



## CHAPTER II

### LITERATURE SURVEY

In the last two decades, crystallization of i-PP in the presence of different nucleating agents has been extensively studied by several authors. There are many factors of nucleating agents that affect the crystallization process such as structure, size, content, surface topology, etc. Theoretical explanation incorporating all of these factors has not yet been established. Nucleating agents can be classified into organic (e.g., sorbitals) and inorganic (e.g., talc, mica,  $\text{CaCO}_3$ ) types. Both the differences in the types and physical and chemical aspects of nucleating agents result in the difference in the nucleation efficiency, which ultimately dictates the physical and mechanical properties of the polymer compounds.

#### 2.1 Effect of Organic Nucleating Agents on Isotactic Polypropylene (i-PP)

In case of organic nucleating agents, Kim and Kim (1991) studied nucleation effect of sorbital derivatives as organic nucleating agents on crystallization behavior of i-PP. For non-isothermal crystallization kinetic analysis of non-nucleated i-PP, the growth process with simultaneous heterogeneous and homogeneous nucleation was considered, while the crystallization kinetics of nucleated i-PP could be described by the growth process with heterogeneous nucleation alone. Addition of nucleating agents up to the saturation concentration of ca. 0.3% by weight in i-PP increased the crystallization peak temperature by  $17^\circ\text{C}$  and increased the number of effective nuclei. If the concentration of nucleating agents was too high, the number of nuclei decreased due to agglomeration.

In addition, Feng *et al.* (1998) reported that addition of dibenzylidene sorbital (DBS) as a nucleating agent increased crystallization rate and reduced fold surface energy ( $\sigma_e$ ). Crystallization rates of nucleated i-PP samples were greater than that of the non-nucleated sample, indicating that DBS was an effective nucleating agent for i-PP. Addition of DBS also reduced the Ozawa exponent, suggesting a change in the crystalline morphology.

## 2.2 Effect of CaCO<sub>3</sub> on Isotactic Polypropylene (i-PP)

### 2.2.1 Effect on Crystallization

Kowalewski *et al.* (1986) studied influence of CaCO<sub>3</sub> on the crystallization behavior of i-PP. They indicated that in both isothermal and non-isothermal crystallization, CaCO<sub>3</sub> acted as a weak nucleating agent. Introduction of liquid oligomer of ethylene oxide as a modifier at polymer-filler interface decreased the nucleating activity of CaCO<sub>3</sub>, as evidenced from the reduction of crystallization temperature in comparison with the unmodified surface. In addition, the number of nuclei of modified CaCO<sub>3</sub> decreased with increasing crystallization temperature.

The nucleation activity of CaCO<sub>3</sub> depends on its crystal structure (calcite or aragonite) and surface morphology. Rybnikar (1991) investigated the crystallization behavior and morphology of i-PP/calcite. He reported that calcite was a weak nucleating agent for i-PP crystallization. This nucleation activity could be increased or decreased by suitable surface treatment. It was shown that nucleation activity of CaCO<sub>3</sub> could be improved by phthalic acid treatment, while it could be reduced by stearic acid treatment.

In contrast, Fujiyama and Wakino (1991) concluded that CaCO<sub>3</sub> was a strong nucleating agent for i-PP. This resulted in the appearance of a second crystallization peak shift of complete crystallization exotherm to a higher temperature. In another case, Mitsushi *et al.* (1991) reported that crystallization temperature in the non-isothermal condition increased with increasing CaCO<sub>3</sub> content and decreasing filler size. However, surface modification of CaCO<sub>3</sub> with alkyl hydrogen phosphate resulted in the reduction in the crystallization temperature of i-PP when compared with that of the unmodified system.

In 1997, Tjong and Xu studied the non-isothermal crystallization of high purity  $\beta$ -phase and  $\alpha$ -phase i-PP and their CaCO<sub>3</sub>-filled composites. The results showed that the crystallization temperature and crystallization rate coefficient of  $\beta$ -PP are higher than those of neat  $\alpha$ -PP homopolymer. This was due to the  $\beta$ -PP containing nucleating agent (adding an effective  $\beta$ -nucleator), which acts as nucleus for  $\beta$ -spherulites. The Ozawa equation describes reasonably well the non-isothermal

crystallization behavior of the  $\beta$ -PP polymer and its filled composites. Furthermore, the  $\text{CaCO}_3$  content showed little or no effect on the Ozawa exponent and crystallization rate coefficient of the  $\beta$ -phase PP in the composites. This means that the addition of  $\text{CaCO}_3$  to  $\beta$ -PP does not influence the mechanism of nucleation or growth of the PP crystals.

Goldman and Copsey (2000) indicated that the presence of  $\text{CaCO}_3$  markedly influenced the crystallization behavior of i-PP. The crystallization temperature of  $\text{CaCO}_3$ -filled i-PP was as much as  $10^\circ\text{C}$  lower than that of the unfilled i-PP. In addition, the subsequent melting temperature was lower than that of the neat i-PP, a direct result of the much thinner lamellar crystallites.

Recently, Ren *et al.* (2001) investigated the crystallization and melting behavior of i-PP filled with  $\text{CaCO}_3$ ,  $\text{BaSO}_4$ , and talc with various modifiers. They reported that crystallinity of the i-PP composites decreased drastically with increasing filler content. Talc was a strong nucleating agent owing to its low surface free energy (ca.  $140 \text{ mJ}\cdot\text{m}^{-2}$ ), while  $\text{CaCO}_3$  and  $\text{BaSO}_4$  acted as weak nucleating agent because they were unable to shift the peak of crystallization exotherm to a higher temperature but only decrease the degree of crystallinity. This paper proved that various surface treatments of the nucleating agents influenced their nucleating efficiency. Silicone is a more effective surface modifier than titanate in enhancing crystallinity because of good dispersion of the filler resulting in better growth of the crystals.

### 2.2.2 Effect on Mechanical Properties

Incorporating of particulate fillers in polymer is well known that this can change the properties of polymer such as physical and mechanical properties. The crystallization behavior of semi-crystalline PP composites is closely related to the mechanical properties such as modulus and impact strength. The mechanical behavior of PP compounds depends on the properties of matrix, size, shape, composition and surface chemistry of filler.

In 1991, Maiti and Mahapatro reported the tensile and impact properties of i-PP/  $\text{CaCO}_3$ . Their study clearly showed that addition of  $\text{CaCO}_3$  greatly

modified the mechanical properties and morphology of i-PP. They indicated that  $\text{CaCO}_3$  could be useful filler for i-PP even at high loading. When  $\text{CaCO}_3$  content increased, tensile modulus increased at an expense of tensile strength and the ultimate strength. Impact strength increased with increasing filler content up to 4% by volume and then decreased with further increasing filler content. Surface treatment of filler with titanate coupling agent enhanced the adhesion of filler and polymer, which further modified the strength properties. In case of the stearate-coated  $\text{CaCO}_3$  (McGenity *et al.* 1992), impact strength could be enhanced by the energy required to pull particle out of the polymer. Use of stearate-coated  $\text{CaCO}_3$  can improve both stiffness and impact strength at the same time.

Mitsubishi *et al.* (1991) studied the mechanical properties of  $\text{CaCO}_3$ -filled i-PP with respect to the crystallization temperature. When crystallization temperature increased, impact strength decreased but modulus of both modified and unmodified  $\text{CaCO}_3$  increased with decreasing particle size because of tie chain.

In 1997, Tjong *et al.* studied mechanical behavior of  $\text{CaCO}_3$ -filled  $\beta$ -crystalline phase in i-PP. Tensile measurement showed that increasing  $\text{CaCO}_3$  content in  $\beta$ -PP resulted in an increase in elastic modulus, at an expense of yield strength. The fracture impact toughness of  $\beta$ -PP composite decreased with increasing  $\text{CaCO}_3$  content, because of the reduced tougher  $\beta$ -PP matrix and the increase in the amount of weaker filler-matrix interphase. The filler particle tends to form large agglomerates when the filler loading was close to 20%.

Mlecnik and La Mantia (1997) studied the mixing of different polyolefins with several calcium-based fillers and sunflower oil. They studied the effects of viscosity and type of polyolefins on young's modulus, yield stress, and elongation at yield. Four types of polyolefins (a low- and high-viscosity high density polyethylene (HDPE) and PP) and four types of fillers (two different sizes of  $\text{CaCO}_3$ , a stearate-coated  $\text{CaCO}_3$  and a building grade calcium hydroxide) were used. The influence of the filler content showed that the yield properties decreased with increasing filler content while elastic modulus increased. Polyolefins filled with the larger particles gave similar tensile strength and improved elongation at yield and

modulus when compared with those filled with smaller size. SEM micrographs indicated the formation of agglomerates and filler/matrix adhesion.

Goldman and Copsey (2000) showed that the toughness of PP/CaCO<sub>3</sub> composites at room and low temperatures was better than that of PP/rubber blends. They concluded that stiff particles had some advantages over rubber at low temperatures.

### 2.2.3 Effect on Rheological Properties

Li and Masuda (1990) measured viscoelastic properties of isotactic polypropylene filled with small (0.15  $\mu\text{m}$ ) and large (4.0  $\mu\text{m}$ ) CaCO<sub>3</sub>. The effects of particle size, particle loading, and rheological history on the dispersion were investigated. The dynamic modulus and viscosity increased with filler loading, especially at low frequencies. For high-loaded compounds appeared a second plateau in the storage modulus (G') curve in low frequency region and the height of the second plateau depends on particle size, particle loading and rheological history. The second plateau was attributed to a formation of an agglomerated structure of particles, especially for small particle (0.15  $\mu\text{m}$ ).

In 1999, Wang and Wang studied the rheological properties of calcium carbonate-filled isotactic polypropylene under a steady test, a transient stress growth test, and a dynamic oscillatory shear flow. They reported that the viscosity and the apparent yield values increased with increasing volume loading of CaCO<sub>3</sub> particles. The surface treatment of filler with titanium coupling agent reduced the interaction between the filler particles and the extent of agglomeration, results in viscosity reduction and decrease in the apparent yield values.

## 2.3 Crystallization in Syndiotactic Polypropylene (s-PP)

Syndiotactic polypropylene (s-PP) was first synthesized in the early 1960s by Natta *et al.* based on Ziegler-Natta catalysis, but resulting in s-PP with high level of regio-irregular defects. A much improved s-PP was successfully synthesized in 1988 by Ewan *et al.* based on novel metallocene catalysis. The new catalyst systems made it

possible to produce s-PP with much improved purity and yields, which led to renewed interest in this material.

In 2000, Supaphol and Spruiell investigated the crystalline memory effects in isothermal crystallization of s-PP after partial or complete melting. On partial melting, the total concentration of predominated nuclei decreased with increasing fusion temperature  $T_f$ , and increasing time that the sample spent at a specific fusion temperature. On complete melting, the total concentration of predominated nuclei approached a constant value after melting the sample at long holding times and sufficiently high fusion temperatures ( $T_f > 160^\circ\text{C}$ ).

In 2000, Supaphol analyzed the non-isothermal crystallization of five different s-PP samples according to three different macrokinetic models, namely the Avrami, the Tobin, and the Ozawa models. All three models were shown to describe the experimental data fairly well, where as the Ozawa model was found to describe the non-isothermal crystallization kinetic of s-PP very well. For each s-PP sample, s-PP crystallized faster with increasing cooling rate.

In the same time, Supaphol and Spruiell (2000) studied the isothermal crystallization and subsequent melting behavior of five s-PP resins by DSC. Subsequent melting of the s-PP samples after isothermal crystallization at a specified crystallization temperature (from  $60^\circ\text{C}$  to  $97.5^\circ\text{C}$ ) exhibited double melting endotherms. The low-melting endotherm corresponded to the melting of primary crystalline aggregates formed at the specified crystallization temperature, whereas the high-melting one was a result of the melting of crystalline aggregates formed by recrystallization of unstable crystals during the reheating process. Comparison with some other polymers revealed that s-PP crystallizes much slower than Nylon 6, i-PP, and Nylon 66, while it crystallizes faster than isotactic polystyrene.