

**Properties of Kenaf Bast Powder Filled High Density Polyethylene/Ethylene
Propylene Diene Rubber Composites**

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DECLARATION

I hereby declare that this thesis is the result of my own research except for quotations and citations that have been acknowledged. I also declare that it has not been previously or currently submitted for any other degree at USM or any other institutions

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LIST OF SYMBOLS

Symbols	Description
W_0	Original Dry Weight
W_t	Weight After Exposure
M_t	Moisture Absorption
t	Time
CrI	Crystallinity Index
%	Percentage

LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
CaCO ₃	Calcium carbonate
CO ₂	Carbon dioxide
EPDM	Ethylene propylene diene monomer
EPM	Ethylene propylene rubber
FTIR	Fourier transform infrared
HCl	Hydrochloric acid
HDPE	High density polyethylene
KBr	Kalium bromide
LDPE	Low density polyethylene
MAH	Maleic anhydride
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NBR	Nitrile butadiene rubber
NR	Natural rubber
OH	Hydroxyl group
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PVCr	Recycled poly(vinyl chloride)
RHP	Rice husk powder
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis

TMTD	Tetramethyl Thiuram Disulfide
TPE	Thermoplastic elastomer
TPO	Thermoplastic polyolefins elastomer
UTS	Ultimate tensile strength
UV	Ultraviolet
XRD	X-ray diffraction

Sifat-sifat Serbuk Kenaf *Bast* Terisi Polietilena Ketumpatan Tinggi / Getah Etilena Propilena Diena Komposit

ABSTRAK

Sifat-sifat termoplastik elastomer komposit serbuk kenaf *bast* terisi HDPE/EPDM telah dikaji. Komposit telah disediakan melalui pencampuran leburan pada nisbah 70/30 phr HDPE/EPDM dengan perbezaan bebanan pengisi, iaitu; 10,20,30 and 40 phr. Sifat-sifat serbuk kenaf *bast* telah dikaji dengan menggunakan pembelauan sinar-x (XRD), Fourier Transform spektroskop inframerah (FTIR), mikroskop elektron penskanan (SEM) dan analisa termogravimetrik (TGA). Serbuk kenaf terawat daripada kombinasi rawatan kimia natrium hidroksida (NaOH) dan asid hidroklorik (HCl) menunjukkan indeks penghabluran (CrI) dan kestabilan terma yang lebih tinggi berbanding serbuk kenaf *bast* tidak terawat. Permukaan licin serbuk kenaf *bast* terawat dapat dilihat melalui mikroskop elektron penskanan (SEM) selepas penyingkiran lilin dan pengurangan lignin dan hemiselulosa. Daripada kajian, peningkatan modulus tensil dan penyerapan air dapat dilihat dengan peningkatan bebanan terisi bagi semua komposisi komposit. Walaupun begitu, kekuatan tensil dan pemanjangan takat putus menurun dengan peningkatan bebanan pengisi. Komposit juga menunjukkan penurunan kestabilan terma dengan peningkatan bebanan pengisi. Serbuk kenaf *bast* terawat terisi HDPE/EPDM komposit menunjukkan kekuatan tensil, pemanjangan takat putus, modulus tensil lebih tinggi dan penyerapan air yang rendah berbanding serbuk kenaf *bast* tidak terawat terisi HDPE/EPDM komposit. Komposit dengan penambahan maleik anhidrida (MAH) dalam campuran leburan menunjukkan kestabilan terma dan penyerapan air yang rendah berbanding komposit tanpa MAH. Analisa SEM mikrograf menunjukkan

kehadiran MAH meningkatkan pelekatan antara matrik dan pengisi. Kesan pemvulkanan dinamik pada serbuk kenaf *bast* terawat terisi HDPE/EPDM komposit menunjukkan kekuatan tensil yang tinggi pada 10 phr bebanan pengisi. Kestabilan terma pemvulkanan dinamik pada serbuk kenaf *bast* terawat terisi HDPE/EPDM komposit tidak menunjukkan sebarang perbezaan ketara daripada serbuk kenaf *bast* terawat terisi HDPE/EPDM komposit tanpa pemvulkanan dinamik.

Properties of Kenaf Bast Powder Filled High Density Polyethylene/Ethylene Propylene Diene Rubber Composites

ABSTRACT

The properties of thermoplastic elastomer composites of kenaf bast powder filled HDPE/EPDM were investigated. The composites were prepared by melt blending at 70/30 phr ratio of HDPE/EPDM with different filler loading, e.g; 10, 20, 30 and 40 phr. The properties of kenaf bast powder was investigated by using X-ray diffraction (XRD), fourier tranform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Treated kenaf bast powder from combination of chemical treatment of sodium hydroxide (NaOH) and hydrochloric acid (HCl) shows higher crystallinity index (CrI) and thermal stability as compared to untreated kenaf bast powder. The smooth surface of treated kenaf bast powder can be observed from scanning electron microscopy (SEM) after the removal of wax and reduction of lignin and hemicelluloses. From the investigation, the increasing of tensile modulus and water uptake was observed with the increasing of filler loading for all composition of composites. On the other hand, tensile strength and elongation at break decrease with increasing of filler loading. The composites also show the decreasing of thermal stability as the filler loading increased. Treated kenaf bast powder filled HDPE/EPDM composites have higher tensile strength, elongation at break, tensile modulus and low water uptake as compared to untreated kenaf bast powder filled HDPE/EPDM composites. Composites with the addition of maleic anhydride (MAH) during melt blending process shows low thermal stability and water uptake as compared to composites without MAH. SEM micrograph

analysis shows that the presence of MAH increased the adhesion between matrix and filler. Effect of dynamic vulcanization on treated kenaf bast powder filled HDPE/EPDM composite showed higher tensile strength at 10 phr filler loading. Thermal stability of dynamic vulcanization of treated kenaf bast powder filled HDPE/EPDM composites show no significant difference from treated kenaf bast powder filled HDPE/EPDM composites without dynamic vulcanization.

CHAPTER 1

INTRODUCTION

1.1 Natural Filler As a Potential Filler in Polymer Composites

The use of natural resources in polymer composites received an extra attention from many researcher due to development of high performance materials made form natural resources and have connected to consumer demands and expectations. The development of natural resources used in polymer composites in worldwide also increased a demands on global resources, leading major issues of material availability and environmental sustainability (Faruk et al., 2012). Nowadays, filler from natural and synthetic fibers are used in many applications. This is because fillers that consist of fiber especially from natural resources have many advantages. They are easy to obtain with unlimited resources, low cost and environmental friendly (Ismail et al., 2000).

According to Joseph et al. (1996), natural fiber thermoplastic composites is more economical than other thermoplastic composites and the strength and plasticity can be increased. Natural fiber in polymer composites increased the water absorption since natural fiber is sensitive to moisture with the presence of hydroxyl groups (OH) and as a result limit the use of natural fiber in polymer composites (Santiagoo et al., 2011). To overcome this problems, the treatments were used on the filler. According to Onyeagoro (2012), the highest tensile strength, elongation at break and good resilience can be obtained with the combination of chemical treatment when natural fiber was treated with sodium hydroxide (NaOH) followed by wash with hydrochloric acid (HCl). By using the chemical treatment process, the content of

lignin and hemicelluloses are reduced and at the same time reduce the biodegradability of the composites. This is because the reduction of hemicelluloses reduce the moisture absorption and increased the thermal stability while the reduction of lignin reduce the UV degradation of natural fiber (Saheb and Jog, 1999).

1.2 The Use of Various Fillers in Thermoplastic Elastomer Composites

Recently, rigid particles and elastomer have drawn great attention in thermoplastic industry. These rigid particles generally strengthened the composites while elastomeric materials toughened the materials. In principle, incorporation of rigid particle is intended to improve the strength, hardness and high heat distortion temperature of materials but generally increased the brittleness. On the other hand, the addition of rubber component often increased toughness but reducing the rigidity of composites (Wu, 1985). As a result, there is increasing interest in the use of multi-component thermoplastics/rubber/filler in polymer composites because of the possibility of increasing both the strength and toughness of the materials (Scott et al.,1987; Pukanszky et al., 1995).

Thermoplastic elastomer (TPEs) have many advantages than vulcanized rubber especially in economic aspect. This is because TPEs can be processed as a thermoplastic and the scrap can be recycled. According to Varma et al. (1989), further addition of EPDM rubber to HDPE resulted in a decreased of tensile strength and improvement of impact strength. However, the properties of HDPE/EPDM blends depend on properties of each components and other variables that can affect the final properties such as interface and crosslink in rubber component. HDPE/EPDM blends has been used mainly in non-tire products such as kitchen

wears, packaging, furniture, roofing, toys and etc. Mohamed et al. (2011) found that the mechanical properties in HDPE/EPDM composites can increase with the decreasing size of the filler particles.

The used of TPEs reduce the cost with the combination of expensive rubber and cheaper cost of plastic and at the same time increased some mechanical properties such as toughness and impact properties (Saroop and Mathur, 1997). Palm ash, rice husk, and kenaf as a filler have been studied in plastic and rubber (Ishak et al., 1998; Santiagoo et al., 2011; Ismail et al., 2010;). Santiagoo et al. (2011) have studied rice husk powder in PP/rNBR and found that the tensile modulus increased with the increasing of filler loading but decreasing of elongation at break and tensile strength. The same result have been reported by Ismail et al. (2010) on kenaf fiber filled natural rubber compound.

One of the recently used natural fiber is kenaf (*Hibiscus cannabinus* L.). It can be used as reinforcing material in polymer composites. Kenaf that consist of 31 to 39% cellulose, 21.5% hemicelluloses, and 15 to 19% lignin were used as an alternative materials for wood-based application (Yao et al., 2008). However, Clark and Wolff (1969) found that there are changes in the chemical composition where the lignin and α -cellulose increase with age. The crystallinity value of kenaf decreased as the plant matured. This is also supported by Nishimura et al. (2012) in their study on the characterization of kenaf phloem fibers in relation to stem growth. Therefore, the properties of kenaf depends on the chemical composition that present in kenaf fiber. For example, cellulose responsible for strength of the fiber and high content of cellulose gives better mechanical properties (Saheb and Jog, 1999). Kenaf bast fiber

have higher cellulose content than kenaf core. Kenaf bast fibers were composed of cemented bundles of phloem fiber cells and constructed with intrinsic cellulose-hemicellulose networks (Nishimura et al., 2012).

1.3 Problem Statement

Kenaf fiber received attention because of their superior properties over other natural fiber, such as oil palm fiber (Chin and Yousif 2009). For example, investigation on kenaf filled PP/EPDM composites have been reported by Anuar and Zuraida (2011). However, the use of kenaf fiber in HDPE/EPDM composites has never been reported. In the previous studies HDPE/EPDM was studied with the various ratio of HDPE/EPDM. Different types of filler such as carbon black, silica and calcium carbonate filled HDPE/EPDM have been studied (Varma et al., 1989; Mohamed et al., 2011).

The greatest challenge in working with natural filler reinforced plastic composites is their large variation in properties and characteristics. The incompatibility between polar natural filler and non-polar matrix become critical issue in development of natural fiber composites. This is because a polar natural fiber tends to form agglomerates during processing due to strong attraction between polar-polar group and poor resistance to moisture that can reduce the potential of natural fiber as reinforcement materials. The presence of lignin and hemicelluloses whose responsible for biodegradability reduce the performance of natural fiber in the composites. which they responsible for biodegradability of kenaf bast powder (Nishino et al., 2003; Ochi, 2008; Ruksakulpiwat et al., 2009; Ismail et al., 2001; Santiagoo et al., 2011).

There are many chemical treatment were used to improve the adhesion between kenaf bast powder and HDPE/EPDM matrix and increased the thermal and mechanical properties of kenaf bast powder (Bai and Li, 2009; Kabir et al., 2012; Onyeagoro, 2012; Gurgel et al., 2012). However, the structure of kenaf bast powder are difficult to penetrate with single chemical solution and the combination of NaOH and HCl chemical treatment were used. Kenaf bast powder was first immersed into NaOH solution at room temperature remove the foreign materials and open the pore inside the fiber so that the HCl easy to penetrate the fiber and remove the lignin and hemicelluloses. The removal of lignin and hemicelluloses improved the mechanical and thermal properties and reduce the biodegradability of kenaf bast powder.

1.4 Objectives

The objectives of this study are:

1. To characterize the kenaf bast powder with and without chemical treatment of NaOH and HCl on kenaf bast powder.
2. To study the effect of kenaf bast powder filler loading on the properties of HDPE/EPDM composites.
3. To investigate the effect of treated kenaf bast powder filler loading on the properties of HDPE/EPDM composites.
4. To study the effect of MAH on the properties of HDPE/EPDM-treated kenaf bast powder composites by melt blending process
5. To study the effect of dynamic vulcanization on the properties of HDPE/EPDM-treated kenaf bast composites in terms of tensile properties, thermal, morphological and water absorption.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Composites

A polymer composite is made by combining two or more polymeric materials such as thermoplastic or rubber and reinforcement (e.g: carbon black, silica, mica and etc) that have very different properties and give the composite a unique properties. However, within the composites these different materials can easily distinguish as they do not dissolved or blend into each other. Most composites are made of just two materials which is thermoplastic or thermoset as a matrix or binder and filler as a reinforcement. The advantages of composite materials is that they are light, flexible that they can be moulded into complex shape and strong than metal (Lei and Wu, 2010; Joshi et al., 2004).

2.1.1 Natural Fiber Polymer Composites

Natural fiber reinforced composites in polymer science are biodegradable and non-abrasive and have potential to act as biodegradable reinforcing materials. In this past decade, polymer have replaced many conventional metals and materials in various applications due to the polymer offers the advantages over conventional materials when a specific properties are compared (Lei and Wu, 2010; Saheb and Jog, 1999). In 1990s natural fiber composites become one of the realistic alternatives in many composites applications. Natural fiber is a low cost material, low density, easy to obtain, and more importantly it is environmentally friendly compared to synthetic material such as glass fiber. The advantages of natural fiber compared to glass fiber are (Joshi et al., 2004):

- Natural fiber has less environmental impacts compared to glass fiber
- High fiber content can be used in natural fiber composites, reducing more polluting base polymer content
- In automotive application, light-weight natural fiber can reduce the emission and improve fuel efficiency.
- The end of life incineration of natural fibers can recovered energy and carbon credits.

In natural fiber composites, matrix phase play an important role in the performance of the polymer composites. The processing temperature is restricted to temperature below 200°C to prevent the natural fiber from thermal degradation. Dispersion of natural fiber in polymer composites is also an important parameter to achieve consistency of the sample where the fiber-matrix interface govern the properties of the composites. The surface adhesion between the fiber and the matrix is very significant in stress transmission from matrix to the fiber and contributes to performance of the composites (Saheb and Jog, 1999).

Polymer composites are able to absorb moisture especially natural fiber polymer composites. The moisture absorption leading to poor mechanical and thermal properties of the composites (Dhakal et al., 2007). Natural fibers are highly hydrophilic due to the hydroxyl group (O-H) which is a polar group that can form a hydrogen bonds with water molecules and increased the moisture content. The mechanism of water transportation in natural fiber polymer composites which is by fiber/matrix interface is when the natural fiber polymer composites is exposed to moisture. The water will penetrate and attached onto the hydrophilic groups of

natural fibers. As a result, the interfacial adhesion is reduced between fiber and matrix (Azwa et al., 2013). Figure 2.1 shows an effect of water on fiber-matrix interface. The moisture absorption caused fiber to swell within the matrix. As a result, weak bonding at interface will form and lead to dimensional stability, matrix cracking and poor mechanical properties (Kabir et al., 2012).

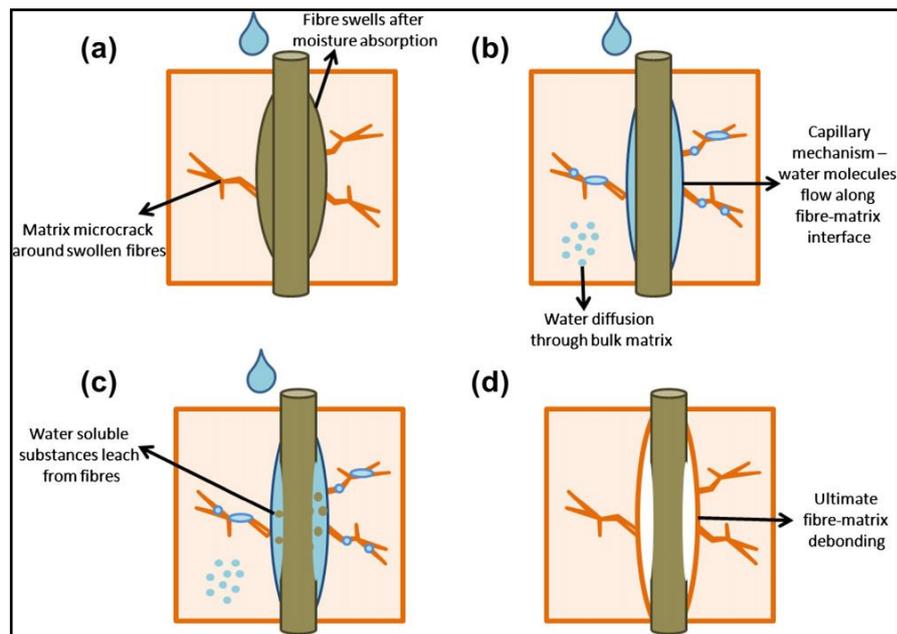


Figure 2.1: Effect of water on fiber-matrix interface (Azwa et al., 2013)

2.2 Thermoplastic Elastomers

Thermoplastics and elastomers are the main class of polymer material that mostly used in industry. Thermoplastics materials are semicrystalline, soluble, linear or branched polymer which can be reversibly melted or solidified while elastomers display rubber characteristic due to their low cross-linkage density and their flexible segments (Holden et al., 1996; Müller and Rieger, 2002).

The first thermoplastic elastomers (TPEs) become available in 1959. Thermoplastic elastomers (TPEs) are a class of polymers with the combine properties of rubber and thermoplastics (Holden et al., 1996). They are processed like thermoplastics, yet perform like rubbers. TPEs can be stretched and unlike rubber-like elastomers, they can be processed without curing or vulcanization because they are true thermoplastics (Mohamed et al., 2011). Vulcanization process is a slow and irreversible process which takes place on heating and leading to a crosslinking network are irreversible that cannot be softened or melt with heat, therefore they are not reprocessable. However, TPEs are generated by transition from melt to solid, which solid takes place on cooling. TPEs can be softened and melt, therefore the process are reversible which they can be reprocessed. TPEs also can be process with the rapid a processing technique. The process was developing by the thermoplastic industry resulting in fast process cycles by using injection and blow molding and higher extrusion rates.

TPEs polymer become significant because they can cut cost saving due to their ability to be processed on plastic machinery and the process is reversible and the products can be processed and remoulded. TPEs processing scrap, reject parts or end of life products can be easily reprocessed, while thermosetting elastomer polymers end up as land fill (Ismail et al., 2002; Ismail et al., 2004). The additional advantages provided by thermoplastic elastomer are excellent colorability and a lower density. By varying the temperature, transitions between the elastomeric and the melt state can be initiated (Holden et al., 1996).

The plasticity behavior results from the melting characteristics of the hard thermoplastic phase, while the rubber properties arise from the rubbery domain. Therefore, TPEs almost heterogeneous in their phase morphology in definition. Such materials can be blends or block polymers. Block polymer in the rubbery phase is not crosslinked chemically. However, the thermoplastic phase happen to be the hard segment of the block polymer which separate from the composition by agglomeration during cooling from the molten state. In the blend polymer, the hard and soft materials are separated, however, there are some form of interaction that makes its properties is useful in certain applications (Holden et al., 1996; Müller and Rieger, 2002).

2.2.1 Thermoplastic Polyolefin Elastomers (TPOs)

Thermoplastic polyolefin elastomers (TPOs) are an important part of thermoplastic elastomers (TPEs) family. They can be classified as blends or physical mixtures of semicrystalline polyolefin thermoplastic and an amorphous elastomer. At ambient temperature, TPOs show properties such as modulus and yield strength similar to rubber. Thermoplastic such as PP, PE, nylon, PS, polyester and etc and elastomer such as EPDM, natural rubber, SBR, NR and etc were used as a component in blending. TPOs shared all the TPEs fundamental characteristics and they process like a thermoplastic material (Holden et al., 1996).

According to industry report in 2010, the combined world consumption of TPOs and TPVs increase from 2009. In 2008-2009 global recession had a depressing effect on demand for almost all end uses of thermoplastic polyolefin elastomer, especially in the automotive industry. Furthermore, TPOs have been used to replaced

thermoset rubber and win competing factor in certain applications. TPOs is a generous TPEs and low performance compare to thermoset rubber. However, it is still suitable in certain application that not required a resistant to fluid and serve at medium temperature ($\sim 80^{\circ}\text{C}$). Thus, TPOs can compete in rubber market for its price not performance.

2.2.2 Natural Fiber in Thermoplastic Elastomer

Ruksakulpiwat et al. (2009) have found that with rubber content more than 20% by weight, the impact strength and elongation at break is significantly increased in natural fiber/PP composite by using NR and EPDM rubber. However, higher viscosity, tensile strength and impact strength was observed in PP/EPDM composites PP/NR composites. This also was supported by Anuar and Zuraida (2011) in PP/EPDM-kenaf fiber composites. Santiagoo, (2011) has studied rice husk powder in PP/NBRr and found that the addition of rice husk powder into PP/NBr composites increased the processing torque, tensile modulus, water absorption and swelling in oil but decreased in tensile strength and elongation at break due to poor adhesion between rice husk powder and PP/NBRr matrix with the increasing of filler loading. The increased of swelling percentage in PP/NBRr/RHP composites is due to the properties of lignocellulosic fiber (RHP) that can absorb oil in its surface (Satyanarayana et al., 2009; Saheb and Jog et al., 1999; Premalal et al., 2002). The same result can be seen in the incorporation of white rice husk ash filled NR/LDPE blends which the increasing of filler loading increased the tensile modulus and hardness but decrease in tensile strength due to poor filler-matrix interaction, poor dispersion of filler and size irregularity (Ismail et al., 2001).

2.3 Polyethylene (PE)

Today PE is one of the most widely used plastics and usually were used in packaging materials. Generally, PE is characterized based on ease of processing, toughness, and chemical and electrical properties and basically classified according to their density.

2.3.1 High Density Polyethylene (HDPE)

HDPE is the high density version of PE plastic. HDPE is prepared from ethylene by a catalytic process. It is harder, stronger and a little heavier than LDPE due to the absence of branching results in more closely in more closely packed structure. The appearance of HDPE is wax-like, lusterless and opaque. HDPE received attention in the past and it is highly resistant to many acids, alkalis, solvents, low cost plastics and often considered as a 'model' polymer for the study of the mechanical behavior of crystallized polymers (Lei and Wu, 2010).

Several studies has been done regarding natural fiber filled HDPE composites (Li et al., 1998; Barone, 2005; Clemons, 2010; Arrakhiz et al., 2013; Chang et al., 2006; Supri et al., 2011). The strength and stiffness can be achieved by using natural fiber with varying the fiber volume fraction and controlling the bonding between fiber and matrix in composites. This study have been done in flax fiber/HDPE composites. However, it found that the thermal conductivity, thermal diffusivity and specific heat of flax fiber/HDPE composites decreased with increasing fiber content (Singleton et al., 2003; Li et al., 2007; Faruk et al., 2012; Wang et al., 2006).

2.3.2 Various Filler in Polyethylene

Supri et al., 2010, studied eggshell powder in LDPE composites and found that increasing of eggshell powder increased the tensile strength and tensile modulus of composites but decreased in elongation at break. The addition of PE-g-MAH as a compatibilizer improved the adhesion between eggshell powder and LDPE matrix. Arrakhiz et al. (2013) has studied Doum/LDPE composites and found the issue of compatibility between polar Doum fiber and non-polar LDPE matrix. Thus the alkali treatment have been done on Doum fiber to improve the interaction between Doum fiber and LDPE matrix and it shows a significant increased in Young's modulus, flexural modulus and torsion modulus however, the thermal analysis decrease in properties compared to neat LDPE. Lei and Wu, (2010) in their investigation found that the mechanical properties of HDPE improved the addition of PET and 40% of wood flour.

2.4 Ethylene Propylene Diene Rubber (EPDM)

EPDM rubber was produce with variations of ethylene/propylene ratios is the one of the most widely used and fastest growing synthetic rubbers. It was produce with a different amount and type of diene used, the molar mass and the amount of long chain branching. EPDM rubber have both specialty and general purpose applications that were used in a wide variety of applications and offer a good processing and finish product performance beyond the capabilities of natural and general-purpose synthetic rubbers . EPDM is an elastomer that is comprised of ethylene, propylene and diene. The letter M in its name come from its ASTM classification, which indicates that it features a saturated chain of the propylene type. Hence, that letter make ups its name. Low crosslink density in EPDM rubber due to

fewer double bonds resulting a good oxidative stability and excellent weather resistance compared to major synthetic elastomer such as SBR, BR, NBR, and IR and natural rubber. EPDM also exhibit ozone resistance, long service life in extreme environmental conditions and sustained flexibility. In industry, EPDM was preferred due to their high resilience properties, good resistance to salt solutions, oxygenated solvents and synthetic hydraulic fluids.

The composition and structure of EPDM can greatly affect the degradation characteristics with ENB (5-ethylidene-2-norbornene) as third monomer are well known to be more sensitive to photo-oxidation when compared to ethylene-propylene copolymer (EPM). However, EPDM is more stable than highly unsaturated elastomer (e.g. styrene-butadiene and isoprene rubber) (Snijers et al. 2005). Figure 2.2 shows an EPDM rubber structure.

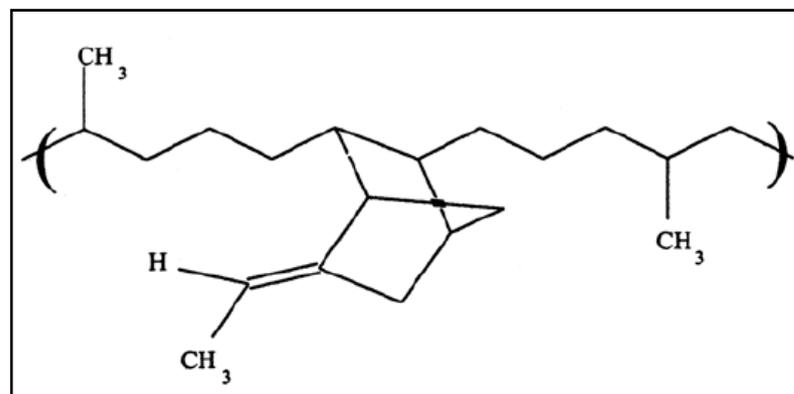


Figure 2.2: An EPDM polymer structure

2.5 Natural Fibers

Natural fibers is a substances produced by plants and animals. Natural fibers not including man-made artificial or synthetic fibers such as nylon, polyester and

rayon. Hemp, leaf, sisal, flax, kenaf and palm ash are a type of plant fibers. Wool, hair and silk are a type of animal fibers.

2.5.1 Natural Fiber Microstructure

Natural fibers themselves are cellulose fiber reinforced materials and mostly constituted of cellulose, a biopolymer of the plant sugar glucose. The other principal components are hemicellulose, lignin and waxes (Espert, 2003). These fiber consist of several fibrils that run all along the length of the fiber. The hydrogen bonds and other linkages provide the necessary strength and stiffness to the fibers. Natural fiber have different percentage of chemical composition depending upon the type of fiber. The properties of each constituent (cellulose, hemicelluloses, pectin and lignin) contribute to the overall properties of the fiber. For example, hemicelluloses is responsible for the biodegradation, moisture absorption and thermal degradation of the fiber, while lignin is thermally stable but responsible for the UV degradation (Saheb and Jog, 1999). The chemical composition is varies for different types of plant and depends upon geographic locations, ages, climate and soil conditions. Besides, chemical composition also often altered during production steps. For example, during pulping, lignin and hemicelluloses are removed.

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose unit and can be seen in Figure 2.3. A large numbers of strong intra-molecular hydrogen bonds are formed in crystalline region of cellulose which creates a cellulose block that able to makes it difficult for other chemical to penetrate (Kabir et al., 2012). Figure 2.4 shows a schematic model of cellulose

molecules in the annular and spiral vessels. Cellulose found in the form of slender rod like crystalline microfibrils that aligned along the fiber length is resistant to hydrolysis, strong alkali and oxidizing agent but degrade when exposed to chemical and solution treatment at some amount of concentration. Cellulose is the most common organic compound on Earth. About 33% of all plant matter is cellulose (the cellulose content of cotton is 90% and that of wood is 40–50%) (Klemm et al., 2005).

Hemicelluloses are made of polysaccharides act as cementing matrix between cellulose microfibrils while lignin is made of a complex hydrocarbon polymer that gives rigidity and on the transportation of water. The main constituents of hemicellulose are glucose, mannose, lose, galactose, xylose, arabinose. Hemicellulose is different from cellulose; contain various sugar units, with shorter chains and by branching of the chain molecules. Thus, its molecular weight is significantly lower than cellulose (Li et al., 2007). In addition, hemicellulose is more active than cellulose which is mainly due to their amorphous nature. Hemicellulose is easily dissolved in water, alkali and hydrolyzed in acids because of its open structure containing many hydroxyl and acetyl groups (John & Thomas, 2008). Lignin resists acid hydrolysis but soluble in hot alkali. Other component in natural fiber are pectin that gives plants flexibility, wax and oil used to protect fiber. The strength of fiber determine by the microfibrillar angle where the smaller angle leads to higher strength and stiffness while larger angles provide higher ductility. Mechanical strength also can be determined by cellulose content, longer cell length and lower mirofibrillar angle.

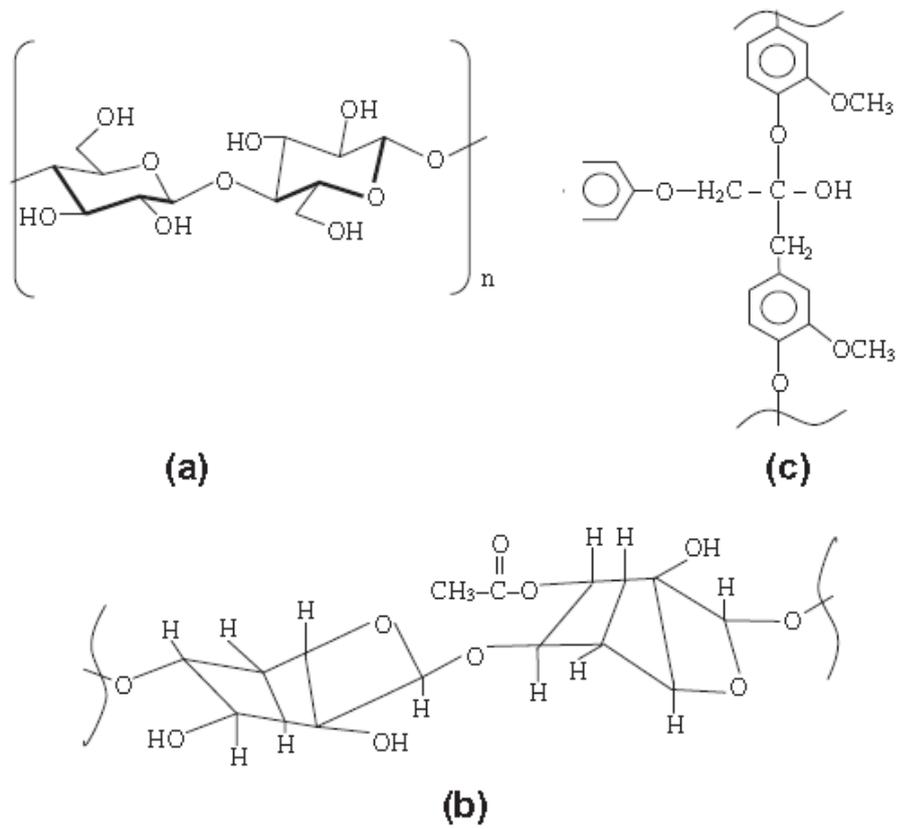


Figure 2.3: Chemical structure of (a) cellulose (b) hemicelluloses (c) lignin (Kabir et al., 2012)

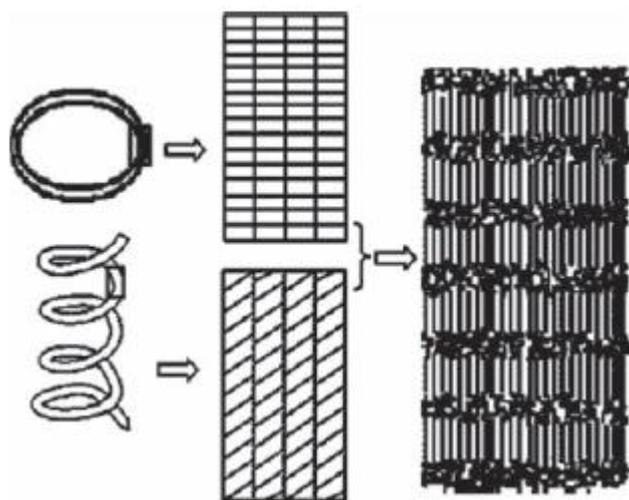


Figure 2.4: Schematic model of cellulose molecules in the annular and spiral vessels (Yu et al., 2005)

2.5.2 Advantages and Disadvantages of Natural Fibers

Natural fibers are well known for their low price, economical production with few requirements for equipment and low density. This characteristic of natural fibers resulting higher specific strength and stiffness compared to glass reinforced composites (Bismarck et al., 2002). The non-abrasive natural fibers during mixing and compounding can contribute to significant equipment maintenance cost reductions. They also appear to be safer handling and working conditions compared to synthetic reinforcement such as glass fiber, which the processing atmosphere is friendly with better working conditions. Therefore, there will be reduced dermal and respiratory irritation compared to glass fiber (Bogoeva-Gaceva et al., 2007). Natural fibers has positive environmental impact which they are renewable resource with production requiring little energy and biodegradable. They are also carbon dioxide neutral such they do not return excess carbon dioxide into atmosphere when they are composed or combusted (Joshi et al., 2004; Mohanty et al., 2002).

However, natural fibers have major drawback which they are sensitive to moisture that lead them to degrade. Hydroxyl group in natural fibers makes it hydrophilic in nature. Mixing between hydrophilic natural fibers and hydrophobic plastic will resulting a poor mechanical properties composites due to non-uniform fiber dispersion in the matrix and inferior fiber matrix interphase. High moisture absorption in natural fiber based composites leading to swelling of fiber and voids in fiber matrix interphase and could also cause deterioration in mechanical properties and loss in dimensional stability (Alvarez et al., 2004). These problems generally can be solved by fiber surface treatment using acid or alkaline or matrix modifications (Alvarez et al., 2004).

Another major limitation for exploitation of natural fibers is face higher risk of degradation when exposed to outdoor applications and low thermal stability. Natural has low thermal stability which natural fibers undergo degradation when processed beyond 200°C, this further limits the choice of plastic materials to be used as matrix (Bismarck et al., 2002; Glasser et al., 1999). Natural fibers are also susceptible to rotting and posses low resistance to microbial attack which attributed to the characteristic biodegradation of natural fiber. The problems are solved by adding anti fungal additives to the composites (John and Thomas, 2008; Verhey et al., 2002).

2.6 Kenaf

Kenaf belongs to the genus Hibiscus known as Hibiscus cannabinus L. and there are about 300 species. They have three distinct fiber types: bast, core and wood (Webber et al., 1999; Wang et al., 2010). Harvesting the plants at the right time is very important because harvesting before the flowering generally results in lower yields and weaker fiber. The optimum time for harvesting kenaf is about ten flowers are in bloom (Rowell and Stout, 2010). The generally harvesting process of kenaf plant as following below:

- The plants are harvested by hand with sickle and cut close to the ground.
- The cuts stems are then tied into bundles, the removed as much as possible and the bundles was submerged in water for retting.
- Stripping the fiber from stem is done by hand, after the fibers are washed and dried.

The advantageous of kenaf plant to environment other than use as reinforcement in polymer composites which is kenaf plant absorbs CO₂ from the atmosphere more than any other crop. It also can absorb toxic elements, such as heavy metal from the soil (Faruk et al., 2012; Rowell and Stout, 2010).

In the past, separation of bast fiber and core fiber was done by biological retting. Extensive research has been done on the mechanical separation of the bast from the core on kenaf. By using mechanical retting, it was found that separation efficiencies of 42 to 48% were achieved which the moisture content become a critical factor in separation process of kenaf, if controlled the separation was cleaner and quicker. Kenaf bast consist of 31 to 39% cellulose, 21.5% hemicelluloses and 15 to 19% lignin (Yao et al., 2008). Compared with kenaf core fibers, kenaf bast fibers have higher crystallinity index, lower moisture content, higher bulk density and higher tapping density when treated with HCl (Wang et al., 2010; Mohanty et al., 2000).

2.7 Chemical Treatment on Kenaf and Other Natural Fillers

Despite their promise as potential reinforcing materials, natural fiber still have some drawbacks, such as low thermal stability and high moisture absorption. These fibers are usually treated to improve their thermal stability and tensile strength. The cementing region composed of lignin, wax and some hemicelluloses is removed through acid hydrolysis to increase thermal stability, crystallinity and crystallite size (Bai and Li, 2009; El-Sakhawy and Hassan, 2007; Gurgel et al., 2012; Kabir et al., 2012).