SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

KINETICS OF CRYSTALLIZATION FOR POLYPROPYLENE/POLYETHYLENE/HALLOYSITE NANOTUBE NANOCOMPOSITES

By

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Dissertation submitted in partial fulfillment

The requirements for the degree of Bachelor of Engineering with Honours

(Polymer Engineering)

Universiti Sains Malaysia

JUNE 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Kinetics of crystallization for polypropylene/polyethylene/ halloysite nanotube nanocomposites**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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Date: 25 June 2018

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my supervisor Prof. Dr. Chow Wen Shyang from School of Material and Mineral Resources at University Sains Malaysia. The door to Prof. Chow's office was always open whenever I faced problems or when I have enquiries about my research or writing. I appreciate the advice and suggestions given as he reviewed my work from time to time.

I would also like to thank our Master students, Ms. Ivy Gan and Ms. Keemi Lim for guiding me especially when I am conducting the research. Without their passionate guidance and motivation, the research could not have been successfully conducted. They gave me technical and conceptual knowledge on how to carry out the research.

I would also like to acknowledge Mr. Mohd. Faizal bin Mohd. Kassim, Mr. Mohd. Suharudin bin Sulong, Mr. Shahril Amir bin Saleh and Mr. Mohammad Bin Hasan who willingly guide me the technical knowledge to handle the equipment and machines in order to complete my research. I am gratefully indebted to be able to learn the knowledge of the machines used from them and the proper way to analyse the results. Besides, I would like to thank all the laboratory technicians of School of Material and Mineral Resources Engineering, University Sains Malaysia for giving me guidance to complete my research.

Finally, I must express my very profound gratitude to my family for providing me with unfailing support and continuous encouragement throughout my studies and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thank you.

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LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimetry
HDPE	High Density Polyethylene
HNT	Halloysite Nanotube
phr	parts per hundred
PP	Polypropylene

LIST OF SYMBOLS

ΔH_m°	Endothermic Enthalpy of 100% Crystallized Sample
ΔH_m	Endorthermic Enthalpy of Samples
χ_c	Degree Of Crystallinity
α	Alpha
β	Beta
X_t	Relative crystallinity at crystallization time t
n	Avrami exponent associated with the crystallization mechanism
Z_c	Modified crystallization rate constant
Z_t	Crystallization rate constant related to both nucleation and growth rate parameters
E_a	Crystallization activation energy
R	Gas constant
T_p	Peak temperature
$\propto$	Mo exponent
$F(T)$	Cooling rate chosen at unit crystallization time
$K(T)$	Cooling function
m	Ozawa exponent
T_g	Transition temperature
T_m	Melting temperature
T_c	Crystallization temperature
w	Fraction of the polymer contained in the composites.

$t½$	Half crystallization time
dH_C	Crystallization enthalpy released in an infinitesimal temperature range dT
T_0	Initial crystallization temperature
T	Crystallization temperature at time t
T_∞	Final crystallization temperature,
ϕ	Cooling rate
$k_0(T)$	Cooling or heating crystallization function

KINETIK PENGHABLURAN NANOKOMPOSIT POLIPROPILENA/ POLIETILENA/TIUB NANO HALLOYSIT

ABSTRAK

Polipropilena (PP) mempunyai prestasi yang tinggi dan harga yang berpatutan. Walaubagaimanapun, kekuatan hentamannya yang rendah mengehadkan pengunaannya, dan ini boleh diselesaikan dengan adunan polietilena berketumpatan tinggi (HDPE). Kadar penghabluran PP/HDPE adalah rendah dan memerlukan pengisi nano sebagai agen penukleusan seperti tiub nano halloysit (HNT). Tumpuan thesis ini dijalankan adalah untuk mengkaji kesan HNT terhadap sifat terma adunan PP/HDPE. Kinetik penghabluran tak sesuhu nanokomposit PP/HDPE/HNT telah dikaji dengan menggunakan model Avrami, Kissinger dan Mo. Penambahan HNT didapati menurunkan suhu penghabluran (T_c) dan meningkatkan darjah kehabluran (χ_c). Eksponen Avrami (*n*) dalam lingkungan 1 hingga 2 bagi semua nanokomposit PP/HDPE/HNT dan ini menunjukkan nukleasi ketika. Nilai pemalar kadar penghabluran (Z_t) bagi PP/HDPE juga meningkat dengan penambahan peratusan berat HNT. Hal ini menunjukkan peningkatan kadar penghabluran. Penurunan masa penghabluran separuh ($t_{1/2}$) bagi PP/HDPE dengan penambahan peratusan berat HNT menunjukkan peningkatan kadar penghabluran. Model Kissinger menunjukkan tenaga pengaktifan penghabluran (E_a) untuk PP/HDPE menurun dengan penambahan HNT. Dengan menggunakan model Mo, nilai *F(T)* untuk PP/HDPE berkurang dengan penambahan HNT. Secara keseluruhannya, amount HNT yang sesuai untuk PP/HDPE adalah 8 wt% disebabkan ia dapat meningkatkan kadar penghabluran nanokomposit tersebut.

KINETICS OF CRYSTALLIZATION FOR POLYPROPYLENE/POLYETHYLENE/HALLOYSITE NANOTUBE NANOCOMPOSITES

ABSTRACT

Polypropylene (PP) is commonly used due to its affordable price and high performance but its low impact strength limits its applications which can be improved by blending with high density polyethylene (HDPE). Crystallization rate of PP/HDPE is lower compared to pure PP. Therefore, provides the need to use nanofiller as nucleating agent such as HNT. The aim of this thesis is to investigate the effects of HNT on the thermal properties of PP/HDPE blends and the kinetics of non-isothermal crystallization of PP/HDPE/HNT nanocomposites by using Avrami, Kissinger and Mo model. In this study, the incorporation of HNT nanoparticles decreases the crystallization temperature (T_c) and increases the degree of crystallinity (χ_c). From the Avrami model, the Avrami exponent (n) is in the range of 1 to 2 for all PP/HDPE/HNT nanocomposites indicating instantaneous nucleation while the crystallization rate constant (Z_t) values of PP/HDPE increased with the addition of HNT. This indicates that addition of HNT increases crystallization rate. The reduction of half crystallization time ($t_{1/2}$) for PP/HDPE as the increasing HNT loading indicates faster crystallization rate. Kissinger model showed that the activation energy (E_a) of crystallization for the PP/HDPE decreases with the addition of HNT. In Mo model, the cooling rate chosen at unit crystallization time $F(T)$ values for PP/HDPE decreases with the addition of HNT. In summary, the most suitable HNT loading for PP/HDPE blend is 8 wt% HNT as it increases the overall crystallization rate of PP/HDPE blend.

CHAPTER 1

INTRODUCTION

1.1 Background

According to Maddah (2016), polypropylene (PP) has gained strong popularity profoundly fast due to the fact that it has the lowest density among commodity plastics. It is a rigid and semi-crystalline polymeric material which is widely used due to its excellent chemical resistance, good mechanical properties and good processability which enables it to be processed through many different methods such as injection molding and extrusion. One of the biggest advantage of PP is its ability to withstand high temperature during its application. This special characteristic permits its use in production of instrument jars that have to be sterilized frequently for use in a medical environment. (Yuan *et al*., 2006). Other useful properties of PP also include high heat distortion temperature, good transparency and dimensional stability which broadens its application. PP is also commonly used as a matrix material because it possesses suitable characteristics for composite fabrication. It is also a candidate that is suitable to be used for filling, reinforcing and blending (Shubhra *et al.*, 2011).

The biggest drawbacks of PP which limits its usage is its low impact strength and brittleness which can be improved by a toughening modification. Therefore, a simple and effective method to improve the impact strength of PP is by polymer blending. Polymer blending is an easy, versatile and cheap method for creating a new polymeric material. The polymer blends can have desirable properties of all the constituent components without synthesizing a totally new material which has proven to be too expensive for certain applications (Supaphol *et al*., 2004). Polyblends are defined as a product of melt-blending or solvent-blending of two or more polymers. The mechanical or physical properties of polyblends is highly dependent on the phase morphology and interaction between the continuous and dispersed phase. The component ratios also affect the final properties of polyblends. Phase morphology depends on the processing technique used to prepare the polymer blend. For example, injection molding and processing parameters which includes temperature and shear force. A suitable polymer to be blended with PP to improve impact strength is High Density Polyethylene (HDPE) because it has a similar structure to PP, good processability, cheap and has high impact resistance. (Lin *et al.*, 2015). HDPE is made up of carbon and hydrogen as backbone elements and has less branching. HDPE also has stronger intermolecular forces and tensile strength than LDPE. Physically, it has higher hardness and can withstand higher temperatures. HDPE also is more opaque than LDPE. Thus, it has extensive industrial and day-to-day applications (Madhu *et al.*, 2014).

The blends of polyethylene and polypropylene are very important and this is a result of their synergy of high impact strength and low temperature toughness. Moreover, both polyolefins are the main contributor of plastic wastes. Recycling PP and PE as blends is sought to be an efficient solution to the waste problem and the final products can be of considerable value. Addition of polyethylene into polypropylene increases the impact strength of polypropylene and addition of polypropylene into polyethylene improves the environmental stress crack resistance of polyethylene (Jose *et al.*, 2004). The crystallization behaviour, processing technique, and phase morphology are important factors which have to be taken into consideration as they have a large impact on the structure and properties of the PP/PE polyblends. For example, the processing temperature and the HDPE amount in the blends is inversely proportional to the interfacial tension of the PP/HDPE polyblends (Lin *et* *al.*, 2015).

At crystallization temperatures (Tc) below 127°C, the number of PP nuclei increased with increasing PE content. However, crystallization temperatures above 127°C show a decrease in the number of nuclei. This was attributed in part to the migration of heterogeneous nuclei from the PP phase to the PE phase during melt mixing. The existence of PE does not influence the spherulite growth rate (Blom *et al.*, 1998). The crystallization orders of PP and HDPE are very similar when the non-isothermal temperature decreases. In this case, their crystallization peaks are not distinguishable which is caused by the high crystallinity rate of HDPE. HDPE has a higher rate of crystallization compared to PP. Furthermore, blending PP with HDPE also speeds up the heterogeneous nucleating of PP in the polyblends. Thus, PP will also show quick crystallization, and the crystallization peaks of PP and HDPE cannot be distinguished from each other (Shankar *et al.*, 2016). However, PP/HDPE blends has a slower crystallization rate compared to pure PP which forms a research gap for improvement of this problem. A solution to this problem is to incorporate halloysite nanotube (HNT) which is further discussed in this research.

The crystallinity of the polymer and crystalline morphology have significant effects on the physical and mechanical properties of polymers. The analysis of crystallization kinetics can provide important information for the control of polymer based composites formulation and performance. Crystallization kinetics analysis can also provide knowledge to control processing parameters such as cycle time, blend ratios and processing temperature in injection moulding. For nanocomposites, it is necessary to understand the effect of additives on the crystallization behaviour of the polymers. It is known that nanoscale fillers can provide nucleation sites that induce heterogenous nucleation which improves the crystallization process. Halloysite nanotube (HNT) are a natural nucleating agents and it has significant promotion effects in many polymers. Halloysite nanotube could serve as a nucleation agent in PP/halloysite nanocomposites which brought about an enhancement of the overall crystallization rate and the non-isothermal crystallization. The crystallization behavior of nanocomposite is strongly dependent on the dispersion and surface conditions. Incorporation of HNTs plays a role in increasing the crystallization temperature of PP and also promoting the nucleation and overall crystallization rate by acting as a heterogeneous nucleating agent (Bao *et al.*, 2015).

Nucleating agents are of major importance in processing of semi-crystalline polymers as they allow for tailoring of the polymer microstructure and allow engineers to have enhanced control over the macroscopic properties of these materials. In addition, Incorporation of nucleating agents in semi-crystalline polymers is economically beneficial, as they increase the polymers’ crystallization temperature, resulting in shorter processing cycles and associated energy savings (Bernland, 2010). Nucleating agents are being widely used in order to improve mechanical and optical clarity of polypropylene and its copolymers. Besides, they are also commonly used to accelerate polypropylene crystallization kinetics, reducing injection moulding cycle times and as a result reducing production costs. The nucleating agent efficiency is highly dependent on its particle size, morphology, chemical structure and behaviour when incorporated into the polymer. Nucleating agents have been evolved and different variations are made to ensure maximum nucleation, efficiency in processing as well as better profit without compromising on quality (Simanke *et al.*, 2016).

Halloysite nanotubes (HNTs) reinforced polymer nanocomposites are extremely popular in research and industrial sectors. This is because HNT has significant effects on the mechanical and flame resistance properties. Advantages of HNT are contributed by its characteristics which includes high length to diameter (L/D) ratio, low hydroxyl group density found on the surface and flame resistance. These benefits allows the widespread usage of HNT in various application sectors. HNTs were commonly used as reinforcing filler for almost all commercial polymer matrices which gives enhancements in their performance properties (Rajan, 2016).

Incorporation of unmodified HNTs into PP exhibit excellent distribution of nanotubes in PP matrix. Mechanical properties of PP also improved with the incorporation of HNT and it was reported that 6 wt% of HNT showed optimum properties (Prashantha *et al.*, 2011). Du *et al.* (2009) studied the kinetics of thermal decomposition and thermal ageing behaviour of HNT reinforced PP. The activation energy for thermal degradation increased with an increase in HNT content. The incorporation of HNT has resulted in a remarkable enhancement of thermal stability and reduction in flammability of the resulting nanocomposites. The crystallisation behaviour of PP/HNT nanocomposites were investigated and the result of the investigation showed that HNT acted as a nucleating agent and thereby resulted in improvement of crystallisation rate and crystallisation temperature of PP. The nucleating effect of HNT for PP was also further investigated. Tailoring of surface microstructure and the wettability characteristics of PP by incorporation of HNT have brought about a conclusion that the size of the spherulites, surface roughness and the surface wetting characteristics of PP can be fine-tuned by proper incorporation of HNT (Rajan, 2016).

The crystallization kinetics of isotatic PP (iPP) has been widely studied by different methods. Generally, crystallization kinetics are analyzed by the Avrami model. However, although the typical value of the Avrami exponent, *n*, is about 3, some authors have reported values in the range of 2 and 4 that were attributed to different nucleation mechanisms (Avalos *et al.*, 1996). The crystallization behavior of PP nanocomposites was investigated for different halloysites weight contents. The results evaluated from the Differential Scanning Calorimetry (DSC) proved that both degree of crystallinity and crystallization temperature increase upon incorporation of halloysites nanotubes into PP. Hence, the results suggests a positive nucleation effect induced by the nanotubes (Prashantha *et al.*, 2011).

Practically, thermoplastic composites are usually produced and processed under non-isothermal conditions including injection and extrusion molding. Thus, it is important to investigate the crystallization behaviour to optimize processing technology of PP blend nanocomposites. Avrami and Mo model are commonly used to analyze the non-isothermal crystallization kinetics of PP blend nanocomposites. The crystallization activation energy (E_a) of the specimens can be calculated with the method introduced by Kissinger (Niu *et al.*, 2011).

The rate of crystallization plays an important role in facilitating polymer fabrication operations such as spinning, extrusion, compression, injection moulding and film processing. A faster crystallization rate is desired in polymer processing industries as it can lead to a reduction in cycle times which improve productivity in moulding operations. Besides, the energy savings and efficiency are improved. In addition, normally in plastic film extrusion, a faster crystallization rate results in the formation of smaller and poorly developed crystals that results in improved optics. Moreover, a faster crystallization rate reduces and to an extent eliminates post-fabrication dimensional changes arising from secondary crystallization. This dictates the need to monitor the changes in the crystallization rate of a polymer brought about by modifiers such as nucleating agents (Khanna *et al.*, 2012).

1.2 Problem Statement

Incorporation of High Density Polyethylene (HDPE) into Polypropylene (PP) can improve the mechanical properties such as impact strength and low temperature toughness. However, crystallization rate of PP/HDPE is lower than pure PP. The nucleation in HDPE is also more difficult to control than in PP due to HDPE's faster crystallization rate.

Addition of HNT into PP/HDPE blend could influence their crystallization behavior. Thus, it is a need to study the crystallization behavior and kinetics of non-isothermal crystallization for PP/HDPE/HNT nanocomposites.

1.3 Research Objectives

The research objectives of this project are as follow:

(a) To investigate the effects of HNT on the thermal properties of PP/HDPE blends.
(b) To investigate the kinetics of non-isothermal crystallization of PP/HDPE/HNT nanocomposites by using Avrami, Kissinger and Mo models.

1.4 Thesis Structure

This thesis comprises of 5 chapters.

Chapter 1 shows the introduction part which explains the research background and problem statement of this research and an outline of the dissertation.

Chapter 2 represents the literature review of this thesis which discuss in details on the literature review of the general information about polypropylene (PP), High Density Polyethylene (HDPE), Halloysite Nanotube (HNT), PP/HDPE/HNT nanocomposites and kinectics of crystallization.

Chapter 3 denotes the material used, preparation methods and characterization methods. The complete methodology for the fabrication of PP/HDPE/HNT nanocomposites will be discussed later in this chapter. The characterization method of PP/HDPE/HNT nanocomposite will be explained further in chapter 4.

Chapter 4 discusses on the results obtained from the research. Elaboration on the problems encountered such as the adverse effects on kinetics of crystallization after addition of HNT to PP/HDPE blend followed by its explanation.

Chapter 5 summarizes the highlights of the research and formulate the overall conclusion of the project. Suggestions and recommendation for future studies are also included in this chapter.

1.5 Scope of Study

In this research, PP/HDPE/HNT nanocomposite were prepared using internal mixer and compression molding. The crystallization behavior of the PP/HDPE/HNT nanocomposites were characterized using Differential Scanning Calorimeter (DSC). The effect of cooling rate and amount of HNT on the crystallization behavior of the PP/HDPE blend nanocomposites were studied. This research is done to address the effect of the HNT amount on the kinetics of crystallization of PP/HDPE blend. Different cooling rate also shows different kinetics of crystallization which affects the properties of the PP, PP/HDPE and PP/HDPE/HNT nanocomposite.

CHAPTER 2

LITERATURE REVIEW

2.1 Polypropylene (PP)

Polypropylene (PP) is a semi-crystalline polymer that was first synthesized in 1957 by Gulio Natta in Italy. This has led to a widespread commercial production in Europe. Not only does PP stands out as an affordable polymeric material, it has excellent versatility in its application. PP has a low density which is 0.89 gm/cc and excellent rigidity compared to other polymers. It has won a place in the frequently used polymer after polyethylene and polyvinyl chloride. The main reason behind its widespread usage is due to its superior strength to weight ratio, good chemical resistance and excellent thermal stability. Moreover, Polypropylene copolymers containing ethylene content up to 25% are recognized for its superior low-temperature impact strength as well as improved clarity compared to PP homopolymers. Polypropylene production is possible by using common process methods such as injection molding, extrusion, thermoforming and compression molding. The applications of PP are commonly found in furniture products, consumer goods, automotive products, textile fibers, sanitary diapers and clothing (Taheri *et al.*, 2014).

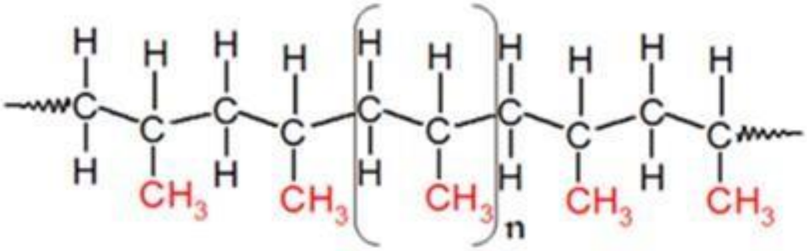

Figure 2.1: Polypropylene structure (Maddah, 2016).

The substantial use of polypropylene (PP) in a wide range of applications has encouraged an immense interest in conducting research for improvement of this common polymer. Aromatic polyesters generally known for its overall superior properties have found a niche as candidates to improve PP properties via blending and various nanocomposite technologies. However, polypropylene is acknowledged as a difficult sample to perform isothermal crystallization. This is mainly due to its very high crystallization rate and very high activation energy. Hence, PP can act as a performance standard to explore isothermal crystallization capabilities by comparison methods. If success is achieved with PP, then it ensures the success for virtually all other polymers to be tested (Jafari *et al.*, 2012).

Propylene resins comes from a family of versatile thermoplastics. Their semi-crystalline nature and their structural stereo-regularity enables engineers to tailor their physical and mechanical properties according to the desired performance. The properties of PP can be controlled by manipulating their molecular structure, molecular weight and molecular weight distribution, co-monomer content and distribution, degree of crystallinity and morphology. Advancements in the catalytic system, polymerization process and post reactor changes and addition of different additives can help overcome the limitations of polypropylene, giving it the chance to compete with other polymers and materials. The wide range applications of polypropylene and its copolymers range from durable parts such as exterior and interior parts of automobiles to disposable packaging such as bags. Although polypropylene faces some restrictions in applications that require outstanding optical properties but these can be improved by propene copolymerization with co-monomers such as ethylene and butane. Besides, optical clarity can also be enhanced by the incorporation of additives such as nucleating agents. For example, foreign particles such as silica, talc and organic salts can be added to polypropylene to accelerate the crystallization rate as they act as seeds of nucleation process (Simanke *et al.*, 2016).

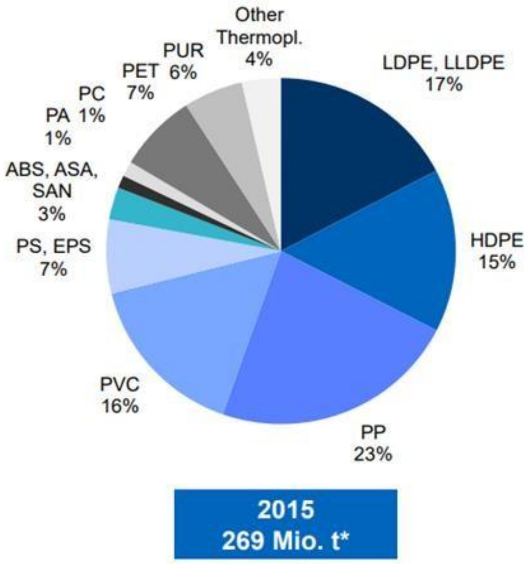

Figure 2.2: Global demand for types of plastic statistic in 2015 (Plastics Europe Market Research Group (PEMRG), 2015).

In the year 2015, polypropylene (PP) have been reported by global market demands as the most demanded plastic compared to the other plastics. The production of PP has represented in 23 wt% of the total amount of plastic consumed in the world (Plastics Europe Market Research Group (PEMRG), 2015). The biggest concerns that caused PP to become controversial are its application in plastic items that are for short term usage such as packaging, bottles, bags and containers. Current waste management plans are not capable enough to accommodate the increasing levels of plastic wastes. In fact, large amounts of waste did not reach proper disposal sites or treated. Instead these waste contribute to the litter in the landscape and are washed into the rivers polluting the environment. As the demand of plastic increases dramatically, this leads to increasing amounts of plastics ending up in the waste stream. In 2013, only 2.66 million tons out of the total 39.3 million tons of plastic waste of the American Municipal Waste Stream have been recycled. Even though, polyolefins have good recycling properties, they make up of over 50% of the non-recycled plastic (17.80% HDPE, 19.60% LDPE, 13.90% PP). This has fueled the interest in reusing and recycling plastic (Aumnate *et al*., 2016).

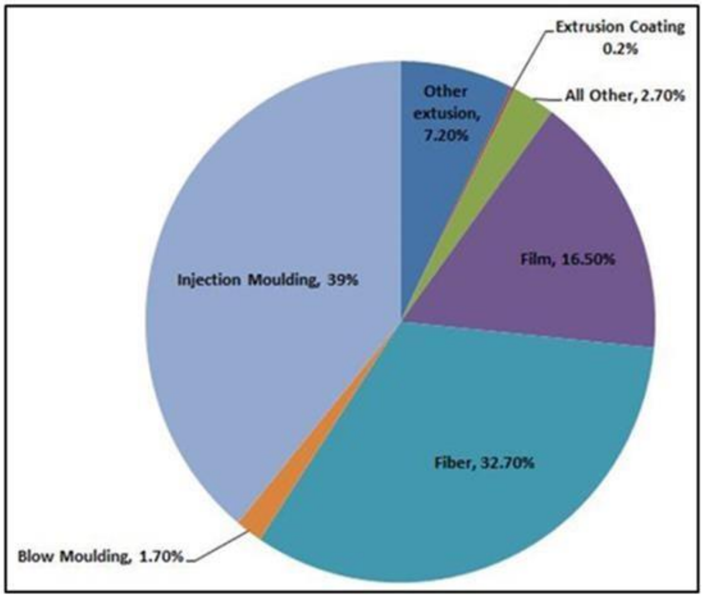

Figure 2.3:Global consumption of polypropylene by end use application (Maddah, 2016).

In 2005, a research showed that the global consumption of polypropylene (PP) is mainly used in injection molding and fibers. Besides, other applications of PP include plastics in medical, laboratory tools, plastic tubs, plastic containers, wastebaskets, pharmacy prescription bottles, plates, cooler containers, pitchers, rugs, electrical insulation cables, stationery folders, light shades, storage boxes, loudspeaker drive units and water filters. Moreover, PP is also widely used to manufacture clothes and related products such as disposable diapers or sanitary products where PP is modified to absorb water which makes it hydrophilic as unmodified PP is naturally water-repellent or known as hydrophobic. PP is an excellent material to fabricate base layer for cold weather clothing and under-armor clothing. Another interesting application of PP is called polypropylene sheet foam (Maddah, 2016).

Polypropylene grades mainly produced are homopolymer, co-polymer, and impact copolymer. In addition, there are four crystalline modifications of polypropylene that is α, β, ɣ and smectic. The differences in the crystalline structure can contribute to significantly different properties as the modes of chain packing of each structure are distinct. The special structure of β-polypropylene gives it interesting properties. Different type of nucleating agent and processing method can also attribute dissimilar β-crystalline content. This can greatly affect the physicochemical properties of the final material. β-polypropylene is well recognized for its superior mechanical performance, toughness, elongation at break and impact strength which is comparatively higher than that of α-form of polypropylene. The unique behaviour of β-PP can be attributed to the banded structures that the β-spherulites exhibit due to their broad lamellae. The specific lamellae form coplanar stacks and its plane tends to twist along the growth direction (Papageorgiou *et al*., 2015).

2.2 High Density Polyethylene (HDPE)

High density polyethylene (HDPE) is a thermoplastic material made from petroleum and it consist of carbon and hydrogen atoms joined together which contributes to its high molecular weight. It is known for is high strength-to-density ratio and has become a very common and useful commodity plastic due to its good chemical resistance, superior electrical insulation, environmental resistance, and it can be easily molded into any shape. The relative amounts of crystalline and amorphous contents present in the polymer can determine the final properties of HDPE. Besides, the mechanical properties and thermal properties of HDPE also depend on the crystal structure and molecular weight of HDPE. The type of branching in HDPE is less compared to LDPE which contributes to a greater density and higher strength. The properties of polyolefins can be improved by the addition of various kinds of fillers to achieve the desirable final properties at low cost. The addition of a filler can cause alterations to the polymer microstructure. For example, crystallization, glass transition, crosslinking, phase splitting, and orientation can be changed as they are closely related to various types of molecular motions. Addition of organic or inorganic particles into the polymer matrix can allow tailoring of the properties of HDPE such as mechanical strength and optical clarity. HDPE is a stable material due to its carbon-carbon bonds which have strong interactions that slow down degradation as more energy is required to break the bonds. HDPE's low rate of degradation is one of the reasons that encouraged the efforts of finding new alternatives for disposal reduction (Kadhim, 2017).

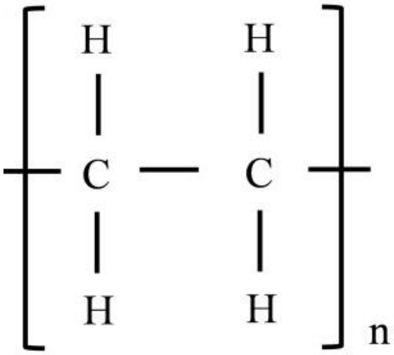

Figure 2.4: High density polyethylene structure (Haghighatpanah *et al.*, 2014).

Polyethylene (PE) is characterized as a semi-crystalline polymer. It is made up of crystalline regions and amorphous regions. PE is gaining popularity over the years and is used extensively in many industrial and biomedical applications. Its exceptional features like regular chain structure, great biocompatibility, reasonable cost and low energy demand for processing and superior mechanical properties allow PE to expand its application continuously. The advantages of PE products over metal products is due to their light weight, low costs, and high corrosion resistance. On the other hand, there are some shortcomings of PE which includes low creep resistance, low environmental stress cracking resistance, and poor compatibility with various additives, resulting in a restriction of its use for cretin purposes. Thus, there have been many attempts to improve the properties of polyethylene by blending (Alothman, 2012).

Polyethylene is a chemically simple polymer consist of carbon and hydrogen atoms with the basic repeating unit ($-\mathrm{CH}_2-\mathrm{CH}_2-$). It is a semi-crystalline polymeric material with crystalline and amorphous phases. The crystalline phase give PE its structural integrity, while the amorphous parts contributes to its elastic properties. Generally, it is impossible to obtain polyethylene single crystals of close to one hundred percent crystallinity in dilute solutions. However, polyethylene is usually crystallized from a melt in practical applications. It is found that melt-crystallized PE shows a spherulite morphology. In this morphology, the lamellae is made up of spherulites that are embedded in a matrix of amorphous material. The spherulites are made up of thin flat lamellae illustrated in Figure 2.5. Moreover, the lamella has a structure consisting of regular chain-folding arrangements where the molecular chains are perpendicularly aligned to the lateral lamellar surfaces as shown in Figure 2.5 and Figure 2.6a. The lamella which has regular chain-folding growth produces crystals with lateral direction dimensions (1-50 μm) which are much larger than their thickness (2-25 nm). Besides the chain folding model, a different type of lamella structure is proposed. This structure is made up of a growing crystal which feeds on whatever chains available and forms an arrangement as shown in Figure 2.6b. Research suggests that both type of crystalline structures proposed by different models can exist in melt-crystallized polyethylene. For polyethylene research studies, the regularly folded chain model is preferred than the non-regularly folded chain model (Cheng, 2008).

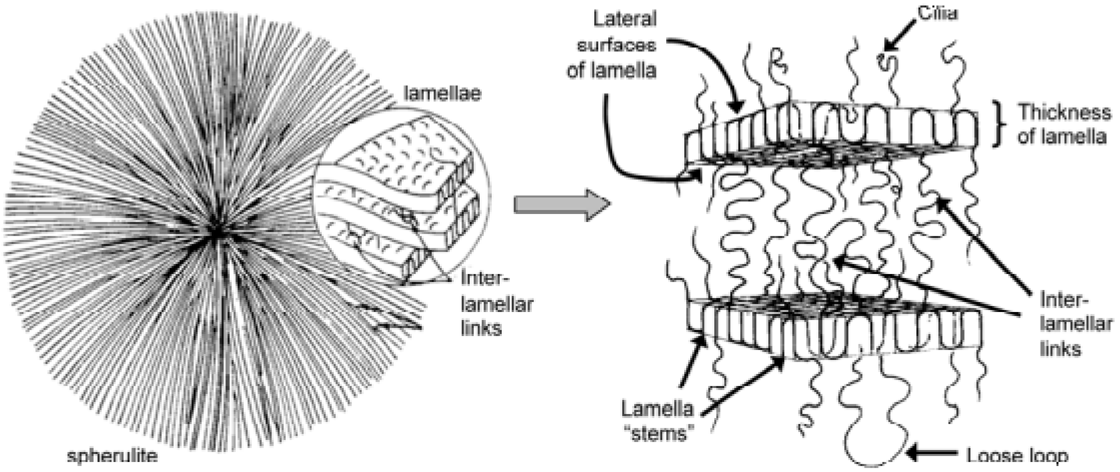

Figure 2.5: Schematic illustration of spherulite, lamella, and amorphous phase structures (Cheng, 2008).

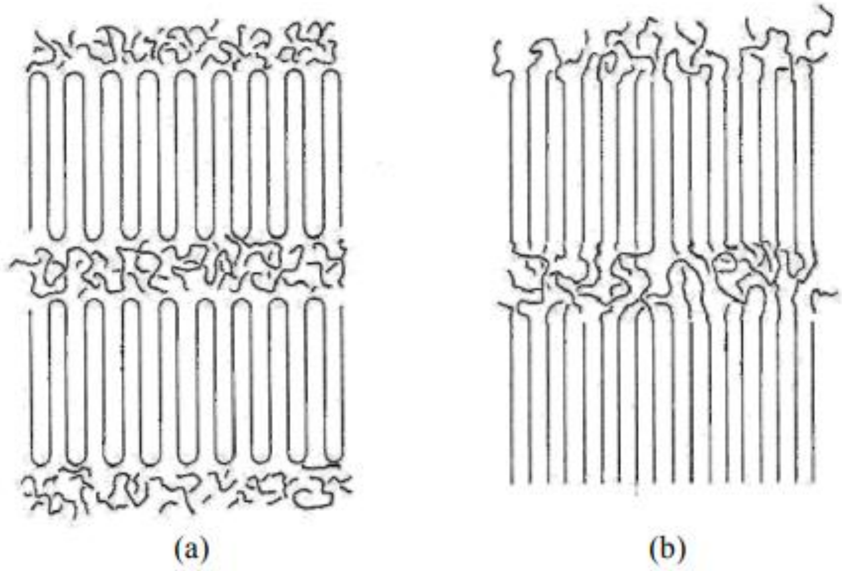

Figure 2.6: Structures of lamella; (a) the regularly folded chain model for semi-crystalline polymer; (b) non-regularly folded chain model for semi-crystalline polymer (Cheng, 2008).

Polyethylene (PE) are polymers of great industrial importance and has been known for its wide applications. The flexibility of polyethylene application is a result of its intrinsic abilities to be produced in many different forms based on molecular structures. There are several types of polyethylene but the most common is high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). All three types of PE have distinct degree and regularity of branching. HDPE has the least branches and a linear structure which allows close packing of molecular chains. Hence, HDPE has superior rigidity compared to the branched PE and is suitable for applications where rigidity is of concern. LDPE is characterized by a larger degree of branching with irregular branches at irregular intervals, contributing to the soft, tough and flexible properties of LDPE (Omar, 2012). In contrast, LLDPE is characterized by short chain branches of regular length at regular intervals. These structural differences contribute to the difference in physical properties of these polymers such as crystallinity and melting point (Furukawa *et al.*, 2006).

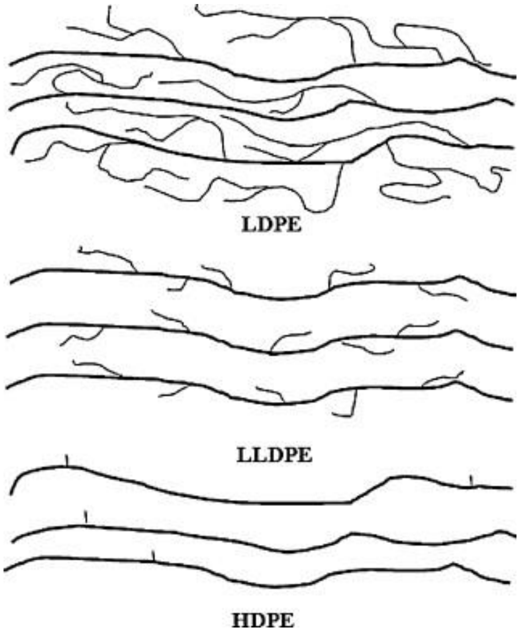

Figure 2.7: Schematic molecular structures representation of different types of polyethylene (Omar *et al.*, 2012).

2.3 PP/HDPE Blends

Polymer blending is an alternative route for development of polymers with optimized properties. In application, performance is an important factor to consider. The final properties of the blends depend on their individual polymer components. The miscibility of the polymer blends and whether the blends exist as a single phase is of importance to the performance of the blend. Most blends of high molecular weight polymers exist as two-phase materials. Morphology of the phases is also an important factor to take into considerations. It is found that there are many different morphologies present such as dispersed spheres of one polymer in another, lamellar structures, and co-continuous phases. The drawbacks of PP is that it has relatively low impact strength especially at low temperature and poor environmental stress cracking resistance. This has encouraged the blending of PP with PE to obtain the combination of properties. Incompatible immiscible polymer blends show synergy of mechanical properties when the processing parameters and composition are at an optimum level. Blending PP and HDPE can improve tensile strength, enhance fracture strength, increase young modulus, improve hardness, increase creep rate and creep modulus compared to PP/LDPE blend. The blend ratio of 20% HDPE and 80% PP gives superior mechanical properties. The results from the scanning electron microscope (SEM) images show that PP/HDPE and PP/LDPE are immiscible blends. (Salih et al., 2013).

The combination of polyethylene (PE) and polypropylene (PP) are difficult to separate due to their similar structure. The blends of polyethylene and polypropylene are important in commercial applications because they exhibit both high impact strength and low temperature toughness. In addition, PE and PP are major contributors of plastic wastes and scraps due to their popular demand. Recycling PP/PE blends also has more value than their pure counterparts. Polyethylene enhance the impact strength of polypropylene while polypropylene improves the environmental stress crack resistance of polyethylene *(*Jose *et al.*, 2004).

The properties of the blends that have two crystallisable components depend strongly on their crystallinity, crystalline morphology and degree of dispersion. The existence of dispersed particles will affect the morphology of the continuous phase, the overall kinetics of crystallization and spherulite growth rate. Many studies related to blends of isotactic polypropylene (iPP) with high density polyethylene (HDPE) have been carried out. The results showed that iPP is immiscible with polyethylene and the blend forms a heterogeneous two-phase system. PE inclusions in iPP matrix form geometrical obstacles to spherulitic growth and cause huge alterations in their morphology but they have insignificant effect on the growth rate. In comparison, significant changes are observed in the overall kinetics of crystallization and in the spherulite nucleation in blends compared to pure polypropylene. Polypropylene blended with high density polyethylene exhibit enhancement in nucleation, reduction in size of crystallities and a lower degree of crystallinity in the (Zhang *et al.*, 2000).

Polypropylene is not only familiar due to its good mechanical properties, heat resistance, low cost, ease of processing and full recyclability. The major limitation of PP is that it has low impact strength which can be improved by polymer blending. Blending be used as it is the most efficient and easiest method. The main reasons that HDPE is chosen to blend with PP is because it has a similar structure to PP, easier to process, low cost and show good impact resistance. The final properties of the PP/PE polymer blends depends on the crystallization behavior, phase morphology and processing methods. Moreover, the compatibility of polymer blends depends on the processing parameters such as temperature, blending ratios and polymer structure. In addition, the combination of two polymers prepared with the same process conditions or possess similar physical properties contributes to greater mechanical properties of the compounds (Lin et al., 2015). PP/HDPE blends exhibit superior impact strength and fracture toughness values as compared with PP/LDPE blends due to the compatibility between PP and HDPE as a result to their structure which applicable in LDPE since the molecular chains in the LDPE have higher degree of branching. This forces the molecular chains farther apart from each other, weakening the bonding forces between the chains. Thus, PP/LDPE blend has lower strength compared to PP/HDPE blend (Smith & Hashemi, 2006).

HDPE dispersed in the iPP /HDPE blend crystallizes below 125-127ºC with a rate close to that of crystallization of iPP. It is found that crystalline HDPE inclusions in iPP matrix induce additional nucleation of a number of iPP spherulites. As a result, nucleation density of iPP spherulites in the iPP /HDPE blends increases with increasing content of HDPE in the blend during crystallization below 127 ºC. It is interesting to note that because of the phenomenon migration of HDPE inclusions become richer in impurities, thus the crystallization is enhanced. This in turn induces a large increase of nucleation density of iPP in that blend because of a large number of HDPE crystallized inclusion contacting iPP melt. During nonisothermal crystallization a simultaneous crystallization of both PP/HDPE components is possible. Already crystallized inclusions of a dispersed polymer accelerate the crystallizaiton of a matrix acting as a nucleating agent. And induce the formation of additional spherulites. Finally the average spherulite radius in those blends becomes smaller than in plain iPP crystallized under the same conditions (Karger-Kocsis, 2012).

In melt blended PP/HDPE samples containing 5 to 25 wt% HDPE, the results indicate that the addition of HDPE to PP results in an increased degree of crystallinity of PP, a faster rate of nucleation and a reduction in the crystalline size distribution (Nicholas, 1989). In rapidly quenched iPP/HDPE blends, the crystallization behavior is studied. By using differential scanning calorimetry (DSC) to imitate the quenching conditions used during preparation of the samples for mechanical testing, results show that both homopolymers crystallized at higher temperatures in the blends than in their individual state. It suggested that some synergistic crystallization effects were responsible for this behaviour. Heterogeneous nucleating agents in the polypropylene migrate to the polyethylene regions and act as nucleating agents for the polyethylene enabling it to crystallize at higher temperatures in the blend than on its own. The polyethylene crystals will then act as nucleating agents for the polypropylene facilitating it to crystallize at higher temperatures than it normally would. Polypropylene can also nucleate polyethylene. It is reasonable to assume that polyethylene can nucleate polypropylene. It was suggested that the higher crystallization temperatures of the components led to higher component moduli (Finlay *et al.*, 2003)

Over the years, PP and PE blends have been extensively investigated to improve their versatility. Out of all the known polymers, PP/PE blend has the most background research studies as its combination of properties is a game changer in commercial plastic production. Both of the thermoplastic PP and PE components are crystallizable. So, knowledge on the kinetics of crystallization and crystalline morphology of either component in the blend is important to understand the relationship between the structure and properties of the blend. The incorporation of organoclays into PP/PE blend significantly enhance its properties and contribute to a more complex phase morphology as well as crystallization kinetics for both of the crystalline components. Very few studies are conducted to study on the fabrication and characterization of polyolefin blend-based nanocomposites (Chiu *et al.*, 2010). It is worth noting that a high HDPE content (above 25 wt%) causes the tensile modulus and flexural modulus of the PP/HDPE polyblends to decrease. High HDPE content in the blends may cause phase separation of HDPE which causes and increase in HDPE particles that serve as the nucleating agent for PP. The spherulite size of PP is then decreased, resulting in reduction of the crystallinity of PP. The second reason is that HDPE has a lower tensile modulus and flexural modulus compared to PP. Thus, the optimum formulation of PP and HDPE in the polymer blends is very important to obtain the desired properties (Lin *et al.*, 2015).

2.4 Halloysite Nanotube

Halloysite nanotube (HNTs) polymeric nanocomposites are composed of both an organic matrix and a dispersed inorganic phase. Halloysite nanotubes are a natural mineral formed in the earth for many years. Compared to conventional composite materials, the mechanical properties and thermal of polymers can be improved with a very low HNTs loading. HNTS have high aspect ratio and its nanosize dimensions makes it a very desirable candidate to be used as reinforcement materials for different polymers. In order to improve the interfacial adhesion between the HNTs and polymers, the interfacial interactions can be tailored using chemical or physical approaches. Modifications can be made to the surface of HNTs. HNTs can improve the mechanical properties of the polymers at high temperatures under both dynamic and static conditions. Besides, incorporation of HNTs have proven to enhance the mechanical strength, modulus, stiffness and impact resistance of polymers (Ferrari *et al.*, 2017).

Halloysite nanotube (HNTs) has a tube like morphology which is commercially used due to its low electrical, thermal conductivity and strong hydrogen interactions which the inner hydroxyl groups show greater stability than the surface hydroxyl groups in halloysite (Ibrahim *et al.*, 2012). Moreover, halloysite nanotubes (HNTs) are used as nanofillers at certain amounts to enhance the mechanical properties, physical properties and thermal properties of the polymer. The addition of HNTs have become a popular choice as reinforcement materials for polymers compared to conventional nanofillers such as carbon nanotubes (CNTs). This is due to its affordability and good processability. Structurally, the geometric size of HNTs are in the range of 300 to 1500 nm in length, 15 to 100 nm in inner diameter and 40 to 120 nm in outer diameter. HNTs do not have to be exfoliated because the layers are intact although HNTs can aggregate or entangle to each other, unlike kaolinite plate like morphology. The crystal structure of HNTs consists of two layers of tetrahedral and octahedral sheets joined mainly by hydrogen bond. The tetrahedral structure siloxane groups (Si-O-Si) belongs to the external surfaces of the HNTs while the internal surface consists of octahedral (Al-OH) structure. HNTs are characterized by the average pore size of 80–100 Å and aspect ratio of 10–50. A higher aspect ratio indicates better reinforcing effect. HNTs have 75–82 $\mathrm{m^2/g}$ BET surface area and 2.14–2.59 $\mathrm{g/cm^3}$ density which performs better than the other mineral fillers in producing a lightweight polymer composite (Gaaz *et al.*, 2017).

Halloysite nanotubes (HNTs) are a class of natural clays which share the same chemical composition as kaolinite and have a hollow tubular morphology, resulting from the wrapping of the clay layers. Basically, 10 to 15 aluminosilicate layers roll into a cylinder. The difference of HNTs are due to its structure and chemistry of the precursor mineral phase from which is formed and the environmental conditions, resulting in crystallization in different forms. The main difference between HNTs and the other aluminosilicate minerals is their unique nanotubular structure, good biocompatibility and very low cytotoxicity make them promising to the development of new products, especially polymeric nanocomposites as carriers for drugs (Ferrari *et al.*, 2017). Halloysite nanotubes are eco-friendly nanotubes and are relatively cheaper than carbon nanotubes. In the recent years, there has been growing concern about the effect of carbon nanotubes on human health and the environment because of their potential toxic nature. This has promoted the use of HNTs in commercial applications such as polymer additives, biocompatible implants, drug delivery vehicles, catalytic supports and molecular sieves, cosmetics and personal care products (Kamble *et al.*, 2012).

Halloysite nanotubes (HNTs) is a type of aluminosilicate clay with a chemical formula $Al_2Si_2O_5(OH)_4.2H_2O$ which is chemically similar to kaolinite, but the unit layers in halloysite are separated by a monolayer of water molecules. The natural deposits of halloysites nanotubes are found in countries like China, Mexico, America, Brazil, and France. Halloysite nanotubes are naturally formed in the earth over millions of years. Halloysite nanotubes are unique and versatile nanomaterials that are formed by surface weathering of aluminosilicate minerals and are composed of aluminum, silicon, hydrogen and oxygen. Halloysite is a fine clay mineral consisting of tubular particles with multi-layered wall structure. The variations in the symmetry of the finishing structure of halloysites are due to the water molecules present between two consecutive layers. Halloysites may be platy, fibers tubular or cylindrical particles of different dimentions. The existence of tubular or cylindrical particles is the indication of halloysites but if the samples are with platy particles then they are named as kaolinite. In terms of crystallization behaviour, HNTs can affect the