COMPATIBILITY AND DEGRADABILITY OF KENAF-FILLED LINEAR LOW DENSITY POLYETHYLENE/POLYVINYL ALCOHOL COMPOSITES

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by

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LIST OF ABBREVIATIONS

AFTA	ASEAN Free Trade Area
APTES	3-aminopropyltriethoxysilane
ASTM	American Society for Testing and Materials
COCA	Coconut oil coupling agent
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogravimetric
EFCA	Eco-friendly coupling agent
EVA	Ethylene vinyl acetate
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared
HDPE	High density polyethylene
KCF	Kenaf core fiber
KNF	Kenaf bast fiber
KF	Kenaf fiber
KP	Kenaf powder
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MAPE	Maleated polyethylene
$NaHCO_3$	Sodium hydrogen carbonate
NaOH	Sodium hydroxide
NKTB	National Kenaf and Tobacco Board
NR	Natural rubber
PA	Phthalic anhydride
PALF	Pineapple leaf fiber
PE	Polyethylene

PE-g-MA	Polyethylene-grafted maleic anhydride
PLA	Poly (lactic acid)
pMDI	Polymeric methylene diphenyl diisocyanate
PP	Polypropylene
PSP	Peanut shell powder
PU	Polyurethane
PVC	Poly (vinyl chloride)
PVOH	Poly (vinyl alcohol)
rHDPE	Recycled high-density polyethylene
rPP	Recycled polypropylene
SEM	Scanning Electron Microscopy
SS	Sago starch
TGA	Thermogravimetric analysis
TMS	3-3-(trimethoxysilyl)propyl methacrylate
TPSS	Thermoplastic sago starch
UV	Ultra-violet
WMCF	Waste maize cob flour
WTD	Waste tire dust

LIST OF SYMBOLS

E_b	Elongation at break
Kg	Kilogram
cm^3	Centimetre cube
rpm	Revolutions per minute
phr	Parts per hundred resin
wt.%	weight percent
MPa	MegaPascal
℃	Degree celcius
mm	Millimetre
µm	Micrometer
N/m	Newton per metre
mW	Miliwatt
ΔH_f	Heat of fusion
T_m	Melting temperature
T_c	Crystallization temperature
%	Percentage
X_c	Degree of crystallinity
J/g	Joule per gram
$T_{5\%}$	Temperature at 5% weight loss
$T_{50\%}$	Temperature at 50% weight loss
W_t	Total water absorption (in weight)
W_1	Weight of specimen before immersion
W_2	Weight of specimen after immersion
W_b	Weight of sample before degradation test
W_a	Weight of sample after degradation test

KESERASIAN DAN KEBOLEHDEGRADASI KOMPOSIT POLIETILENA BERKETUMPATAN RENDAH LINEAR/POLIVINIL ALKOHOL TERISI KENAF

ABSTRAK

Penyelidikan berkaitan komposit polimer gentian semula jadi sedang meningkat dengan cepat disebabkan permintaan tinggi pada produk polimer yang mesra alam dengan harga yang berpatutan. Usaha-usaha yang berterusan adalah tertumpu untuk meningkatkan sifat-sifat komposit ini. Di dalam kajian ini, adunan polietilena berketumpatan rendah linear (LLDPE)/polivinil alkohol (PVOH) telah digunakan sebagai matrik polimer dengan komposisi yang telah ditetapkan pada 60/40 (wt. %), manakala gentian kenaf bast (KNF) digunakan sebagai pengisi. Kesan pembebanan pengisi dan pelbagai rawatan kimia terhadap pengisi semula jadi tersebut ke atas ciri-ciri pemprosesan, sifat-sifat tensil, struktur, morfologi, termal dan biodegradasi komposit LLDPE/PVOH/KNF telah dikaji. Komposit LLDPE/PVOH/KNF mengandungi pembebanan KNF yang berbeza (0, 10, 20, 30 and 40 phr) telah disediakan menggunakan pencampuran leburan dan pengacuanan mampatan. Didapati bahawa peningkatan pembebanan KNF, tork pemprosesan, modulus tensil, kestabilan termal dan penyerapan air komposit telah meningkat. Walau bagaimanapun, kekuatan tensil dan pemanjangan pada takat putus komposit telah didapati menurun. Ini menunjukkan lekatan antara muka yang lemah di antara matrik LLDPE/PVOH dan KNF sebagaimana dibuktikan dalam kajian SEM. Pencuacaan semula jadi dan penanaman di dalam tanah telah memberikan kesan negatif kepada sifat-sifat komposit LLDPE/PVOH/KNF, sebagaimana ditunjukkan oleh kemerosotan di dalam sifat-sifat tensil, kerosakan permukaan yang terdedah, dan peratusan kehilangan berat yang lebih tinggi. Seterusnya, keputusan daripada spektra FTIR mengesahkan kehadiran degradasi dengan kemunculan puncak karbonil yang jelas. Kehadiran perawatan kimia ke atas KNF telah meningkatkan sifat-sifat tensil, morfologi, sifat terma dan juga mengurangkan penyerapan air komposit LLDPE/PVOH/KNF. Perawatan kimia KNF telah disahkan melalui spektroskopi FTIR. Berdasarkan keputusan yang diperolehi, didapati penambahan KNF terawat 3-(trimetosisilil)propil metakrilat (TMS) ke dalam matrik LLDPE/PVOH telah meningkatkan tork pemprosesan, kekuatan tensil, modulus tensil, kestabilan terma dan mengurangkan penyerapan air komposit. Ini dibuktikan dengan peningkatan lekatan antara muka di antara KNF terawat TMS dan matrik LLDPE/PVOH melalui analisis SEM. Penambahan KNF terawat dengan agen pengkupel mesra alam (EFCA), kromium (III) sulfat dan lisin ke dalam matrik LLDPE/PVOH juga didapati meningkatkan tork pemprosesan, sifat-sifat tensil, kestabilan terma dan mengurangkan penyerapan air komposit. Keputusan daripada analisis SEM menunjukkan peningkatan di dalam lekatan antara muka di antara KNF terawat dan matrik LLDPE/PVOH. Keputusan FTIR juga mengesahkan pembentukan ikatan kimia di antara agen-agen pengkupel dan KNF, seterusnya menghasilkan pautan di antara KNF and matrik LLDPE/PVOH.

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ABSTRACT

The research on natural fibres polymer composites are rapidly growing due to an increasing demand on environmentally friendly polymer products with reasonable price. The on-going efforts are focused on the improvement in overall properties of these composites. In this research work, linear low-density polyethylene (LLDPE)/poly (vinyl alcohol) (PVOH) blend were utilized as polymer matrices with a fixed composition at 60/40 (wt. %), whereas kenaf bast fiber (KNF) was used as filler. The effect of filler loading, as well as various chemical treatments on the natural filler towards the processing characteristic, tensile, structural, morphological, thermal and biodegradability properties of LLDPE/PVOH/KNF composites were explored. LLDPE/PVOH/KNF composites containing different KNF loadings (i.e. 0, 10, 20, 30 and 40 phr) were prepared by means of melt-mixing and compression moulding. It was found that with increasing KNF loading, the processing torque, tensile modulus, thermal stability and water absorption of composites were increased. Nevertheless, tensile strength and elongation at break of composites were found declined. This indicated weak interfacial adhesion between LLDPE/PVOH matrices and KNF, as revealed by SEM studies. Natural weathering and soil burial has affected the properties of LLDPE/PVOH/KNF composites, as displayed by the deterioration in tensile properties, damage of exposed surfaces, and higher percentage of weight loss. Results from FTIR spectra further confirmed the occurrence of degradation with appearance of intense carbonyl peaks. The existence of chemical treatments of KNF has enhanced the tensile, morphological and thermal properties, as well as reduced the water absorption of LLDPE/PVOH/KNF composites. The chemical treatment of KNF was further confirmed by FTIR spectroscopy. Based on the results, it was found that addition of 3-(trimethoxysilyl)propyl methacrylate (TMS) treated KNF into LLDPE/PVOH matrices has increased the processing torque, tensile strength, tensile modulus, thermal stability and reduced the water absorption of the composites. This was evidenced by the enhanced interfacial adhesion between TMS-treated KNF and LLDPE/PVOH matrices in SEM analysis. Addition of treated KNF with eco-friendy coupling agent (EFCA), chromium (III) sulfate and lysine into LLDPE/PVOH matrices were found respectively increased the processing torque, tensile properties, thermal stability and reduced the water absorption of composites. Results from SEM analysis revealed an improvement in the interfacial adhesion between treated KNF and LLDPE/PVOH matrices. FTIR results also confirmed that chemical bonds were formed between coupling agents and KNF, subsequently provide linkages between KNF and LLDPE/PVOH matrices.

CHAPTER ONE

INTRODUCTION

1.1 Background

For the past few decades, the rising global awareness in renewable resources and environmentally compatible materials has resulted in an extensive research done on natural fibers (particularly, plant fibers/lignocellulosic) (Sdrobis et al., 2012; Zaini et al., 2013; Ayadi et al., 2017). The combination of specific properties and environmental friendly characteristics of natural fibers has positively impact their applications in polymer based composites (Fiore et al., 2016). Furthermore, the need to produce economically feasible products has intensified the development of natural fibers-based polymer composites in various research fields and industries (Yee et al., 2011; Nirmal et al., 2014). Natural fibers are generally classified according to their origins (animal, plant/lignocellulosic and mineral), and currently many types of plant/lignocellulosic fibers are available such as kenaf bast fiber (KNF), jute, sisal, hemp, wood and etc (Akil et al., 2011; Farsi, 2012). The attractive attributes of these natural fibers are their low price, low density, biodegradability, renewability, non-abrasive and high specific mechanical properties (George et al., 2015; Fiore et al., 2016). Nevertheless, natural fibers possess several demerits including poor fiber-matrix adhesion, high moisture absorption, low processing temperature (limiting matrix selection) and low resistance to microorganisms attack (Carvalho et al., 2013; Pickering et al., 2016).

Among various types of plant/lignocellulosic fibers, KNF has been exploited in various sectors (particularly in academic research) over the past few years, because of their fast growing speed over a wide range of climatic conditions (Akil et al., 2015; Ramesh, 2016). Moreover, KNF has been recognised as an important cellulose source for composites and other industrial applications (Datta and Kopczynska, 2015). The applications of KNF-based composites have been found in industries like sports, automotive, furniture, and construction (structural and non-structural elements) (Mahjoub et al., 2014; Saba et al., 2015). Similar to other natural fibers, the challenges encountered during the incorporation of KNF into polymer matrix is the lack of good interfacial adhesion between KNF and polymer matrix (Akil et al., 2011). This is a result of poor compatibility between hydrophilic KNF and hydrophobic polymer matrix, thereby forming a weak filler-matrix interface (Akil et al., 2011). A good interfacial adhesion between KNF and polymer matrix is essential to obtain optimum mechanical properties, since the stress is transferred between matrix and filler across the interface (Pickering et al., 2016).

In natural fibers based polymer composites, the polymer matrix functions as a binder material that holds the fibers in position, protects the fiber surface from mechanical abrasion, and transfers load to fibers (Kabir et al., 2012; Pickering et al., 2016). According to Pickering et al. (2016), polymeric matrices are the most frequently used in natural fibers-based composites due to its light weight and low processing temperature. Both thermoplastics (polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS)) and thermosets (unsaturated polyester, epoxy resin, and phenol formaldehyde) are commonly used matrix materials for natural fibers-based composites (Kamal et al., 2014; Pickering et al., 2016). Thermoplastics possess many benefits over thermosets such as low processing cost with simple molding methods (extrusion, injection molding), flexible in design, capable of undergo repeated heating and cooling, as well as have better potential to be recycled (Pickering et al., 2016). However, thermoplastics like PE, PP, PVC and

PS are non-degradable materials. In conjunction with the environmental concerns and stringent regulations and standards, blending or replacement of petroleum-based with biodegradable matrices or renewable biofibers has been explored (Tajeddin et al., 2010; Carvalho et al., 2013). Polyvinyl alcohol (PVOH) is a synthetic biodegradable polymer that is soluble in water and it is extensively used in agricultural mulch film or packaging applications due to its good strength and biodegradability (Nordin et al., 2012; Tan et al., 2015). PVOH has been used for the fabrication of blends and composites with synthetic polymers like polyethylene and with natural polymers such as lignocellulosic fillers, starch or chitosan (Tan et al., 2015).

In this study, linear low density polyethylene (LLDPE)/polyvinyl alcohol (PVOH) blend with fixed composition ratio of 60:40 (wt. %) was used as polymer matrices because this composition ratio gives the best overall properties as confirmed by Ismail et al. (2009). Meanwhile, KNF was selected as filler materials for LLDPE/PVOH blend because of several reasons. First of all, KNF is a fiber crop that grown commercially in Malaysia (easily available) and has been proven to be environmental friendly cellulose source by Kyoto Protocol (Kamal et al., 2014; Akil et al., 2015; Ramesh, 2016). Moreover, the short growing cycle of KNF (4 to 5 months) enable a stable supply of raw materials (Kamal et al., 2014). Additionally, there is limited research reported for the KNF-based LLDPE/PVOH composites. Hence, the highlights of this study are to explore the potential of KNF in LLDPE/PVOH matrices, its effect on the overall properties of composites, the degradability of composites under natural weathering and soil burial for time of exposure up to 6 months and the influence of different chemical treatments of KNF on the properties of LLDPE/PVOH/KNF composites.

1.2 Problem statement

The increased environmental consciousness has led to the usage of natural fibers based polymer composites to replace the commonly used synthetic fibers reinforced polymer composites (Pickering et al., 2016). One of the most widely used natural fibers is KNF. KNF has been found to possess attractive merits such as low density, less abrasive, biodegradable, high specific mechanical properties, short growth cycle, ease of cultivation and require minimal maintenance (fertilizers, water, pesticides) (Akil et al., 2011; Pang and Ismail, 2013a). Despite of all these advantages, there are certain demerits and challenges need to overcome prior to the usage of KNF in polymer composites.

First, the poor compatibility between hydrophilic KNF and hydrophobic LLDPE from polymer matrices lead to lack of good interfacial adhesion between KNF and polymer matrix. According to Pickering et al. (2016), the incompatibility between filler and matrix generates a weak interface between them, thereby causing the applied stress inefficiently transferred from matrix to filler via the interface. Moreover, the incompatibility between KNF and polymer matrix may cause difficulties in compounding and lead to non-uniform filler dispersion, subsequently impairs the properties of composites (John and Anandjiwala, 2008). Another demerit is the high moisture absorption of KNF when contacted with aqueous media or subjected to high humidity environment (Sarifuddin et al., 2013). The poor water resistance of KNF adversely affects the dimensional stability and mechanical properties of the KNF-based polymer composites.

In order to improve the interfacial adhesion between KNF and polymer matrix, modification of KNF can be made to enhance the properties of composites. There are two types of modification methods such as physical and chemical, with the most commonly used are chemical treatments (Akil et al., 2015; Datta and Kopczynska, 2015). Numerous researchers have reported improvement in the properties of KNF-based polymer composites due to formation of strong interface between KNF and polymer matrix after chemical treatments (Pang and Ismail, 2013b; Cao et al., 2014; Majid et al. 2010).

1.3 Research objectives

The main objective of this research is to develop LLDPE/PVOH/KNF composites with desirable performance. There are several aims need to be tackled to facilitate the achievement of main objective. The aims are listed as below:

- To compare the effect of KNF loading on the processing characteristics, mechanical, morphological, thermal properties and water absorption of LLDPE/PVOH/KNF composites.
- To determine the degradability of LLDPE/PVOH/KNF composites under natural weathering and soil burial exposure for 3 and 6 months.
- To characterize the effect of different KNF treatments (such as 3-(trimethoxysilyl)propyl methacrylate as silane coupling agent (TMS), glycidyl ester of fatty acid as eco-friendly coupling agent (EFCA), chromium (III) sulphate and lysine) on the processing characteristic, mechanical, structural, morphological, thermal properties and water absorption of LLDPE/PVOH/KNF composites.

1.4 Thesis outlines

This thesis is presented into five chapters as below:

Chapter 1 covers the introduction of the research. It contains brief introduction about research background, problem statements, research objectives and organization of thesis.

Chapter 2 provides the related literature on this research work, along with some review of significant works and findings from previous researches.

Chapter 3 outlines the details of materials, methodology, measurement and analysis used to fabricate and characterize LLDPE/PVOH/KNF composites.

Chapter 4 discuss the outcome of this research work. It includes the processing characteristics, structural, mechanical, morphological, thermal properties, water absorption and degradability of the composites.

Chapter 5 summarize the findings in previous chapter, along with the recommendations for the future work.

CHAPTER TWO

LITERATURE REVIEW

2.1 Non-degradable synthetic polymer/biodegradable polymer blend

2.1.1 Linear low-density polyethylene (LLDPE)

A polyolefin is referred to a class of polymers (general formula of C_nH_{2n}) that derived from a simple olefin as a monomer (Sam et al., 2014). Polyethylenes (PEs) and polypropylene (PP) are the examples of commercial polyolefin that extensively utilized in various applications which include food packaging, retail bags, household and automotive components (Sam et al., 2014; Amer and Saeed, 2015). PEs provides many characteristics, thereby making them one of the most extensively used thermoplastic polymers as matrix materials for fiber composites (Tajeddin et al., 2010). PEs is known for its good mechanical properties, moisture resistance, chemical resistance, easy process-ability, low electrical conductivity and low cost (Noorunnisa and AlMaadeed, 2015). In general, there are three major types of mass-produced PE, namely high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). The basic difference between these three types of PEs is their degree of branching (Ahmad and Luyt, 2012).

LLDPE is a linear PE with a significant number of short branches, and was recognized for its good process-ability, great recyclability and preferable compatibility with other polyolefin (Das et al., 2015; Guo, 2016). Comparing to other types of PEs, LLDPE has grown rapidly due to its good balance of mechanical properties and process-ability (Noorunnisa et al., 2016). Recently, LLDPE is observed fast replacing LDPE as packaging films due to its comparable cost and better mechanical properties (Roy et al., 2010). LLDPE has higher tensile strength, impact resistance and heat tolerance than LDPE (Nwanonenyi et al., 2013; Kim and Lee, 2017). Comparing to HDPE, LLDPE has better resistance to environmental stress cracking and higher impact strength (Kim and Lee, 2017). It is also very flexible and able to elongate under stress (Francis et al., 2012). Moreover, LLDPE is known for its moisture, chemicals and corrosion resistance, as well as good barrier properties (Nwanonenyi and Chike-Onyegbula, 2013). LLDPE has broad applications including in the production of plastic bags and sheets (thinner than that of comparable LDPE plastic bags), cable and wire covering, toys, pipes, containers, etc (Nwanonenyi et al., 2013).

2.1.2 Polyvinyl alcohol (PVOH)

Polyvinyl alcohol (PVOH) is a synthetic vinyl polymer that produced commercially from the hydrolysis of polyvinyl acetate (Chiellini et al., 2003, Ismail et al., 2009). The direct polymerization of vinyl alcohol monomer to obtain PVOH is impossible due to an unstable nature of the corresponding monomer, in which it tends to convert spontaneously into acetaldehyde (Leja and Lewandowicz, 2010; Tan et al., 2015). PVOH is recognized as one of the few vinyl polymers that are biodegradable and water-soluble with high mechanical properties, chemical and abrasion resistance, as well as excellent adhesive and gas barrier properties (Dorigato and Pegoretti, 2012; Francis et al., 2012). PVOH is widely used in medical field as it is non-toxic to human body, thereby being utilized to made medicine cachets, yarn for surgery, dialysis membrane, tissue engineering scaffold and artificial cartilage (Panaitescu et al., 2011). Furthermore, the other common applications of PVOH are including agricultural film and environmental friendly packaging (Abdulkhani et al., 2013; Tan et al., 2015).

Nevertheless, the cost of PVOH is a limiting factor for their utilization in various applications (Yee et al., 2011; Ooi et al., 2012). In conjunction with the economical and environmental issues, it is preferable that PVOH to be blended with low cost thermoplastic polymers (PE and PP) and/or renewable resources such as natural fibers (Ismail et al., 2010; Tan et al., 2015). According to Tan et al. (2014), PVOH has a good potential as biodegradable matrix in the development of environmental friendly polymer blends and/or composites. They also observed high water absorbency in kenaf/PVOH composites with 2 wt. % and 10 wt. % of PVOH, respectively. In another study by Pua et al. (2013), they modified kenaf/PVOH composites with sodium hydroxide and citric acid solutions and reported an increase in the properties of modified composites. Moreover, the modified composite film was found biodegradable in natural environmental condition.

2.1.3 Linear low-density polyethylene/polyvinyl alcohol (LLDPE/PVOH) blends and composites

The stringent environmental regulations associated with the management of non-degradable synthetic polymers waste have increased the opportunity for the usage of biodegradable polymers in a wide range of applications. It is obvious that the utilization of biodegradable materials in application like packaging has provides partial solution to handle the problem of solid waste (Tajeddin et al., 2010). The blending of non-degradable synthetic polymer (like LLDPE) and biodegradable polymer such as PVOH are potential in reducing the volume of plastic wastes when they undergo partial degradation (Ismail et al., 2009; Francis et al., 2012).

Several researchers have successfully prepared the LLDPE/PVOH blend and also investigated on the properties as well as biodegradability of the blend. For instance, Ismail et al. (2009) studied on the effect of blend ratio on properties and miscibility of LLDPE/PVOH blends. It was reported that tensile strength and elongation at break decreased whilst the modulus increased with increasing PVOH content. They also noted that both LLDPE and PVOH are immiscible, as revealed by the scanning electron microscopy (SEM). Meanwhile, the biodegradability of LLDPE/PVOH blends exposed in two different environments such as culture medium containing *Vibrio sp* bacteria and soil environment was explored by Francis et al. (2012). They observed that the biodegradation of LLDPE/PVOH blends in culture medium is more rapid than in soil environment, as indicated by the loss in tensile properties and surface defects.

The effect of in-situ silane treatment on the performance of LLDPE/PVOH blend was studied by Nordin et al. (2012). They observed that the thermal stability and tensile properties of the blend increased in the presence of silane. Moreover, better compatibility between LLDPE and PVOH was demonstrated by SEM morphology of the blend. In another study by Raghul et al. (2014), who examined the effect of marine bacteria on biodegradation of PVOH-LLDPE blended plastic films, observed a drop in tensile strength of the plastic film after exposed to marine bacteria, thereby evidence the degradation of PVOH-LLDPE has occurred.

Moreover, the effect of sago starch (SS) content on the tensile properties of hybrid blends of LLDPE/SS/PVOH was studied by Rahmah et al. (2013). They observed that an increase in the SS content increased the tensile modulus, but decreased the tensile strength of the hybrid films. Additionally, they also found that the optimum SS content to be used in LLDPE/SS/PVOH films was 20%.

2.2 Natural fibers filled polymer composites

2.2.1 Characteristic of natural fibers

Natural fibers are grouped into three categories such as plants (or lignocellulosic fibers), animals and minerals (Figure 2.1), depending on their origins (Akil et al., 2011; Farsi, 2012). Among these three groups, plants fibers are the most widely used natural fibers for composites application (Pai and Jagtap, 2015). Natural fibers from plant, also known as lignocellulosic fibers, have attracted interest from both academia and industry to be used as filler and/or reinforcing agent in polymer composites (Muniyasamy et al., 2013).

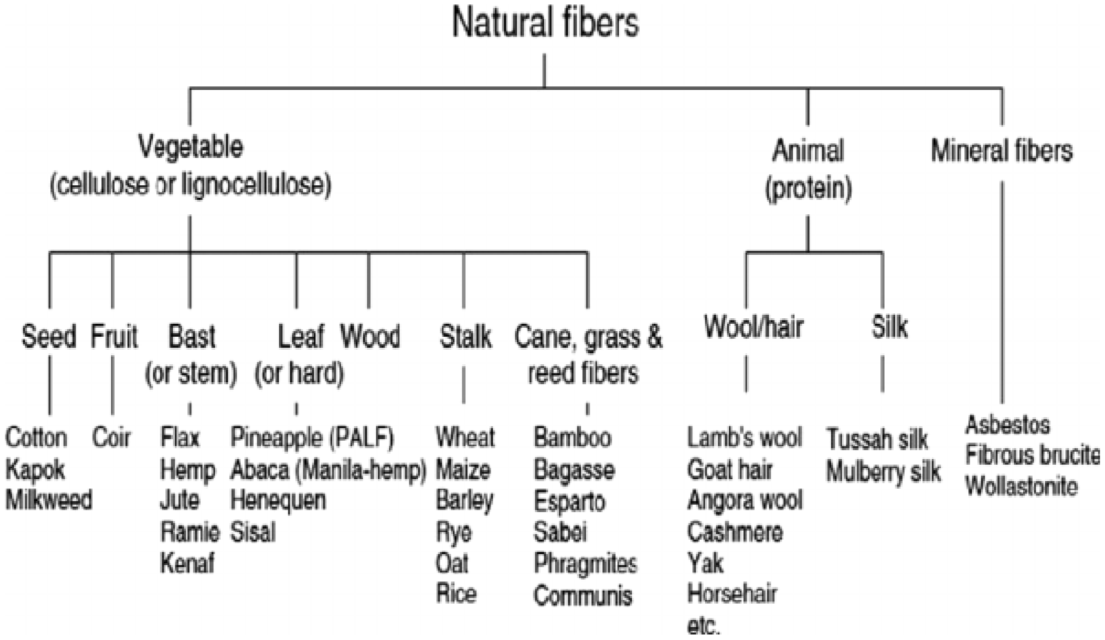

Figure 2.1. Classification of natural fibers (Akil et al., 2011)

The attractive attributes of lignocellulosic fibers are including low cost, low abrasiveness, renewable, light weight, biodegradable, flexible during processing, and acceptable specific mechanical properties (Malkapuram et al., 2009; Fiore et al., 2015). Moreover, the growing environment concerns and regulations have contributed to the fast-growing utilization of lignocellulosic fibers in the design and development of polymer composites (Muniyasamy et al., 2013; Kamal et al., 2014). Natural (plant/ lignocellulosic) fibers can be categorized into two types: agricultural residues and planted crops that grown specifically for their fiber (Muniyasamy et al., 2013; Tahir et al., 2015). The examples of agricultural residues are such as wheat straw, sugarcane bagasse, cotton stalk, coconut coir, oil palm stems, empty fruit bunch and rice straw (Saini et al., 2015; Tahir et al., 2015). Meanwhile, the examples of planted crops are including kenaf, hemp, sisal, jute, ramie, flax, abaca, etc (Muniyasamy et al., 2013).

Natural fibers can be regarded as composites that consist of cellulose microfibrils link together by lignin and hemicelluloses matrix (John and Anandjiwala, 2008, Miao and Hamad, 2013). The chemical compositions of most natural (plant/lignocellulosic) fibers, except for cotton are comprised of celluloses, hemicelluloses, lignins, pectins, and other extractives (ash, wax, etc) (Malkapuram et al., 2009; Akil et al., 2011). The three major constituents of natural fibers are cellulose, hemicelluloses and lignin (Anwar et al., 2014). Cellulose is the main structural component of the plant cell walls (Akil et al., 2011; Anwar et al., 2014). Cellulose is a natural linear polymer made up by (1,4)-D-glucopyranose units, which are connected to each other by β-(1,4)-glycosidic linkages (Kalia et al., 2011; Farsi, 2012). The hydroxyl (O-H) groups present in the cellulose structure units allow formation of intermolecular (between other cellulose molecules) and intramolecular (within the cellulose itself) hydrogen bonding, which gives the hydrophilic nature to plant fibers (Huang et al., 2012; George et al., 2015). Generally, cellulose molecules exist in the form of microfibrils which are bound together by hydrogen bonding, and aligned along the length of the plant (Jonoobi et al., 2009; John, 2017). Cellulose is resistant to oxidizing agents and strong alkali, but easily hydrolyzed by acid to water-soluble sugars (John and Anandjiwala, 2008; Farsi, 2012). The general formula of cellulose is $C_6H_{10}O_5$ and its chemical structure is shown in Figure 2.2.

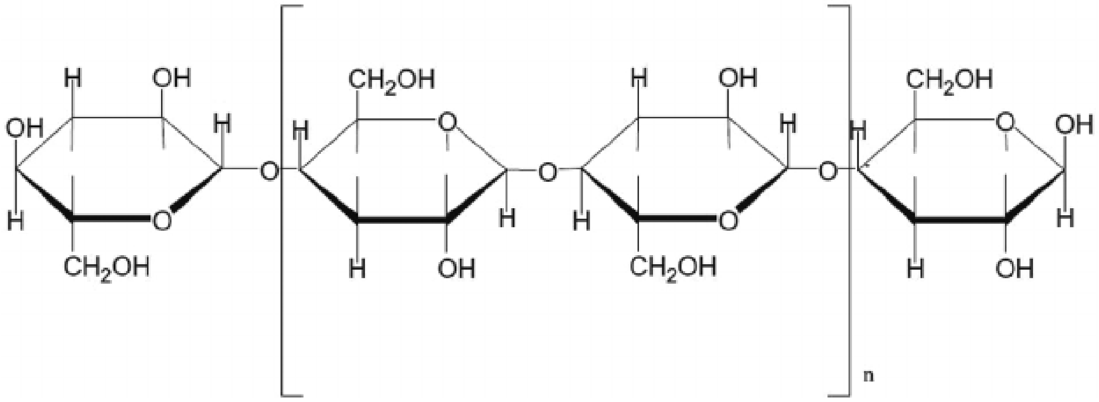

Figure 2.2: Chemical structure of cellulose (Akil et al., 2011)

Hemicellulose is another important component of plant fibers. Hemicellulose is a heterogenous polymer (mostly branched) that consists of xylans, glucomannan and polysaccharides (Farsi, 2012; Anwar et al., 2014). Hemicellulose serves as a bridge between the cellulose and lignin (cellulose-hemicellulose-lignin network), and provides more rigidity to the plant fiber (Huang et al., 2012). Based on Kalia et al. (2011) and John (2017), they found that hemicellulose could be function as a compatibilizer and cementing material between cellulose and lignin, respectively. The hemicellulose is hydrophilic in nature, soluble in alkali and easily hydrolyzed in acids (John and Anandjiwala, 2008).

Lignin is a long chain heterogenous polymer made up of phenyl-propane units, which commonly linked by ether bonds (Anwar et al., 2014). Lignin comprises of a mixture of complex aromatic and aliphatic hydrocarbons with very high molecular weight (Farsi, 2012; John, 2017). Lignin is found insoluble in most solvents and cannot be broken down to smaller units (John and Anandjiwala, 2008). The inherent nature of lignin is amorphous and hydrophobic, thereby decreases the permeation of water across the plant cell walls (Farsi, 2012). Furthermore, lignin imparts rigidity to the plant structure (Farsi, 2012; John et al., 2017). According to Kalia et al. (2011), lignin functions as a stiffener that provide the plant stem its resistance to gravity forces and wind. Additionally, lignin acts as protection against oxidative stress and micro-organisms attack (Kalia et al., 2011; Huang et al., 2012; Farsi, 2012).

Despite the numerous research efforts have been done to use natural (plant/lignocellulosic) fibers in polymer composites, however natural fibers (hydrophilic nature) are inherently incompatible with the hydrophobic polymer matrix (Cicala et al., 2010; George et al., 2015). The addition of hydrophilic natural fibers to hydrophobic polymer matrix results in composites with poor mechanical properties, attributed to inferior fiber-matrix interface (Pickering et al., 2016). Moreover, the utilization of natural fibers in polymer matrix possesses difficulty in mixing due to poor wetting or dispersion of fibers with the matrix (John and Anadjiwala, 2008; Cicala et al., 2010). The hydrophilic natural fibers tend to result in high moisture absorption by its respective polymer composites, leading to swelling and presence of micro-voids at the fiber-matrix interface (Akil et al., 2011; Ramesh, 2016). Subsequently, the mechanical properties and dimensional stability of the composites is reduced. Another limitation is that the processing temperature of natural fiber-based polymer composites is restricted to 200 ℃, as the fibers undergo degradation at higher temperature (John and Anandjiwala, 2008; Farsi, 2012). The degradation of hemicelluloses, celluloses and lignin occurred between the temperature range of 200 ℃ to 260 ℃, 240 ℃ to 350 ℃ and 280 ℃ to 500 ℃, respectively (Peng et al., 2014). This phenomenon will further restrict the choice of polymers to be used as matrix material (Akil et al., 2011).

2.2.2 Kenaf fiber

Kenaf belongs to the non-wood lignocellulosic fibers and primarily contains cellulose, hemicelluloses and lignin (Kamal et al., 2014). The word kenaf is originated from Persian, describing that the plant is grows in short day and annually in the warm season (Saba et al., 2015; Ramesh, 2016). Figure 2.3 shows the kenaf plant.

Figure 2.3. Kenaf plant (Akil et al. 2015)

Kenaf is categorized as a hard, strong and tough fiber plant that is resistance to the attack by insect and requires minimum or no pesticides (Saba et al., 2015). Kenaf is able to grow effectively under a wide range of climatic conditions and soils (Ramesh, 2016). Kenaf comprises of three types of fibers which are bast, core and pith (Saba et al., 2015; Ayadi et al., 2017). According to Tahir et al. (2015), the pith particles dried up during the fiber processing and subsequently detached from the rest of the fibers. Hence, kenaf is characterized by the outer bast and inner core fibers around 30-40% and 60-70% of the stalk dry weight, respectively (Saba et al., 2015; Ayadi et al., 2017). The outer bast fiber is long and has thick cell wall; the inner core fiber, on the other hand, are shorter in length and thinner (Tahir et al., 2015).

According to Ashori et al. (2006) and Abdul Khalil et al. (2010), kenaf bast and core fibers are quite different in respect to their chemical constituents. Table 2.1 shows the chemical composition of different constituents of kenaf fibers.

Table 2.1: Chemical composition of different constituents of kenaf fibers (Abdul Khalil et al., 2010)

Constituents (%)	Kenaf whole	Kenaf core	Kenaf bast
Extractive	6.4	4.7	5.6
Holocellulose	87.7	87.2	86.8
α-cellulose	53.8	49.0	55.0
Lignin	21.2	19.2	14.7
Ash	4.0	1.9	5.4

Kenaf bast fibers (KNF) contained higher percentage of alpha-cellulose which is accounted for its higher mechanical strength compared to kenaf core fibers (Ashori et al., 2006). Hence, the present work chose KNF as filler in LLDPE/PVOH composites. Additionally, the mechanical properties of a few selected natural (plant/ lignocellulosic) fibers and synthetic fibers are listed in Table 2.2.

Table 2.2: Mechanical properties and density values of selected natural (plant/ lignocellulosic) and synthetic fibers (Akil et al. 2011; Ku et al. 2011)

Fibers	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Density (g/cm^3)
Flax	345-1500	27.6	2.7-3.2	1.5
Hemp	690	70	1.6-4	1.47
Jute	393-800	13-26.5	1.16-1.8	1.3-1.49
Kenaf	930	53	1.6	1.45
Ramie	400-938	61.4-128	1.2-3.8	1.55
Sisal	468-700	9.4-22	2-7	1.45-1.5
Cotton	287-800	5.5-12.6	7-8	1.5-1.6
Coir	131-593	4-6	15-40	1.15-1.46
E-glass	2000-3500	70-73	0.5-2.5	2.5-2.55
Aramid	3000-3150	63-67	3.3-3.7	1.4
Carbon	3400-4800	230-425	1.4-1.8	1.4-1.78

Kenaf fiber was recognised by Kyoto Protocol as an environmental friendly cellulose source that effective in reducing global warmness (Kamal et al., 2014; Ramesh, 2016). In Malaysia, the government highly encourage the development of kenaf as a potential crop to replace tobacco, in conjunction with the ASEAN Free Trade Area (AFTA) that comes into effect in 2010 (Basri et al., 2014; Karimi et al., 2014). Under AFTA, the government is requires to reduce the import duties for tobacoo, and this could affect the competitiveness of Malaysian tobacoo planters with their competitor in Thailand and Indonesia (Basri et al., 2014). Moreover, Malaysia is the third largest exporter of wood in the world, and the growing demand for the wood industries has increase the rate of deforestation (Basri et al., 2014).

Therefore, the introduction of kenaf (non-wood lignocellulosic) plantation could help to preserve the destruction of forests and fulfill the demand for raw material in the production of paper and other fiber products.

Worldwide, kenaf has been considered as a potential substitute for wood pulp due to its extensive adaptation, strong resistance, rich in cellulose, high production yield and sustainable properties (Tahir et al., 2015; Ramesh, 2016). Furthermore, kenaf is well known as environmental friendly natural resources because of several reasons: (i) kenaf plant absorbs carbon dioxide from the environment at a significantly high rate; (ii) kenaf plant absorbs nitrogen and phosphorus from the soil; (iii) kenaf is renewable and biodegradable; and (iv) kenaf-based composites are lighter in weight and require low fuel consumption and emission, particularly for automotive industries (Mahjoub et al., 2014; Ramesh, 2016).

The traditional uses of kenaf were to produce rope, cords, clothes, protective packing for fruits and vegetables, paper products and animal bedding (Ayadi et al., 2017). Nowadays, there are plenty of applications for kenaf-based polymer composites including automotive components (interior lining, door panel, dashboard), construction and housing industry (particle boards, ceilings, furniture), as well as oil and chemical industry (adsorbent materials, feedstock) (Akil et al., 2015; Ramesh, 2016; Ayadi et al., 2017). The pioneer automotive company that utilized kenaf as raw material for their interior automotive components is Toyota Boshoku Corporation from Japan (Kamal et al., 2014). The company choose to use kenaf biocomposites in the production of lighter weight door trim and seat back board, attributed to benefits such as improving fuel efficiency and minimizing emission of carbon dioxide (CO_2) (Kamal et al., 2014).

2.3 Kenaf-based polymer composites

2.3.1 Introduction

A tremendous number of researches over the past few years have utilized kenaf as reinforcement and/or filler in polymer composites (Akil et al., 2015; Saba et al., 2015). For example, Anuar and Zuraida (2011) developed thermoplastic elastomer composites reinforced with kenaf fiber. They observed enhancement in stiffness, tensile, flexural and impact strengths of composites in the presence of kenaf fiber. Similarly, Sarifuddin et al. (2013) noted that addition of kenaf core fiber (KCF) imparts a considerable improvement in tensile strength, modulus and thermal stability of LDPE/thermoplastic sago starch (TPSS)/KCF composites. The water uptake, tensile and thermal properties of PP/waste pulverized tire (WPT)/kenaf composites was studied by Pang and Ismail (2013a). It was observed that the water uptake, tensile modulus and thermal stability of composites increased with increasing kenaf loading. On the contrary, tensile strength and elongation at break were decreased. In another study, the properties of kenaf bast fiber reinforced poly (vinyl chloride) (PVC)/thermoplastic polyurethane (TPU) composites as a function of fiber content were examined by El-Shekeil et al. (2014). They found that the composites exhibited lower tensile and impact strengths, but higher tensile modulus and thermal stability with an increase in the fiber content.

However, similar to all natural fibers, the hydrophilic kenaf is incompatible with the hydrophobic polymer like LLDPE, subsequently lead to poor interfacial adhesion between fiber and matrix. Furthermore, the hydrophilic nature of kenaf tends to cause high water absorption which can impair the mechanical properties of the fibers and also their respective composites (Ramesh, 2016; Pickering et al., 2016). Moreover, the low thermal-degrade temperature of kenaf may also render their efficiency as reinforcement or filler during the processing of composites (Tahir et al., 2015; Srinivasarao et al., 2017). In order to overcome these disadvantages, various chemical treatments were applied with the aim to modify the chemistry, changing the polarity, lower the moisture uptake, and increase the roughness of fibers' surface, as well as enhance the fiber-matrix interface adhesion (Cicala et al., 2010, Farsi, 2012). A good adhesion between kenaf and matrix interface is very important because it facilitates the uniform stress transfer within the composites, thereby allows composites to withstand the effect of load without failing (George et al., 2015).

2.3.2 Chemically-treated kenaf-based polymer composites

Generally, the chemical treatment of kenaf fibers was carried out by using reagents which have the functional groups that are able to bond with the hydroxyl group from the kenaf fibers (Ramesh, 2016). According to Kabir et al. (2012), chemical treatments expose the reactive groups on the fiber surface, and hence facilitate an efficient coupling with the matrix material. In order to improve the adhesion of the fibers with the matrix, chemical treatment is an essential consideration. There are many investigations have been conducted to enhance the interfacial adhesion between kenaf and polymer matrices through chemical treatments. The followings described the reviews of various chemical treatments on kenaf and their effects on the composite properties.

The influence of alkaline treatment on the physical and mechanical properties of kenaf/PP composites was investigated by Akhtar et al. (2016). The compatibility between kenaf and PP was improved with alkaline treatment, attributed to better interfacial adhesion and stronger bonding between them. Furthermore, alkali-treated composites exhibited higher tensile and flexural properties than that of untreated composites. Fiore et al. (2015) examined the effect of treated kenaf fibers in 6 % NaOH solution for two different immersion periods (44h and 144h), on the mechanical properties of kenaf-epoxy composites. They observed that 48 hr of alkaline treatment improved the mechanical properties, whereas treatment for 144 hr resulted detrimental effect on fiber surface and impaired the mechanical properties of composites.

In another work by Pang and Ismail (2013b), they employed 3-aminopropyltriethoxysilane (APTES) as coupling agent in PP/waste tire dust (WTD)/kenaf composites. They found that composites with APTES showed higher stabilization torque, tensile strength and modulus compared to untreated composites. This is because of better filler-matrix interfacial adhesion was established in the presence of APTES, as observed in SEM. Whereas, the combined effect of alkali and silane treatments on properties of recycled HDPE/natural rubber (NR)/kenaf powder (KP) biocomposites were studied by Cao et al. (2014). It was found that the tensile strength, modulus and thermal stability of composites increased after treatment. Furthermore, SEM analysis showed better interfacial adhesion between rHDPE/NR matrix and KP. The water absorption and elongation at break, on the other hand, were observed decreased with the effect of treatment.

The modification of PP/waste tire dust (WTD)/kenaf composites with phthalic anhydride (PA) as coupling agent was studied by Pang and Ismail (2014). It was observed that composites with PA possessed higher tensile strength and tensile modulus, as well as more water resistance than composites without PA. Furthermore, the interfacial adhesion between kenaf and PP/WTD matrices was enhanced in the presence of PA, as shown by SEM analysis. On the other hand, Noranizan and

Ahmad (2012) investigated the effect of polyethylene-grafted maleic anhydride (PE-g-MA) on mechanical and morphological behaviours of HDPE filled with kenaf fiber (KF). They observed that the tensile strength and modulus were optimal at 20 % KF loading, with treated composites showed higher mechanical properties than untreated composites. The morphology analysis shows presence of strong interface between HDPE and KF in the presence of PE-g-MA as compatibilizer.

In another work by Nurfatimah et al. (2014), they examined the effect of methyl methacrylate grafted-kenaf fiber on the mechanical properties of poly (vinyl chloride)/ethylene vinyl acetate (PVC/EVA) composites. They noted that the grafting of kenaf fiber with methyl methacrylate has improved the adhesion between kenaf fiber and PVC/EVA matrix, thereby enhanced the stress transfer efficiency between them and subsequently increased the composites' mechanical properties. Whereas study by Pua et al. (2013) showed that kenaf/PVOH composite films with citric acid treatment exhibited higher elongation characteristic as compared to composite films with alkaline treatment. The good elongation property of this composite film serves as a basic advantage for packaging products.

El-Shekeil et al. (2012) compared the tensile properties of kenaf fiber reinforced thermoplastic polyurethane composites under the effect of 4 % polymeric methylene diphenyl diisocyanate (pMDI) and combination of 2 % sodium hydroxide (NaOH) + 4 % pMDI. It was noted that 4 % pMDI has negligible effect on tensile properties, whereas the treatment of 2 % NaOH and 4 % pMDI has enhanced the tensile strength and modulus of composites by 30 % and 42%, respectively. Meanwhile, Datta and Kopczynska (2015) compared the influence of different chemical treatments such as acetylation, blocked isocyanate, maleic anhydride and potassium permanganate treatment on properties of kenaf/thermoplastic polyurethane composites. It was observed that all the treated composites showed improvement in tensile properties, hardness and water resistance, particularly at low fiber loading. However, composites with potassium permanganate treatment exhibited better interfacial adhesion between the kenaf and the thermoplastic polyurethane matrix, in comparison to other chemical treatments.

Despite of numerous published studies on the chemical treatments of kenaf fibers and its composites, however the chemical treatment of KNF using 3-(trimethoxysilyl)propyl methacrylate (TMS) and glycidyl ester of fatty acid as coupling agents in LLDPE/PVOH/KNF composites was not elaborated. Coupling agent can be regards as a third material that used to improve the compatibility between two materials which are incompatible (Kalia et al., 2011). Furthermore, coupling agent also referred to a chemical reagent that interacts with both the filler and the polymer, thereby bridging the two components (Supri et al., 2012). Silanes are recognized as efficient coupling agents that may respectively react with the hydroxyl group (O-H) of the natural fiber and the functional groups of the polymer matrix, thereby improving interfacial adhesion of the composites (Xie et al., 2010; Ramesh, 2016). Generally, the concentration of silanes used for natural fibers-based polymer composites are varied and ranged from 0.5 wt. % to 5 wt. % (with respect to fiber weight) (Rangel-Vazquez and Leal-Garcia, 2010; Kushwaha and Kumar, 2010; Pang and Ismail, 2013b; Eng et al., 2014a; Le Moigne et al., 2014).

Furthermore, in this work, an eco-friendly coupling agent (EFCA) namely glycidyl ester of fatty acid was developed from the virgin coconut oil. The EFCA is produced by reacting epichlorohydrin and sodium salt of fatty acid derived from virgin coconut oil, based on the method by Chun and Husseinsyah (2017). Figure 2.4 shows the schematic synthesis of EFCA. The EFCA shows a few advantages in comparison to commercial coupling agents like silanes and maleated polymers, as EFCA is produced from sustainable resources (coconut oil), reactive to natural fibers and less expensive.

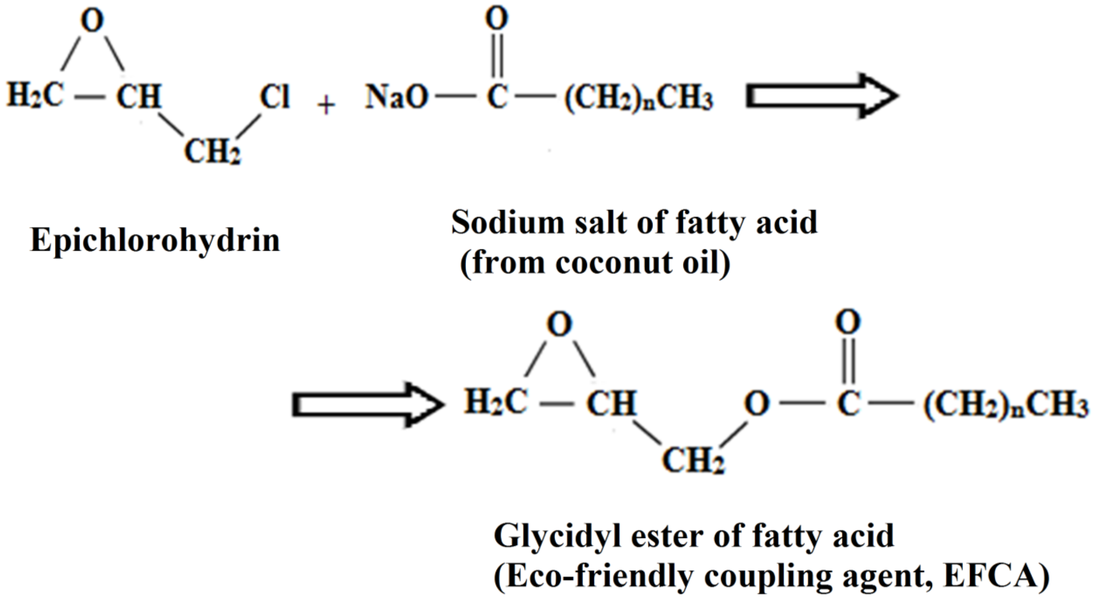

Figure 2.4. Schematic synthesis of eco-friendly coupling agent, EFCA

Moreover, the chemical treatment of KNF using chromium (III) sulfate solution was not widely explored, especially in LLDPE/PVOH/KNF composites. Generally, chromium (III) sulfate mainly exists as hexa-aquachromium (III) ion ($[Cr(H_2O)_6]^{3+}$ or Cr^{3+}) in an acidic solution (pH below 4) (Miretzky and Cirelli, 2010; Liu et al., 2017). According to Miretzky and Cirelli (2010), Cr^{3+} exists as bulky species in acidic solution and less likely to penetrate the negatively-charged adsorbent surface, thereby undergo partial hydrolysis to form $[Cr(OH)]^{2+}$ and $[Cr(OH)_2]^{+}$ ions which are able to bind with the negatively-charged functional groups by electrostatic attraction. They also noted that the concentration of Cr^{3+} species declined with an increase in pH of the solution, rendering both $[Cr(OH)]^{2+}$ and $[Cr(OH)_2]^{+}$ ions as essential for proper adsorption. Based on works done by Miretzky