

CHAPTER II

LITERATURE SURVEY

In the last two decades, crystallization of iPP in the presence of different nucleating agents has been extensively studied by several authors. There are many factors of nucleating agents, such as structure, size, content, and surface topography, that affect the crystallization process of the resulting compounds. 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, CaCO₃) types. The difference in both the physical and chemical aspects of different nucleating agents result in the difference in the ability for these nucleating agents to nucleate polymers, which finally dictates both the physical and mechanical properties of the final polymeric products.

2.1 Effect of Organic Nucleating Agents on Isotactic Polypropylene (iPP)

Kim and Kim (1991) studied nucleation effect of sorbital derivatives as organic nucleating agents on crystallization behavior of iPP. For non-isothermal crystallization kinetic analysis on non-nucleated iPP, the growth process with simultaneous heterogeneous and homogeneous nucleation was considered, while the crystallization kinetics of nucleated iPP 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 iPP increased the crystallization peak temperature by 17°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.

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

2.2 Effect of CaCO₃ on Isotactic Polypropylene (iPP)

2.2.1 Effect on Crystallization

Kowalewski *et al.* (1986) studied the influence of CaCO₃ on crystallization behavior of iPP. They indicated that in both isothermal and non-isothermal crystallization, CaCO₃ acted as a weak nucleating agent. Introduction of liquid oligomers of ethylene oxide as a modifier at polymer-filler interface decreased the nucleating activity of CaCO₃, as evidenced from the reduction in the crystallization temperature in comparison with that of CaCO₃ of unmodified surface. In addition, the number of nuclei of modified CaCO₃ decreased with increasing crystallization temperature.

The nucleation activity of CaCO₃ depends on its crystal structure (calcite or aragonite) and surface morphology. Rybnikar (1991) investigated the crystallization behavior and morphology of iPP/calcite. He reported that calcite was a weak nucleating agent for iPP. This nucleation activity could be increased or decreased by a suitable surface treatment. It was shown that nucleation activity of CaCO₃ could be improved by phthalic acid treatment, while it could be reduced by stearic acid treatment.

In contrast, Fujiyama and Wakino (1991) concluded that CaCO₃ was a strong nucleating agent for iPP. This results in the appearance of a second crystallization peak shift in a 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 CaCO₃ content and decreasing filler size. However, surface modification of CaCO₃ with alkyl hydrogen phosphate resulted in the reduction in the crystallization temperature of iPP when compared with that of the unmodified system.

Tjong and Xu (1997) studied the non-isothermal crystallization of high purity β -phase and α -phase iPP and their CaCO₃-filled composites. The results showed that the crystallization temperature and crystallization rate coefficient of β -PP are higher than those of neat α -PP homopolymer. This was due to the β -PP containing a nucleating agent (adding an effective β -nucleator), which acts as

nucleus for β -spherulites. The Ozawa equation described reasonably well the non-isothermal crystallization behavior of the β -PP polymer and its filled composites. Furthermore, the CaCO_3 content showed little or no effect on the Ozawa exponent and crystallization rate coefficient of the β -phase PP in the composites. This means that the addition of CaCO_3 to β -PP did not influence the mechanism of nucleation or growth of the PP crystals.

Goldman and Copsy (2000) indicated that the presence of CaCO_3 markedly influenced the crystallization behavior of iPP. The crystallization temperature of CaCO_3 -filled iPP was as much as 10°C lower than that of the unfilled iPP. In addition, the subsequent melting temperature was lower than that of the neat iPP, a direct result of the much thinner lamellar crystallinities.

Recently, Ren *et al.* (2001) investigated the crystallization and melting behavior of iPP filled with CaCO_3 , BaSO_4 , and talc with various modifiers. They reported that crystallinity of the iPP 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 CaCO_3 and BaSO_4 acted as a weak nucleating agent because they were unable to shift the peak of crystallization exotherm to a higher temperature but only to decrease the degree of crystallinity. This work suggested that various surface treatments of the nucleating agents influenced their nucleating efficiency. Silicone is a better surface modifier than titanate in enhancing crystallinity, due possibly to the good dispersion of the filler.

2.2.2 Effect on Mechanical Properties

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

Maiti and Mahapatro (1991) reported the tensile and impact properties of iPP/ CaCO_3 . Their study showed that addition of CaCO_3 greatly

modified the mechanical properties and morphology of iPP. They indicated that CaCO_3 could be a useful filler for iPP even at high loadings. When CaCO_3 content increased, tensile modulus increased at an expense of the tensile 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 a titanate coupling agent enhanced the adhesion of filler and polymer, which further modified the strength properties. In case of the stearate-coated 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 CaCO_3 can improve both stiffness and impact strength at the same time.

Mitsuishi *et al.* (1991) studied the mechanical properties of CaCO_3 -filled iPP with respect to the crystallization temperature. When crystallization temperature increased, impact strength decreased but modulus of both modified and unmodified CaCO_3 increased with decreasing particle size because of the increased amount of tie chains.

Tjong *et al.* (1997) studied mechanical behavior of CaCO_3 -filled β -crystalline phase in iPP. Tensile measurement showed that increasing CaCO_3 content in β -PP resulted in an increase in the elastic modulus, at an expense of the yield strength. The fractured impact toughness of β -PP composite decreased with increasing CaCO_3 content, because of the reduced amount of the tougher β -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 filler and sunflower oil. They studied the effect 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 were two different sizes of CaCO_3 , stearate-coated CaCO_3 , and a building grade calcium hydroxide. The influence of the filler content showed that the yield properties decreased with increasing filler content while the elastic modulus was found to increase. Polyolefins filled with particles of larger sizes gave similar tensile strength and improved

elongation at yield and modulus when compared with those filled with particles of smaller sizes. SEM micrographs indicated the formation of agglomerates and partial filler/matrix adhesion.

Goldman and Copsey (2000) showed that the toughness of PP/CaCO₃ 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.

2.3 Crystallization in Syndiotactic Polypropylene (sPP)

Syndiotactic polypropylene (sPP) was first synthesized in the early 1960s by Natta *et al.* based on Ziegler-Natta catalysis, but the resulting sPP contained high levels of regio-irregular defects. A much improved sPP was successfully synthesized in 1988 by Ewan *et al.* based on novel metallocene catalysis. The new catalyst systems made it possible to produce sPP with much improved purity and yield, which led to renewed interest in this material.

Supaphol and Spruiell (2000) investigated the crystalline memory effects in isothermal crystallization of sPP after partial or complete melting. On partial melting, the total concentration of predominated nuclei decreased with increasing 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 ($T_f > 160^\circ\text{C}$).

Supaphol (2000) analyzed the non-isothermal crystallization of five different sPP 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, whereas the Ozawa model was found to describe the non-isothermal crystallization kinetic of sPP very well. For each sPP sample, sPP crystallized faster with increasing cooling rate.

At the same time, Supaphol and Spruiell (2000) studied the isothermal crystallization and subsequent melting behavior of five sPP resins by DSC. Subsequent melting of the sPP samples after isothermal crystallization at a specified crystallization temperature (from 60 to 97.5°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 sPP crystallizes much slower than Nylon 6, IPP, and Nylon 66, while it crystallizes faster than isotactic polystyrene.

The crystallization behavior and mechanical properties of CaCO₃-filled sPP were investigated by Supaphol *et al.* (2004). They studied the effect of CaCO₃ with varying particle sizes, contents, and surface modifications. By means of DSC, the results indicated that CaCO₃ acted as a good nucleating agent for sPP. Nucleation efficiency of CaCO₃ was found to depend strongly on its purity, types of surface treatment, and average particle size. Tensile strength was found to decrease, while Young's modulus increased, with increasing CaCO₃ content. Surface treatment of CaCO₃ with stearic acid or paraffin reduced tensile strength and Young's modulus, but helped improve impact resistance. Furthermore, steady-state shear viscosity of CaCO₃-filled sPP was found to increase with increasing CaCO₃ content and decreasing particles size.