CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/ RECYCLED ACRYLONITRILE BUTADIENE RUBBER/ RICE HUSK POWDER COMPOSITES

by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Characterization and Properties of Polypropylene/ Recycled Acrylonitrile Butadiene Rubber/ Rice Husk Powder Composites". I also declare that it has not been previously submitted for the degree or other similar title of this for any other examining body of University.

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DEDICATION

This work is special dedicated to my beloved wife and children for their endless love, patience, support and encouragement.

My Family

SUMATHY, DANIEL, JESLINE, MELVIN

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LIST OF ABBREVIATIONS

ANM	Agensi Nuklear Malaysia
ASTM	American Standard for Testing and Materials
BRHA	Black rice husk ash
DGEBA	Diglycidal ether of bisphenol A
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Derivate thermogravimetric analysis
EB	Electron beam
ENR	Epoxidized natural rubber
EPDM	Ethylene Propylene Diene Monomer
FESEM	Field emission scanning electron microscope
FRP	Fibre reinforced polymer
FTIR	Fourier Transform Infra-Red
HDPE	High density polyethylene
HVA-2	N, N-m pehylenebismaleimide
IR	Infra-red
KBr	Potassium bromide
LCD	Liquid crystal display
LOI	Loss of ignition
MAPP	Maleic anhydride grafted polypropylene
MMC	Matrix Material Classification

MSC	Matrix Structure Classification
MW	Microwave
NaOH	Potassium hydroxide
NBRr	Recycled Acrylonitrile butadiene rubber
NBS	N-Bromosuccinimide
NR	Natural rubber
NBR-RCOOH	Carboxylated Acrylonitrile butadiene rubber
OH	Hydroxyl
PB-1	Polybutene-1
phr	Part per hundred resin
Ph-PP	Phenolic modified polypropylene
PLA	Poly(lactic acid)
PE	Polyethylene
PFM	Poly-functional monomer
PMP	Polymethylpantane
PP	Polypropylene
PP-g-MAH or PPMAH	Polypropylene grafted maleic anhydride
PTFE	Polytetraflouroethylene
PU	Polyurethane
PVA	Polyvinyl alchohol
PVC	Polyvinyl chloride
RH or RHP	Rice husk or rice husk powder

SEM	Scanning electron microscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric analysis
TMPTA	Trimethylolpropane triacrylate trifunctional coagent
TPE	Thermoplastic elastomer
TPO	Thermoplastic olefins
UV	Ultra-violet
WRHA	White rice husk ash
XPS	X-ray photoelectron spectroscopy
XRF	X-Ray fluorescence

LIST OF SYMBOLS

Ac	Acetic anhydride
E_b	Elongation at break
µm	Micrometer
T_g	Glass transition temperature
T_m	Melting temperature
ɤ-APS	ɤ-aminopropyltriethoxysilane
Kg	Kilogram
wt	Weight
NaOH	Potassium hydroxide
nm	Nanometer
T_0	Initial degradation temperature
T_{deg}	Final degradation temperature
X_{com}	Crystallinity of composite
X_{pp}	Crystallinity of PP fraction
ΔH_f	Melting enthalpy
ΔH_c	Crystallisation entropy
ɤ	Gamma
MeV	Electon potential
W_f	Weight fraction of PP in composites

LIST OF PUBLICATIONS AND SEMINARS

Note: (A – Journal, B – Conference)

PENCIRIAN DAN SIFAT-SIFAT KOMPOSIT POLIPROPILENA/ GETAH KITAR SEMULA AKRILONITRIL BUTADIENA/ SERBUK SEKAM PADI

ABSTRAK

Komposit elastomer termoplastik bagi adunan polipropilena (PP)/ getah kitar semula akrilonitril butadiene (NBRr)/ serbuk sekam padi (RHP) telah dikaji. Kesemua sampel ujian disediakan dengan menggunakan pencampur dalaman Haake Rheomix Polydrive R600/ 610 pada suhu 180°C dan kelajuan rotor 50 rpm. Sampel tersebut kemudian dibentuk menggunakan pengacuanan mampatan pada suhu 180°C. Saiz partikel bagi RHP dan NBRr yang digunakan di dalam kajian ini adalah 150 - 300 μm. Perekatan di antara pengisi dan matriks telah ditingkatkan dengan menggunakan asetik anhidrida (Ac) sebagai agen penserasian dan ɤ-APS sebagai agen pengkupel. Sifat-sifat mekanikal dan terma bagi kesemua komposit yang dirawat telah meningkat. Rawatan Ac telah menambahkan ciri-ciri hidrofobik RHP dan meningkatkan lekatannya dengan matrik tak berpolar PP/NBRr. Peningkatan sifat-sifat seperti tensil, kestabilan terma dan penghabluran komposit yang lebih baik ditunjukkan oleh komposit yang dirawat dengan Ac berbanding pengkupelan ɤ-APS. Teknik penserasian matrik dengan menggunakan Eter Diglycidal Bisphenol A (DGEBA) dan maleik anhidrida tercantum polipropilena (PPMAH) juga telah dikaji. Perekatan di antara pengisi dan matrik telah ditingkatkan oleh DGEBA dan PPMAH. DGEBA didapati lebih berkesan dalam meningkatkan perekatan antara pengisi dan matrix. Radiasi alur elektron turut dikaji bagi menghasilkan sambung silang di dalam komposit. Radiasi alur elektron pada dos 40 kGray dengan kehadiran TMPTA (promoter sambung silang) telah digunakan. Keputusan menunjukkan komposit

mempunyai sifat-sifat tensil, kandungan gel, kestabilan terma dan kehabluran komposit yang paling tinggi tetapi penyerapan air yang paling rendah.

CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/ RECYCLED ACRYLONITRILE BUTADIENE RUBBER/ RICE HUSK POWDER COMPOSITES

ABSTRACT

Themoplastic elastomer composite of polypropylene (PP)/ recycled acrylonitrile butadiene rubber (NBRr)/ rice husk powder (RHP) was investigated. All test samples were prepared using Haake Rheomix Polydrive R600/ 610 internal mixer at temperature of 180°C and rotor speed of 50 rpm. The samples were later moulded using compression moulding at temperature of 180°C. The particle sizes of the RHP and NBRr used in this research were 150 - 300 µm. The composites properties were enhanced by treating the RHP using Acetic Anhydride (Ac) and ɤ-APS as a coupling agent. Mechanical and thermal properties of all treated composites were improved. The treatment with Ac increased the hydrophobic characteristic of RHP and improves its adhesion with non-polar PP/NBRr matrixes. Better properties such as tensile, thermal stability and crystallinity of composites showed by Ac treatment compared with ɤ-APS coupling agent. Matrix compatibilization techniques were also investigated by using Diglycidal ether of bisphenol A (DGEBA) and Polypropylene grafted maleic anhydride (PPMAH). The adhesion between filler and matrix was improved for both DGEBA and PPMAH. DGEBA was found to be more effective in improving the adhesion between filer and matrix. Electron beam irradiation was also evaluated to introduce cross-linking in the composites. Electron beam irradiation at 40 kGray in the presence of TMPTA (irradiation crosslink promoter) was used. Results showed that composites have highest tensile properties, gel content, thermal stability and crystallinity but lowest percentage of water absorption.

CHAPTER 1

INTRODUCTION

1.1 Overview

The awareness on environmental conservation and green products has been highly emphasized in the past few decades. This concern includes the product manufacturing both in industries and domestic applications. Over the years, intensive research and development efforts have been focused towards waste minimization. Eco-friendly substance is constantly been developed and used by many researchers to minimize the adverse effect to the environment. One of the prominent efforts undertaken is to reduce the usage of traditional pure petroleum based plastic products towards natural fibre reinforced polymer composites. Currently, natural fibre reinforced polymer composites have been used widely in many sectors such as automotive, construction, packaging and other industries (Espert, 2003). This materials are found to have many advantages and able to be tailored for specific engineering applications. They are also re-processable with recyclable capacity up to few times without significant loss of material properties (Naderi et al., 1999). The types of natural fibre commonly incorporated into polymer composites includes rice-husk, bagasse, rice straw, coconuts, banana skin, sisal, pineapple skin, rubber wood, palm oil fruit bunch, sago, short silk fibre, jute fibre, rubber wood, hemp, cotton stalk, kenaf, cellulose and etc. (Satyanarayana et al., 2009; Saheb & Jog, 1999; Tajvidi et al., 2006; Sgriccia et al., 2008). They are found to be exhibiting reinforcement capacity with biodegradable characteristic at low fibre loading percentages (Ismail & Suryadiansyah, 2002a).

Asian rice (*Oryza sativa*) was first planted as agricultural commodity in large scale in Malaysia in late 1870. Today, it has become the 4th country's agricultural sector, with a planted area of 3.8 million hectares and it is forecasted to double by the year 2020 (Chuah et al., 2005). In this industry, although rice is the major product, there are varieties of wastes created such as rice husks. In 2010 alone, the amount of rice husk generated is approximately 20.4 million tones and it creates huge disposal problem. Rice husk is the outer covering of paddy which accounts for 20% of its weight (http://www.knowledgebank.irri.org). Currently, they are burned to fertilize the field or been thrown away with no specific application. The open burning at the end of each harvesting seasons cause serious environmental problem such as air pollution due to emission of particulate matter less than 10μm and smoke release that inhibit vision of drivers.

Hence, many researches have been carried out to utilize the rice husk powder (RHP) as filler in polymers composites (Razavi et al., 2006; Fuad et al., 1995; Premalal et al., 2003; Siriwardena et al., 2002). They are many advantages of RHP filled polymer composites compared to synthetic fibres. This natural RHP fibre filled polymer composites was found to inherit good characteristics such as low density, recyclable, low production cost in moulded products, and biodegradable (Premalal et al., 2003).

In order to produce low cost and degradable polymers, lignocellulosic based materials are commonly used in composites or as filler in polyolefin. Polyolefins are polymer produced from a simple olefin (also called an alkene with the general formula [C_nH_{2n}]) as a monomer such as polyethylene (PE), polypropylene (PP), polyvinyl alcohol (PVA),polymethylpentene (PMP), polybutene-1 (PB-1) and some other elastomeric polyolefins (Pasquini., 2005).

Addition of polyolefin such as PP with lignocellulosic fibre RHP in the presence of elastomeric material such as synthetic rubber are found to inherit energy absorbing capacity with good mechanical and thermal properties of the resulting composites. A hard thermoplastic phase such as PP is combined with a softer rubber elastomer phase. The resulting composite inherits its dual characteristics of elastomer and thermoplastic properties phases (Arnold & Rader, 1992). These types of material are called as Thermoplastic elastomers (TPEs). TPEs have emerged as a highly demanding class of polymeric materials and already started replacing many other conventional materials in various applications. TPEs are found to be low cost and also inherit attractive properties such as superior mechanical properties, light weight, corrosion resistance and applicable at elevated temperature besides its ability to be tailored for specific engineering applications and to meet the customer requirements (Naderi et al., 1999).

PP is a conventional polyolefin polymer which are widely used in TPEs as hard segment due to its excellent mechanical strength (highly crystalline molecule arrangement), low density (0.9 g/cm^3), low cost for manufacturing, highly resistance to solvent and high temperature workability besides PE and PVA (Holden, 2000). Acrylonitrile butadiene rubber is a synthetic rubber with superior strength, excellent resistance to abrasion, oil, water, alcohols, heat and heat resistant over a wide range of temperature (George et al., 1995). NBR rubber is gaining its attention in TPEs due to its huge volume of acrylonitrile butadiene rubber (NBR) base products generation from the synthetic rubber industries. These products such as surgical gloves, urine catheter and etc are commonly discarded after a single use and have become a major environment issue for disposal (Noriman, 2011). Hence, NBRr was preferred

compared to pure/ virgin NBR as soft segment (elastomeric material) of the TPEs lately.

Therefore, this study is focused on the development of a new class of TPE material by blending PP with NBRr such as waste nitrile gloves generated from the nitrile glove manufacturing industry in the presence of grounded RHP lignocellulosic fibres as fillers. It is hopeful that at the end, the final product developed would find useful applications in building, construction and automotive industries.

Even though mixing of RHP with PP/NBRr looks to be very attractive for fabrication of TPEs due to its excellent mechanical properties, easy processability and thermal resistance, these composite are found to be highly incompatible due to their large difference in surface energy between PP and NBRr (Soares et al., 2006).

Numerous techniques have been developed to solve the problem and to find more effective ways to utilize waste NBR and RHP. These include reclaiming, surface treatment, compatibilization and etc. Mechanical grinding of gloves and rice husk would be one of the simplest recycling methods of converting waste gloves and rice husk into useful form of reclaimed rubber and cellulosic fibre in the powder form (Zulkepli et al., 2009; Premalal et al., 2002). The composite are fabricated by melt mixing techniques to ensure good properties of resulting TPE composite.

1.2 Applications

Fibre reinforced polymer (FRP) have been utilized mainly in diverse applications viz. automotive, construction, packaging and aerospace application (Bledzki & Gassan, 1999). This application primarily due to its characteristic such as light weight, corrosion resistant, non-magnetic, radar transparency, dimensional stable, good strength to weight ratio (http://www.mdacomposites.org/mda/psgbridge_CB_print_materials.html).

In United States of America, legislative such as "End of Life Vehicle Directives" have been enforced, which sets recycling target of 95% by 2015, have contributed in higher utilization in FRP (http://www.netcomposites.com). Currently, big companies such as Volkswagen, Audi, Mercedes-Benz, Ford and others have start using FRP in their vehicles (Gulati, 2005).

Construction sector also indicated similar trend towards FRP since polyolefins are non-degradable as they are chemically stable. Therefore, generation of solid and domestic waste is highly anticipated for disposal. As an alternative measure, FRP is preferred in the construction such as door frames, door shutters, roof tile, decking and roofing sheets (Mahlberg et al., 1998). PP also shows potential benefits when combined with natural fibres besides epoxy resin in making composites for construction and industrial application (Jin & Park, 2008).

Packaging industries has also move on from conventional plastic packing materials to biodegradable material with comparable mechanical properties. Currently, fibres from various sources are incorporated with polymer to provide reasonable life span of packing material called "Green Packing" (Kalia et al., 2009).

Therefore, FRP have enormous increasing potential as an alternate material in many sectors.

1.3 Problem Statements

TPE fabrication using PP/NBRr and RHP sounds very promising with excellent mechanical and thermal properties. However, these components are found to be also highly incompatible. The major issue associated with integrating RHP into PP/NBRr is due to the chemical incompatibility between hydrophilic fibres and hydrophobic polymer. Therefore, the physical and chemical interactions across the phase boundaries are very poor, giving rise to a very weak interface. The incompatibility leads to poor adhesion and reduction in the ability of the matrix to transfer stress to the fibres. Researchers have evaluated that the differential scanning calorimetry (DSC) of PP/NBRr without RHP filler showed no significant changes in onset of melting ($T_{m,onset}$) and melting temperature (T_m) for the blend and the percentage of crystallinity (X_c) remained almost unaffected by the addition of NBR (Joseph et al., 2006). This indicates very poor interaction between the PP and NBR phase and incompatibility of both phases in the absence of RHP filler. Thus, such incompatibility between the phases needs to be resolved, to achieve good mechanical and thermal properties of the composites.

Therefore, compatibilization of this TPE system may be essential to attain desired properties of the composites. Study by Soares et al. (2006) has discover the use of maleic anhydride functionalized PP (PP-g-MAH) and carboxylated NBR (NBR-RCOOH) as a compatibilizing system and found that there is an improvement in tensile and swelling properties of PP/NBR blends. George et al. (1996) revealed

enhances resistance to tearing on PP/NBRr blends compatibilized (PP-g-Ph) due to reduction of NBR particle size in the compatibilized blend.

Alternative techniques to improve PP/NBR blend properties such as introduction of crosslinker in the rubber phase of the blend has also been reported by several researchers. The effect of dynamic vulcanization on properties of PP/NBRr blends has been investigated by Ismail et al. (2009b) also reveal the improved tensile properties and oil resistance of the blends. The same research group has also revealed electron-beam irradiation of PP and NBRr blends improve the tensile properties Ismail et al. (2010). However, there is no work reported in PP with NBRr in the presence of hydrophilic rice husk power as filler. Hence, the properties of PP/NBRr/RHP composites must be evaluated to obtain the best mechanical and thermal properties.

1.4 Objectives of Study

The aim of this research is to develop new TPEs using PP/NBRr and RHP as filler. The main objectives of study are:

1. To investigate the physical and chemical properties of the RHP filler and evaluate the effect of RHP loading in PP/NBRr/RHP composites.
2. To determine the effect of NBRr loading on the properties of PP/NBRr/RHP composites;
3. To study and compare the effects of RHP treatment with Acetic Anhydride (Ac) and ɤ-aminopropyltriethoxysilane (ɤ-APS) coupling agent on properties of PP/NBRr/RHP composites;

4. To study the effects of polypropylene maleic anydride (PPMAH) and diglycidyl ether of bisphenol-A epoxy resin (DGEBA) on properties of PP/NBRr/RHP composites;

5. To determine the effect of electron beam irradiation in the presence of trimethylolpropane triacrylate (TMPTA) trifunctional coagent (crosslink promoter) on properties of PP/NBRr/RHP composites.

1.5 Outline of Thesis Structure

The thesis has been divided into nine chapters and each chapter deals with an aspect of the overall problem of understanding the behaviour of the PP/NBRr/RHP composites.

- Chapter 1 covers the introduction of the thesis. It provides an overall introduction for the study including a brief introduction about research background, a problem statement, an objective of study and the outline of the thesis;

- Chapter 2 provides a comprehensive review on natural fibre in polymer matrices, along with some review of related works reported in the literature;

- Chapter 3 details the materials, instruments and experimental procedures applied in this research;

- Chapter 4 focuses the preliminary studies on RHP filler loading on the behaviour of PP/NBRr/RHP composites;

- Chapter 5 focuses the preliminary studies on NBRr loading on the behaviour of PP/NBRr/RHP composites;

- Chapter 6 provides the comparison of reinforcing efficiency of RHP treatment with Ac and ɤ-APS coupling agent with untreated RHP in PP/NBRr/RHP composites;

- Chapter 7 discusses the effect of PP modification with PPMAH and DGEBA coupling agent on PP/NBRr /RHP Composites;

- Chapter 8 discusses the effect of irradiation-induced crosslinking with incorporation of polyfunctional momoners (PFMs), namely, TMPTA in PP/NBRr/RHP composites; and

- Chapter 9 presents conclusions on the present work and suggestions for future work.

CHAPTER TWO

LITERATURE REVIEW

2.1 Composite Materials

Composite materials are made aware since thousands of years even before the modern calendar came in place. Man understood that fact use of making bricks with straw to enhance the structural integrity of the pyramids in the days of Pharaohs (Sharma, 2000). Current composites have progressed from glass fibre for automobile parts to specific composites for aerospace applications. The general term for composite is mixture of two or more distinctly identifiable constituents. The different physical or chemical constituent of the material usually results in different properties of the resulting materials. Inspite the distinctly different constituent, they are suitably arranged or distributed with an interface separating between them (Chawla, 1987). The importance of composite materials was further researched due to its ability to inherit the combine properties of the individual material in a single mixture. Composite materials were developed to meet desired properties since there is no single and homogeneous structural material had all desired characteristics for a given application. The fabrication of composites materials may enhance characteristics such as mechanical strength, stiffness, toughness and strength at high temperature that unable to be attained by individual constituents such as metal alloys or polymers (Callister, 2000).

The composite materials generally consist of three major phases (matrix phase, matrix-filler interphase and dispersed phase) resulting from matrix and filler. The properties of a composite depend critically on the microstructure and properties of the interface or inter-phase between the filler and the matrix. “Inter-phase” is a

region where the filler and matrix phases are chemically and/or mechanically combined or otherwise indistinct. The inter-phase may be a diffusion zone, a nucleation zone, a chemical reaction zone, a thin layer of filler coating or any combination of above. An “Interface” is a boundry demarcating distinct phase such as filler, matrix, coating layer or inter-phase as shown in Figure 2.1 (Sharma, 2000).

Figure 2.1 (a) and Figure 2.1 (b) show the schematic diagram of composite material with interface and inter-phase. The matrix/matrix phase provides uniform load distribution to the reinforcing constituent (dispersed phase) by holding the reinforcement (filler) in place. A good matrix is able to bind the reinforcement together by virtue of its matrix interphase and reinforcement phase and holding reinforcement in proper orientation or position, in order to carry loads and transfers them evenly. The good transfer stresses between the reinforcement and matrix provide shear strength, de-lamination resistance, fatigue, crack resistance and corrosion resistance (Sharma, 2000). Matrix must also be able to absorb energy by deforming under stress, primarily, due to high modulus of reinforcement materials.

A filler-matrix interface is a composite interface between a matrix and filler. Whereby, matrix usually does not inter-diffuse into the filler surface but may bond and adhere to it (Sperling, 2006). The theories that outline the mechanisms of interfacial adhesion are inter-diffusion, electrostatic attraction, chemical bonding and mechanical interlocking and adsorption and wetting (Kim & Mai, 1998; Pukanzsky, 2000; Ismail, 2004a).

Strong interfacial adhesion is a primary condition of good stress transfer, assuring the proper performance of the composites. The interfacial adhesion itself is

depends on the morphology and the chemical structure of both the filler and the matrix (Wypych, 2000).

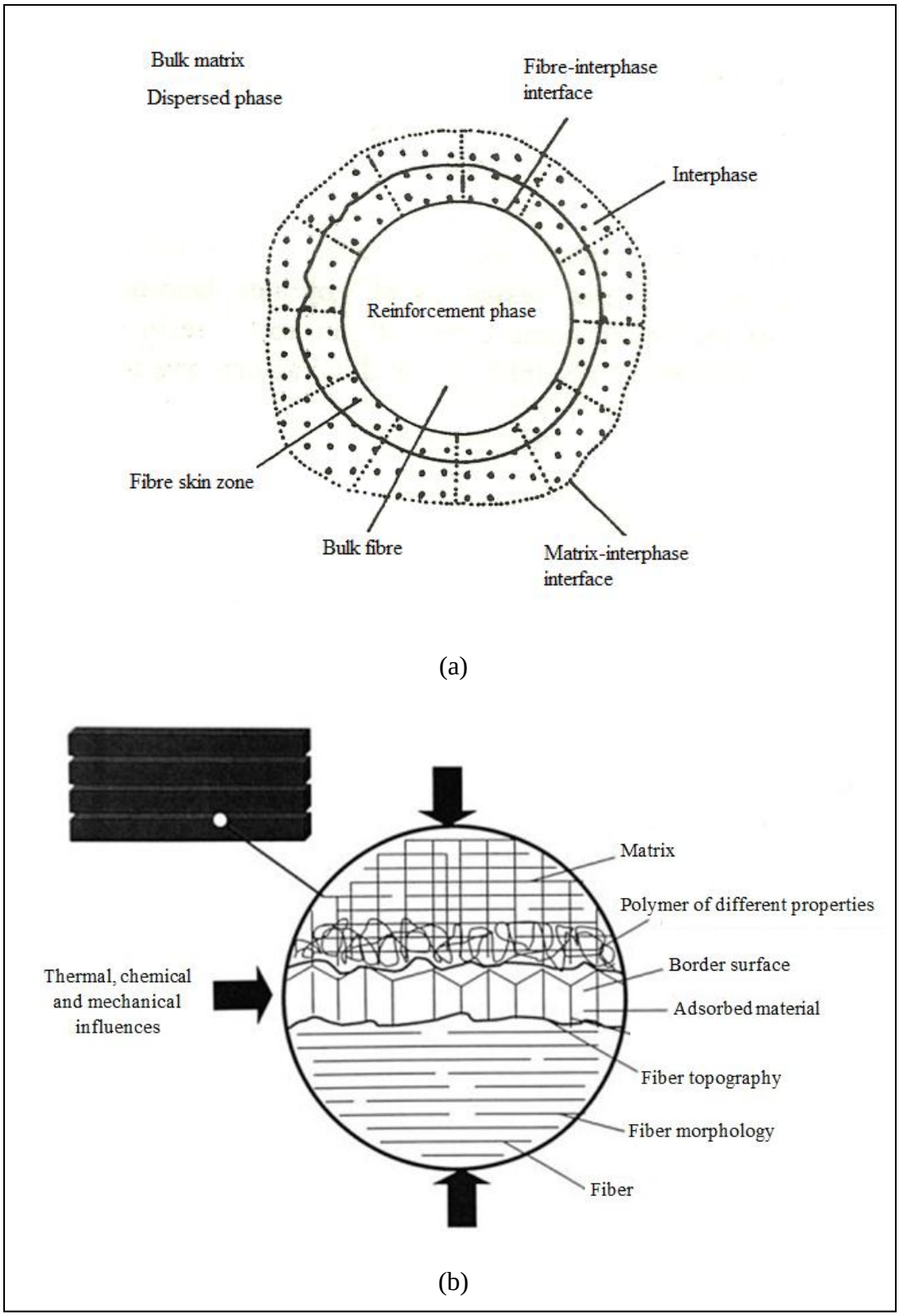

Figure 2.1 Schematic diagrams of composite material with interface and inter-phase (Sharma, 2000)

Dispersed phase is the solid material of an organic or inorganic nature appears in various shapes such as fibre, particulate, flake, filler or laminate. They are usually added to improve mechanical and physical properties of the composites, mainly, the strength, toughness and stiffness (Sharma, 2000). With an addition of the dispersed phase in the polymer matrix, it may lead to increase in rigidity, stiffness and hardness, regulate thermal expansion and shrinkage, improve heat resistance, improve or regulate electrical characteristics, increase strength and reduce creep, modify rheological properties, aid processability, modify appearance and alter density (Peters, 1998; Leong, 2003). Types of possible forms of reinforcements in a composite and reinforcement classification are as shown in Figure 2.2 and Figure 2.3.

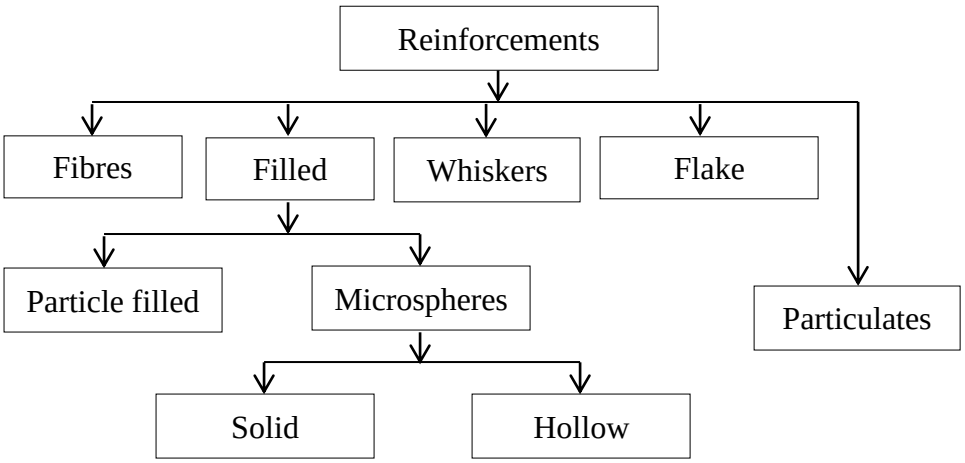

Figure 2.2 Types of reinforcements in composite (Gupta, 2005)

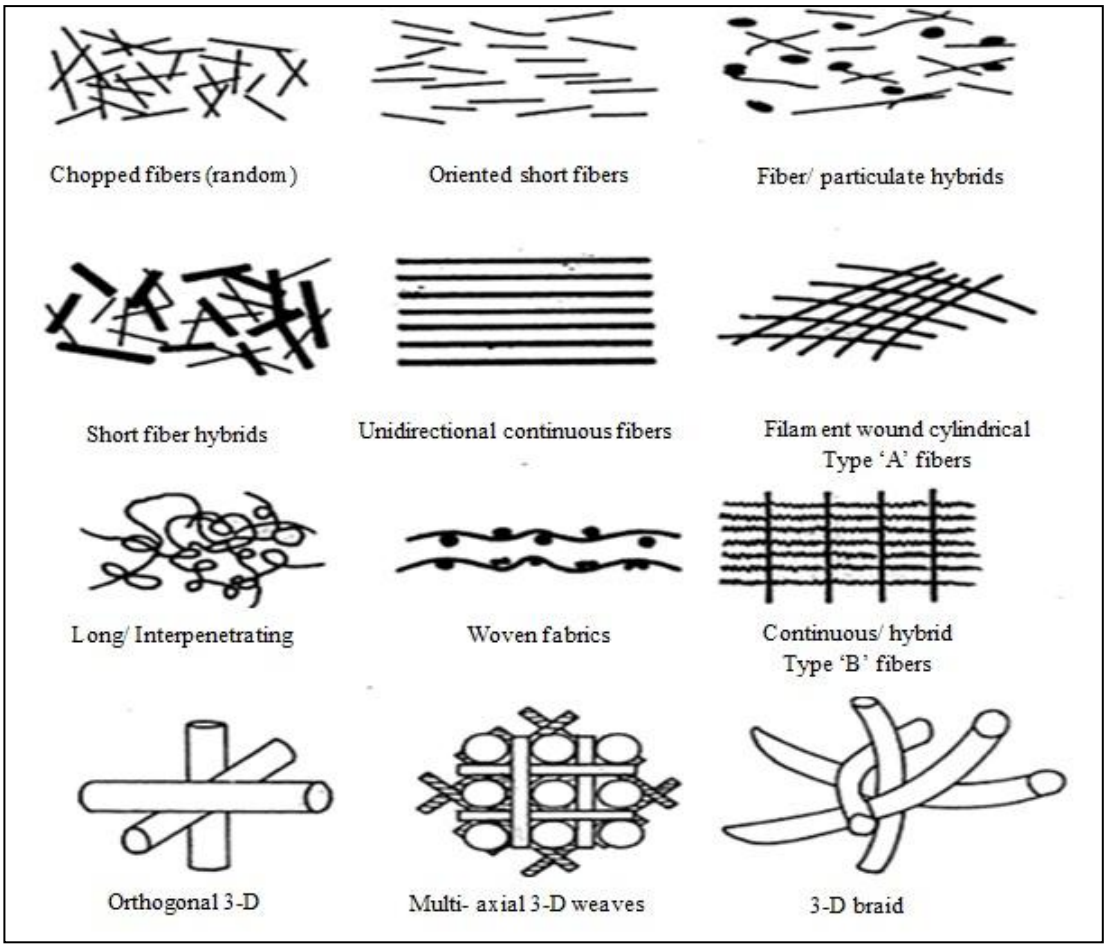

Figure 2.3 Types of possible forms of reinforcements in a composite

(Gupta, 2005)

Matrix is substance mean to provide uniform load distribution to the reinforcing constituent by holding the reinforcement (filler). Classification of composite materials are usually done base on two aspects. According to Ahmad (2006), they are matrix material classification (MMC) or matrix structure classification (MSC). Figure 2.4 shows the classifications of composite materials base on matrix material.

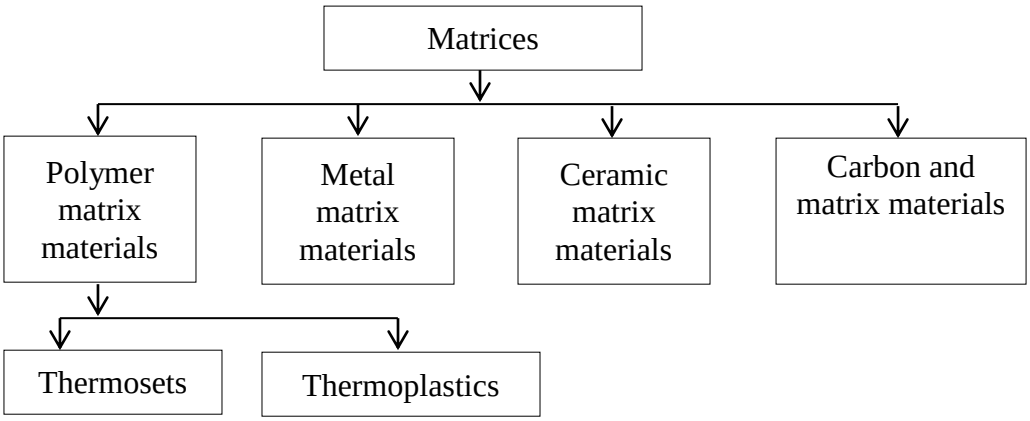

Figure 2.4 Classifications of composite materials base on MMC (Sharma, 2000)

2.2 Polymer Matrix Materials Composites

Polymer matrix materials composites or commonly known as polymer composites, is a mixture of two or more materials in which usually the matrix constituent is a polymeric material (Dyke et al., 2007). It also is defined as a mixture of polymers with solid particulate or fibrous fillers of inorganic or organic nature which are dispersed throughout the continuous matrix (Anandhan et al., 2003). When the filler and the matrix are joined to form a composite, they retain their individual properties. Both directly influence the composite's final properties (Khanbashi & Kaabi, 2005).

2.3 Classification of Polymer Composites

According to Hakimah (2010), polymer composites can be classified with many parameters such as number of components (binary, ternary, quaternary and etc), type of constituent (thermoplastic, thermosetting or elastomer), nature of the polymer architecture (graft or block polymer), compatibility among the constituent

(compatible, incompatible) and method of producing (physical or chemical blending). Among the listed parameters, type of constituent is the most commonly used indicator. The polymer composites are classified into four main categories, based on the polymer matrix, namely as, thermoplastic, thermoset, elastomer and thermoplastic elastomer (TPE) composites. Figure 2.5 shows the classification of polymer composites (Sharma, 2000).

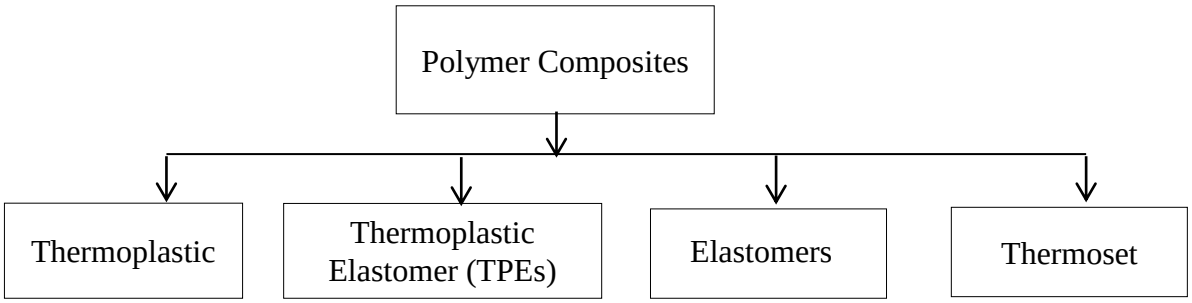

Figure 2.5 Classification of polymer composites (Ismail & Suryadiansyah, 2002a)

2.3.1 Thermoplastic Elastomers (TPEs)

TPEs usually consist of at least two polymeric phases. They generally exhibit a phase-separated system in bulk. A hard thermoplastic phase is combined with a soft elastomer phase, and the properties of the resulting TPE will be derived from the properties of each of the two phases and from the interaction between these phases. The two phases may result from simple mixing of two different polymers, as in a blend of a hard thermoplastic with a soft elastomer (Arnold & Rader, 1992). The hard phase gives these TPEs their strength and the elastomeric phase provides elasticity and flexibility to the system.

The performance characteristics of a TPE depend on the melting point (T_m) of the hard thermoplastic phase and the glass-transition temperature (T_g) of the soft

elastomeric phase. The useful temperature range of a TPE is between T_m and T_g and the TPE displays its desirable elastomeric properties within this range. At temperature above T_m, the thermoplastic phase melts and the TPE becomes fluid and can be processed by usual thermoplastic techniques. Below T_g, the TPE becomes brittle and loses all of its useful elastomeric properties (Arnold & Rader, 1992). TPE composites usually are produced by addition of fillers materials into the TPE.

The majority of TPEs function as rubber at temperature as low as -40^{o}C or even lower as measured by their brittle point. The upper temperature limit is determined by the maximum temperature at which it can give satisfactory retention of tensile stress-strain and hardness properties. TPEs generally extend to high elongation and often in some cases with residual elongation or permanent set. Their set properties are in between elastomers and thermoplastics. As the temperature rises in TPE, the modulus and the strength decrease due to softening of hard domain. In the vicinity of softening point, the properties decrease drastically and the material cannot be used as TPE. Most of the TPEs are in the high rubber hardness range. Most of the TPEs have fair to good compression set resistance at ambient temperature. The chemical resistance of the TPE is greatly influenced by its chemical composition of the TPE (Dutta et al., 1997).

2.3.2 Thermoplastic Elastomer Olefin

According to Hakimah (2010), the thermoplastic elastomer olefin (TPO) is categorized as a polymer blend and can be produced by melt mixing technique using thermoplastic olefin (e.g., PP, PE, PVC, etc.) and an elastomer (e.g., NR, EPDM, ENR, etc.) under high shearing action. It is commonly does not inherit strong

chemical bond between the plastic and the elastomeric phases. This is due to incompatibility of the non-polar olefin and other polar elastomeric materials. However, the introduction of compatibilizers and electron beam radiation may significantly influence the adhesion and compatibility of the resulting material. The most common olefin used in fabrication of TPO is shown in Figure 2.6.

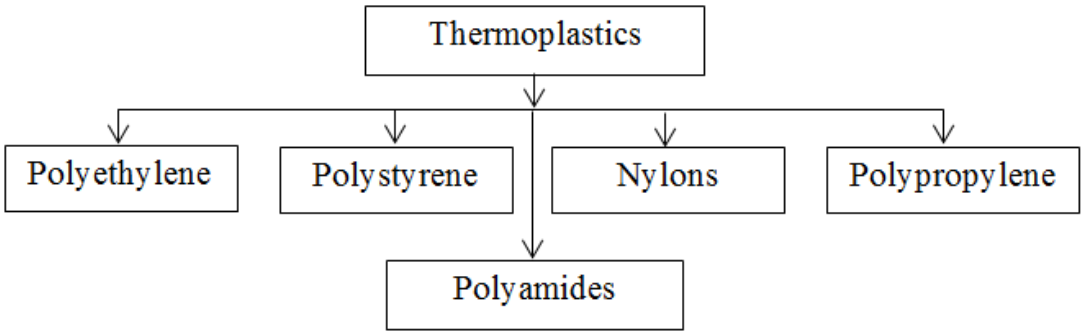

Figure 2.6 Common olefin used to fabricate TPO (Gupta, 2005)

2.3.3 Polypropylene

According to Ulrich (1993), polyethylene, polypropylene, polyvinyl chloride and polystyrene are four main type of polyolefins produce from petrochemicals monomers by cracking or refining crude oil.

PP is similar to polyethylene in structure except for the substitution of one hydrogen group with a methyl group on every other carbon. This change allows for the preparation of different stereoisomers, namely, syndiotactic, isotactic and atactic chains. PP is synthesized by the Natta polymerization of propylene that is derived from petroleum products. The repeating unit of polypropylene is shown in Figure 2.7.

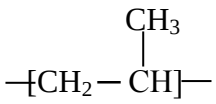

Figure 2.7 Repeating unit of polypropylene

The most significant research finding by Natta was a variation of methyl groups of the PP that lead to products of different tacticity. The mechanical and thermal properties of PP are dependent on the tacticity, the molecular weight and on other structure features. Methyl groups of isotactic PP are aligned on one side of the chain, the methyl groups of syndiotactic and atactic are alternating and randomly positioned respectively. The isotactic PP is stiff, highly crystalline and with a high melting point whereas the atactic PP is an amorphous. Different tacticity of PP can be seen in Figure 2.8.

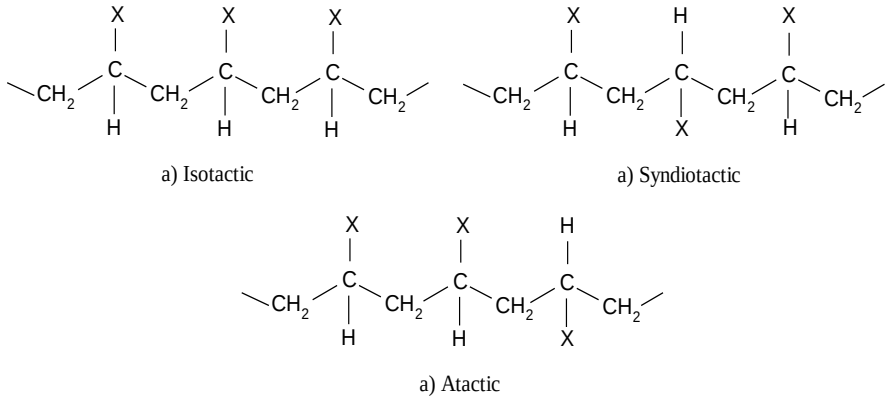

Figure 2.8 Tacticity of polypropylene structure

Isotactic and syndiotactic PP can pack into a regular crystalline array giving a polymer with more rigidity, where as, atactic PP has a leser amount of crystallinity due to its irregular structure, thus, it behaves as a soft flexible material. The isotactic PP is the most commercially important form (Pasquini, 2005). Commercial polymers are about 90-95 % isotactic. The amount of isotacticity present in the chain will influence the properties. As the amount of isotactic material increases, the amount of

crystallinity will increase resulting in increased modulus, softening point and hardness.

PP is a versatile thermoplastic offering a useful balance of heat at 160°C and chemical resistance, good mechanical and electrical properties, processing ease and etc. The discovery and development of PP as one of large tonnage thermoplastics material has been developed since World War II. In 1954, G. Natta of Milan following on the work of K. Ziegler in Germany, found that certain Ziegler-type catalysts were capable of producing high molecular weight polymers from propylene. In the mid of 1980s, the production growth rates for PP have generally been higher than for the other major tonnage plastics and moved into third place after PE and PVC in the plastics production league (Brydson, 1999). The advantages and disadvantages of PP according to Leong, (2003) can be list as in Table 2.1.

Table 2.1 Some advantages and disadvantages of polypropylene (Leong, 2003)

Advantages	Disadvantages
- Low specific gravity (density)	- More flammable
- Excellent chemical resistance	- Low temperature brittleness
- High melting point (relative to volume plastics	- Moderate stiffness
- Good stiffness/ toughness	- Difficult printing, painting and gluing
-Adaptability to many converting methods	- Low UV resistance
- Great range of special purpose grades	- Reduced extruder output
- Excellent dielectric properties	- Haziness
- Low cost (per unit volume)	- Low melt strength

However, the effect of molecular weight on the bulk properties of PP is opposite to its tacticity. Although an increase in molecular weight leads to an increase in melt viscosity and the impact strength, it also causes decrease in melt flow index, consequently reduces tensile strength, hardness, stiffness, brittle point and softening point. This effect is believed to be due to the fact that high molecular weight of PP does not crystallize so easily as lower molecular weight material. Instead of tacticity and molecular weight, the properties of the PP is also depend on the size and type of crystal structure formed and this will in turn be dependent on the relative rates of nucleation to crystal growth. The ratio of these two rates can be controlled by varying the rate of cooling and by the incorporation of nucleating agents. In general, the smaller the crystal structures, the greater the transparency and flex resistance and the less the rigidity and heat resistance.

Polypropylene has many applications such as in automotive uses, packaging applications and etc. Some of the automotive applications are dome lights, kick panels, car battery cases, mount and engine covers. Elastomer filled PP is used for bumpers, fascia panels, and radiator grills in automotive industry. Also, PP is used in house ware applications and in the outer tank of washing machines. PP films are used for carpet backing and sacks. Fabrics prepared from PP are used in both woven and nonwoven cloth manufacturing (Baker & Mead, 2002).

PP is a linear hydrocarbon polymer containing little or no unsaturation. Therefore, it is not surprising that PP and HDPE have many similarities in their properties, particularly in their swelling and solution behaviour and electrical properties. The two polymers have similar solubility parameters and tend to be swollen by the same liquids. With many solution such as silicone oil, PP shows the lowest permeability but not with hexane. Despite of the many similarities, the

presence of a methyl group attached to alternate carbon atoms on the chain backbone can alter the properties of the polymer in a number of ways included interfere with the molecular symmetry. The methyl groups can also influence some aspects of chemical behaviour. For example, the tertiary carbon atom provides a site for oxidation at elevated temperature, so that, the PP is less stable than polyethylene (PE) to the influence of oxygen. In addition, thermal and high-energy treatment leads to chain scission rather than cross-linking. Similar effects were found when the polymer is exposed to high-energy radiation and when heated with peroxides. Substantial improvements can be made by the inclusion of antioxidants and such additives, including fillers, rubbers, ultraviolet absorbers and nucleating agents.

2.3.4 Acrylonitrile Butadiene Rubber (NBR)

Nitrile rubber, or Buna-N, is a synthetic rubber copolymer of acrylonitrile (ACN) and butadiene with the many trades name such as Breon, Butaprene, Butacril, Chemigum, Chemivic, Elaprim, FR-N, Hycar, Krynac, Nysyn, Nysynblak, Paracril, Paracril OZO, Perbunan N, Tylac and Nipol (Long, 1985). Acrylonitrile Butadiene Rubber (NBR) is a family of unsaturated copolymers of 2-propenenitrile and namely, with two types of butadiene monomers (1, 2-butadiene and 1, 3-butadiene). Figure 2.9 shows the repeating unit of acrylonitrile butadiene rubber.

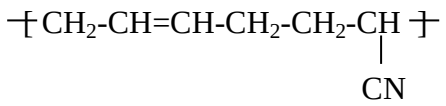

Figure 2.9 Repeating unit of acrylonitrile butadiene rubber (Blow, 1998)

NBR are commonly classified very broadly according to acrylonitrile content as low (10-25%), medium (25-35%) and high (35-50%). The actual level of acrylonitrile in the polymers varies from nearly 50 per cent for the very high range to about 10 % for polymers of low acrylonitrile content (Ulrich, 1993). As the acrylonitrile content is increased, so the molecule becomes less hydrocarbon and more polar. The primary properties affected are the T_g and the solubility parameter which both increase with increasing percentage of acrylonitrile content (Blow, 1998; Brydson, 1978). Also, the level of acrylonitrile content has an important effect on the properties of the final product. According to Blow (1998), as acrylonitrile content increases, the following are the advantages and the disadvantages of acrylonitrile content increases in NBR Rubber, as shown in Table 2.2.

Table 2.2 Advantages and disadvantages of acrylonitrile content increases in NBR rubber (Blow, 1998)

Advantages	Disadvantages
- Increase oil and solvent resistance	- Decrease permeability
- Increase tensile strength	- Low temperature resistance becomes poorer
- Increase hardness	- Decrease Resilience
- Increase abrasion resistance	- Decrease Plasticizer compatibility
- Increase heat resistance	

NBR is found to be resistance to gases, to abrasion, to heat and to many solvents and chemicals as well as compatibility with certain resins (Lufter, 1964). Hence, in industrial applications acrylonitrile butadiene rubbers are widely used in oil contacting parts due to its oil resistant characteristics. It is used in the automotive

application such as hoses, oil seals, shaft seals, bushings, gaskets, carburetor parts, oil filter gaskets O-rings, gaskets, V- belts, synthetic leather, belts, cable jacketing and etc. NBR's ability to withstand a range of temperatures from −40 °C to +108 °C makes it an ideal material for extreme applications such as blowout preventers, drill-pipe protectors, pump piston elements and rotary drilling hose in oil-drilling industry (Blow, 1998). The high temperature tolerance and its ability to withstand stiffening at low temperatures enable NBR to use for other applications such as footwear, adhesives, sealants, sponge, expanded foams, and floor mats. On the other hand, nitrile rubber is also used in plastic modifications to improve impact strength and flexibility (Morton, 1995). NBR also exhibits good resilience properties compared to natural rubber gloves. It is found to be three times more puncture-resistant than natural rubber gloves**.** Hence, it becomes a perfect material for disposable lab, cleaning and examination gloves.

The use of NBR in the glove production has increased all over the world due to its excellent resistance to puncture and tears as well as the non-existence of leachable allergenic proteins, unlike natural rubber latex. Nitrile gloves are made of a synthetic polymer formed by combining the monomers acrylonitrile, butadiene and carboxylic acid. Each monomer contributes a unique property. Acrylonitrile provides penetration resistance from a number of solvents and chemicals such as hydrocarbons oils, fats and solvents. The chemical resistance and stiffness of the glove increase as the acrylonitrile concentration increases. Natural rubber on the other hands is not very resistance to chemicals. Butadiene adds softness and flexibility and contributes the elasticity of the glove. Carboxylic acid contributes to the tensile strength or the tear strength of the glove. By changing the composition of these monomers, the characteristics of the glove can be changed. Many of the