman, 1983; Hoffman and Miller, 1988; Hoffman, 1992; Hoffman and Miller, 1997). The theory starts by considering the formation of the first stable stem and following by the deposition of subsequent stems in a stepwise manner. The minimum lamellar thickness needed to form a thermodynamically stable nucleus can be expressed as

$$l_{\min} = \frac{2\sigma_e T_m}{\Delta H_f \Delta T_c} \quad (2.17)$$

where ΔT_c or supercooling is defined as $T_m^0 - T_c$. Furthermore, the lamellar thickness which gives the fastest stem deposition rate and thus the maximum overall crystal growth rate is more favorable than l_{\min} would be express as

$$l_g^* = l_{\min} + \left[\frac{kT}{2b_0\sigma} \right] \left[\frac{\Delta G_f + 4\sigma a_0}{\Delta G_f + 2\sigma a_0} \right] = l_{\min} + \delta l \quad (18)$$

where k is the Boltzman constant, a_0 is the width of the molecular stem, b_0 is the thickness of a surface nucleus, and δl is the increment above the l_{\min} which makes the crystal to enter the thermodynamically stable state at the fastest rate and prevents the anomaly $T_m = T_c$.

2.4.3 Equilibrium Melting Temperature Determination

The equilibrium melting temperature T_m^0 is an important thermodynamic parameter for determining the degree of undercooling, which, in turn, influences the kinetic driving force for crystallization of a crystallizable polymer. It is simply said that no crystallization can occur at temperatures greater than the T_m^0 . Theoretically, T_m^0 is defined as the melting temperature of an infinitely large stack of extended-chain crystals in the directions perpendicular to the chain

axis and with the chain ends establishing an equilibrium state of pairing (Marand *et al.*, 1998).

2.4.3.1 Gibbs-Thomson Extrapolation Method

According to equation (16), the equilibrium melting temperature can be obtained by plotting the observed melting temperature, T_m , versus $1/l$. The lamellar thickness, l , is often obtained from SAXS or TEM experiment, while T_m is usually obtained using DSC technique.

2.4.3.2 Linear Hoffman-Weeks Extrapolation Method

Hoffman and Weeks (1962) proposed a method for determining the T_m^0 which states a finite linear relationship between the observed melting temperature T_m and the crystallization temperature T_c . As mention previously in equation (18), $l_g^* = l_{min} + \delta l$, the thickening ratio, β , was introduced to be the ratio of l/l^* , then the observed melting point, T_m , of a crystal which has been thickened by a factor β can be expressed using Gibbs-Thomson equation as

$$T_m = T_m^0 \left[1 - \frac{2\sigma_e}{\beta l^* \Delta H_f^\infty(T_m^0)} \right] \quad (2.19)$$

In case of $\delta l = 0$ (i.e. non-thickening), the melting temperature is related to its crystallization temperature as

$$T_c = T_m^0 \left[1 - \frac{2\sigma_e}{l^* \Delta H_f^\infty(T_m^0)} \right] \quad (2.20)$$

Based on equation (19) and (20), Hoffman and Weeks (1962) derived the following equation:

$$T_m = \frac{T_c}{2\beta} + T_m^0 \left[1 - \frac{1}{2\beta} \right], \quad (2.21)$$

So the linear extrapolation of T_m versus T_c data to the line $T_m=T_c$ yields the equilibrium melting temperature value, and the thickening ratio as the slope. It should be noted that this method is only valid when the slope of the plot of observed T_m versus T_c is a constant value close to 0.5, at which condition the β is close to 1.

2.4.3.3 Non-Linear Hoffman-Weeks Extrapolation Method

Recently, Marand *et al.* (1998) proposed a new mathematical derivation that states a relationship between the observed T_m and the corresponding T_c by considering the possibility for the stem length fluctuation during secondary nucleation. The new equation reads

$$\frac{T_m^0}{T_m^0 - T_m} = \beta^n \frac{\sigma_e^1}{\sigma_e^{GT}} \left[\frac{T_m^0}{T_m^0 - T_c} + \frac{D_2 \Delta H_f^0}{2\sigma_e^1} \right], \quad (2.22)$$

where β^n is the thickening coefficient, σ_e^{GT} is the basal interfacial free energy associated with nuclei of critical size including the extra lateral surface energy due to fold protrusion and the mixing entropy associated with stems of different lengths, σ_e^1 is the interfacial energy associated with the formation of the basal plane of the initial crystals, D_2 is an arbitrary constant, and ΔH_f^0 is the equilibrium enthalpy of fusion. Due to the suggested nonlinear relationship of the T_m - T_c data, this approach should be referred to the nonlinear Hoffman-Weeks extrapolative method.

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