Molecular Modelling of Polypropylene Crystallization

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***Abstract*—. Polypropylene is a semicrystalline polymer where crystallinity is usually in the range 40-70% and it also depends on the level of tacticity of the polymer.. Different crystal modifications can exist depending on the condition of the crystallization process and isotacticity of polypropylene. These changes also create differences in strength, heat resistance and pressure bonding properties. Materials Studio software package is used for the simulation of polypropylene. The molecular simulation is carried out using the forcite module, using the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. The limitation of this research was only isotactic polypropylene was investigated in this paper. In conclusion, the growth of spherulite or the crystallization of polypropylene can be affected by the cooling rates, temperature, tacticity and many more. However as for isotactic propylene, a few types of spherulites can be formed based on the condition of the crystallization process.**

Keywords— Polypropylene, Molecular, Crystallization

I. INTRODUCTION

Polypropylene (PP) is a thermoplastic polymer that is moldable at or above a specific temperature and will solidified when cooling. It is widely used in variety of field and applications, for instance, in packaging and labelling, reusable container such as plastic food containers and microwave- and dishwasher safe containers, polypropylene sheets are used for stationery such as stationery folders and many more. However, in medical field, it is used to make heat-resistant medical treatment. Polypropylene has the characteristic of slippery low-energy surface, meaning that many types of glues will not form adequate/complete joints. Welding processes is used to join polypropylene.

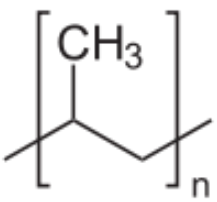

Fig 1: Molecular structure of polypropylene (PP)

The present of methyl group in polypropylene improves the mechanical properties and thermal resistance; however it decreases the chemical resistance of polypropylene. The properties of PP depend on the crystallinity, molecular weight, type, isotacticity and many more. Tacticity is related to the arrangement or order of the molecular structure. For instance, isotactic polymers are when all the substituents are located on the same side of the macromolecular backbone, syndiotactic polymers are when the substituents have alternate positions along the chain and atactic polymers are when the substituents are placed randomly along the chain.

The orientation of each methyl group on polypropylene affects the polymer's ability to form crystals. Different crystal modifications can exist depending on the condition of the crystallization process and isotacticity of polypropylene. These changes also create differences in strength, heat resistance and pressure bonding properties.

Crystallization is a process where a solid forms where the atoms or molecules are highly organized in a structure known as a crystal. The crystallization process affects a few properties of polymer, such as mechanical, thermal and chemical properties. Typically, the degree of crystallinity depends on the method of crystallization and ranges between 10-80% [1], therefore, the crystallization of polymers is usually called 'semi-crystalline'. The size and orientation of the molecular chains also determines the properties of the semi-crystalline polymers.

Table 1: Degree of crystallininty (D,%), densities of crystalline (ρ_c) and amorphous (ρ_a, g/cm^3)

Polymer	D	ρ_c	ρ_a
Isotactic polypropylene	70-80	0.95	0.85
Atactic polypropylene	~ 0	-	-

However, It is stated in the journal[2] that the degree of crystallinity is usually in the range 40-70% and it also depends on the level of tacticity of the polymer. The syndiotactic polypropylene will form either an orthorhombic unit cell or a planar zigzag conformation and triclinic unit cell conformation and isotactic polypropylene have the possibility to crystallize into three different forms depending on the polymer structure and crystallization condition. The three possible forms are again the α form with a monoclinic, the ϒ form with an orthorhombic and the β form with a hexagonal unit cell. The schematic diagram of the cylindritic morphology is shown in figure 2.

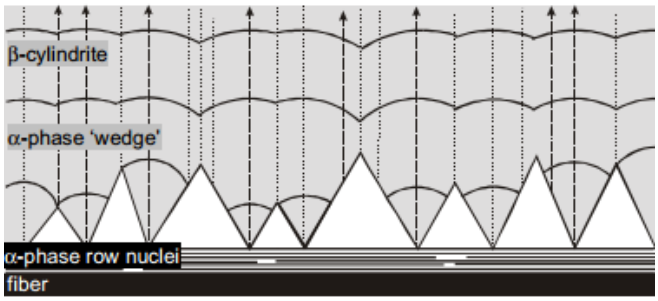

Fig 2: Schematic diagram of the cylindritic morphology. The arrows indicate the direction of growth.

II. METHODOLOGY

Materials Studio software package is used for the simulation of polypropylene. The molecular simulation is carried out using the forcite module where it is a collection of molecular mechanics tools that allow a wide range of systems to investigate. It is typically used to optimize the geometry of a system prior to a molecular dynamics simulation or a quantum mechanical calculation. Using the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. The COMPASS force field is widely used in molecular simulation for common organic and inorganic materials [3]. It is the first force field that used for accurate and simultaneous prediction of gas-phase properties and condensed-phase properties for a broad range of molecules and polymers.

The limitation of this research was only isotactic polypropylene was investigated in this paper.

III. RESULTS AND DISCUSSION

The carbon atom carrying the substituent (a methyl group in PP) is a stereogenic center and the microstructure of the polyolefin is described in terms of the meso [m] or racemo [r] enchained neighboring substituents. Isotactic polypropylene is characterized by a high fraction of [m] position of the methyl groups. For the theoretical treatment of isothermal crystallization kinetics, there are several models proposed. Avrami model proposed for isothermal model which described the polymer crystallization kinetics [7]. The change in crystallinity with time t can be expressed as:

$$\theta(t) = 1 - \exp(-k(T)t^n)$$

Where θ is the relative crystallinity at time t; n, the Avrami index (crystal geometry information); T, the crystallization temperature; and k, the isothermal crystallization rate constant containing the nucleation and growth rates. The equation above can be transform into logarithmic form.

$$\ln[-\ln(1-\theta(t)] = n\ln(t) + \ln(k)$$

Applying the Avrami theory, a plot should get straight line with slope n and intercept k. In many cases, isothermal models are experimentally accessible only over a narrow temperature range that is often well above that where crystallization occurs in processing. Non-isothermal modeling is therefore essential for the understanding of the crystallization behavior of a semicrystalline polymer.

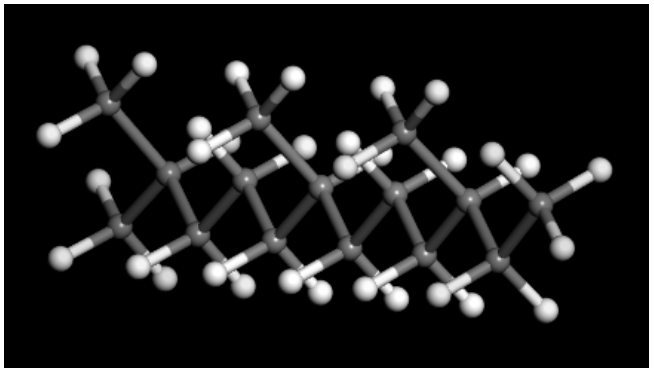

Fig 3 : Molecular model of isotactic Polypropylene

The molecular model of polypropylene was simulated using the Material Studio software as in figure 3. The cutoff distance is 12.5 Å. The simulated model in figure 3 is the best structure of isotactic polypropylene.

A Ziegler-Natta catalyst which is crystalline α-$TiCl_3$ in combination with $Al(C_2H_5)_3$, is used to restrict the linking of polypropylene to a specific orientation such as isotactic polypropylene that affects the ability for it to crystallize. The macromolecules coil into a shape of helical and line up next to each other to form the crystals. Commercially, isotactic polypropylene synthesis is produced using the medium of liquid propylene or in gas-phase reactors[4].the potential function of molecular potential energy is describe as follows;

$$E = E_{bonds} + E_{angle} + E_{dihedral} + E_{non\text{-}bonded}$$
$$E_{non\text{-}bonded} = E_{electrostatic} + E_{van\ der\ waals}$$

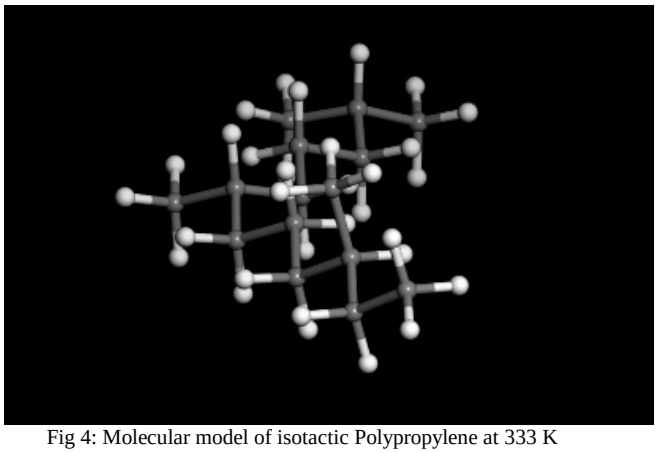

Fig 4: Molecular model of isotactic Polypropylene at 333 K

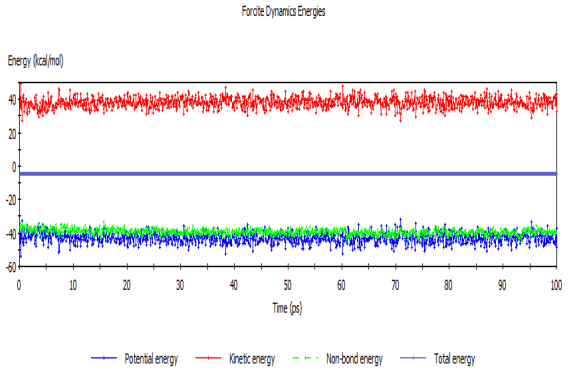

Fig 5: Dynamic energy of isopolypropylene at 333K in 100ps simulation time

The molecular model of polypropylene at 333K was simulated as in figure 4. The simulated model in figure 4 is the best structure of isotactic polypropylene, where it starts to crystallize. Figure 5, it can be concluded that it has the total energy of -4.960 kcal/mol which includes the valance energy, bond energy and many more. As for isotactic polypropylene, the methyl groups are located at one side of the molecule which make is easier to crystallize due to the regular spaced side groups.

Comparing figure 6 to journal from University of South Africa [6], at temperature 435 K where it exists as melt, and it is hard to crystallize-, the chain conformation of isotactic propylene exists with the configuration of right-up helices. The helix conformation leads to the lowest interaction energy between the methyl groups. From figure 7, it can be concluded that it has the total energy of 11.245 kcal/mol which includes the valance energy, bond energy and many more. The cutoff distance is 12.5 Å. The simulated model in figure 2 is the best structure of polypropylene.

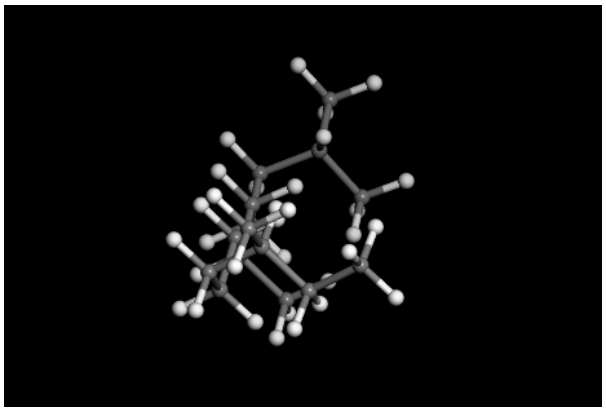

Fig 6: Molecular model of isotactic Polypropylene at 435 K

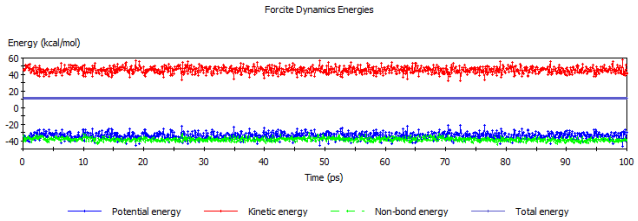

Fig 7: Dynamic energy of isopolypropylene at 435K in 100ps simulation time

Based on the research, the homogeneous polypropylene melts in heating stage, shows that when the temperature in slowly lowered to below the melting point, the crystallization process will form not spherically surfaces but circle-shape surfaces(spherulite) that eventually make contact with each other. As a result, there are straight lines boundaries formed which represent plane surfaces due to the uniform speed of growth [5]. Spherulites are three-dimensional structures that form from branching and twisting of lamellae which grow in radial direction starting from a central nucleus and polymer chains lie perpendicular to the radius.

However, at rapid cooling, the crystallization process starts at multiple different points simultaneously as in figure 8, compare to slow cooling which starts only at a few points that eventually grow until they make contact with each other.

Since the melting point of polypropylene is between 130-170^{o}C, the polypropylene exist as melt in this temperature range. The crystallization process starts when it is cooled to temperature below than the melting temperature which is in the range of 70-80^{o}C under standard polymerization conditions.

Polypropylene formed a few different phases or types of spherulite during crystallization which are α, β, ϒ or smectic phases. The formation depends on the helical conformation of polypropylene with 6.5 A repeat distance [10].

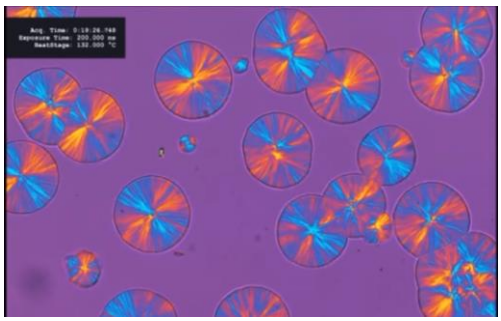

Fig 8: Multiple spherulite growth in Polypropylene measured by polarized light microscopy

When slow cooling, the crystallization of isotactic polypropylene was predominant by the α spherulites, because the alpha phase is denser than the mesomorphic one, which in turn is denser than amorphous one. When fast cooling, it is predominant by β spherulites and when thermal gradient, it is predominant by the ϒ spherulites. However, the β spherulites can transform or further crystallize into α spherulites when it is quenched or recrystallized. When the cooling rate increases, the crystallization process occurs at lower temperature. In other word, as the cooling rate increases, the temperature of crystallization decreases [11]. Other than that, the size distribution of spherulites growth will also decrease, which results in the larger number of spherulite and lower stability. The strain energy release rate of a β-PP (19.8 kJ/m^2) is at least twice as large as that of α-PP (8.5 kJ/m^2) [8]. It is concluded that the toughness of β-PP is the result of the combined effect of the microstructure and phase transformation from β to α.

The α crystals has two modification which are α_1; limit disorder, α_2; limit-ordered. However the α_1 modification can transform into α_2 when it is annealed at high temperature (higher than 110^{o}C and saturates at 140^{o}C). These two froms can be diffetiate by using x-ray analysis at high diffraction angles.

The crossover of α and β crystal can be seen at temperature of 90^{o}C and 133^{o}C where at temperature below 90^{o}C and higher than 133^{o}C, α crystal growth rate is higher that β crystal [9]. It is found that, comparing pressure crystallized isotactic propylene and isotactic crystallized at atmospheric condition, the pressure crystallized has a slightly lower density than the other, however there are no conclusive was found to explain this.

IV. Conclusion

In conclusion, the growth of spherulite or the crystallization of polypropylene can be affected by the cooling rates, temperature, tacticity and many more. However as for isotactic propylene, a few types of spherulites can be formed based on the condition of the crystallization process. It can be conclude that, the ratio of the growth rate of the β-phase with the growth rate of the α-phase (Gβ/Gα) increases steadily with decreasing crystallization temperature. When the β-phase is crystallized below $T_{\beta\alpha}$, 141°C (but above $T_{\alpha\beta,}$ 100-105°C), the growth rate of the β-phase

exceeds that of the α-phase (Gβ>Gα). In all other cases the growth rate of the α-phase is larger than that of the β-phase.

However, there are not many research made regarding this topic. A further investigation and research have to make to fully understand the topic. It is recommended to investigate not only isotactic polypropylene, but also the other types with different tacticity.

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