

CHAPTER II

LITERATURE SURVEY

Studies of the kinetics of polymer crystallization are of great importance in polymer processing, due to the fact that the resulting physical properties are strongly dependent on the morphology formed and the extent of crystallization during processing. It is therefore very important to understand the processing-structure-property interrelationships of the studied materials, which in this case are PET, PTT and PBT.

2.1 Isothermal and Nonisothermal Crystallization Kinetics

The first study on the nonisothermal crystallization of PET was carried in 1971, when Ozawa proposed a new method to analyze data for the solidification of polymers cooled at a constant cooling rate. The cooling rates that used to analyze kinetic parameters of PET were 1, 2 and 4°C min⁻¹. The Avrami exponents estimated by using Ozawa equation, were 3.4, 3.6 and 3.6 at 220, 222 and 235°C, respectively.

In 1992, Nadkari *et al.* studied the effect of blending on the crystallization behavior of PET by blending PET with other thermoplastics such as poly(phenylene sulfide) (PPS), high density polyethylene (HDPE) and a copolyester (PETG). The non-isothermal crystallization studies showed that blending of PET with PETG had a retarding influence on PET crystallization. No non-isothermal crystallization peaks were observed at intermediate blend compositions, whereas the crystallization peak width was considerably broadened in the 90/10, 25/75, 10/90 PET/PETG blends. The degree of crystallinity in the blends was also significantly reduced as compared to virgin PET. These blends exhibited melting-point depression, implying partial miscibility of the component polymers. The isothermal crystallization studies showed that both nucleating and crystal growth of PET were clearly retarded in the PET/PETG blend, confirming the findings of the non-isothermal studies.

Moreover, the crystallization kinetics of PET and its blend with poly (ethylene 2,6-naphthalate) (PEN) was studied by Shi and Jabarin (2001). Isothermal crystallization kinetics was evaluated in term of the Avrami equation. The Avrami exponent was found to be 4 for all the blend samples but for pure PET and PEN, it was found to be 3 and 3 or 4, respectively. From these results, indicated that the blends used the different crystallization mechanism than those in pure polymers. The activation energies of crystallization were calculated from the rate constant, by using an Arrhenius-type expression. The activation energy showed a jump from pure PET, when plotted against blend composition, due to the different nucleation.

The crystallization kinetics of PBT and its blends with polyarylate was studied by Runt *et al.*(1992). They found that PBT has a regime II \rightarrow III transition near 210°C ($\Delta T \sim 30^\circ\text{C}$) and the fold surface free energy was found to be 57-75 erg cm⁻². This leads to a work of chain folding of $\sim 3\text{-}5$ kcal mol⁻¹.

The kinetics of isothermal and nonisothermal crystallization of PBT and its blends with liquid crystalline polymer (LCP), Vectra A950 (VA) was also studied by Kalkar and Deshpande (2001) using a differential scanning calorimetry (DSC). Isothermal crystallization study was carried out at the crystallization temperature of 190 to 205°C and analyzed based on the Avrami equation. The values of the Avrami exponent indicated that the crystallization process of PBT/VA blends was governed by three-dimensional morphology growth preceded by heterogeneous nucleation. The presence of VA in the blends enhanced the overall crystallization rate of PBT. However, the degree of crystallinity of PBT remained almost the same. For nonisothermal crystallization study, the data were evaluated based on the combination of Avrami and Ozawa equations, known as Liu's approach. It was observed that at a given cooling rate, the overall crystallization rate of PBT increased with VA content in the blends.

Ziabicki (2000) studied nonisothermal crystallization of PTT using a DSC at different cooling rates, the data were then analyzed by modified Avrami equation. He found that the temperature at maximum crystallization rate moved to a lower temperature from 189 to 163°C when cooling rate increased from 2.5 to 35°C min⁻¹.

Moreover Kim *et al.*(1997) also studied PTT nonisothermal crystallization, and reported an Avrami exponent of 2.7 and an activation energy of 165 kJ mol⁻¹.

The crystallization kinetics of PTT based on Avrami theory was also studied by Chuah (2001) studied. It was found that PTT has crystallization rate in between those of PET and PBT when compared at the same degree of undercooling. PBT has the highest crystallization rate with Avrami rate constant (k_a) in the order of 10⁻² to 10⁻¹ min⁻ⁿ. It is about an order of magnitude faster than PET with rate constant (K) of 10⁻⁴ to 10⁻² min⁻ⁿ, which in turn is an order of magnitude faster than PET with K of 10⁻⁴ to 10⁻² min⁻ⁿ. The same result was also reported by Huang *et al.* (2001).

Wang *et al.* (2001) studied the effect of molecular weight on isothermal, and nonisothermal crystallization and melting behavior of PTT using a DSC and polarized light optical microscope (POM). For isothermal crystallization studied based on Avrami equation, they found that the crystallization rate constant increased with increasing molecular weight. The Avrami exponent, n, was found to be ca. 2 and was nearly independent of both molecular weight and temperature. In case of nonisothermal crystallization, the modified Avrami was used to evaluate the data. It was found that at same cooling rate, the higher molecular weight showed the narrower crystallization peak, higher onset crystallization temperature, and larger rate constant. The Avrami exponent were found to be varied from 3.4 to 3.8 and the average value of the Ozawa exponent changed from 2.3 to 2.6 as the molecular weight change from 13,000 to 67,000.

Chung *et al.* (2002) investigated the melting behavior of isothermally crystallization of PTT in DSC heating traces. The multiple melting peaks were found because of two populations of lamellar stacks were formed during primary crystallization and the recrystallization at heating process, respectively. Moreover, he also calculated the equilibrium melting temperature (T_m°) of PTT based on the Hoffman-Weeks equation, which was equal to 525 K. From the enthalpy of fusion by using DSC and the degree of crystallinity from Wide angle X-ray Diffractometer (WAXD), the value of the equilibrium-melting enthalpy (ΔH_f°) was found to be ca. 28.8 kJ mol⁻¹.

In 2000, Supaphol used the Avami, Tobin, and the Ozawa models to analyze the data obtained from nonisothermal bulk crystallization kinetics of syndiotactic polypropylenes (s-PP). The results showed that both Avrami and Tobin models provided a fair description of the experimental data. The Ozawa model was found to describe the nonisothermal crystallization kinetics of s-PP very well. The ability of the s-PP samples to crystallize from the melt was investigated based on the Ziabicki's kinetic crystallizability approach, and was found to be in the range of 0.93 to $1.40^{\circ}\text{C s}^{-1}$. The activation energy for nonisothermal crystallization was calculated using Augis-Benett, Kissinger and Takhor methods.

For isothermal crystallization of s-PP, Supaphol (2001) used various macrokinetic models, namely, the Avami, Tobin, Malkin, and Urbanovici-Segal models to describe the kinetics of primary crystallization from the melt state of s-PP. The experimental data obtained from DSC were fitted directly to each model using a non-linear multi-variable regression program. The results showed that the experimental data of s-PP can be best described by the Urbanovici-Segal model.

2.2 Polyester Blending

Miscibility and crystallization behavior of polymer blends have been widely and intensively studied in order to provide valuable information on the miscibility, interactions between the ingredients and even on degree of dispersion.

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 (ΔH_m), the interaction parameter (χ_{AB}), the entropy of mixing (ΔS_m) and the free energy of mixing (ΔG_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°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 disturbed 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 melted-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 (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 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 BaSO_4 particle, a block copolymer-like architecture was obtained with a BaSO_4 linkage. The

formation of the block copolymer-like structure for the polyester stuck to the BaSO₄ 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 nonisothermal crystallization study, the depression of crystallization temperature of PTT also depended on 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.