



## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Theories of Polymer Crystallization

Overall crystallization process of semi-crystalline polymers can be divided into two main processes: primary crystallization and secondary crystallization. Primary crystallization process is a macroscopic development of crystallinity as a result of two consecutive microscopic mechanisms: primary nucleation and subsequent crystal growth (i.e., secondary nucleation). Primary nucleation is the process by which a crystalline nucleus is formed in the melt state: nuclei can be formed homogeneously, by means of statistical fluctuation in the melt phase, or heterogeneously, when catalyzed by the presence of heterogeneities. Very often nucleation of polymers is heterogeneous and starts on surfaces, cavities or cracks of insoluble impurities. After the nucleus is formed, crystalline lamellae develop and form three-dimensional superstructures. The most common morphology encountered on crystallization from the melt is the spherulite, but other superstructures, such as hedrites or dendrites, are also observed. Generally, crystallization does not stop with the growth of crystals but a process called secondary crystallization is also occurred, resulting in the increase of crystallinity and thickness of already formed lamellar crystals.

Over the last several years, both theoretical and empirical models have been proposed and worked out in order to provide description and prediction of crystallization in polymer. However, these models are divided into two types: macroscopic and microscopic crystallization, which depend on the scope of kinetics studies.

##### 2.1.1 Kinetics of Macroscopic Crystallization

Isothermal bulk crystallization kinetics of semi-crystalline 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)

$$\theta(t) = \frac{\int_0^t \left( \frac{dH_c}{dt} \right) dt}{\int_0^{\infty} \left( \frac{dH_c}{dt} \right) dt} \in [0,1] \quad (2.1)$$

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:

$$\theta(t) = 1 - \exp \left[ - (K_a t)^{n_a} \right] \in [0,1] \quad (2.2)$$

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.  $k_a = K_a^n$ ). 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 (Tobin, 1974). The original theory was written in the form of a nonlinear Volterra integral equation, of which the zero-order solution is given by:

$$\theta(t) = \frac{(K_t t)^{n_t}}{1 + (K_t t)^{n_t}} \in [0,1] \quad (2.3)$$

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  $(\text{time})^{-1}$ .

Malkin et al. (1984) developed a macrokinetic crystallization 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, They arrived at a totally different kinetic equation:

$$\theta(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)} \in [0,1] \quad (2.4)$$

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:

$$\theta(t) = 1 - \left[ 1 + (r-1) \left( K_{us} t^{n_{us}} \right) \right]^{1/(1-r)} \in [0,1] \quad (2.5)$$

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  $(\text{time})^{-1}$ .

For non-isothermal conditions, on the basis of isokinetic conditions and the assumption that the number of activated nuclei is constant. Nakamura et al. (1973) developed the following equation from the Avrami theory:

$$\theta(t) = 1 - \exp \left[ - \left( \int_0^t K(T) dt \right)^{n_a} \right] \quad (2.6)$$

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

$$K(T) = [k(T)]^{1/n_a} = \ln(2)^{1/n_a} \left[ \frac{1}{t_{0.5}} \right] \quad (2.7)$$

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

Based on the mathematical derivation of Evans, Ozawa (1971) extended the Avrami model to be able to describe the non-isothermal case. Mathematically, the relative crystallinity can be written as a function of cooling rate  $\phi$  according to the following equation:

$$\theta(T, \phi) = 1 - \exp \left[ - \frac{k_o(T)}{\phi^{n_o}} \right] \quad (2.8)$$

where  $k_o(T)$  is the Ozawa crystallization rate function and  $n_o$  is the Ozawa exponent (which is similar to the Avrami exponent).

### 2.1.2 Kinetics of Microscopic Crystallization

The Lauritzen and Hoffman secondary nucleation theory is the most widely used in the evaluation of microscopic crystallization process. 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:

$$G = G_0 \exp\left(-\frac{U^*}{R(T_c - T_\infty)} - \frac{K_g}{T_c(\Delta T)f}\right) \quad (2.9)$$

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  $1500 \text{ cal mol}^{-1}$ ,  $T_c$  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:

$$K_g = \frac{\xi b_0 \sigma \sigma_e T_m^\circ}{k \Delta H_f^\circ} \quad (2.10)$$

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 constant, and  $\Delta H_f^\circ$  is the equilibrium heat of fusion.

Referring to Equation (2.9), 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 (2.9) corresponds directly to the secondary nucleation rate, observation of the relationship between  $G$  and  $I$  can be determined by rearranging the logarithmic product of Equation (2.9), which results in the equations:

$$\log G + \frac{U^*}{2.303R(T_c - T_\infty)} = \log G_0 - \frac{K_g}{2.303T_c(\Delta T)f} \quad (2.11)$$

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 (2.11), 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 be expressed as:

$$\Psi(T) = \Psi_0 \exp\left(-\frac{A}{R(T_c - (T_g - C))} - \frac{B}{T_c(\Delta T)f}\right) \quad (2.12)$$

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.  $2T_c / (T_c + T_m^\circ)$ ).

## 2.2 Crystallization in Miscible Blends

As in one component systems, spherulite growth rates in binary blends for which the two components are miscible at molecular level mainly depend on the energy related to the transport of macromolecular chains towards the growing crystals and on the energy barrier for creation of secondary nuclei of critical size (according to the Hoffman and Lauritzen model). In blends, both terms are functions of the molecular characteristics of each component, hence  $G$  is more complex function of all the parameters that characterize the system such as the crystallization temperature, composition, glass transition and melting temperatures, and molecular mass (Di Lorenzo, 2003).

For polymer blends system, the variation of the glass transition temperature  $T_g$  of a blend is generally related to the change of mobility of crystallizable units, hence it affects the energy related to the transport of crystallizable polymer chains in the melt across the liquid-solid interface ( $U^*$  of Equation (10)). When a new polymer molecule is added to a crystal, first a small part of it nucleates on the growing substrate, then the remaining part of chain is drawn from the entangled melt. Diffusion from the melt towards the growing crystal is delayed by friction with the neighboring macromolecules, whose magnitude depends linearly on chain length and decreases with progressive attachment onto crystal. The friction forces are affected by mobility of the environment, and by possible interactions with neighboring chains. In the majority of miscible polymer blends, the diluent component has a  $T_g$  higher than that of major component, which contributes to reduce the chain mobility in the melt, and, as consequence, the spherulite growth rate  $G$  decreases with

composition. In addition, another factor that affect spherulite growth rate in blends is the reduction of the equilibrium melting temperature upon addition of a miscible component. The reduction of the equilibrium melting temperature produces a decrease in crystallization rate since, for same crystallization temperature, crystallization takes place at a lower undercooling compared to the pure polymer. A small undercooling corresponds to a lower thermodynamic driving force towards crystallization that, in turn, results in a lower spherulite growth rate (Di Lorenzo, 2003).

## 2.3 Related Research Works

### 2.3.1 Crystallization Kinetics: Macrokinetic

Supaphol (2000) studied the non-isothermal bulk crystallization and subsequent melting behaviour of syndiotactic polypropylenes crystallized from the molten state. The crystallization kinetics was described with various macrokinetic models, namely, the Avrami, the Tobin, and the Ozawa models. It was found that both Avrami and Tobin models provided a fair description of the experiment data. The rate parameters (i.e.  $k_a$  and  $k_t$ ) suggested that s-PP crystallizes faster as the cooling rate increases. For Ozawa model, it also found to describe the non-isothermal crystallization kinetics of s-PP very well. The Ozawa rate constant  $k_o$  was found to decrease with increasing temperature.

Piccarolo et al. (2000) studied the non-isothermal crystallization kinetics of PET. From the variation of density with cooling rate, one can observed the expected monotonous density decrease with cooling rate, from the semi-crystalline to the amorphous phase. This observation was confirmed by WAXS patterns.

Supaphol (2001) used DSC to study the isothermal crystallization of syndiotactic polypropylene. The Avrami, Tobin, Malkin, and Urbanovici-Segal models have been applied to describe the kinetics of primary crystallization from the melt state. It was found that the quality of each model, judging from the values of the correlation coefficient  $\chi^2$



parameter, in describing the isothermal crystallization data of s-PP falls in the following order: (1) the Urbanovici-Segal model, (2) the Avrami model, (3) the Malkin model, and (4) the Tobin model. This led to the rejection of the Tobin model in describing the isothermal crystallization of s-PP. For crystallization rate parameters (i.e.  $t_{0.5}^{-1}$ ,  $K_a$ ,  $K_t$ ,  $C_1$ , and  $K_{us}$ ) were found to be very sensitive to changes in the crystallization temperature. Within the crystallization temperature range studied (i.e.  $70^\circ\text{C} \leq T_c \leq 95^\circ\text{C}$ ), the values of the rate parameters were all found to increase with decreasing temperature, suggesting that the range of temperature in this study falls in the region where nucleation mechanism is the rate determining step.

Chuah (2001) studied the bulk isothermal crystallization kinetics of poly(trimethylene terephthalate). It was found that PTT had a crystallization rate between PET and PBT with PBT being the fastest. From this result, it suggested that PTT did not follow a previous study that aromatic polyesters with odd numbers of methylene units were more difficult to crystallize than the even-numbered polyesters.

Supaphol and Spruiell (2001) studied the overall crystallization kinetics of syndiotactic polypropylene under isothermal quiescent condition from both the melt and glassy state. When plotted as a function of crystallization temperature, the overall crystallization rate parameters for melt crystallization process showed an unmistakable double bell-shaped curve, while those for cold-crystallization process showed the typical bell-shaped curve. Comparison of the overall crystallization rate parameters obtained for both melt- and cold-crystallization processes indicated that crystallization from the glassy state proceed at a much greater rate than from the melt state.

Kalkar and Deshpande (2001) studied kinetics of isothermal and non-isothermal crystallization of poly(butylenes terephthalate)/liquid crystalline polymer blends. From the non-isothermal crystallization of PBT, the peak crystallization temperature  $T_c$  occurs at higher undercooling temperatures with increasing cooling rate as would be expected in a nucleation-controlled crystallization.

Qiu et al. (2003) studied crystallization behavior of biodegradable poly(ethylene succinate) from amorphous state using DSC. From the non-isothermal cold crystallization, it shown two crystallization exotherms. The major crystallization located at low temperature range corresponded to the real cold crystallization of PES and the other minor one located at high temperature range was from the melt-recrystallization of the unstable crystal formed earlier. It was confirmed by using TMDSC.

Supaphol et al. (2003) studied the non-isothermal melt-crystallization kinetics for three linear aromatic polyesters. The Ziabicki equation was used to determine the ability of polymer to crystallize. The Ziabicki's kinetic crystallizability parameter  $G$  for these polyesters was found to be of the following order: PBT>PTT>PET. The effective energy barrier for non-isothermal crystallization process of these polyesters was determined by the differential isoconversional method of Friedman.

### 2.3.2 Crystallization Kinetics: Microkinetic

Huang and Chang (2000) studied the crystallization kinetics of poly(trimethylene terephthalate). The polarized light microscope (PLM) was used to study the spherulite morphology. The Lauritzen-Hoffman theory was used to describe the growth rate. The nucleation parameter  $K_g$  was obtained from the slope. The lateral surface energy and the fold surface free energy were calculated from  $K_g$ . It was found that a transition regimes III and II was found in the vicinity of 194 °C. However, Hong et al. (2002) reconsidered the value of the work of chain folding for nucleation by considering effect of chain stiffness. The average work of chain folding for nucleation was ca. 6.5 kcal mol<sup>-1</sup>. The crystallite morphologies of PTT, observed from the melt and cold crystallization, exhibited typical negative spherulite and sheaf-like crystallite, respectively. Moreover, the regime I→II→III transition was accompanied by a morphological transition from axially-like or elliptical-shaped structure to banded spherulite and then non-banded spherulite, indicating that the formation of banded spherulite is very sensitive to regime behavior of nucleation.

Wang et al. (2001) studied the effect of molecular weight on crystallization and melting of poly(trimethylene terephthalate). The morphology studies indicated that both the isothermal crystallization and the dynamic crystallization of PTT from the melt were thermal nucleation processes, and for fixed temperature between 190°C and 210°C, the nucleation density increased with increasing the molecular weight.

### 2.3.3 Multiple Melting Behaviors in Polymer

Multiple melting is not an exclusive phenomenon for PTT. In fact, various investigators reported similar observations on a number of semi-crystalline polymers, including some flexible polymers such as syndiotactic polypropylene (s-PP) (Supaphol, 2001). In syndiotactic polypropylene (s-PP), triple melting endotherms were also observed in samples crystallized at “low” temperature. The minor endotherm, located closed to the corresponding crystallization temperature, was postulated to be the melting of the secondary crystallites formed at  $T_c$ . The low-temperature melting peak was found to be the melting of the primary crystallites formed, and the high-temperature melting peak was a result of the melting of the crystallites recrystallized during a heating scan. The triple-melting behavior observed in subsequent melting endotherms of s-PP was therefore described as contributions from melting of the secondary crystallites and their recrystallization, partial melting of the less stable fraction of the primary crystallites and their recrystallization, melting of the primary crystallites, and remelting of the recrystallized crystallites formed during the heating scan.

Srimoan et al. (2003) reported that the isothermally crystallized PTT exhibited triple melting peak for crystallization temperatures lower than 192°C, double melting peak for crystallization temperatures higher than 192°C but lower than 210°C, or single melting peak for crystallization temperature higher than 210°C. In addition, they also reported the values of the equilibrium melting temperature  $T_m^0$  using linear and non-linear Hoffmann–Weeks extrapolation. It was about ca. 243.6 and 277.6 °C, respectively.

#### 2.3.4 Polyester Blending

The first study on crystallization behavior of PET/PBT blends was carried out by Escala and Stein (1979). They found that the blends were compatible in amorphous phase and showed single glass transition temperature varied with composition. The effects of time and temperature in the melt showed that no transesterification occurred during preparation of the samples within at least three minutes. X-ray, DSC and IR studies demonstrated that the crystallization resulted in separate crystals of the two components rather than co-crystallization. Crystallization rates were primarily affected by the degree of supercooling of each component in the blends and by the influence of blending on the glass-transition temperature.

The miscibility of PET/PBT blends can be predicted by using the heat of mixing ( $\Delta H_m$ ), the interaction parameter ( $\chi_{AB}$ ), the entropy of mixing ( $\Delta S_m$ ) and the free energy of mixing ( $\Delta G_m$ ) (Mishra and Deopura, 1985). The results showed that the system behaved as a compatible polymer pair and could be served as a good guide to solve practical problems. After that in 1987, Mishra and Deopura studied the mechanical behavior of fibers from PET/PBT blends and found that the fibers showed a sharp decrease in tensile strength and modulus when blends were on the verge of phase segregation. The modulus values of pure polymers were different from the blends due to the differences in chain configuration and their methylene groups. Moreover, it was observed that on the drawing process of 90/10 blend, the blend probably had a fine grain structure due to an interconnected with high density of tie molecules, resulting in high modulus and comparatively high strength.

In 1991, Avramov and Avramova studied the crystallization behavior of PET/ PBT blends. The blends were prepared by ultra quenching in a liquid nitrogen bath and then studied by using DSC and WAXS. The results shown that the blends were amorphous regardless of the composition, and the as-quenched 0.5PET/0.5PBT blend had two glass transition temperatures. The activation energies determined from the dependence of each  $T_g$  on the heating rate were approximately the same. Moreover in 1995, the miscibility and properties of amorphous PET/PBT blends after three years of storage at  $-15^\circ\text{C}$  were also studied by Avramova. It was

found that after a long period of storage at low temperature, the physical properties of the as-quenched samples changed significantly. In contrast to the results for the as-quenched blends, a single glass transition temperature was intermediate between those of pure components was observed at each composition after a long period of low temperature relaxation. Implying that the blends were miscible in the amorphous state and both components could crystallize simultaneously at all compositions of the quenched blends. Each component formed its own crystal phase and the presence of the other component did not disturb and even enhanced the crystallization process.

In 1992, the miscibility of PET/PBT blends reinforced with glass fiber was investigated by Shonaike. The double glass transition temperatures over the whole composition range of PET/PBT blends in the first heating scans was observed due to the occurring of phase segregation in the amorphous phase of the as-received glass fiber reinforced blends. On the second scans, a single glass transition temperature appeared in all cases conclusively showing that PET was miscible with PBT. In the PET-rich region, the higher the PBT content the lower the miscibility was obtained and the lowest miscibility was observed at 50/50 blend.

The glass transition temperature and the crystallization of PET/PBT blends were studied by Yu and Choi (1997). The blend was prepared by melt-mixing in a Brabender cam mixer at different mixing speeds and then the sample was analyzed by using a DSC. At the same composition, the blend exhibited the similar glass transition temperature, but different crystallization properties. It can be concluded that the crystallization behavior from glassy state influenced by the entanglement and the transesterification of polymer chains.

The equilibrium melting temperature and crystallization behavior of PBT/amorphous copolyester (PETG) blends were studied by Nabi Saheb and Jog (1999). The experiment was carried out using a DSC with a Thermal Analysis Data Station (TADS). The results showed a single composition-dependent glass-transition temperature with a reduced crystallization rate. The composition-dependent melting point depression was obtained using the method suggested by Hoffman and Weeks (1962). The interaction parameter for PBT/PETG blends were calculated by using the melting point depression according to the Flory-Huggins theory (1953) and

further exemplified by Nashi and Wang (1975). The blends exhibited composition-dependent negative interaction parameter confirming thermodynamic miscibility. The retardation in crystallization rate as evidenced by increase in half-time of crystallization ( $t_{0.5}$ ) values were ascribed to the increase in  $T_g$  and hindered mobility of crystallizing polymer chains due to the presence of amorphous PETG.

In 2001, Lee et al. studied the effect of the barium sulfate ( $\text{BaSO}_4$ ) on the transesterification reaction of the PBT/PET blends. They found that the transesterification reaction could be suppressed by the addition of the modified surface of  $\text{BaSO}_4$  with a coupling agent. Due to the blocking with chemical reaction of the polyester chain ends with the surface hydroxyl groups of the  $\text{BaSO}_4$  particle, a block copolymer-like architecture was obtained with a  $\text{BaSO}_4$  linkage. The formation of the block copolymer-like structure for the polyester stuck to the  $\text{BaSO}_4$  particle facilitated crystallization by providing a crystallization nucleus without significant transesterification reaction, resulting in higher mechanical properties.

Recently, The blending of poly(trimethylene terephthalate) (PTT) with poly(ether imide) (PEI) was studied by Huang and Chang (2001). The miscibility, melting, and crystallization of these blends were observed using DSC, thermogravimetric analysis (TGA), and polarized light microscopy (PLM). The single and composition-dependent glass transition temperatures over the entire composition range were obtained, indicating that these blends were fully miscible in amorphous region. The enthalpy of the middle melting endotherm of the primary crystallization decreased with increasing PEI content in the blend. Recrystallization of PTT during heating scan in DSC was either retarded or fully inhibited by the presence of PEI. For non-isothermal crystallization study, the depression of crystallization temperature of PTT depends on both the blend composition and cooling rate. The presence of PEI decreased the PTT segments migrating to the crystallite-melt interface. The effects of temperature and PEI content on spherulite growth rate of PTT were evaluated by PLM. The spherulite growth rate decreased with increasing PEI content, implying that it was a thermodynamically dominant process. Both thermodynamic and kinetics factors cause total inhibition of PTT crystallization at higher PEI content in the blend.