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**EFFECTS OF HALLOYSITE NANOTUBE ON  
THE MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES  
OF POLYPROPYLENE/POLYAMIDE BLENDS**

By

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Dissertation submitted in fulfillment  
of the requirements for the degree of Bachelor of Engineering with Honours  
(Polymer Engineering)

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “**Effects of Halloysite Nanotube on the Mechanical, Thermal and Morphological Properties of Polypropylene/Polyamide Blends**”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this in any other examining body or university.

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## LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetry
FESEM	Field Emission Scanning Electron Microscope
HNT	Halloysite Nanotube
KAS	Kissinger-Akahira-Sunose
MMT	Montmorillonite
PA6	Polyamide 6
PP	Polypropylene
TGA	Thermogravimetric Analysis
VMT	Vermiculite

## LIST OF SYMBOLS

$\alpha$	alpha
$\beta$	beta
$\gamma$	gamma
$\chi_c$	crystallinity
$\Delta H_{f^\circ}$	enthalpy change of fusion at 100% crystallinity
$\Delta H_m$	enthalpy change of fusion
$E_a$	activation energy for thermal decomposition
$T_d$	temperature at end of decomposition
$T_c$	crystallization temperature
$T_{max}$	temperature at maximum rate of decomposition
$T_m$	melting temperature
$T_{onset}$	temperature at onset of decomposition

**KESAN TIUB NANO HALLOYSIT TERHADAP SIFAT MEKANIKAL,  
TERMA DAN MORFOLOGI BAGI ADUNAN POLIPROPILENA/POLIAMIDA**

**ABSTRAK**

Poli(propilena)/Poliamida 6/tiub nano hallosit telah disediakan melalui ekstruder dan diikuti dengan pengacuan suntikan. Adunan nisbah PP/PA6 telah ditetapkan dalam nisbah 80:20 dan pembebanan tiub nano halloysit (HNT) adalah daripada 2 hingga 8 wt%. Kajian ini dijalankan untuk menyiasat kesan HNT terhadap sifat lenturan dan terma bagi adunan PP/PA6. Daripada ujian lenturan tiga titik, ia menunjukkan modulus lenturan dan kekuatan lenturan PP/PA6 meningkat apabila kandungan HNT bertambah. Hasil daripada Mikroskop Medan Pancaran Pengimbasan Elektron (FESEM) menunjukkan bahawa saiz PA6 (fasa serakan) menurun selepas HNT dimasukkan dan ini menunjukkan kesan penyerasian HNT dalam adunan PP/PA6. Analisis Termogravimetrik (TGA) menunjukkan bahawa penguraian terma PP/PA6 dipengaruhi oleh kandungan HNT. Dalam kajian kinetik penguraian terma, model Kissinger-Akahira-Sunose (KAS) telah digunakan. Adalah didapati bahawa tenaga pengaktifan penguraian terma ( $E_a$ ) nanokomposit PP/PA6/HNT adalah lebih rendah daripada adunan PP/PA6 tanpa HNT. Hasil Kalorimetri Pengimbasan Pembezaan (DSC) telah menunjukkan bahawa darjah pengabluran PP dan PA6 meningkat dengan kehadiran HNT dan ini membuktikan kesan penukleusan HNT terhadap adunan PP/PA6.

**EFFECTS OF HALLOYSITE NANOTUBE ON THE MECHANICAL,  
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**ABSTRACT**

Poly(propylene)/Polyamide 6/halloysite nanotube nanocomposites were prepared using extruder followed by injection molding. PP/PA6 blend ratio was fixed at 80:20 while the halloysite nanotube (HNT) loading was ranged from 2 to 8 wt%. This study is aim to evaluate the effects of HNT on flexural and thermal properties of the PP/PA6 blends. From the 3-point bending test, it was shown that the flexural modulus and strength of PP/PA6 was increased as the increasing loading of HNT. Field emission scanning electron microscopy (FESEM) results demonstrated that the droplet size of PA6 (minor phase) reduced after incorporation of HNT, which indicates the possible compatibilization effects of HNT in the PP/PA6 blends. Thermogravimetric analysis (TGA) results showed that the thermal decomposition of PP/PA6 is influenced by the loading of HNT. For the study of kinetics of thermal decomposition, Kissinger-Akahira-Sunose (KAS) model was applied. It was found that the activation energy of thermal decomposition ( $E_a$ ) of the PP/PA6/HNT nanocomposites is lower than that of unfilled PP/PA6. Differential Scanning Calorimetry (DSC) results showed that the crystallinity of PP and PA6 was increased in the presence of HNT, which evidenced the nucleating effects of the HNT for the PP/PA6 blends.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

Polypropylene (PP) is a type of thermoplastic that is very much versatile as it can be manufactured through several processing methods and can be seen to be in the usage of numerous commercial products. It is a very light thermoplastic with only  $0.9 \text{ g/cm}^3$ . PP with its relatively low cost and desired properties gives rise to its strong growth rate. Many different grades in the market with various properties that make PP widely used in various applications such as injection molded parts for automobiles, food packaging, appliances and consumer products (Karian, 2003). PP is one of the major materials used in the automotive industry. However, for a long-term thermal stability is an important consideration in the application. Despite the many advantages of PP, low dimensional and thermal stability limits the scope of PP in various fields (Lomakin, 2006).

Usually at the processing stage, PP may experience damage in their backbone chain which may result in crosslinking, chain scission and conjugation. Excessive shear forces, heat and having impurities and oxygen may damage the polymer chains which result in highly reactive radicals situated at the chain ends. These radical can recombine, but they can also able to form peroxy radicals and hydroperoxides in the presence of air. Excessive degradation can cause severe chain scission in the back bone chain, branching and crosslinking that may alter different properties (Yin, 2017).

Incorporation of nanofiller to a polymer was found to be beneficial to the mechanical and thermal stability of a polymer system. In terms of physical, nanofiller form a surface barrier layer that is thermally stable and decrease the heat transfer to the underlying material. On the chemical side, it favours the formation of solid rather than gaseous decomposition product that serves the purpose like the physical barrier (Mitchell & Tojeira, 2016).

Polyamides come with numerous chemical compositions that is comprise of a large family of materials which also known as nylons. One of these types of nylon is the ring polymerized nylon, polyamide 6 (PA6). Generally, the family of nylons have good mechanical properties, chemical resistance and heat resistance. However, one of these drawbacks of PA6 is the brittleness at low temperature. Development had been done to modify the commercially nylon resin to improve its performance (Keskkula, 1999). In the polyamide family due to its good performance over the cost ratio, nylon 6 is widely used in the automotive field (Vaidya, 2011).

Polymer blends is a new polymeric system which is formed by having two or more polymers mix together having both traits of the individual polymers. It eliminates the need to synthesize new polymers that required long and expensive route (La Mantia et al., 2017). Polymer blends had been recognized as one of the most versatile and cost saving methods to give rise new multiphase polymeric materials that are able to fulfil the requirement for certain high end performance. For the past decades, different types of polymer blends had been developed and researched intensively. The design and performance of the mentioned multiphase polymer blend is highly influenced by the control of the interface and also the morphology (Harrats et al., 2006). Polymer blends

had been extensively selected as materials in the current polymer industry as they provide a broader range of properties as compared to its respective single polymer alone. Thus, this gives polymer blends to be used in various fields such as biocompatible materials, adhesion and design of composite (Mittal, 2012).

PP and PA6 are two important class of polymer. PP is commercially used due to ease of processing and considerably cheap and it has high barrier properties to moisture due to its hydrophobicity. On the other hand, PA6 is relatively expensive and hygroscopic in nature (Sanderson & Pasch, 2002). Thus, blending PA6 with PP is expected to improve the overall properties and achieve a balance between the properties (Tokumitsu et al., 2016).

Polymer nanocomposites are composites that comprised of a polymer matrix and fillers with at least one dimension less than 100 nm were incorporated into the polymer matrix. The fillers that were incorporated can be in various forms such as plate-like (clays), high aspect ratio nanotubes and also equiaxed nanofillers. Attention was given to nanocomposites due to its unique combinations of properties that were not acquirable by traditional composite (Schwarz et al., 2004). Nowadays, various types of commercial nanofillers are added in the formation of polymer nanocomposite. Due to this variety, researchers can tailor made the properties by selecting the type of nanofiller that can achieve the desired outcome (Koo, 2016). There are various nanofillers that are commercially used in polymer system. These nanofillers include carbon nanotubes, metal-oxide nanoparticles and clay-based nanocomposites. The reason for this is that they show an improvement for the polymer system in the aspect of thermal and mechanical properties (Gao, 2012).



In this recent decade, the advancement and research on clay minerals in nano scale had been beneficial. Nanosized tubular clay minerals are clay mineral with hollow tubular nanostructure having at least one dimension between 1 and 100 nm. Several microscopic and spectroscopic methods were used to identify different structures of nanosized tubular clay minerals, such as chrysotile, imogolite and halloysite (Yuan et al., 2016). As compared to other layered silicate nanofillers such as montmorillonite (MMT) and vermiculite (VMT), halloysite nanotube (HNT) had been research intensively due to its unique cylindrical structure (Thakur et al., 2017). The tubular shape and the hydroxyl groups found on the HNTs surface enables the HNTs to be easily dispersed in the polymer matrix by the means of direct melt mixing. This eases the processing as compared to other forms of mineral nanoparticles (Lvov et al., 2017). HNT is seen as a potential replacement for carbon nanotubes as reinforcing filler for polymers. The structure of HNT is similar to the tubular structure of carbon nanotubes but relatively cheaper and non-toxic in nature (Saharudin et al., 2017).

The tubular form of halloysite with combined of high mechanical properties and aspect ratio can be used to reinforce the nanocomposite (Yuan et al., 2016). HNT is surprisingly flexible that can be bend without being fractured. This can contribute to some of the mechanical properties of the nanocomposite. HNT has the ability to act as a heterogeneous site for nucleation. This gives HNT the potential to increase the degree of crystallinity of nanocomposites and its effect tends to increase with increment of nanotubes loading (Mitchell & Tojeira, 2016).

## **1.2 Problem Statement**

PP and PA6 blending has been used to obtain improvement in mechanical, thermal and barrier properties, where PP offers good processability and less moisture absorption while PA6 offers mechanical and thermal properties. Note that, blending of PP (major matrix) and PA6 (minor phase) need to be melt-compounded at temperature about 260 °C ( $T_m$  of PA6) may induce thermal degradation of PP. Adding antioxidant is one approach. However, it is rather complicated for example the selection of suitable primary and secondary antioxidant. Also, some of the antioxidant would be affecting the mechanical properties of the polymer blends. It is believed that nanofiller for example, Halloysite Nanotube (HNT) is a feasible alternative for the PP/PA6 blends to achieve a balance of mechanical and thermal properties by compensating the possible properties reduction due to thermal degradation during the melt processing.

## **1.3 Objectives**

This research is mainly to develop a PP/PA6 blend nanocomposite that is reinforced with halloysite nanotube (HNT) via single screw extruder and injection moulding. In order to accomplish this main objective, this project was divided into three specific objectives:

1. To improve the flexural properties of PP/PA6 blends.
2. To evaluate the effects of HNT on the thermal properties of PP/PA6 blends.
3. To evaluate the kinetics of thermal decomposition of the PP/PA6 nanocomposites by using Kissinger-Akahira-Sunose (KAS) model.

## 1.4 Thesis Structure

This thesis consists of five chapters.

**Chapter 1** represents the introduction part of the thesis, which consists of the research background, problem statement, objectives and the outline of the dissertation.

**Chapter 2** contains literature review of thesis, which presents background literature on the general information about polypropylene, polyamides, polypropylene blend and a comprehensive literature review of PP/PA6 nanocomposites.

**Chapter 3** represents the material approaches and the research methodology. Detailed methodology will be provided regarding sample preparations including the machineries used and also the processing parameters. The characterization methods used for PP/PA6 nanocomposites will also be discussed in this chapter.

**Chapter 4** comprised of the results and the discussion of this dissertation. Elaborations of the problem and the explanation will also be included in this chapter.

**Chapter 5** denotes conclusion of the project. This chapter provide conclusion that based on the objectives of the projects and suggest recommendations for future studies.

## 1.5 Scope of Study

In this study, PP/PA6 blend nanocomposite was prepared. The selected polymer used to blend with the polypropylene was polyamide 6. The blend ratio of the PP/PA6 blend was in 80/20. Halloysite nanotube (HNT), a nanofiller was incorporated into the polymer blend system to study its effect and possibly to improve on the thermal and mechanical properties. The parameter that was studied was the different loadings of

HNT, 2%, 4%, 6% and 8%. The polymer nanocomposite was prepared via melt mixing by using a single screw extruder and the samples were formed by injection moulding. The influences of the HNT and its loadings on the flexural, morphology and thermal properties were studied. The kinetics for activation energy of thermal decomposition for PP was investigated by using Kissinger-Akahira-Sunose (KAS) model.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Polypropylene

Polypropylene had long been discovered 45 years ago and been commercialized since 40 years. Further research and development of polypropylene still continued until today (Otto, 2007). Propylene is manufactured as a by-product through the cracking process of different types of hydrocarbon which is originally from the crude oil or natural gas (Alger, 1997).

Polypropylene is formed through the addition polymerization process of the monomer propylene. The chemical structure of polypropylene is usually known as the repeating unit of 2-methyl ethylene. Figure 2.1 shows the chemical structure of propylene and polypropylene which gone through the addition polymerization. The molecular weight of polypropylenes in within the range  $M_n = 38\ 000 - 60\ 000$  with  $M_w$  220 000 – 700 000 thus giving  $M_w/M_n$  approximately in the range of 5.6 – 11.9 (Murphy et al., 2016).

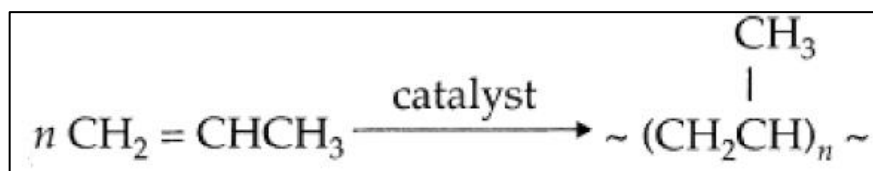


Figure 2.1: Polymerization of polypropylene (Malpass & Band, 2012).

The polymerization can be in many different condition and polypropylene compositions also varied extensively in structure and properties. The subscript  $n$  is known as the degree of polymerization (DP) and is usually larger than 1000 for most of the commercially available grades of polypropylene. After the manufacturing process from industrial scale reactors in ambient conditions, stereoregular polypropylene is basically in a form of white powdery or granular solid (Malpass & Band, 2012).

There are different stereo chemical configurations exist in polypropylene which is in the form of isotactic, syndiotactic and atactic. The resulting stereo chemical configuration is highly dependent on the orientation of the pendant methyl groups polymerized with the neighbouring carbon atoms. In isotactic, all the pendant methyl groups are in the same configuration and at the same side of the polymer chain. On the other hand, syndiotactic is when the pendant methyl groups are in an alternate manner on opposite sides of the polymer chain. Atactic polypropylene will have the random orientation along the polymer chain (Ugbolue, 2017). Figure 2.2 shows the different stereo chemical configurations of polypropylene.

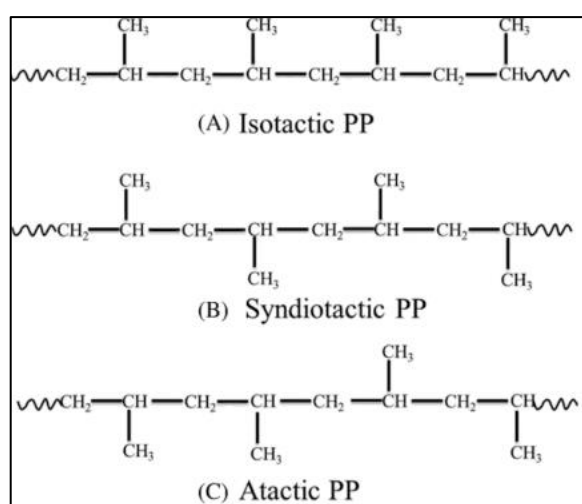


Figure 2.2: Different stereo chemical configurations of polypropylene (Ugbolue, 2017).

The stereo chemical configurations had a great impact on the properties and thus the applications of polypropylene. For instance, atactic polypropylene is amorphous which resulted in soft and limited in applications such as adhesives. On the other hand, isotactic polypropylene is relatively higher crystalline and stiffer which is suitable for molded parts (Baugh & Canich, 2008). As far as the stereo chemical configuration concerned, it can be specify through the usage of Ziegler-Natta catalysts. Ziegler-Natta catalysts are highly capable of producing isotactic polypropylene (Padsalgikar, 2017). The function of a Ziegler-Natta catalyst is to destabilize the double bond between adjacent alkene carbons. The catalyst which is in the crystalline form catalyzes the polymerization on the edge sites of the crystal metal centered complex by forming a bond between the metal atom and the propylene. At the same time, the electrons from the double bond delocalized making the addition polymerization can be continued (Wagner, 2016).

Besides that, it is possible to copolymerize polypropylene with various olefins such as ethylene and  $\alpha$ -olefins such as 1-butene, 1-hexene and so on. The olefins used to copolymerize are named as comonomers and added into the growing polymer chain. For example, ethylene is the widely used comonomer. However, there are products also used higher  $\alpha$ -olefins. Normally, the polymerization from this comonomer along the polymer chain is rather random because of differences in reactivity. This often led to random of copolymer in content and a distribution of comonomers along the polymer chain. Thus, random blocks of ethylene comonomer resulting from multiple insertions may exist along the backbone chain (Malpass & Band, 2012).

Referring to Table 2.1 and Figure 2.3, it is shown that the market share for the consumption of polyethylene (PE) is the highest at 33% to 39% and this is followed by PP at 21% – 22%. Although, the market share of PP is lower, its annual growth rate is high (Biron, 2013).

Table 2.1: Market shares by weight for different thermoplastics (Biron, 2013).

Thermoplastics	Market share (%)
PE	33 – 39
(LDPE/LLDPE)	(18 – 22)
(HDPE)	(15 – 17)
PP	21 – 22
PVC	13 – 14
PET	8 – 11
Styrenics: PS and others	7 – 11
PA	1 – 2
PC	1
PMMA	1
Acetal	<1
Other engineering	6
TPEs	1
Bioplastics	<1
Total thermoplastics	100



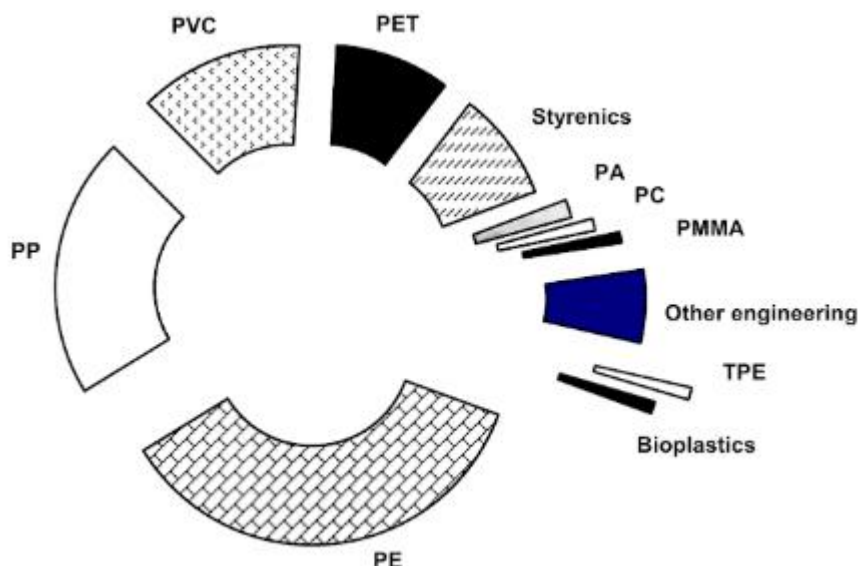


Figure 2.3: Proportion of market share on total thermoplastic consumption (Biron, 2013).

PP is a widely used polymeric material for wide range of applications due to its good properties and processability in mass production processes such as through extrusion, injection moulding and casting. The products manufactured from PP can be made from several different types of PP. These include isotactic PP, crystalline PP homopolymers, random copolymer and impact or heterophasic copolymers. PP came in many advantages such as it is lightweight, unaffected by moisture and acid resistant. The structural of PP products have excellent impact capability, high strength, high toughness and good dimensional stability under service conditions. In addition, PP is cheap and easily available in the market. PP can exist in various forms to be used in applications such film and sheet, filament and fibres, pipes, profiles and wire coating (Abdel-Bary, 2003).

PP exhibits several interesting on mechanical properties such as good strength at room temperature and different rates of deformation. The incorporation of inorganic fillers has been further discussed in the toughening mechanism polypropylene (Eiras & Pessan, 2009). The deformation mechanism of unmodified polypropylene is through shear yielding. This deformation leads to a permanent change of the dimension and gives translational motions of the polypropylene chains. The molecular entanglements of PP which act as resistant points give great deformations for PP. The deformation process is represented in Figure 2.4. On the other hand, for a filled system the toughness characterization depends on the matrix voiding initiated by the rigid inclusion and matrix shear deformation that surrounding the particles. The presence of a plastic zone affects the fracture initiation and the propagation values. Figure 2.5 showed the stages of crack formation (Arencon & Velasco, 2009).

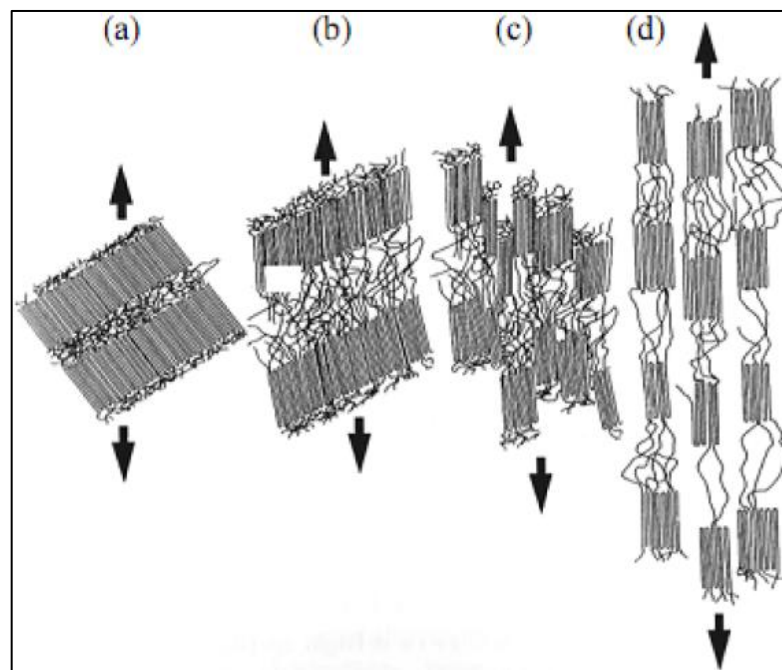


Figure 2.4: Schematic representation of the deformation process in PP: (a) no deformation, (b) chain motion inside lamellae, (c) lamellae fragmentation and (d) tension alignment (Arencon & Velasco, 2009).

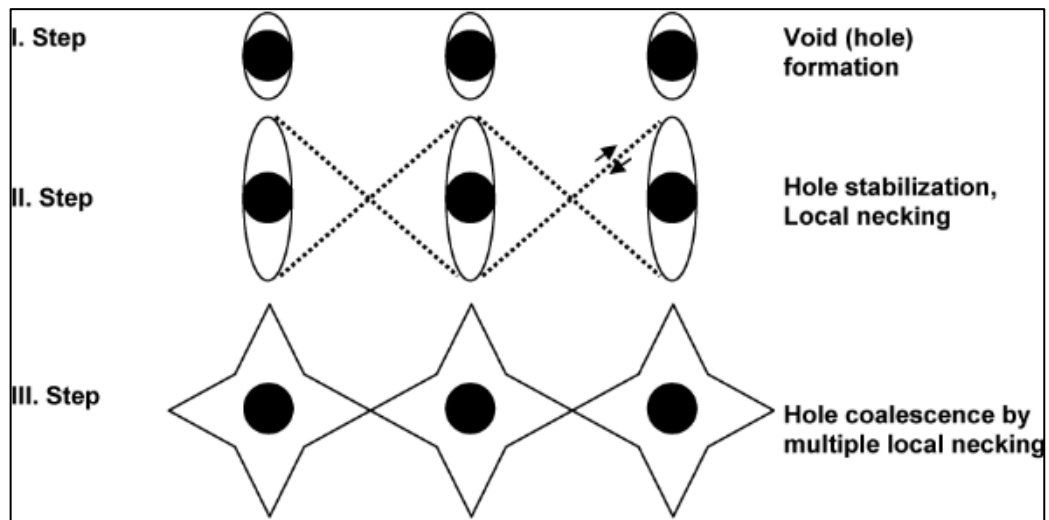


Figure 2.5: Stages of crack formation around rigid particles in a ductile matrix (Arencon & Velasco, 2009).

## 2.2 Polyamide 6

Polyamide was first discovered from the research of Wallace Hume Carothers and with the cooperation of the Du Pont Chemical Co. of America in the aim of discovering synthetic fiber forming material. Polyamides are formed as a result of condensation reactions from diamine with dibasic acid (Kohli & Bhatia, 2013). During the condensation reaction, small molecules like water or ammonia is released as a result of the di- or multifunctional chains condensed with each other. Figure 2.6 showed the condensation process in the formation of polyamides with the release of water molecules. However, for polyamides that represented by one number such as nylon-6, are produced by the ring-opening polymerization of cyclic amides such as caprolactam as shown in Figure 2.7 (Agarwal et al., 2006).



PA6 is an aliphatic polyamide that is commonly used among the polyamides. PA6 has the ability to crystallize in a fast manner up to 30 – 40% range. This helps PA6 to have high modulus even reaching above the glass transition temperature (Paz et al., 2016).

Figure 2.9 showed the proportion of polyamide type usage. From Figure 2.9, it was shown that PA6 showed the most usage among the polyamides in the nylon family. On the other hand, Figure 2.10 showed the usage of polyamide in various fields. It was shown that PA6 was highly used in the automotive field. This was in respect to its good mechanical and thermal properties. Moulded polyamide parts have the ability to absorb energy in failure and crash situations (Page, 2001). Despite the relatively higher strength and stiffness of PA66, PA6 still remains a preferable choice. The reason for using PA6 over other classes of PA is that PA6 produces lower mould shrinkage. Besides that, the processing of PA6 is relatively easier than PA66 (Platt, 2003).

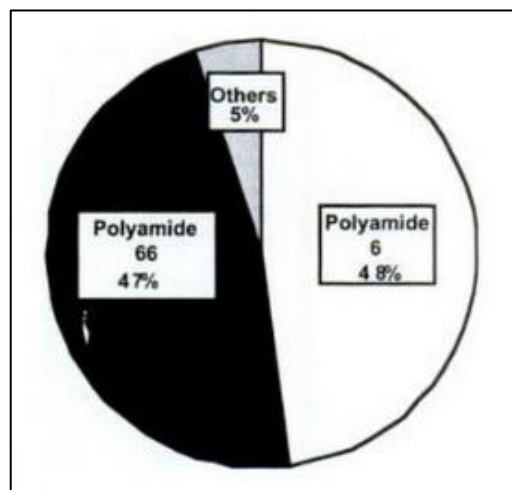


Figure 2.9: Usage of polyamide based on the type (Page, 2001).

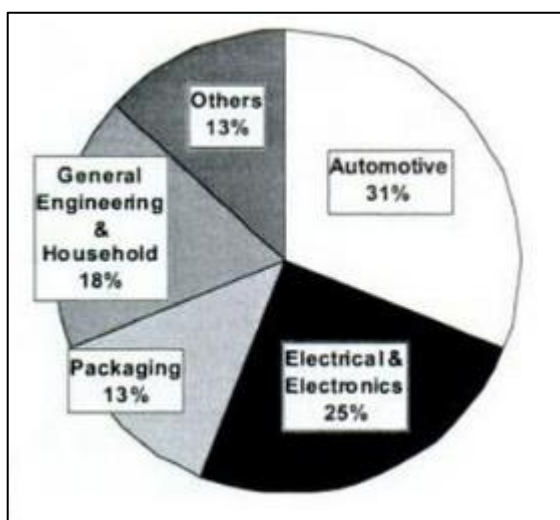


Figure 2.10: Usage of polyamide in various fields (Page, 2001).

PA6 is extensively used in the engineering field due to its high performance in terms of rigidity, thermal stability and high mechanical performance. Despite these, the cost of PA6 is rather high and its brittleness has limited to some applications (Xu et al., 2017). PA6 can be blended with other polymers in order to enhance the properties such as impact, dyeability, vapour permeation and antistatic (Haponiuk & Balas, 1995). A lot of studies had been done and through the static mechanical analysis, it was found that the tensile strength, tensile modulus and flexural strength increase with the increase of clay loading (Venkataramani et al., 2008).

### 2.3 PP Blends

PP is a commodity polymer that is commonly used in many applications, such as home appliances, automotive parts, construction and other important industrial applications. However, the usage of PP is often limited due to its low impact strength and Young's modulus properties, particularly at low temperatures and high temperature loading conditions. Blending PP with different polymers is an economic and effective way to improve these drawbacks (Dikobe & Luyt, 2009). The fact that PP excels in the price/performance ratio, made PP blend to be researched extensively. Numerous investigative research works has been conducted in the field of PP blends.

There was a study of PP incorporated with epoxidized natural rubber (ENR). The aim of that research was to improve the flexibility and behaviour at low temperatures of PP through the blending with ENR. From the end of that study, it was found that there was an improvement in the toughness and flexibility. Toughness in terms of the elongation at breaks and impact strength significantly increases as the rubber content of the blend increases. However, mechanical properties such as tensile strength, Young's modulus and hardness of PP had found to be reduced. This was associated with the crosslinking in the rubber matrix from ENR that contributed to the elastic behaviour and resulted in the reduction of Young's modulus of PP blend (Mohamad et al., 2013).

PP which is a commercially used plastic material experienced difficulty in decomposition by microorganism in the environment. On the other hand, poly- $\epsilon$ -caprolactone (PCL) is aliphatic polyester that is capable to undergo biodegradation. A study was done in blending of PCL with oxidized PP in order to increase PP biodegradability. This is due to the fact that the backbone chain of the PCL can be

hydrolysed easily by the microbial activity. The findings show that the weight loss of the polymer due to biodegradation with different blend ratio. The results showed that the biodegradability increased as the content of PCL in the blend increased. The oxidized PP and PCL blend degraded relatively higher than the original as a result from the compatible part changes that induced lower crystallinity of PCL and susceptible to biodegradation (Arcana et al., 2007).

In the study of PP/SEBS (Styrene-ethylene-butadiene-styrene), it was showed that the blends able to decrease the flow temperature. Melt viscosity was observed to be decreased with increasing SEBS content. Thus, melt fracture experienced by PP alone was reduced through this blending. Besides that, through the blending of PP/PBR (Polybutadiene rubber), it was found that the rate of crystallization of PP increased in the presence of PBR. The tensile properties decreased but the impact strength was improved through the addition of PBR. The PP/PET (Polyethylene terephthalate) blend was seen to have an improvement in terms of mechanical properties and processability (Martuscelli et al., 1980).

## **2.4 PP/PA6 Blends**

From many PP blend systems, the blending of PP and PA6 had received some attention in these recent years as they combine the thermomechanical characteristics of PA 6 with the ease of processing of the PP. PP is commercial plastic which has good overall mechanical performance, good moisture resistance and low cost, but it shows relatively poor chemical and heat resistance (Kusmono, 2008). Polyamides on the other hand are the family of engineering thermoplastics whose wet affinity limits their



application. Their combination with lower-module but hydrophobic polymer-like polyolefins has become a matter of interest (Marco et al., 2002).

One of the advantages blending PA6 into PP is that PA6 act as both a polymeric matrix and a carbonization agent because of its unique mechanical properties and processability. PA6 as a charring agent can make the intumescent char layer thicker and more compact. Thus, the introduction of PA6 into PP composites can increase the thermal stability of the composites (Chen et al., 2015).

Polyamide has good barrier properties to gases such as oxygen and carbon dioxide. Thus, blending of polypropylene with polyamide is capable to improve the barrier properties and mechanical properties. Experimentally, oxygen permeability is measured according to ASTM D3985 and predicted with some models such as Maxwell model, Fricke model and Series model. Figure 2.11 showed the experimental and the predicted values in oxygen permeability of PP/PA blend. From the findings it was showed that lesser oxygen was able to permeate as the PA content increased. However, the decrement gradually decreased as the PA content increased further (Kim & Kim, 2003).

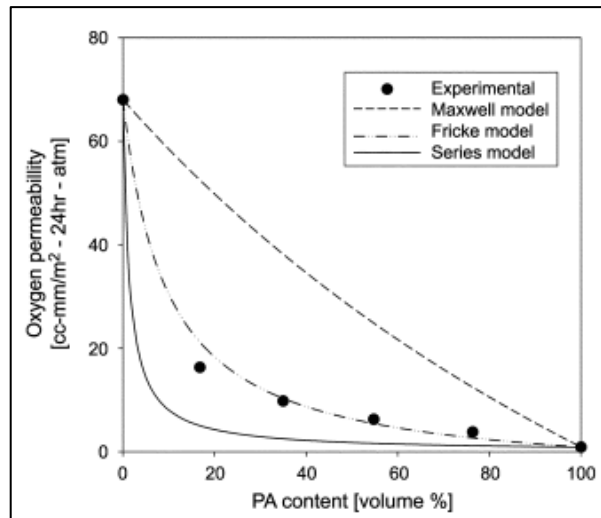

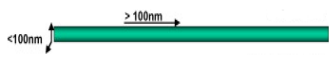
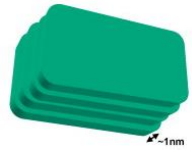


Figure 2.11: Comparison of measured permeabilities of PP/PA blend film as a function of PA content with the values predicted from various model (Kim & Kim, 2003).

## 2.5 PP/PA6 Nanocomposites

A nanocomposite is a class of composite material which consist at least one of the components to have one dimension that is of nanoscopic size. It consists of a continuous matrix and a discontinuous reinforcing phase. Large interest is devoted to the nanofiller-based nanomaterials as it shows exceptional improvement in the properties. The aspect ratio and effective surface area of the nanofillers are high compared to those conventional fillers. Nanofillers are mainly additives and comprised of inorganic solid materials that differ from the polymer matrix (Davim & Charitidis, 2013). Table 2.2 showed the classification of nanofiller based on the shape.

Table 2.2: Classification of nanosize material according to shape (Kumar et al., 2009).

Terminology	Nanoparticles	Nanotubes	Nanolayers
Dimension	Three dimensions of particulate are in order of nanometers	When two dimensions are in nanometer scale and the third is larger, forming an elongated structure,	The particulates which are characterized by only one dimension in nanometer scale
Shape	Equiaxed (isodimensional) nanoparticles, nanogranules or nanocrystals	Elongated structure or nanofibers/nanotube	Sheets form of one to a few nanometer thick and hundreds to thousands nanometers long.
Example	Silica	carbon nanotube (CNTs), cellulose whiskers, HNT	Clay (layered silicates), layered double hydroxides (LDHs).
Illustration			

The nanocomposite of PP/PA6 was developed and is widely used for lightweight automotive parts with improved mechanical properties. PA6 exhibits good mechanical properties and is used widely as an engineering plastic. PP component was blended to manufacture the exterior automotive parts as a weight reduction and increase water resistivity. The blending of these two polymer achieved an intermediate between the properties of each respectively polymer. However, in order to compensate the loss of mechanical properties, nanofillers are added. For example, carbon nanotubes (CNT) are used as filler because of its exceptional mechanical and physical properties. Finding showed that CNT was able successfully reinforce the nanocomposites even without any surface treatment (Nguyen-Tran et al., 2018).

A study was done in order to investigate the influence of incorporation of functionalized titanium dioxide ( $\text{TiO}_2$ ) nanoparticles on the crystallization and melting behaviour of PP/PA6 blend. In that study, the isothermal crystallization kinetics was analysed based on the Avrami equation. The result of the study showed that the presence of functionalized  $\text{TiO}_2$  nanoparticles in PP/PA6 blend increases the crystallization rate due to the induction of heterogeneous nucleation of PP and PA6 chains (Ou et al., 2012).

Nanofillers such as carbon black can be incorporated into a polymer system to improve properties and also induce electrical conductivity. Recently, a study was done to study the effect of polyamide 6 and carbon black on the electrical conductivity of polypropylene. From the result obtained, it was seen that the surface resistivity decreased with the increment of carbon black content. Furthermore, generally the blending of PA6 decreased the surface resistivity as compare to pure PP. Thus, the

percolation threshold can be further reduced where the conductive filler was incorporated into an immiscible polymer blend system (Zhang et al., 2017).

Besides that, there was also investigation on the mechanical properties of PP/PA6 blend, which organo-montmorillonite (OMMT) nanoclay was added into the system. From the storage modulus and tan delta obtained, it was seen that the storage modulus of the nanocomposites increased with the increased of OMMT loading. This is due to the fact that OMMT possesses high stiffness in which restrict and result in the decrease in the mobility of the polymer chain (Somwangthanaroj et al., 2010).

## **2.6 Halloysite Nanotubes**

Besides the stated nanofillers that are used in PP/PA6 blend, halloysite nanotubes (HNT) had been studied intensively. HNT with the chemical formula of  $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \times n \text{H}_2\text{O})$  is a two-layered (1:1) natural aluminosilicate clay minerals which exist in the form of nanotubular. The sizes of the HNT are within 0.5 – 1.5 microns of length with 15 nm of inner diameter and 50 nm of external diameter. Figure 2.12 showed the schematic diagram of a 7 Å HNT (Abdullayev & Lvov, 2010).