

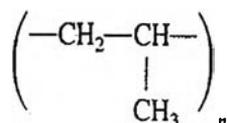
CHAPTER II

THEORETICAL BACKGROUND

2.1 Isotactic polypropylene (iPP)

2.1.1 Structure and morphology

Isotactic polypropylene is one of the most widely used polymer. Its value and significance originally stem from both commercial and scientific viewpoint, which are primarily related to the iPP's morphology studies. It was reported during the late 1950s by Natta and Corradini that the chain conformation of iPP is a threefold helix, which can be either right or left-handed, with a periodicity of 6.50 Å. The molecular structure of polypropylene:



Commercial polypropylenes generally have about 0.95 or higher isotactic indices. High isotactic index contributes to higher crystallization of the polymer and much improved mechanical properties of the products. It increases, for example, the yield stress, elastic modulus, hardness, and brittle point of the polymer itself [11]. The position of the methyl group (CH₃) with respect to the chain axis can be either up or down. As a consequence, four possibilities relatively to a reference axis can be determined for a three-fold helix of iPP in the crystalline state as shown in Figures 2.1 and 2.2.

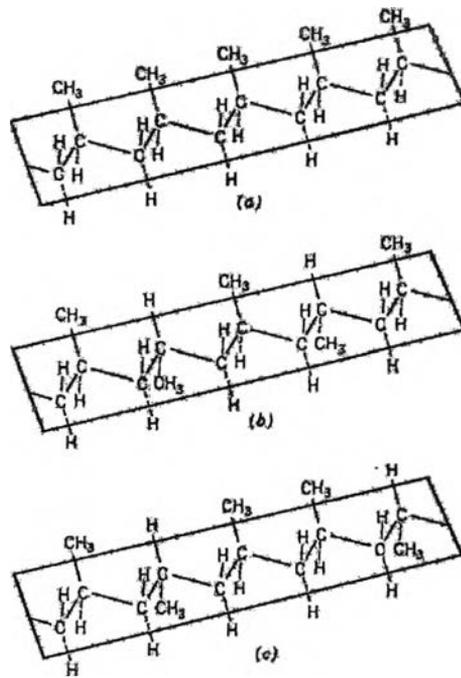


Figure 2.1 Representation of the spatial disposition of CH₃ in (a) isotactic, (b) syndiotactic, and (c) atactic polypropylene chain segments.

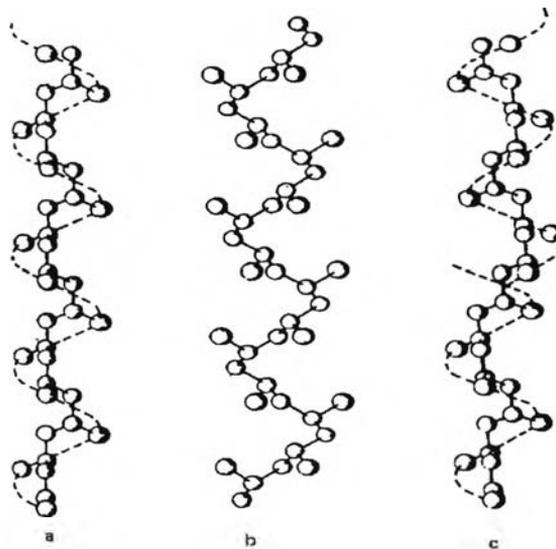


Figure 2.2 Models of (a) isotactic, (b) syndiotactic, and (c) stereobloc iPP.

The stereospecificity (isospecific or syndiospecific) refers to the consistency of the methyl group placement. Atactic chains do not have any consistent placement of methyl groups as shown in Figure 2.3. The level of tacticity can be varied considerably in PP. Tacticities of 100% are ideal, but often are not reached in practice. Crystallization of either isotactic or syndiotactic PP chains can result in a relatively high degree of crystallinity, in the range of 40% to 70%. High crystallinity requires high tacticity, which implies the presence of long, uninterrupted, stereospecific sequences along the chain. As the tacticity along the polymer chain is reduced, the crystallinity decreased. This discussion focuses on chains of isotactic PP and Figure 2.3 illustrates a simplistic view of stereoisomerism in homopolymer PP [1].

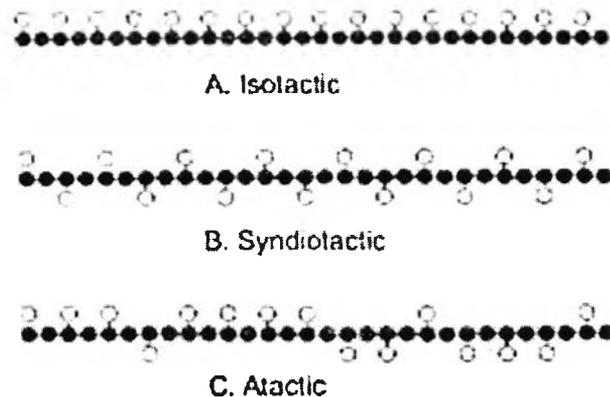


Figure 2.3 Schematic illustration of the stereochemical configurations of PP: (a) isotactic, (b) syndiotactic, and (c) atactic PP chains.

On the crystal lattice level, isotactic PP shows four well-known crystalline forms, namely monoclinic: α -form, hexagonal: β -form, triclinic: γ -form and smectic: δ -form (partial order of micro crystal of hexagonal and/or monoclinic). The α -form dominates in the crystallization of the PP grades used in mostly industrial applications. Among these four crystalline structures, the β -form demonstrates higher performance such as higher values of tensile elongation and higher impact resistance. Moreover, the α -

form can undergo phase transformation into the other crystal form through different conditions or methods such as orientation, tensile deformation and heat treatment, etc [5, 6, 7].

Mainly three crystal forms are their arrangement chains. Each of its form has been defined using wide angle X-ray scattering (WAXS) that is shown specific peaks as Figure 2.4.

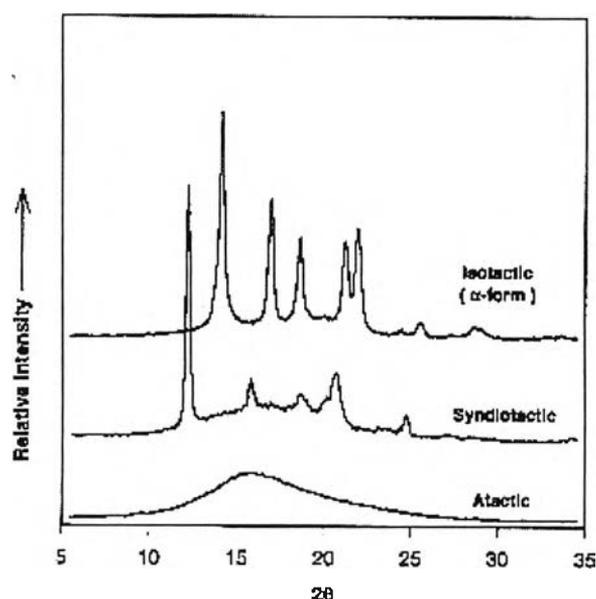


Figure 2.4 Wide angle X-ray scattering patterns of isotactic, syndiotactic, and atactic PP.

2.1.2 α - Modification of iPP

The occurrence of these iPP in the isotactic form (α -form) exhibits a unique tendency for lamellae to organize into a “cross-hatched” pattern. The principal form was first observed by Natta [12] in melt crystallized material. It is normally observed also in solution-grown crystals [13]. The structure determinations carried out on α phase iPP [14] showed that the crystal structure is monoclinic and the chains assume a helical conformation according to Figure 2.2(a). From the x-ray data it follows that the identity

in the main direction of the chain comprises three monomer units. The symmetry of the helix is characterized by a threefold screw axis. Consequently, right- and left-handed helices are possible. They are arranged in a regular pattern, a left-handed helix always facing a right-handed one.

2.1.3 β - Modification of iPP

The β -form is generally formed in mixture with the α -form by quenching the melt at temperatures between 100 and 120°C. In these conditions the relative amounts of the α and β forms are dependent on the efficiency of the quenching conditions and on the tacticity and molecular weight of the specimen [14]. This form has been observed in melt-crystallized spherulites formed in particular conditions [15] and in thin films [16] or when crystallization has occurred in the presence of shearing forces [17, 18].

The use of a nucleating agent can affect the physical and/or optical properties of PP products. Regardless of which effect is desired, it is brought about by the same mechanism: increased nucleation of the crystallizing PP. In general, PP can crystallize to give one of its crystalline forms, depending on the nucleating agent type which is used. Homoepitaxy is where the PP crystallizes on a PP crystal, often forming lamella branching. Heteroepitaxy is where the polymer crystallizes on an inorganic or organic compound [19]. Commercially available nucleators can be broken down into two classifications, which term “melt sensitive” and melt insensitive” [1]. For melt sensitive nucleators include the sorbitol-based compounds, they melt below or near the processing temperature. As a group, they are characterized by providing the PP which enhanced clarity, and are thus called “clarifiers”. On the other hand, melt insensitive nucleants do not melt below normal processing temperatures. Typical nucleating agents are shown in following Table 2.1.

Table 2.1 Nucleator types

Nucleator types	Crystal form provided
1) Lithium, Sodium, Potassium benzoate	α - crystalline form
2) Sodium salts or organophosphates	
3) Talcum, finely divided (<40 nm) clays	
4) Millad, bis-(3,4-dimethylbenzylidene sorbitol diacetal)	
5) Quinacridone dye	β -crystalline form
6) Triphenol ditrazine	
7) Aluminium quinizarin sulfonic acid	
8) Disodium, Calcium phthalate	
9) Wallastonite	

The β -forms PP are easily identified by X-ray diffraction, polarized optical microscopy, and scanning electron microscopy due to its high birefringence. The β -form has been obtained by crystallization at higher temperatures ($T_c = 120$ - 140°C) and can only be studied if the sample temperature is maintained above 110°C . Moreover, β crystallization is reduced in copolymers of propylene with ethylene [20, 21, 22].

Numerous investigations have been carried out involving the subject of the β -iPP crystal structure but most previous studies were only concentrate on the technique that obtains a higher level of the β -form and on the morphological structure of it. Three techniques used to promote the β -form are the following:

1. Addition of β -nucleators.
2. Crystallization in a temperature gradient/ thermal gradient.
3. Shear-induced technique.

From all above techniques, the addition of β -nucleator was found to be a very high effective method for promoting β -form in iPP [8]. With reference to previous studies on quinacridone pigment (permanent Red E3B) that has been of great interest due to its high efficiency in creation of the β -form iPP. Recently, a composition of pimelic acid with calcium stearate was patented as a most efficient β -nucleator [9, 10]. Many earlier studies by adding bicomponent of pimelic acid and calcium stearate as β -nucleator modified homopolymer PP had been investigated thermal behaviour, morphology characterization and drop weight impact property. At meanwhile, there was research paperwork to study effect of β -form iPP on drawing behavior as well.

2.1.3.1 Determination of β -crystalline form

A typical X-ray diffraction diagram showing both α and β form crystallinity. Turner Jones et al. [23] obtain the relative proportions of α and β forms by an empirical ratio K defined as

$$K = \frac{H\beta}{H\beta + (H\alpha_1 + H\alpha_2 + H\alpha_3)}$$

where $H\alpha_1$, $H\alpha_2$, and $H\alpha_3$ are the heights of the three strong equatorial α -form peaks (110), (040), and (130), and $H\beta$ the height of the strong single ($hk0$) peak at $d = 5.495 \text{ \AA}$, as shown in Figure 2.8. The K parameter is an empirical one. It tends to zero when no β form is present, and $K = 1$ when α form is absent. Table 2.2 shows the lattice parameters of β -form iPP and Figures 2.5, 2.6 and 2.7 show a typical X-ray diffraction diagram.

Table 2.2 Lattice parameters of β -form iPP

Bravais Lattice	Lattice parameters (Å)	No.repeat unit	Density (g/cm^3)	References
Hexagonal or Trigonal	a = 6.36	3	0.92	8
	a = 11.01	9		9
	a = 12.72	12		58
b = a, c = 6.49, $\gamma = 120^\circ$, $\alpha = \beta = 90^\circ$	a = 19.08	27	0.92	9
	a = 22.03	36		9
	a = 25.43	48		9
Orthorhombic	a = 6.36	6	0.92	58
	b = 11.01			
	c = 6.49			
	a = 19.08	18		9
	b = 11.01			
	c = 6.49			
a = 12.72	24	9		
b = 22.03				
c = 6.49				

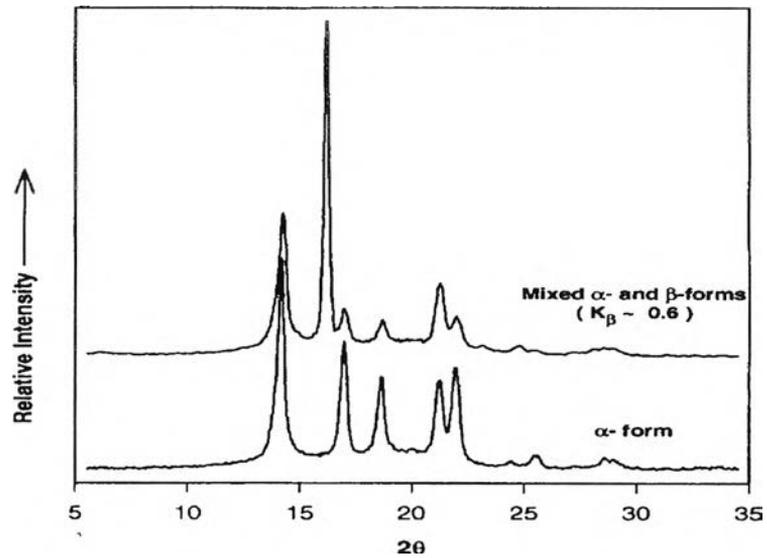


Figure 2.5 A comparison of WAXS patterns for a sample of iPP in the α -form, and a sample with a mixture of α -and β -forms. The latter sample has a value for K_{β} of approximately 0.6 the crystalline phase which exists in the β -form can be made to approach unity.

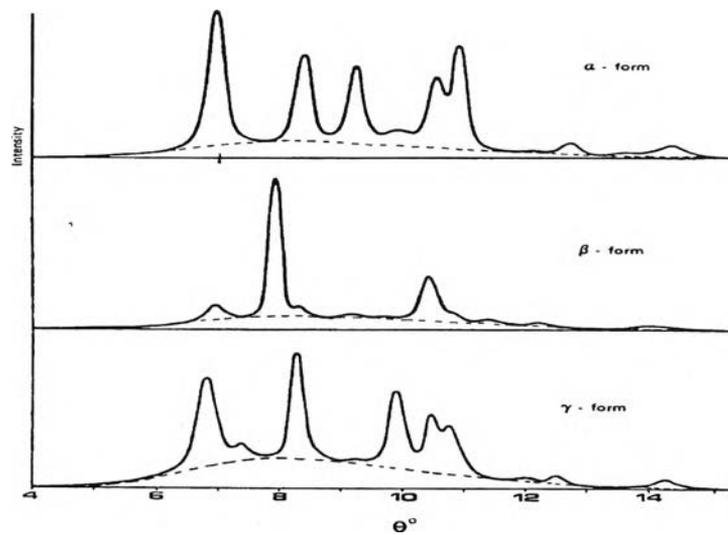


Figure 2.6 X-ray diffraction diagrams of iPP crystalline forms.[23]

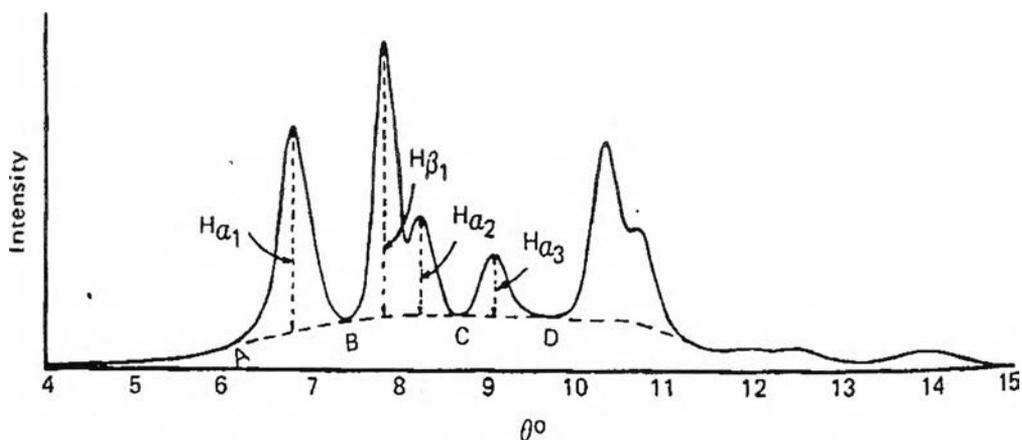


Figure 2.7 X-ray diffraction diagram showing mixed α and β crystalline forms.[23]

2.1.4 γ -Form

The γ -form is also another crystal structure of the iPP. The γ -form is triclinic structure. The γ -form of iPP was first noted during the 1960s and was generated by several methods. It was largely produced by crystallization at elevated pressures. However, under specific conditions, low molecular weight fraction ($M_w < 6000$) of iPP can be used to generate γ -form or even single crystals. Another procedure of γ -iPP formation is crystallization from the melt of high molecular weight stereoblock copolymer with small amounts (3 to 10%) of ethylene. It appears; that the presence of interruption, rather than the specific nature of the interruptions, of isotacticity is the main feature promoting the γ crystallization at atmospheric pressure.

Early studies mainly involved the formation of the γ -phase by introducing chemical heterogeneity in the polypropylene chain caused by atacticity or by copolymerization. A new study demonstrates that the γ -phase is produced at elevated pressures from high molecular weight homopolymer and the developed γ -phase has the same diffraction patterns as the low molecular weight polymers. This study has also confirmed that the γ -phase is not the result of some unexpected degradation reaction at

elevated pressures. Turner-Jones considered some copolymers of propylene with ethylene (as well as other co monomers) and found that the presence of a comonomer enhanced the formation of the γ -phase. The polymers at that time contained atactic material, and there was no a priori way of separating the effects of atacticity from the effects of copolymerization, which would be complementary. Polymers available now have >99% isotacticity and so the effect of the microstructural variables can be separated. More recent studies conducted by Mezghani and Phillips, using variable amounts of ethylene content in > 98% isotactic propylene copolymers, confirmed the results reported by Turner-Jones and also indicated that the amount of the γ -form is proportional to the ethylene content and to the crystallization temperature. Accordingly, the amount of the γ -form is higher at low supercoolings.

When the pressure is varied, only the α and γ -forms are observed. As the crystallization pressure increases, the γ -form started to coexist with the α form until it becomes dominant at 2 kbar. Furthermore, it appears from experiment that the lower the supercooling, the higher the amount of γ -form produced at a specific pressure. Like β -form, all attempts at obtaining oriented fibers of γ -phase resulted in a transformation into the oriented α -crystals. Consequently, all the x-ray diffraction data available in the literature are obtained either from powder or bulk samples, although diffraction patterns from γ -single crystals have been reported.

The γ -form was first identified as triclinic with the unit cell similar to that of the α form, with a slip along the c-axis direction ($a = 6.54^\circ\text{A}$, $b = 21.40^\circ\text{A}$, $c = 6.50^\circ\text{A}$, $\alpha = 89^\circ$, $\beta = 99.6^\circ$, $\gamma = 99^\circ$). Recent studies of a γ -form generated at atmospheric pressure from low molecular weight iPP ($M_n = 6300$) have led to a reassignment of the structure as a face centered orthorhombic unit cell. The lattice parameters of such orthorhombic cell are $a = 8.54^\circ\text{A}$, $b = 9.93^\circ\text{A}$, $c = 42.41^\circ\text{A}$. The new structure accounts for the diffraction pattern in a more satisfying manner than earlier structure. Figure 2.8 represents a schematic arrangement of chain stems in the γ -orthorhombic unit cell. The

new structure is unique in that it contains sheet of parallel molecules, but the molecular orientation between adjacent sheet becomes nonparallel every two sheets. The angle between the nonparallel stems is about 81° . On the spherulitic level, pure γ -form shows negative birefringence as shown in Figure 2.9. It is clear from Figure 2.10 that the lathlike structure of the α form is absent in the γ spherulites. However, when α and γ -form are present in the same sample the morphological features become complex. The optical studies of microtome sections as reported by Cambell and Phillips show no evidence of Maltese cross formation when less than 10% of the material is in the γ -form.

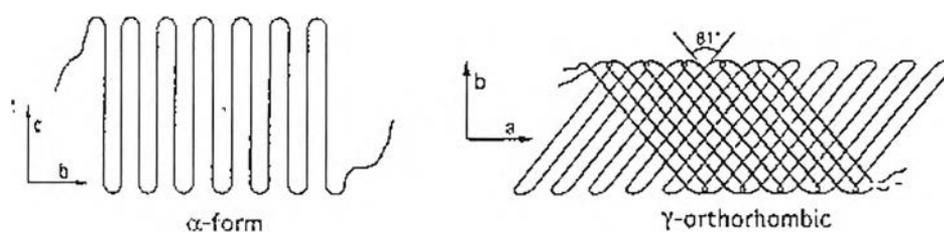


Figure 2.8 Schematic arrangement of chain stems in the α -monoclinic and the γ orthorhombic unit cells.

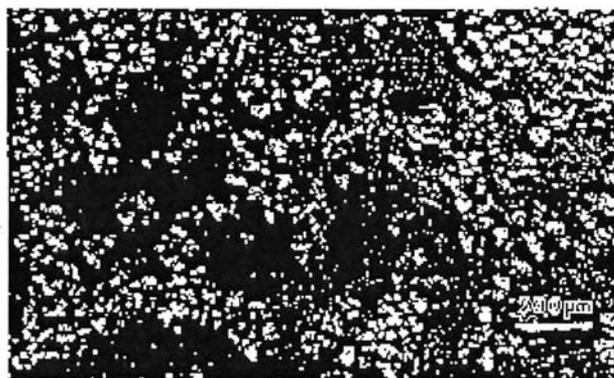


Figure 2.9 Spherulitic morphology of the γ form. Sample is isothermally crystallized at 200 Mpa (2 kbar) and 187.5°C . The spherulites show negative birefringence.

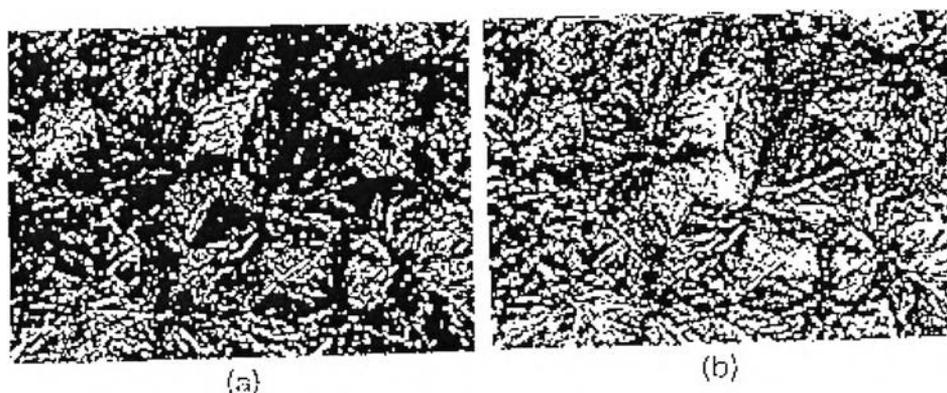


Figure 2.10 The γ -spherulites, isothermally crystallized at 200 Mpa (2 kbar) and 187.5°C, show no lathlike structure of the α form. (a) with red filter (1/4 wave plate); (b) without red filter.

However, when more than 60% γ -form is present, a clear Maltese cross exists. In addition, optical and electron microscope studies of etched specimens reveal no crosshatching in specimens with $> 60\%$ γ -crystals.

The studies of Morrow and Newman, of low molecular weight ($M_n = 1260$), show that solution-crystallized iPP gives rise to needlelike crystals with the presence of both α and γ -form structures. This morphology is also observed for high molecular weight samples crystallized at 125 Mpa (1.25 kbar) where the α form coexists in small amount with the γ -form. The contact faces of epitaxially crystallized γ on α substrates has been investigated by Stocker and coworkers, using electron microscopy and atomic force microscopy. The results show that the contact face with a low density of methyl side chains is preferred over the alternate face with a higher density of methyl groups.

The coexistence of the α and γ -phases at high pressures can be predicted from their thermodynamics parameter differences. Calculated value of the Gibbs free energy (ΔG) plotted for both α and γ -phases as a function of temperature show that at low supercooling the ΔG of the γ -form is lower than that of the α -form. The experimental

results are in good agreement with the theoretical predictions. The γ -phase may be less stable at atmospheric pressure because of its being of an intrinsically higher entropy form than the α -phase. The melting point of the γ -form is mostly reported in the range from 125 to 150°C for low molecular weight samples. In the case of pressure-crystallized samples with high molecular weight iPP, the melting occurs above 150°C.

The results of melting at high pressures show that the equilibrium melting point of iPP is linearly proportional to the pressure. The equilibrium melting point of the γ -form at atmospheric pressure is the intercept of the line and has a value of 187.6°C. This value is in good agreement with the equilibrium melting point determined from the melting temperature versus lamellar thickness, where 100% γ samples were prepared at 2 kbar and melted at atmospheric pressure.

2.1.5 Smectic

The smectic form is an intermediate crystalline order. This mesomorphic form was first named by Natta et al, and was later assigned different names such as Miller suggested that the order existing in this form might be of the type described in general terms by Hosemann as “paracrystalline”. This term was also used by Zannetti *et al.* and Wunderlich while Grebowicz proposed the term “condis crystal,” which means conformational disordered crystal.

The preparation of this form is very simple: quenching thin sheets of iPP from the melt into ice water. The main characteristics of this mesomorphic form are indicated by two broad maxima X-ray diffraction, one at 14.8° and the other at 21.2°. The interpretation of the structure formed is still disputed in the literature. Natta et al, claimed that this form is composed of bundles of parallel three fold helices, right and left-handed, where more order is present in the chain axes. In addition, the smectic form

is transformable into the α form by annealing at temperatures higher than 70°C. This fact led Bodor *et al.*, to conclude that this form is composed of microcrystals of α -iPP. On the other hand, Gailery and Ralston and later Corradini et al, suggested that the smectic form contains small crystals of the β -iPP. This suggestion is based on the position of the two maxima of the smectic form close to the position of the two most intense β -peaks. The density of the smectic form has been reported by Natta et al, to be 0.88 g/cm³, which is higher than that of atactic PP (0.85 g/cm³).

2.1.6 Rubber-modified PP

The addition of rubber to PP has been developed to extend the useful property range of PP resin. The availability of a wide range of PP homopolymers, copolymers, and elastomers with respect to molecular weight and composition has resulted in material with good stiffness and low temperature impact resistance, as well as low modulus, high thermal stability, and improved blush-resistance. This range of properties results from both matrix and dispersed phase composition and part morphology. Illustrative examples of the relationship of morphology to structure, processing, and properties of industrial applications as Figures 2.11-2.12 in order to serve the broad variety usage.

In the early development of PP, the addition of rubber provided an improvement in impact, but results varied significantly depending on the rubber composition and morphology. The basic requirements for impact-modified brittle plastics were established with the development of high impact polystyrene (PS). Similar considerations govern rubber-modified PP, but the crystalline nature of PP complicates the achievement of the desired rubber morphology. From the PS work, it was evident that particles with about 1 micron diameter having good adhesion to the matrix were desired. PP requires a similar morphology.

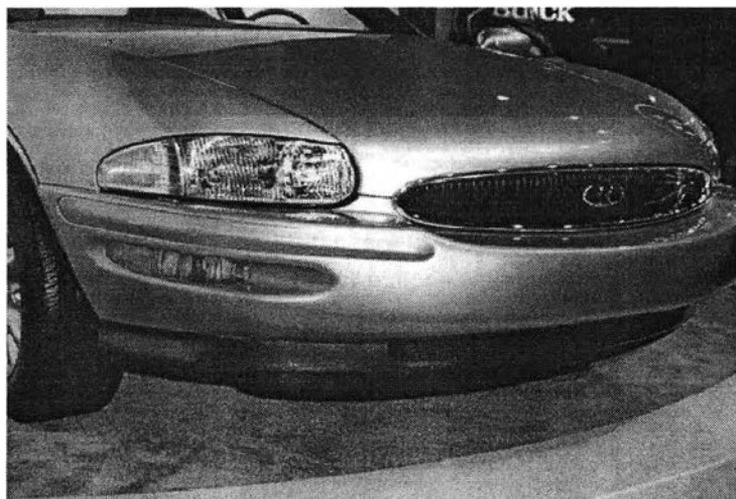


Figure 2.11 High performance car bumper in Europe.



Figure 2.12 For battery applications.

For PP impact modification, ethylene-propylene rubber (EPR) with 30% to 60% C_2 is often used. The rubber is reactor polymerized or introduced through compounding. As discussed earlier, the rubber composition is sufficiently different from PP homopolymer and random copolymer that it is usually immiscible even in the melt. Thus, the final rubber morphology is strongly affected by shear and deformation during melt process operations.

2.1.6.1 Morphology studies

The morphology of rubber-modified PP is determined by the relative chemical composition and molecular weight of the PP and elastomer phases, in addition to the compounding/fabrication process [1-3]. Like other rubber-modified polymers, blends of PP with elastomer separate into distinct phases. Immiscible mixtures can result in blends of PP homopolymer with ethylene-propylene copolymers when the comonomer content is as low as 8% ethylene [4]. Recent advances in multistep polymerization technology have added new dimensions to the control of rubber-modified PP morphology. These advances include the ability to polymerize the elastomer phase directly in the matrix, a choice of monomers and monomer ratio, and molecular weight control. The resultant product yields and as-polymerized finely dispersed elastomer phase which allows for the tailoring of rubber phase morphology and interfacial tension.

The morphologies observed in rubber-modified PPs range from dispersed to cocontinuous phase structures. The rubber phase has its own morphological characteristics resulting from its structure, melt processing, and crystallization history. Note that coalescence and growth of the rubber phase has led to an increase in the average elastomer particle diameter. The crystallinity and MW of the material are not affected by molding conditions. Changes in the macromorphology (skin/core structure), which correlate to orientation, are also small. The decrease in drop weight impact (60% in this case) is due to the increase in average elastomer particle diameter.

2.1.6.2 Viscosity ratio

The effect of viscosity ratio ($\eta_r = \eta_{\text{dispersed}}/\eta_{\text{matrix}}$) on blend morphology is well documented [5-8]. Viscosity ratio is important in determining the effects of melt processing, particularly in blends compounded by extrusion. In these blends, the

original rubber particles are very large, usually several millimeters in diameter. This ratio is also an important factor governing dispersion in reactor produced blends. Downstream melt processing may yield and increase in average particle size from agglomeration caused by particle collisions when the viscosity ratio is high, implying a weak matrix relative to the elastomer phase. The decrease in matrix viscosity reduces its ability to transfer shear stress to the elastomer phase and break it apart. Taylor dispersion, resulting from shear and extensional flow generated in some types of twin screw extruders, is responsible for rubber particle breakup in typical two phase polymer blends. The rheology of immiscible blends is complicated, and generalizations are difficult. The diameter of a fluid droplet dispersed in a matrix is related to the viscosity ratio of dispersed and matrix fluids (η_r), the interfacial tension, and the shear rate. The tendency for droplet breakup in the dilute Newtonian limit is characterized by the dimensionless capillary number (Ca) or Weber number (We) [5-8]. The final particle size of the dispersed phase is also affected by droplet coalescence during processing. As concentration and interparticle collisions increase, small particles can recombine to form larger particles, depending on the nature of the interface between them. The blend with higher viscosity ratio shows a larger average particle size.

2.1.7 EPR blends

2.1.7.1 Morphology studies

In PP/EPR blends, the multiphasic morphology was observed by microscopy and dynamic mechanical tests [9-13]. In microscopic studies, three types of dispersed morphology were observed at different compositions. When EPR forms the minor phase, the average size of dispersed EPR particles depended largely on the relative viscosity between PP and EPR; the morphology of a very fine and uniform distribution of the EPR particles could be obtained when the two component polymers had similar melt viscosities. In the intermediate composition range, the

blends with a lower viscosity EPR showed cocontinuous morphology in a wider range of concentration than those with higher viscosities. At high elastomer content, as expected, EPR forms the matrix and PP droplets are dispersed in it. Dynamic mechanical analysis (DMA) showed that the transition temperatures of the blends were identical to the pure components, indicating total incompatibility between PP and EPR, in spite of the intimate mingling of the phases. The rules controlling the morphologies in PP/EPR blends are also applicable to PP/EPDM systems [9-10, 13-14].

In injection molding of these blends, two distinct morphological layers are generally observed within the cross section [15-16]. Near the top surface, there exists a shear zone having an elongated elastomer phase. Elastomer particles in this zone are highly stretched and oriented with the injection direction as a result of high shear rates near the wall during mold filling coupled with a high cooling rate. It is also possible that, during injection molding, some elastomer particles in the core zone are elongated by flow, and spherulites nucleate along rows due to the shear. However, the slower cooling rates of polymer melt in this region allow the elastomeric inclusions time to relax, yielding spherical droplets. The morphology of the shear zone has significant effects on surface character, while the physical properties depend more on the morphology of the core zone.

The crystallization behavior of PP-based blends containing EPR or EPDM has also been reported. A substantial increase in the number of nuclei in the blends with increasing elastomer content in the system has been found [17-20]. The change in nucleation density was first attributed to nucleation is the result of a greater number of heterogeneous nuclei (inorganic residues and contaminants) that migrate from the EPR phase into PP during the mixing process. Using EPR copolymers with a reduced number of heterogeneities, D'Orazio *et al.* reported that the effects of EPR on nucleation behavior of PP/EPR blends disappeared [21].

Although the rubber is clearly immiscible with PP, the character of the PP spherulites has been shown to be affected by the rubber addition. Melting points and heats of fusion (PP basis) were lower, and the spherulites were more irregular in

texture and boundaries. At the same time, the crystallization temperatures are raised, based on the nucleation mentioned above. Unfortunately, nucleation, by raising the crystallization temperature, would work to reduce impact; smaller, but more dense and more brittle spherulites would result. Many investigators confuse this behavior with the results of higher quench rate, which gives the smaller, less well-defined, and therefore tougher spherulites of the mesomorphic (smectic) form of PP. Thus, the observation of less regular, lower melting spherulites in EPR/PP blends is more likely to explain the improved impact than nucleation.

2.1.7.2 Physical properties

In a tensile test, results obtained from a large number of blends have shown that elastic modulus is not very sensitive to structural differences [22]. In fact, its value depends almost entirely on composition and moduli of constituent components. Young's modulus of PP/elastomer systems, as expected, decreases with increasing the EPR or EPDM content [14,23-25]. Chemical modification of EPR or PP by maleic anhydride grafting did not cause any significant effect on concentration dependence of elastic modulus.

2.1.8 Talc-filled PP

Talc is by far the most widely used inorganic filler in PP, having been compounded with PP for more than thirty years. Its continued growth has been to a large degree due to efforts by the suppliers to offer talc with more consistent properties. Control of the average particle size, particle size distribution, purity, aspect ratio, and color have allowed PP producers to design filled products with as much as 40% by weight of talc.

The surface of talc may be hydrophilic or hydrophobic, depending upon the location of the ore source. In North America, talc mined in Montana have a

hydrophobic character, and those from California, a predominantly hydrophilic surface. Water absorption can be considerable and will affect the surface appearance of the molded product and the adhesion to the matrix if the filler is not modified. Using proprietary technologies, some suppliers offer surface-treated grades to enhance the adhesion between the talc and the PP. Many commercial coupling agents are also available that have shown improved mechanical properties of talc-filled PP [25-26].

Talc-filled PP grades can be based on homopolymers and copolymers of PP. The talc content varies from as little as 10% to as much as 40% by weight, with the highly filled systems being the largest percentage of the products produced. The copolymer version is similar in properties, except that the yield elongation is 25% instead of 3%. These filled products exhibit excellent properties such as high stiffness, surface aesthetics, low coefficient of thermal expansion, low shrinkage, improved scratch and mar resistance, and resistance to some aggressive chemical agents. Good impact strength is also achievable through the use of the appropriate surface-treated filler and PP grade. In some cases, compatible impact modifiers are added to maintain the impact strength, but at the expense of stiffness. For this reason, the balance between the desired stiffness and impact is critically evaluated for specific applications. Flexural modulus increases dramatically with added talc, with minimum sacrifice in tensile strength. The impact strength remains largely unaffected by the talc. Heat deflection temperature and mold shrinkage are also improved by the addition of talc. In general, talc is mainly added to improve the stiffness, use temperature, and shrinkage of the polymer.

2.1.9 Calcium carbonate-filled PP

Calcium carbonate is another filler commonly used in PP resins. It is available from a number of suppliers with chemical coatings and special coupling agents designed for specific polymeric systems [27]. Additionally, various grades of calcium carbonate are produced to meet certain stringent requirements of the plastic,

paint, and medical applications. Besides improvements in the purification processes, calcium carbonates are produced with a mean particle size ranging from 0.8 microns for the finer grades to 40 microns for the coarser grades; and some have reduced particle size distributions.

Calcium carbonate is added to PP at the same loadings as talc, from 20% to 40% by weight. There are some differences between the performance of talc and calcium carbonate. Calcium carbonate-filled PP grades have a higher impact toughness and slightly lower modulus and tensile strength than their similar talc-filled systems.

Although unique properties are achievable with mineral-filled PP resins, there are limits inherent in filled polymers. In highly filled systems, nonuniformity of mechanical properties can result from poor dispersion during the compounding process [28]. Thus, research in the area of compounding technology has intensified. In addition, many compounders are now using coupling agents to enhance the mechanical properties of filled systems. For examples, silane coupling agents are used with some fillers to improve both the wet-out with the matrix and the dispersion of the filler particles in the molten polymer. Others have found the titanate coupling agents to yield similar results [29-31].

2.1.10 Crystallization behavior

It is generally accepted that crystalline polymers have superior impact properties to amorphous ones. This is due to the crystallisation behavior of the polymers. Nevertheless, in the literature one can find lots of papers claiming a toughness deterioration with increasing crystallinity [33]. On the other hand, Karger-Kocsis J. [34] assumed that the toughness of semicrystalline polymer goes through a maximum in function of crystallinity as depicted in Figure 2.13.

Polypropylene is a semi-crystalline polymer. Its properties are determined by its crystalline structure and the relative amount of amorphous and crystalline phases, crystal modification, size and perfection of crystallites, dimensions of

spherulites and the number of tie molecule [34]. The crystalline phase of polymers consists of thin plates or ribbons with the chains oriented along the thin dimension. The amorphous region consists of chain-end cilia, totally occluded chains, and chains which are incorporated into two or more crystals (tie chains). The tie chains determine the mechanical continuity of the system and thereby control the elastic modulus as well as yield strength.

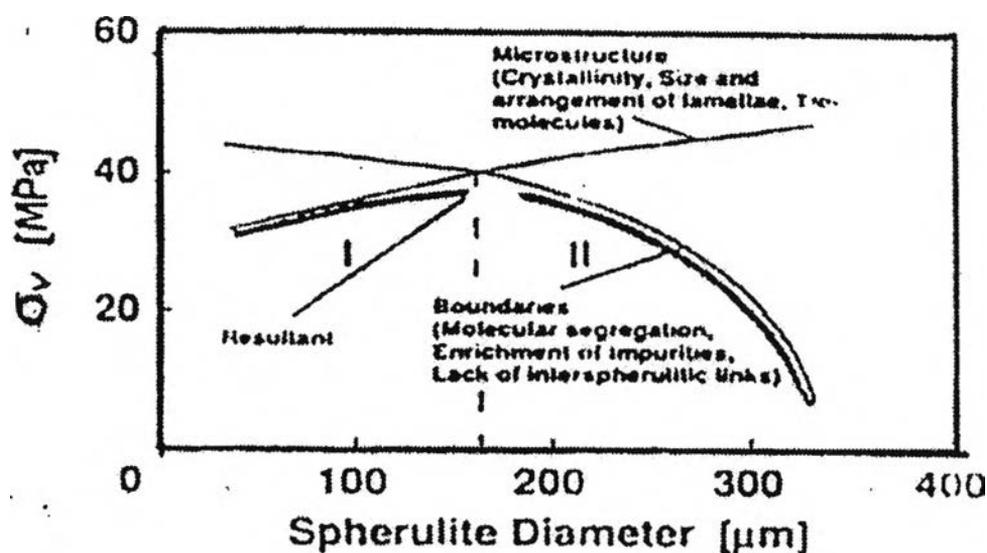


Figure 2.13 Effect of microstructure and boundaries of crystalline polymers as function of spherulite diameter.

2.1.10.1 Crystallisation of polypropylene

The higher crystallinity of the PP with coarse spherulitic structure leads to a larger volume contraction and thus to formation of voids and microcracks. Consequently, the crack path tends to follow the weak spherulite boundaries, resulting in a very low fracture toughness value as shown in Figure 2.14.

In general, it is believed that the spherulitic nucleation takes place at heterogeneities in the melt such as catalyst residues, dust particles low-molecular weight fractions, branch points, stereo-irregular molecules, fillers or

specific nucleating agents. The spherulite size is primarily dictated by the volumetric nucleation rate, which depends on thermal history, nature of the surface and degree of undercooling. The amount of crystallinity and spherulite size influences the modulus and strength of PP [34]. Spherulite size and spherulite boundaries significantly influence the yield and failure behavior of polymers. These effects are manifested in the macroscopic nature of the fracture path.

The fine spherulitic microstructure produced by adding nucleating agents gives rise to greatly enhanced ductility, yield strength, and impact strength. In general, refinement of the spherulite size by either homogeneous or heterogeneous nucleation or by reducing the crystallisation temperature results in improved ductility and strength. It is clear that large spherulites exhibit cracks at spherulite boundaries, whereas systems with smaller spherulites draw smoothly.

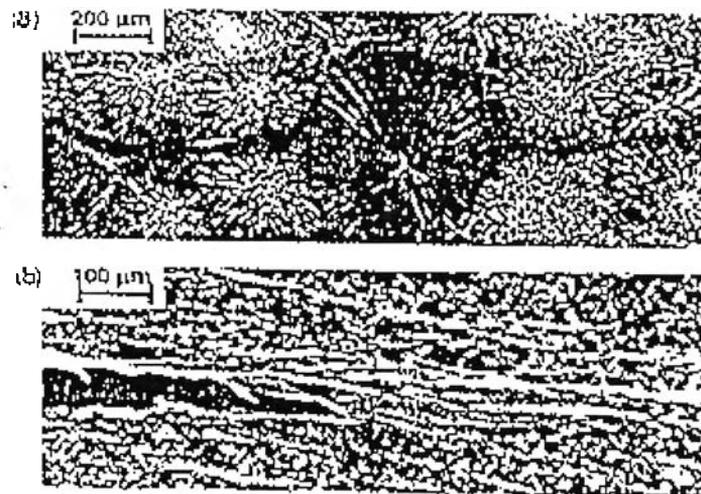


Figure 2.14 Fracture toughness of PP as a function of spherulite size: (a) coarse spherulitic, (b) fine spherulitic morphology [34].

2.1.10.2 Crystallisation of polypropylene blends

The binary crystalline polymer blends and alloys may be categorized in terms of crystalline/crystalline systems, wherein both the component polymers are crystallising, and crystalline/amorphous systems, wherein only one of the components is crystallising. The critical factors governing the extent and direction of change in the rate of crystallization and morphology of a polymer in a blend include miscibility, the glass transition, and melting temperatures of the constituent polymers, their relative melt viscosities, chemical compatibility, inherent crystallisability and phase morphology [35]. The crystallization of a polymer in a blend takes place under conditions different from those involved in its crystallization from those involved in its crystallization from the virgin melt. The physical state of the second component and the temperature range of crystallisation are determined by considerations such as the difference in the melting points of the component polymers their glass transition temperatures and miscibility. Depending on the differences in the melting points and the inherent crystallisability, a polymer may crystallise either concurrently with the other component, in the presence of the solidified second component, or in the presence of the melt of the second component [35]. Thus, in LLDPE/HDPE blends, concurrent crystallization of the two components is feasible since their melting points are close and the temperature range of crystallisation are overlapping. However, in PP/PVDF blends, although the melting points of the two polymers are comparable, PVDF will crystallize first in the presence of supercooled PP melt owing to its higher crystallisability; thus PP would crystallise in the presence of solidified PVDF. The presence of a second component either in the molten or solid state affects both nucleation and crystallisation rate is the net combined effects on nucleation and growth. In general, the presence of the second component physically hinders the transport of the crystallising polymer molecules, thereby adversely affecting crystal growth. The extent of the adverse effect is governed by the blend composition, the relative melt viscosities of the component polymers, and miscibility. The effect of blending on nucleation is more subtle and complex, particularly in the presence of the melt of the second

component. However, in the presence of the molten second component, factors such as miscibility, relative viscosity, and inherent crystallisability all influence the formation of critical size nuclei.

In the case of immiscible blends the addition of a second noncrystallising polymer results in significant changes in the spherulitic morphology. The effect of the second phase on the overall rate of crystallisation was found to be either positive or negative depending on the conditions of crystallisation, composition, molecular structure and the molecular weight of the noncrystallising component. The incorporation of one or more diluents in a crystallisable polymer may lead to the following modifications in its crystallisation behavior;

- noeffect on crystallisation rate or morphology,
- retardation of crystallisation with or without change in morphology,
- prevention of crystallisation at high loading,
- acceleration of crystallisation with or without morphological change,
- crystallisation of normally noncrystallising polymer as a result of induced mobility.

2.2 Literature reviews

Arroyo, et al. [36] investigated the crystallization kinetics and tensile behavior of EPDM/PP blends. The results have shown that PP/EPDM blends are immiscible in the melt, and, at low EPDM percentages in the blend (< 25%), the particles of EPDM act as nucleating agents and co-crystallize with PP. However, at higher percentage, the EPDM obstructs the mobility of PP chains and hence decreases the PP crystallization rate.

Nomura, et al. [37] studied the relationship between the morphology and impact strength for the blends of PP with two kinds of ethylene-propylene (EPR) having different propylene contents. The PP/EPR blends with less than 30% wt. of EPR have the PP matrix-domain structure, whereas these with have than 40% wt. of EPR have the interpenetrating co-continuous structure produced by the liquid-liquid phase separation process resulting from the spinodal decomposition. The blends of PP/EPR having a high propylene content resulted in the thickening of the interfacial region between PP domain and EPR one, because this EPR has good compatibility to PP. This thickening of the interfacial region caused the enhancement of impact strength.

Jacoby P., et al. [38] have produced different levels of the β -form PP by adding a small amount of a quinacridene dye nucleating agent. They reported that PP which contains high levels of the β -form exhibits lower values of the modulus and yield stress, but higher values of the impact strength and elongation at break.

Martinatti and Ricco [39] reported that the tensile yield stress of α -PP specimens tends to increase slightly with increasing talc content. This is due to the alignment of the lamellar shaped talc particulates in the drawing direction. However, the addition of calcium carbonate to PP produces a monotonic decrease in yield stress. This is because calcium carbonate fillers are almost spherical whereas the talc particles are lamellar in shape. Further improvement in the tensile strength and impact properties of the talc-containing PP composites can be achieved by coating talc with phosphate. The incorporation of this coupling agent to the talc-filled PP

composite helps promote the adhesion at the filler-polymer interface, and improves the degree of dispersion.

Morales and White [40] also observed that the talc filler addition does not lead a drastic change in the flexural strength of the PP composites. They attributed this behavior to the orientation of talc particulates along the flow direction during injection molding and also with the high aspect ratio of talc particulates. Thus the addition of low volume fraction of talc filler is considered to be effective in improving the impact toughness of both α -PP and β -PP specimens.

Zhang Z. et al. [41] reported that the β -PP homopolymer is shown to be much tougher than the α -PP polymer as the β -spherulites exhibit curved lamellae and sheaf-like structure. The relative higher toughness of β -PP is attributed to the ease of fibril and microcrazes formation during the impact tests.

Tjong S.C., et al. [42] have conducted a preliminary study on the impact behavior of such high β -form material. They also confirmed that the β -form sample exhibits a much higher Izod impact strength than that of an α -form sample. The above behavior is related to a difference in the spherulitic morphologies between the α - and β -crystallites. The β -spherulite exhibits a sheaf-like structure, whereas the α -spherulite consists of an aggregate of lamellae growing and braching from a central nucleus. The greater impact toughness observed in the β -form PP specimen is due to the larger energy dissipation, which is associated with the formation of microfibrils.

Alonso et al. [43] indicated that talc acts as a heterogeneous crystallization nucleus, which markedly enhances the existence of the α -modification in the PP and suppresses the formation of the β -modification.

Rybnikar [44] investigated talc fillers and identified two features on electron micrographs which were probably related to the relatively low impact strengths of talc-filled composites. Firstly, the talc platelets are arranged parallel to each other in the compound. He also demonstrated that the growth of PP on the talc surface was epitaxial, with PP tending to crystallize with a, c planes being parallel to the a, b planes in talc. Such alignment would probably mean that crack propagation would be

anisotropic, i.e. rather easier parallel to the talc plates than perpendicular to them due to a reduction in crack pinning or blocking. Secondly, the talc particles have very sharp edges, potential sites for high stress concentrations when the composites are deformed.

Shi et al. [45-46] reported that the β -spherulites develop initially as rod-like structures and then by branching of the lamellae, which finally evolve into sheaf-like structures. In this case the spherulite is formed from one crystal via an unidirectional growth mechanism. The spherical shape is attained through continuous branching and fanning via the intermediate stage of sheaves. However, the α -spherulites consist of an aggregate of chain folded lamellae growing from central nucleus. Different crystals nucleate separated during crystallization and the spherulites that are developed have distinct boundaries. These boundaries are weak sites in the polymer as failure of the PP is often initiated at these places. It is generally known that the spherulitic microstructure plays a key role in controlling the fracture behavior and the mechanical properties of polymer. The mechanical responses to tensile yielding differ substantially between the α - and β -spherulites. Tensile deformation of α -form PP usually involves a necking process in which the initial randomly-oriented spherulites structure is converted into a highly oriented one. However, the β -form PP exhibits more homogeneous deformation without obvious necking formation during the drawn process.

Lovinger et al. [47] studied the possible effects on the polymer microstructure which might result from using a nucleating or non-nucleating filler. They note that at certain crystallization temperatures, growth of β -phase crystallites is relatively favoured. It is shown that between 122°C and 138°C, the β -phase grows at a rate which is 20-70% faster than the α -phase, with the difference in growth rates being greatest at low temperatures.

Murphy et al. [48-50] have studied the correlation of mechanical properties and microstructure at different positions in a moulding. They implied that the presence of β -phase polymer reduces the impact strength of unfilled PP. Contrary to this, it has been suggested that the presence of β -phase crystallites actually enhances

impact strength. The β -phase index for PP filled with the coated carbonate is much greater than for the uncoated carbonate.

Varga J. et al. [51-52] reported that calcium salts of pimelic and suberic acids are highly active, thermally stable β -nucleating agents. Isotactic homopolymers and random and block copolymers of propylene crystallize almost purely in β modification, even at a low concentration. Ca-Sub proved to be the most effective β -nucleating agent found iPP crystallized in pure β form up to a temperature of $\sim 140^{\circ}\text{C}$. These additives caused significant changes in crystallization, melting characteristics, and structure of the polymers. The degree of crystallinity of the β -nucleated samples was markedly higher than that of the α -modification. Similar features were found for the melting behavior of α - and β -iPP crystallized isothermally in a wide temperature range.