EFFECT OF CHEMICAL TREATMENT ON MECHANICAL AND THERMAL PROPERTIES OF KENAF FIBER MAT REINFORCED UNSATURATED POLYESTER BIOCOMPOSITES

by

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DECLARATION

I declare that this thesis entitled "Effect of Chemical Treatment on Mechanical and Thermal Properties of Kenaf Fiber Mat reinforced Unsaturated Polyester Biocomposites" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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The Effect of Chemical Treatment on Mechanical and Thermal Properties of Kenaf Fiber Mat reinforced Unsaturated Polyester Biocomposites

ABSTRACT

Kenaf fiber mat (KFM) reinforced unsaturated polyester (UPE) biocomposites have been prepared using hand lay-up and compression moulding technique. To improve fiber matrix adhesion, the KFM was chemically treated with 6% alkaline (NaOH) solution at different soaking time range from 0 to 6 hours. Fourier transform infrared red (FTIR) and thermogravimetric analysis (TGA) were used to investigate the changes of fibers chemical constituents and thermal behavior after alkaline treatment. Mechanical properties such as tensile and flexural strength, tensile and flexural modulus and elongation at break of untreated and alkaline treated KFM-UPE biocomposites were also studied and compared. The incorporation of the alkalized KFM resulted in composites better tensile and flexural properties and 3 hours treatment showed best results. Thermal stability of the KFM-UPE biocomposites were significantly enhanced after alkaline treatment compared to those of untreated KFM-UPE biocomposites. FESEM morphological studies showed that the alkali treatment provided adhesion of the fiber-matrix interaction better. Thus, the chemical treatment on KFM improved fiber-matrix adhesion, which also contributed to the improvement of mechanical properties and thermal stability compared to those of untreated KFM-UPE biocomposites.

Kesan Rawatan Kimia terhadap Sifat Mekanik dan Terma Biokomposit Tikar Gentian Kenaf diperkuatkan Poliester Tidak Tepu

ABSTRAK

Biokomposit tikar gentian kenaf (KFM) bertetulang poliester tidak tepu (UPE) telah disediakan dengan menggunakan teknik pelapisan tangan dan teknik pengacuanan mampatan. Untuk meningkatkan pelekatan gentian-matriks, KFM telah dirawat secara kimia dengan 6% larutan alkali (NaOH) pada julat masa rendaman berbeza daripada 0 sehingga 6 jam. Fourier infra merah (FTIR) dan analisis termogravimetri (TGA) telah digunakan untuk mengkaji perubahan struktur kimia gentian dan tingkah laku haba selepas rawatan alkali. Sifat mekanik seperti kekuatan tegangan dan lenturan, modulus tegangan dan lenturan serta pemanjangan takat putus bagi biokomposit KFM-UPE yang tidak dirawat dan dirawat alkali juga dikaji dan dibandingkan. Penggunaan KFM terawat alkali dalam UPE telah menghasilkan komposit dengan sifat tegangan dan lenturan yang lebih baik dan 3 jam rawatan menunjukkan hasil yang terbaik. Kestabilan terma biokomposit KFM-UPE telah dipertingkatkan dengan ketara selepas rawatan alkali. Kajian morfologi FESEM menunjukkan bahawa, rawatan alkali memberikan interaksi lekatan gentian-matriks yang lebih baik. Oleh itu, rawatan kimia pada KFM meningkatkan pelekatan gentian-matriks yang turut menyumbang kepada peningkatan sifat mekanik dan kestabilan haba berbanding dengan biokomposit KFM-UPE yand tidak dirawat.

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LIST OF ABBREVIATIONS

ALK	Alkali-treated KFM
ALK C	Alkali-treated KFM-UPE Composite
ASTM	American Standard for Testing and Material
KF	Kenaf Fiber
KFM	Kenaf Fiber Mat
KFM-UPE	Kenaf Fiber Mat Reinforced Unsaturated Polyester
NFPC	Natural Fiber Plastic Composite
UK	Untreated KFM
UK C	Untreated KFM-UPE Composite
UPE	Unsaturated Polyester
σ_f	Flexural strength
E_f	Flexural modulus
A	Surface area
D	Thickness of the specimen
F	Maximum load force
L	Span length
m	Slope of the initial straight line portion of the load-deflection curve
P	Load applied
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DTA	Differential Thermal Analysis
DTG	Derivative Thermogravimetric Analysis
FESEM	Field Emission Scanning Electron Microscopy
MPa	Megapascal
GPa	Gigapascal

LIST OF SYMBOLS

%	Percentage
°C	Degree Celcius
mg	Milligrams
g	Grams
h	Hour
mL	Milliliter
mm	Millimeter
wt%	Weight percentage
kN	Kilonewton
cm^{-1}	Reciprocal centimeters
min	Minute
µm	Micrometer

CHAPTER 1

INTRODUCTION

1.1 Background of study

Biocomposites are composite materials formed by the natural fiber or synthetic fiber as reinforcement and thermoplastic or thermoset as matrix which at least one of the components derived from renewable resources (Shamsuri *et al.*, 2015). As for reinforcement, natural fibers include kenaf, jute, hemp, sisal and kapok. While synthetic fibers include glass, aramid and carbon. The major types of resins can be used as matrix in biocomposites include polypropylene (PP), polyethylene (PE), unsaturated polyester (UPE), and epoxy (Mehta *et al.*, 2004).

In the years ranging from 2011 until 2016, the natural fiber plastic composites (NFPCs) industry is at 10% global cultivation (Uddin, 2013). The global NFPCs market was estimated at US$2.1 billion in 2010 and made to rise at US$ 531.3 million in 2016 with an 11% Compound Annual Growth Rate (CAGR) (Faruk *et al.*, 2014). In recent years, many NFPCs industries has renewed interest for thermoset matrix natural fiber-reinforced composites. Thermoset matrix have better strength and stiffness than thermoplastic matrix. All types of natural fibers will be used generally in thermoset matrix natural fiber-reinforced composites. The applications associated with ecological and environmental benefits for thermoset matrix natural fiber-reinforced composites are transportation, load bearing applications, housing industries, and packaging (Mishra *et al.*, 2004).

Kenaf (*Hibiscus cannabinus*) is a warm season annual crop native to Africa and selected as an attractive alternative instead of man-made fibers such as glass and carbon. Kenaf fiber (KF) , obtained from processing the bark of the kenaf plant, offers advantages such as low density, ease of chemical modification, high toughness, good thermal properties, acceptable specific strength, and biodegradability (Kamal, 2014). KF have been used as non-woven mats in the automotive, textiles, fiberboard, civil and electronic industries (Bledzki & Gassan, 1999).

Unsaturated polyester (UPE) is thermosetting resin. UPE has excellent mechanical properties, chemical resistant and relatively thermal stability (Rajpal Girase, 2012). UPE is one of the most important model resins for use in bioderived natural fiber-reinforced UPE composites (Mallick, 2007). UPE has been used in marine, automobile, construction, sport and furniture applications (Atta *et al.*, 2005).

The hydrophilic nature of the natural fibers have contributed poor compatibility with reinforced matrix in mat biocomposites. In order to enhance the adhesion property between the reinforcing fiber and the surrounding matrix, the present study used alkali treatment with 6% NaOH for 0, 3 and 6 h to investigate the properties of kenaf fiber for kenaf fiber mat reinforced unsaturated polyester biocomposites. The effect of alkali modification differ on the mechanical and thermal properties of kenaf fiber mat reinforced unsaturated polyester biocomposite based on parameters including types of chemical treatment, concentration and soaking time can be studied. In this study, three characterization methods will be employed. thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy (FESEM) will be used to characterize the effect of alkali treatment on the thermal and morphological properties of kenaf fiber mat reinforced unsaturated polyester biocomposite.

1.2 Problem Statement

The main disadvantages faced by many researchers are weaknesses of synthetic fiber, fiber-matrix interfacial adhesion and thermal stability. Higher cost, harmful to skin and lower biodegradability are the most frequently stated weaknesses with synthetic fibers. Natural fiber will replace synthetic fiber as an alternative reinforcement, thus creating higher service life in high performance biocomposite.

Fiber-matrix interfacial interaction is generally seen as a factor strongly related to mechanical properties of biocomposite. The hydrophilic nature of KFM can cause loss of mechanical strength resulting from weak interfacial adhesion to a hydrophobic matrix. However, chemical treatment have played a vital role in bringing about superior fiber-matrix interfacial adhesion.

Although natural fibers have advantages of being low cost and low density, they are not fully unrestricted of problems. Natural fibers have lower thermal stability and decomposition at temperatures around 190-200 °C. If natural fibers do high performance biocomposite, they have decreased thermal stability, therefore, chemical treatment is expected to slightly increase the thermal stability of biocomposite.

In this proposed study, 6 % NaOH solution will be used to treat KFM-UPE biocomposites. Both hand lay-up and hot press techniques have been used to produce natural fiber-reinforced UPE biocomposites (Abdullah *et al.*, 2011; Akil *et al.*, 2009). In a follow-up study, Ariawan *et al.* (2015) found that immersion time of 3 hours for alkali treated biocomposite has enhanced thermal stability. The tensile strength and elongation at break of the fiber have been improved by 65 % and 38 %, respectively at elevated temperature with pretreatment of kenaf fiber in 6 % NaOH solution with immersion time of 3 hours (Edeerozey *et al.*, 2007). The treatment of kenaf fibers with

6% NaOH solution at room temperature for 3 h greatly increased the flexural strength and slightly increased the flexural modulus (Lai *et al.*, 2008).

Up to now, far too little attention has been paid to kenaf fiber-reinforced UPE composites with alkali treatment. However, a number of authors have considered the effects of alkali treatment of natural fibers with polyester resins to improve the mechanical properties of composite. There are the effect of alkali treatment conditions on properties of sisal-polyester composites (Sreekumar *et al.*, 2009), coir fiber-polyester composites (Prasad *et al.*, 1983), bagasse-UPE composites (Vilay *et al.*, 2008) and jute-polyester composites using silane over alkali treatment (Kabir *et al.*, 2012). Numerous studies have attempted to explain the effects of alkali treatment conditions of natural fibers with thermosetting resins to improve thermal properties of composites involved banana fiber-reinforced phenol formaldehyde composites (Joseph *et al.*, 2008), sisal fiber-reinforced epoxy composites (Ganan *et al.*, 2005) and hemp fiber-reinforced polyester composites (Aziz & Ansell, 2004).

1.3 Objectives

The objectives of the research are:

i. To fabricate KFM-UPE composite by using hand lay-up and hot press technique.

ii. To investigate the effect of NaOH chemical treatment on the mechanical and thermal properties of KFM-UPE composite.

1.4 Significance of Study

In this present study, both unsaturated polyester and kenaf fiber mat composites are produced. In this study, kenaf fiber was chosen to embed unsaturated polyester resins to increase the strength and stiffness of biocomposite. 0, 3 and 6 hours of immersion time in 6% NaOH solution was selected in this study. A variety of alkali immersion times will show different mechanical, thermal and morphological properties. Understanding the link between alkali treatment conditions such as temperature, soaking duration and concentration and choice of natural fibers will help higher performance biocomposite applications with higher service life. This project provided an important opportunity to advance the understanding of treatment with 6% NaOH solution at room temperature for 3 h can be expected to have greater thermal stability of KFM as well as to contribute an increase in fibre-matrix interfacial adhesion of biocomposite than one that is untreated.

Kenaf is a potential candidate for sustainable applications of renewable raw material source and widely cultivated. It is responsible for large production for conventional and hybrid vehicles. It is found in Malaysia and generally it is hard enough to be widely used with other than waste in industry. Introducing kenaf fiber into thermoset based biocomposite should make an important contribution to the field of automotive industry to reduce the weight for products of NFPCs.

Hand lay-up and compression molding method are selected to produce the KFM-UPE composites. 83.5 g of kenaf fiber mat with 10 wt% together with 100:2:1 of UPE mixures are used to produce KFM-UPE composites. Untreated and treated of kenaf fiber and KFM-UPE composites will be examined, all of which analyses the results of tensile properties, flexural properties, thermal stability, failure morphology and functional groups. Data for this study are collected using softwares called OMNIC and STARe Evaluation. While mechanical tests are carried out according to ASTM D 790 and ASTM D 3039 standards, whereas FTIR analysis is one according to ASTM E168-06 and ASTM E1252-98 standards.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Biocomposites

The word biocomposites can be termed as natural fiber reinforced polymer composite (NFPC). Biocomposite composed of natural fibers (kenaf, hemp, jute, flax, sisal, banana, kapok, etc.) and synthetic thermoplastic or thermoset polymers such as polypropylene (PP), polyethylene (PE), epoxy, and unsaturated polyester (UPE) (Mehta *et al.*, 2004). Biocomposite comes from bioplastic as matrix and either natural fiber or synthetic plastic as reinforcement are “ecocomposites”. “Ecocomposites” have a balance among cost, property, and environment for applications in automotive parts, building materials, electronic parts and packaging (Kozlowskiy, 2000).

2.1.1 Classification of Biocomposites

In Figure 2.1, biocomposites can be divided into two types which are fully degradable and partly degradable, depending upon the nature and origin of the reinforcement as well as the polymer matrix (Drzal *et al.*, 2001). The fully biodegradable biocomposite is made of polymer matrix derived from natural sources and reinforced with natural fibers (Mohanty *et al.*, 2005). Both components of the biocomposite can be degraded by microorganisms and the byproducts of the degradation process are carbon dioxide (CO_2) and water (H_2O). As for partially biodegradable biocomposite, it is fabricated with a combination of petroleum-based matrix and natural fibers (Kamal, 2014).

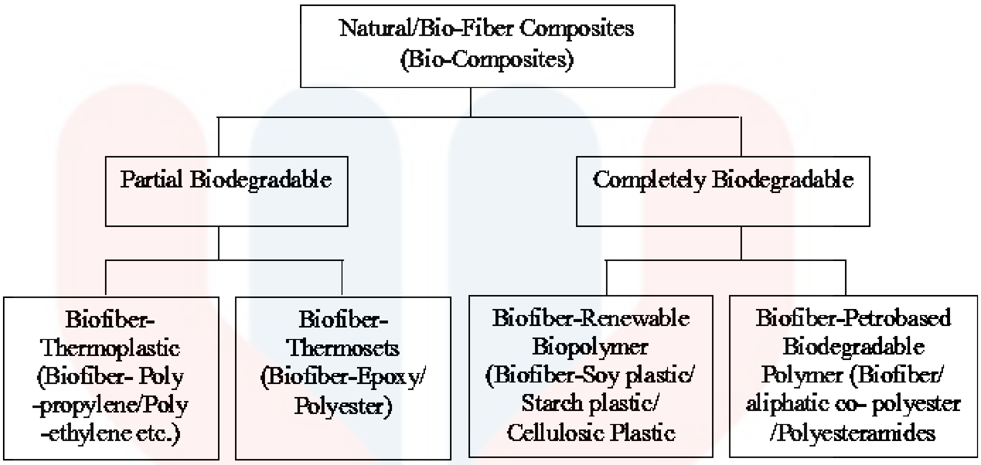


Figure 2.1: Classifications of biocomposites (Drzal *et al.*, 2001).

Furthermore, biocomposites are the combination of natural fibers as reinforcement and petroleum-based or bio-based matrices from both renewable and non-renewable resources (Mitra, 2014). In totally renewable polymer composite material, both the reinforcing materials and the matrix material comes from biorenewable resources. In partly renewable composites, only one component is from biorenewable resources such as a polymer matrix from biorenewable resources and a reinforcement from nonrenewable raw material sources or a polymer matrix from synthetic resources and a reinforcement from biorenewable resources (Thakur, 2013).

A structural biocomposite intends to carry a load in use whereas a nonstructural biocomposite does not intend to carry a load in use. Researcher attempts that kenaf fiber reinforced thermosets and thermoplastics composites are very good to produce two principle products: the first is structural biocomposites, such as bridge as well as roof structure, and the second is nonstructural biocomposites such as window, exterior construction, composites panels, and door frame (Yuhazri & Sihombing, 2011). The nonstructural composites are often used in indoor for a period of time such as wood plastic composites and shown in Figure 2.2 (Netravali & Chabba, 2003).

Figure 2.2: Courtesy of phenix biocomposites (Netravali & Chabba, 2003).

2.1.2 Thermoset based Biocomposites

Thermoset based biocomposites are composite materials composed of natural fibers and petrochemical based polymers like phenolic, epoxy, and polyester resins. Among plant fiber mat-reinforced composites of petrochemical based polymers, the most widely used plant fibers are bamboo, hemp, and kenaf fiber which have high specific bending strength and stiffness . Thermoset based biocomposites are often as a replacement for glass fiber and include building and construction, automotive, leisure and sporting goods, and aircraft interiors.

Commercially, thermoset based biocomposites are still not widely available. Despite wide usage of such composites in different green product demands and it directly considered known relative higher material performance of the thermoset composites than that of the thermoplastic ones. A variety of techniques are used for fabrication of thermoset based biocomposites such as hand lay-up technique, compression moulding and pultrusion so that long and continuous mat reinforcement can be used (Abdullah *et al.*, 2011; Akil *et al.*, 2009). Thermoset based composites are not readily recyclable. However, the methods for dealing with thermoset-based wastes such as energy recovery and recycling as composite fillers can support the trend of cleaner production as well as to save both money and effort (Peijs, 2003).

2.2 Polymers as Matrices for Biocomposites

Generally, polymer matrices used for NFPCs are divided into two groups namely thermoset and thermoplastic. The strength and stiffness of matrix in NFPCs come for the most part from the reinforcing fibers. The polymer matrix in NFPCs acts as a binder to hold the fibers in place and transfers the load onto the reinforcing fiber. Polymer matrix also protects reinforcing fibers from degradation due to environmental attack (Fowler *et al.*, 2006). The polymer chain contributes significantly to the mechanical properties of the structural polymer composites, acting to resist delamination between piles of reinforcements and to inhibit fiber buckling during compression (Fowler *et al.*, 2006).

Thermoplastics polymer is capable of being broken down into small part by action of the living things such as microorganism and ease of recycling material. Molecules of thermoplastics are not chemically joined together and held by weak intermolecular forces like van der Waals bonds and hydrogen bonds (Mallick, 2007). Examples of thermoplastics are low density polyethylene (LDPE), polyether ether ketone (PEEK), polyphenylene sulfide, and polysulfone. LDPE has a density range of 0.910 to 0.940 g/cm^3. Since it is part of the thermoplastics, polymers can be heat-softened, melted, and reshaped. Advantages of thermoplastics are it has high impact strength and fracture resistance, unlimited storage life at room temperature, shorter fabrication time, and post formability (Kabir *et al.*, 2012).

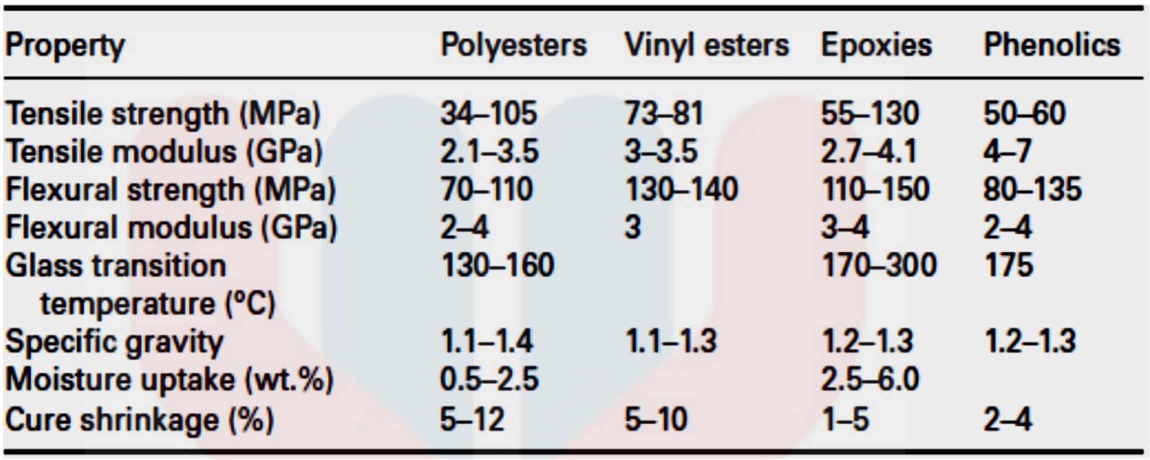
2.2.1 Thermosets

Thermosets are network-forming polymers. These cross-links joined molecules of thermoset together through polymerization to form a rigid and three dimensional network. Thermosets cannot be melted and reshaped by heat since cross-linked. The cross-linked thermosets are tough, high creep resistant, and highly solvent resistant. Most of the thermosets include epoxies, phenolic, and polyester resins. Meanwhile, epoxy resins are less promising potential matrices for use in NFPC not only because they are unlikely to see availabilty worldwide in commercial natural fiber reinforced polymer composites but also due to their relatively high cost. Polyester and vinyl ester are cheaper resins and more widely used in industry. Phenolic resins have good fire resistance but are more difficult to process (Hodzic & Shanks, 2014). Polyesters, vinyl esters, and epoxies probably account for some 90% of all thermosetting resin systems used in structural biocomposites (Scheirs & Long, 2005). The main advantages and disadvantages of each of these resins are given in Table 2.1. Typical properties of thermosets are given in Table 2.2 (Aranguren & Reboredo, 2015).

Table 2.1: Advantages and disadvantages of thermosetting resins (Scheirs & Long, 2005).

Resin	Advantages	Disadvantages
Polyester	Easy to use lowest cost of resin available	Only moderate mechanical properties High styrene emission in open molds High cure shrinkage Limited range of working time
Vinylester	Very high chemical/environmental resistance Higher mechanical properties than polyester	Postcure generally required for high properties High styrene content Higher cost than polyesters High cure shrinkage
Epoxy	High mechanical and thermal properties High water resistance Long working times available Temperature resistance can be up to 140°C (wet)/220°C (dry) Low cure shrinkage	More expensive than vinylesters Critical mixing Corrosive handling

Table 2.2: Properties of common thermosetting matrix materials (Aranguren & Reboredo, 2015).



Property	Polyesters	Vinyl esters	Epoxies	Phenolics
Tensile strength (MPa)	34–105	73–81	55–130	50–60
Tensile modulus (GPa)	2.1–3.5	3–3.5	2.7–4.1	4–7
Flexural strength (MPa)	70–110	130–140	110–150	80–135
Flexural modulus (GPa)	2–4	3	3–4	2–4
Glass transition temperature (°C)	130–160		170–300	175
Specific gravity	1.1–1.4	1.1–1.3	1.2–1.3	1.2–1.3
Moisture uptake (wt.%)	0.5–2.5		2.5–6.0	
Cure shrinkage (%)	5–12	5–10	1–5	2–4

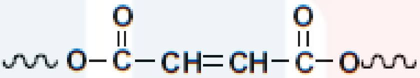
Thermosets have chemical resistance, high dimensional stability, high creep properties, low resin viscosity, excellent thermal stability, chemical resistant, and are good fiber wetting and also easier to impregnate with fillers. Disadvantages of thermoset are it has limited storage life at room temperature, require standard techniques, poor melt flow and has low strain-to-failure which will contribute toward the low impact strengths (Kabir *et al.*, 2012). In industrial applications, such as civil infrastructure and transportation, thermosets are often added as a resin matrix to form fiber-reinforced composites (Kubouchi *et al.*, 2013).

Synthetic thermoset is a plastic isolated from petroleum or natural gas. Synthetic thermoset is used and accepted by most people. Owing to their petrochemical nature, production of synthetic thermosets is conditioned by the rank in society of the oil industry. Conventional plastic market today is continuing to rise in oil price and to look forward a sudden rise in production cost. Therefore, many oil industry seek plastic to stop environmental problems from existing in the world (Kubouchi *et al.*, 2013).

Bio based thermoset is a result of the limitations of thermoplastics. Bio based thermoset is able to be replaced by nature especially derived from plant based resources. Bio based thermoset can take the function of synthetic thermoset. However, the properties of bio based thermoset vary large in size in terms of glass transition temperature, impact strength, stiffness and water absorptivity with all other types of polymers (Kubouchi *et al.*, 2013).

2.2.2 Unsaturated Polyester Resin

Unsaturated polyester (UPE) resin is the first known use in 1940. UPEs are low molecular weight and yellow oily liquid. UPEs are versatile as thermosetting resin in the coatings and composite industry. UPEs are formed by the reaction of ethylene (ethylene glycol) and benzene (maleic acid). Figure 2.3 has shown chemical structure of UPEs. UPEs are relatively inexpensive and have good mechanical properties but are brittle at room temperature and have low fracture toughness (Skrifvars, 2000).



$$\sim\sim O-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}-O\sim\sim$$

Figure 2.3: Chemical structure of UPE resin (Xie *et al.*, 2010).

UPE resins consist of two polymers which are a short chain polyester containing polymerizable double bonds and a vinyl monomer (Skrifvars, 2000). The curing reaction consists of a copolymerization of the vinyl monomer with the double bonds of the polyester. It should be noted that UPE resin is different from polyester resins which have no double bonds in polymer backbone. A mixture of UPE with the vinyl polymer is referred to as an UPE resin. In the path of curing, a three-dimensional network is formed.

The most important advantage of UPE resins is a balance of properties including mechanical, chemical, electrical, dimensional stability, low cost, and ease of handling or processing. Figure 2.4 exhibits chemical reaction of UPE and MEKP (Xie *et al.*, 2010). UPE resins form highly durable structure and coatings when they are cross-linked with a vinyl reactive monomer, the most commonly used being styrene (Johnson & Yang, 2003). This reactive diluent reduces the viscousity of the polyester resin, so that it can be easily processed.

Curing is achieved with a radical initiator and a promoter. For curing polyester resin, cobalt naphthenate was used as accelerator and methyl ethyl ketone peroxide (MEKP) as initiator. UPE can be cured by a free radical reaction. The radical can be generated by suitably adding a small quantity of free-radical initiator under different condition such as heat, UV light, or visible light. However, the initiators used for UPE resins are not capable of producing radicals at room temperature. Therefore, accelerators are used to promote curing at room temperature by activating the initiator, which provides a room temperature curing ability to UPE resin (Skrifvars, 2000).

The control of cross-linking process is important in the commercial processing of UPE composites, both before and after the gel point. The mechanical properties of the cross-linked product depend on the average number of cross-links between the polymer chains (cross-link density) and the average length of the cross-links (branches). Too slow or too rapid cross-linking will determine the properties of a desired product. The properties of the UPE are determined by the types and monomers used, as well as the reaction conditions adopted to polymerize them (Skrifvars, 2000).

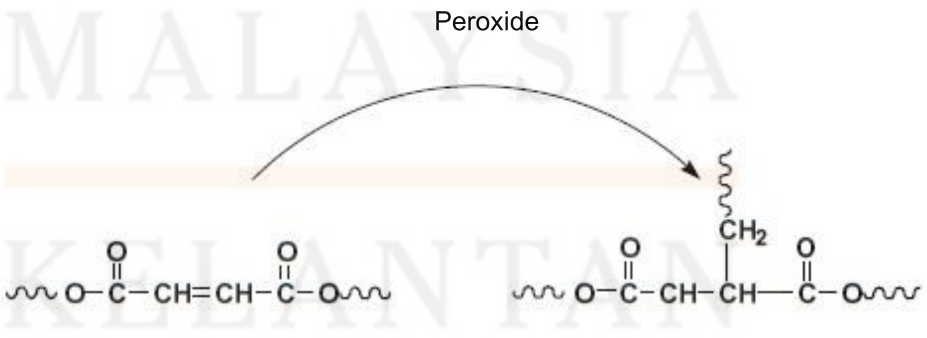


Figure 2.4: Chemical reaction of UPE and MEKP (Xie *et al.*, 2010).

UPE are having many uses or applications because of their ability to hold the building of polymer chains. The applications of unsaturated polyesters are wide-ranging and number in the thousands. Major application categories exist in the marine, construction and transportation industries. Bulks could be generated to rightly list the everywhere uses which range from buttons to bridges. Table 2.3 presents a summary of the significant applications of unsaturated polyesters (Scheirs & Long, 2005). UPE composites will continue to provide solutions to engineering demands for corrosion resistance, strength-to-weight and cost performance.

Table 2.3: Significant applications of unsaturated polyesters (Scheirs & Long, 2005).

Market	Application
Marine	Powerboats, sailboats, canoes, kayaks, personal watercraft
Construction	Bathtubs, shower stalls, hot tubs, spas, cultured marble, building panels, swimming pools, floor grating, doors, electronic boxes and cabinets, countertops, sinks, tanks, pipes, pipe linings, concrete rebar, bridges, concrete forming pans
Transportation	Body panels, ‘under the hood’ components, truck cabs, tractor components, structural elements
General purpose	Buttons, sport equipment, medical equipment housings, computer housings, ladders, utility poles

2.3 Natural fiber as Reinforcement Materials

Natural fibers are divided in three main categories: straw-fibers, non-wood fibers and wood fibers. Natural fibers are derived from renewable resources and often from industrial by-products. Natural fibers can compete with synthetic fibers such as glass and carbon that were already being used as reinforcement materials. Generally natural fibers cannot provide the same mechanical properties as carbon fiber, but some of them can achieve the similar properties to fiberglass. However, natural fibers have some limitations due to their moisture affinity, poor wettability and low thermal stability during processing with synthetic polymers (Thakur *et al.*, 2014).

In composite materials, natural fibers are subject to preparation for operations and modification of its surface before being used. Following the latter, properties for these natural fibers include low cost, low density, acceptable specific mechanical strength, good insulation properties and biodegradability (Cho *et al.*, 2013). Though the degradability of natural fibers can be a disadvantage in durable applications where composites are exposed to harsh environments, it can also be an advantage when degradability is desired.

Natural plant fibers are suitable for polymer composite processing. Figure 2.5 shows plant-based composites. In six basic types of natural fibers, classification depending on the plant origin is made: as seed fibers for cotton and kapok; bast fibers for flax, hemp, jute, kenaf; leaf fibers for sisal, pineapple, banana, palm; fruit fibers for coconut; wood fibers for softwood and hardwood; and grass and reed fibers for bamboo, wheat, rice and corn (Faruk *et al.*, 2014).

Figure 2.5: Door panel (Marsh, 2003).

2.3.1 Kenaf

The word Kenaf came from a Persian word *kanab* which is an African hibiscus (*Hibiscus cannabinus*) widely cultivated for its fiber (Kamal, 2014). Kenaf is an annual plant that has soft stem closely related to cotton and jute which grows throughout warm season in tropical or subtropical lands. It is a new crop in USA and has shown good potential in biocomposite applications. Africa is main producing country for Kenaf. Biocomposite products in automotive industry has found kenaf plant works as substitute of for fiberglass or other synthetic fibers in automotive dashboards, carpet padding and corrugated medium (Kugler, 1988). Kenaf exhibits low density, non-abrasiveness during processing, high specific mechanical properties and biodegradability. Kenaf can be grown very fast under warm weather and soils types. Kenaf not only has short harvest period in six months but also produces stronger fibers. The average plant grows 3 m tall with woody base diameter 3 – 5 cm (Aziz *et al.*, 2005). Kenaf contains two types of fibers such as long fibers which are extracted from bast and short fibers extracted from core.

In long times, kenaf can be used as a domestic supply of cordage fiber in manufacture of rope, twine carpet backing and burlap (Wilson *et al.*, 1965). Nowadays, kenaf are expanding into new markets of paper products, building materials, absorbents and livestock feeds (Edeerozey *et al.*, 2007). The interest in cultivate kenaf is due to kenaf can absorb nitrogen and phosphorus as three to five times faster as forests, and its deep roots can improve that soil by the potential in assimilating a significant rate of carbon dioxide (Ramesh, 2016).

2.3.2 Kenaf Fiber

In general, all plants contain cellulose, hemicellulose, and lignin, the three of which constitute the three major organic constituents of plant cell walls. The chemical composition of kenaf constitutes cellulose (72 %), hemicellulose (20.3 %), lignin (9 %) impacts the properties and surface characteristics (Faruk *et al.*, 2014).

Cellulose is semicrystalline polysaccharide. Cellulose is a substance that is the main part of the cell walls of plants with good strength, stiffness and structural stability

(Kabir *et al.*, 2012). Cellulose begins to degrade after 220° C, amorphous cellulose is much easier degradable than crystalline cellulose and lignin (Rowell *et al.*, 1995).

Hemicellulose is branched polysaccharide containing five and six carbon sugars and has lower molecular weight than cellulose. Hemicellulose is less complex than cellulose and easily hydrolyzable to monosaccharides and other products. The amount of hemicellulose is responsible for biodegradation, moisture absorption, and thermal degradation of the fiber (Thakur *et al.*, 2014).

Lignin is an amorphous polymer related to cellulose that provides rigidity and together with cellulose forms the woody cell walls of plants and the cementing material between them. Lignin is aromatic compound and cross-linked. On the other hand, lignin is thermally stable, but responsible for the UV degradation of the fibers. Lignin will start to degrade at 200° C while the otherwise constituents such as cellulose and hemicellulose at higher temperature will be degraded (Rowell *et al.*, 1995).

Kenaf bast fiber has cellulose content as 60% while kenaf core fiber has cellulose content as 50.6% (Rowell & Han, 1999). The bast fibers have a lower lignin content, higher cellulose content, and lower hemicellulose content compared to the core fibers. For this reason, kenaf bast fibers are longer and stronger when compared to kenaf core fibers. Kenaf bast fibers are strong fiber obtained from the outer fibrous bark and used especially in cordage, matting, and fabrics. The difference between the bast and core fibers in kenaf is shown in Figure 2.6 (Rowell & Stout, 2007). The bast fibers have thicker walls as compared to the core fibers. Kenaf core fibers are used in product applications such as animal bedding, summer forage, and potting media. However, kenaf core fibers are relatively short and thick, which limits their application in making papers and composites. Kenaf stalk is made up of an inner woody core and an outer fibrous bark surrounding the core. Kenaf stalk's average composition was 35% bark and 65% woody core by weight (Lee & Eiteman, 2001).

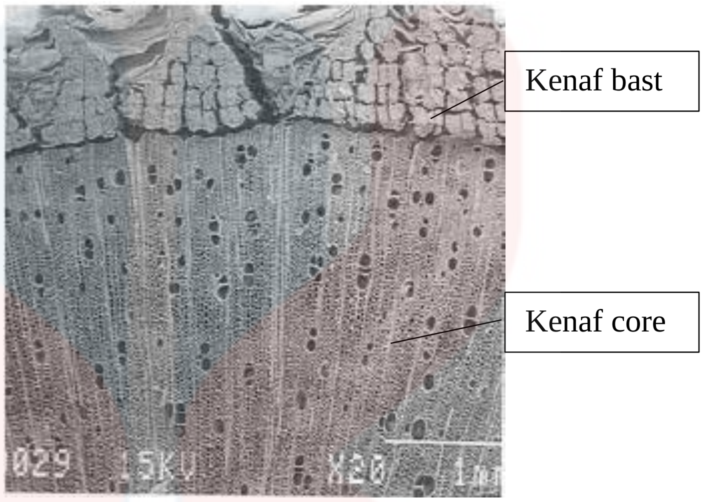


Figure 2.6: Cross section of kenaf bast and core (Rowell & Stout, 2007).

According to Rowell and Stout (2007), kenaf are strong fibers but exhibiting brittle fracture and have only a small breaking elongation. They have a high initial modulus, but show very little recoverable elasticity. In Table 2.4, Li *et al.* (2007) reported that the tensile properties of the kenaf fibers: tensile strength and modulus of about 930 MPa and 53 GPa respectively. The percentage elongation is around 1.6%.

Table 2.4: Mechanical properties of selected natural fibers (Li *et al.*, 2007).

Fiber	**Tensile strength (MPa)**	**Young's modulus (GPa)**	**Elongation at break (%)**	**Density [g/cm^3]**
Abaca	400	12	3-10	1.5
Bagasse	290	17	-	1.25
Bamboo	140-230	11-17	-	0.6-1.1
Flax	345-1035	27.6	2.7-3.2	1.5
Hemp	690	70	1.6	1.48
Jute	393-773	26.5	1.5-1.8	1.3
Kenaf	930	53	1.6	-
Sisal	511-635	9.4-22	2.0-2.5	1.5
Ramie	560	24.5	2.5	1.5
Oil palm	248	3.2	25	0.7-1.55
Pineapple	400-627	1.44	14.5	0.8-1.6
Coir	175	4-6	30	1.2
Curaua	500-1150	11.8	3.7-4.3	1.4

Furthermore, the thermal properties of each natural fiber are critical, and include the fiber maximum decomposition temperatures, thermal stability, glass transition temperature and melting temperature. There are several thermal properties that are important to know about for each natural fiber before that fiber can be used to reach its highest potential. It should be noted from the above literature review, however, that limited studies are available on mechanical properties of kenaf fiber and this has motivated the present study.

2.4 Chemical Treatment in Natural Fiber reinforced Polymer Biocomposites

The chemical methods for natural fiber treatment were more commonly adopted than the physical methods, due to low cost, simple, easy handling and less skill. There are variety of chemical treatments including alkali, silane, acetylation, benzoylation, acrylation, maleated coupling agents, isocyanates and permanganate (Faruk *et al.*, 2014). The most frequently used chemical methods are alkali and silane treatment. An appropriate surface treatment of natural fibers provide positive effect on the properties improvement of the resulting biocomposites. Many research efforts investigated on the effects of chemical treatment of natural fibers on the properties of biocomposites, such as interfacial, dynamic mechanical, thermal, physical, mechanical, fracture behaviour and water absorption.

2.4.1 Alkali Treatment

Alkali treatment is a chemical method adopted for many natural fibers. Natural fiber is immersed in a solution of sodium hydroxide for a given period of time. The effect of alkali treatment depends on the properties of the composites as well as on natural fibers strongly depends on alkali concentration, treatment time and treatment temperature. In order to improve mechanical properties, effectiveness of the treatment depends on alkali treatment condition (Cho *et al.*, 2013).

Alkalization results in sites of mechanical interlocking, hence helping adhesion quality of the bio composites (Aziz & Ansell, 2004). This phenomenon of compatibility with the matrix was achieved by changing surface chemistry with the functional group of matrix. As a result, alkali treatment is essential in improving interfacial adhesion between the hydrophilic natural fibers and the hydrophobic polymer matrix. The important modification achieved with alkaline treatment is the disruption of the hydrogen bonding in the network structure, thereby increasing the surface roughness providing for improved interfacial bonding (Li *et al.*, 2007). Alkali treatment removes fiber constituents including hemicellulose, lignin, pectin, fat and wax which exposes cellulose and cleans the surfaces, depending on the alkali concentration and treatment time used. Therefore, the interfibrillar region is less dense and less rigid and in that way allows the fibrils rearranging themselves along the direction of stress loading when hemicelluloses are removed (Sapuan *et al.*, 2010).

Alkali treatment also modifies cellulose structure; modest treatments have been seen to bring about increased cellulose crystallinity considered to be due to removal of materials that could obstruct cellulose crystallinity, whereas at harsher treatments crystalline cellulose has been converted to amorphous material (Kabir *et al.*, 2012). For crystalline matrices, fiber treatment with alkali has also been seen to influence the degree of matrix crystallinity, with exposed cellulose acting as a nucleation site for crystalline polymer (Sawpan et al., 2012). Improvement of fiber strength has also been obtained using alkali treatment. Many studies observed alkali treated natural fibers where improvements in interfacial shear strength (IFSS) and improved tensile strength, Young's modulus, failure strain, impact strength, fracture toughness and flexural properties of composites as well as thermal stability and long term moisture resistance.

The following scheme represents the chemical reaction of sodium hydroxide with hydroxyl groups in natural fibers:

Natural fiber-OH + NaOH → Natural fiber-O^{-}Na + H_2O ....(Eq. 2.1)

2.4.2 Effect of Alkali Treatment on Mechanical Properties of Natural Fiber reinforced Polymer Biocomposites

Ray *et al.* (2001) subjected jute fibers to alkali treatment with 5% NaOH solution for 0, 2, 4, 6 and 8 h at 30 °C. The modulus of the jute fibers improved by 12, 68 and 79% after 4, 6 and 8 h of treatment, respectively. The tenacity of the fibers improved by 46% after 6 and 8h treatment and the percentage breaking strain was reduced by 23% after 8h treatment. However, the treatment of fibers over a prolonged period makes the fibers stiffer and more brittle. Mishra *et al.* (2004) treated jute and sisal fibers with 5% aqueous NaOH solution for 2 h up to 72 h at room temperature. These researchers observed that alkali led to an increase in amorphous cellulose content at the expense of crystalline cellulose.

Venkateshwaran *et al.* (2013) studied the effect of alkali (NaOH) treatments of various concentrations (0.5%, 1%, 2%, 5%, 10%, 15%, and 20%) on the mechanical properties of abaca-epoxy composite. Mishra *et al.* (2004) reported that 5% NaOH treated sisal-polyester composite had better tensile strength than 10% NaOH treated composites. However, the rising of alkali concentration maybe causes fiber surface damage, leading to a decrease of mechanical properties. The alkali concentration on the fiber surfaces results in better mechanical properties of the resulted composite (Yousif *et al.*, 2012).

Vilay *et al.* (2008) reported that the positive effects of alkali treatment on the mechanical strength of bagasse-UPE composites. Composites of 1% NaOH solution treated fibers showed maximum improvement. 13% improvement in tensile strength, 14% in flexural strength and 30% in impact strength had been found, respectively. After alkali treatment, increase in strength and aspect ratio of the fiber contributed to the enhancement in the mechanical properties of the composites. Sreekumar *et al.* (2009) studied the effect of fiber surface modification on the mechanical properties of sisal-UPE composites. Alkali-treated sisal-UPE composites exhibited 36% increase in tensile strength and 53% increase in Young's modulus.

Prasad *et al.* (1983) reported that the use of alkali treatment on coir fibers improved the mechanical properties of coir-polyester composites. Among the alkali treated coir fiber polyester composites, 2% alkali treated coir composites show better tensile strength (26.80 MPa) whereas 5% alkali treated coir composites show better flexural (60.4 MPa) and impact strength (634.6 J/m) (Rout *et al.*, 2001).

Edeerozey *et al.* (2007) used different concentrations (i.e. 3%, 6% and 9%) of NaOH to pre-treat kenaf fibers for 3 h at room temperature. For the 6% NaOH concentration, two different conditions were used (i.e. immersion at room temperature and immersion in water bath at 95° C). The authors reported that pre-treatment of kenaf fibers in 6% NaOH solution in water bath leads to the best results. Saha *et al.* (2010) studied the influence of alkali treatment (NaOH) on the tensile strength of jute fibers under ambient temperatures and elevated temperatures. The tensile strength and elongation at break of the fiber have been improved by 65% and 38%, respectively at elevated temperature.

The combination effect of alkali treatment and silane treatment to improve the mechanical properties through the interfacial modification between the polar fiber and nonpolar matrix. For jute-epoxy composites silane over alkali treatments showed about 12% and 7% higher strength and modulus properties compared to the alkali treatment alone. Similar treatments reported around 20% and 8% improvement for jute-polyester composites (Kabir *et al.*, 2012).

2.4.3 Effect of Alkali Treatment on Thermal Properties of Natural Fiber reinforced Polymer Biocomposites

Alkali treatment of fibers could affect the thermal stability of natural fiber. The treated fibers exhibited an improved stability of hemicellulose and pectin. Thermal stability of the fiber can be enhanced by removing certain proportion of hemicellulose and lignin constituents. Alkali treatment of rice husks with more than 4% NaOH causes a substantial chemical degradation of rice husks, which subsequently decreases their thermal stability. The thermal stability and final degradation temperatures of the alkali-treated rice husks were also lowered by 24-26°C due to degradation of hemicellulose and lignin during alkali treatment (Mansaray & Ghaly, 1999). However, Mahato *et al.* (1995) reported that thermal stability of alkali-treated coir fiber increases with the increase in activation energy and is highest for 5-15% alkali concentration.

Nguyen *et al.* (1981) reviewed that thermal degradation of lignocellulosic fibers in detail for modified and unmodified materials. Joseph *et al.* (2008) analysed the thermal degradation of treated and untreated banana fiber-reinforced phenol formaldehyde composites. It was found that the thermal stability of the composites was much higher than that of fibers but they are less stable compared to neat PF resin matrix.

Ganan *et al.* (2005) examined the effect of alkali treatments of the fibers on the thermal stability of 30 wt% sisal fiber/epoxy matrix composites. Composites present a region associated with the fiber constituents decomposition appearing at 210 °C to 350 °C. Treated fiber composites present a slight increase on thermal stability with respect to that for untreated fiber composites in this region (Ganan *et al.*, 2005).

Mohanty *et al.* (1989) made attempts to graft the fibers with monomers for improvement of thermal stability. Grafting is possible since the lignin can react with the monomers. Mohanty *et al.* (1989) has evidenced grafting of acrylonitrile on jute improved the thermal stability during degradation temperature has increased from 170 °C to 280 °C. Sabaa (1991) has reported increased initial degradation temperature, lowering of the rate of degradation and the total weight loss gave improved thermal stability for acrylonitrile-grafted sisal fibers.

After the alkali treatment, the temperature at the maximum rate of decomposition of hemp fiber increased, indicating that the alkali treatment leads to an enhancement in the thermal stability of the hemp fiber, weight loss of 10% occurred between 288 and 332°C for the untreated and alkali-treated fibers, while a weight loss of 20% occurred in the range of 329–366°C, and weight loss of 30% was observed in range of 346–378°C for untreated and alkali-treated hemp fibers (Aziz & Ansell, 2004).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The materials that were used in this study are the kenaf fiber mat (KFM). The KFM were collected from local plantation sources located at Bukit Mertajam, Penang. The matrix selected for the study can include unsaturated polyester (UPE) resin. Methyl ethyl ketone peroxide (MEKP) and cobalt napthanate were used together as catalyst and initiator and collected from Dr. Rahmatullah Holdings Sdn. Bhd. respectively. All measurements were taken according to the size of the KFM for five characterizations to be carried out. The mechanical properties such as strength and moduli of tensile and flexural specimens and thermal properties such as mass changes and char residues of untreated and treated composites should be pointed, respectively.

3.2 Methods

Sample preparations were divided into two different groups: untreated and treated KFM. Before the composite samples were fabricated using hand lay-up and hot press technique, alkali treatment was used following different soaking times.

3.2.1 Fiber Treatment

Dried kenaf fiber mat (KFM) was soaked in 900mL NaOH solution using cleaned basin for soaking times of 0, 3 and 6 h. Dried KFM was treated by 6% NaOH solution at room temperature. After treatment, KFM was washed with distilled water containing 1 wt% acetic acid, neutralized the excess NaOH sticking to the fiber surfaces, and finally rinsed with enough distilled water to remove any dirt or impurity. The pH level was tested using a red litmus paper to maintain pH on the litmus paper. Both untreated and treated KFM were left at room temperature for 48 h and then dried up at 80 °C for 24 h in the oven to remove the moisture. The series of designation was depicted in Table 3.1. The samples were kept under 27°C in temperature before testing.

Table 3.1: Preparation of different immersing duration of 0, 3 and 6 h on three samples in 6% NaOH solution.

Designation	Sample	Soaking Duration (Hour)	Constant
UK	Untreated KFM	0	6
ALK3	Alkali-treated KFM in 3 h	3	6
ALK6	Alkali-treated KFM in 6 h	6	6

3.2.2 Composite Preparation

Dried kenaf fiber mats (KFM) was cut using stationary blade and dimension of 150 mm long, 150 mm width and 3 mm thick was taken. The matrix-fiber ratio was 90:10 for KFM-UPE composites. To manufacture the test specimens, treated and conrol samples of KFM were mixed thoroughly to which were added 100% unsaturated polyester (UPE) resin, 2% methyl ethyl ketone peroxide (MEKP) and 1% cobalt naphthanate as initiator and accelerator, respectively. The UPE mixture were then poured over the fiber mat by hands. For making KFM-UPE composite material, the weight (m) and the volume (V) of the KFM was easily determined by simple weighing using the electronic balance. The following calculation was an example procedure for making amount of UPE mixture based on predetermined weight of treated and control samples of KFM. 74.8 g UPE, 1.5 g MEKP and 0.7 g cobalt naphthanate were mixed by spatula for one minute to generate a UPE mixture and do

83.5 g composite material in Figure 3.1. Assuming that the composite material consisted of fiber and matrix material, the weight of the composite material was equal to the sum of the weight of the fibers and the weight of the matrix. Therefore,

$$w_c = w_f + w_m$$

where, w_c= weight of composite material

w_f= weight of fiber

w_m= weight of matrix

The weight fractions of the fiber and the matrix was defined as

$$W_f = \frac{w_f}{w_c} \quad \text{and}$$

$$W_m = \frac{w_m}{w_c}$$

such that the sum of weight fraction is

$$W_f + W_m = 1$$

Table 3.2: Preparation of composites for untreated and treated KFM groups.

Designation	Sample justification
UK C	Untreated KFM-UPE
ALK3 C	Alkali-treated KFM-UPE in 3 h
ALK6 C	Alkali-treated KFM-UPE in 6 h

Figure 3.1: KFM-UPE Biocomposites

The series of designation was depicted in Table 3.2. The sides of stainless steel mold were applied with release agent to prevent resin sticking to the mold. Two pieces of plastic releasing firms were set in a way that were not easily moved on the top of the uncured mixture and steel mold. Before compression was applied for fabrication, efforts were made with the help of a roller in a way to eliminate all bubbles. The mold and the specimen were closed slowly, allowing the UPE mixture to flow and forming a mold shape, and then placed into compression moulding machine. A compression moulding machine called Gotech Testing Machine was operated at 120°C. Steel mold was put onto upper platen of the machine and pressed at pressure of 5 bar for 10 min. The mold was then put in separate press of the machine and cooling was done for 5 min under maintained pressure at room temperature. When the hot-pressing was finished and after the resin was set, the press was opened and the mold was taken out gently from the hot press machine and cooled to room temperature. The KFM-UPE composite block was removed from the mold. Once KFM-UPE composites were cured at 80 °C for 24 h at oven, they were cut to required dimensions for mechanical tests.

3.3 Characterizations

3.3.1 Flexural Test

Flexural test measured the force required to bend a beam under three point loading conditions. The flexural test was performed in accordance to ASTM D 790 procedure, using Instron universal testing machine with span-to-depth ratio of 1:16 and tested at cross head speed of 2 mm/min. Test specimens in rectangular form having 127 mm x 12.7 mm x 3 mm were used for the test depicted in Figure 3.2. The specimens were prepared by cutting from KFM in rectangular form using band saw machine. A specimen rested flatwise on a support span and the load was applied to the center by the loading nose producing three point bending at a specified rate. The specimens were placed onto two supports having a 48 mm span length between the supports. The test was performed using a load capacity of 50 kN and carried out in laboratory environment until bending specimens failed.

All the statistical significant results were obtained as the average value and the standard deviation of three test specimens of treated and untreated KFM-UPE composites after the test. Load-deflection curves determined the flexural strength and modulus. The flexural strength, σ_f and modulus, E_f were measured using the following equations:

$$\sigma_f = (3\mathrm{PL})/2\mathrm{b}d^2 \tag{3.1}$$

$$E_f = L^3 m/4\mathrm{b}d^3 \tag{3.2}$$

where P = load applied, L = span length, d = thickness of specimen, b = width of specimen and m is the slope of the initial straight line portion of the load-deflection curve.

Figure 3.2: Fracture flexural specimens.

3.3.2 Tensile Test

Tensile test involved mounting the specimen in a machine and subjecting it to tension at a constant rate. The test was performed conforming to ASTM D 3039 procedure using Instron universal testing machine, tested at cross head speed of 2 mm/min, and carried out in laboratory environment until tensile specimen failed with load capacity of 50 kN at room temperature. Test specimens were prepared by cutting from KFM in rectangular form using band saw machine. Before the test, the seen surface of specimens were cleaned and polished by a mean of specimens were in rectangular form (150 mm x 20 mm x 3 mm) depicted in Figure 3.3. Abrasive paper was used to polish the edge surfaces so that the specimens did not have bumps.

All the statistical significant results were obtained as the average value and the standard deviation of three test specimens of treated and untreated KFM-UPE composites after the test. Tensile strength, elongation at break and tensile modulus were then recorded for all samples from stress-strain curves. The tensile strength, elongation at break and tensile modulus were measured using the following equations:

$$\text{Tensile strength} = \frac{\text{maximum load force (F)}}{\text{surface area (A)}} \tag{3.3}$$

$$\text{Tensile modulus} = \text{stress / strain} \tag{3.4}$$

$$\text{Elongation at break} = \frac{l - l_0}{l_0} \text{ x } 100\ \% \tag{3.5}$$

l_0 = Original length of test piece
l = Length of test piece at break

Figure 3.3: Fracture tensile specimens.

3.3.3 Fourier Transform Infrared Spectroscopy

Infrared spectra of each samples was obtained in the range of 4000 – 400 cm^{-1} using a FTIR spectrophotometer from NICOLET iZ10. FTIR was employed to determine functional groups and its molecular bond presented in KF by effect of alkali treatment. NICOLET iZ10 measured infrared spectra of each samples at room temperature using KBr pellet. For carrying out the test, 20 mg of KF samples analyzed in this study was crushed in a blender, mixed them with 100 mg of dry powder, potassium bromide (KBr) and then pressed them in a small agate pestle with the effort of hands to create a sample pellet of the untreated and treated KF for FTIR spectroscopy. A hydraulic pressure was applied onto the mixture sample at two bar for 2 min by 3 mm disc. The hydraulic pressure causes the removal of moisture inside spectroscopy. IR spectrum bands were obtained when laser of infrared projected onto the mixture pellets. All the information obtained was characterized according to ASTM E168-06 and ASTM E1252-98 standards used by Bakri and Jayamani (2016).

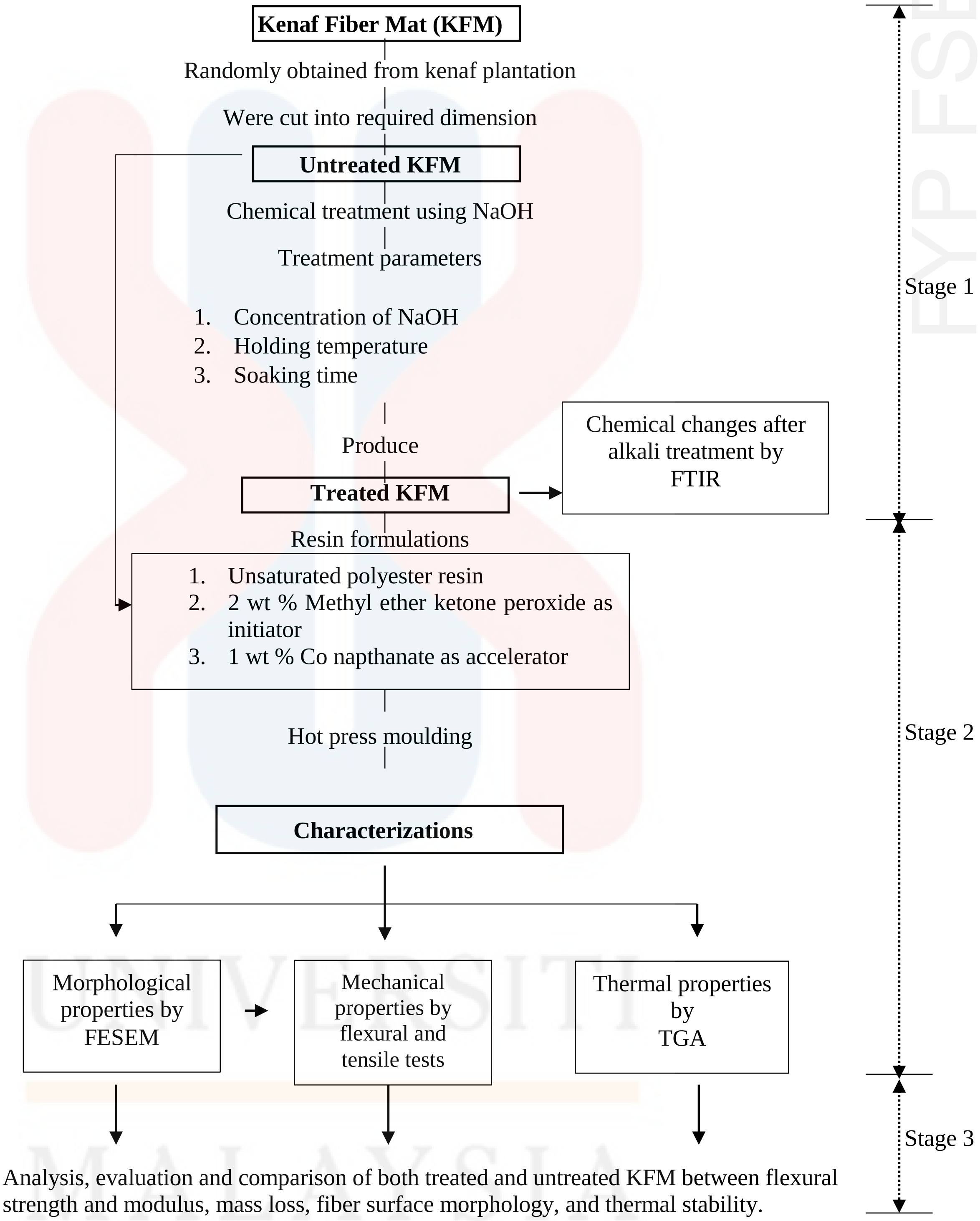
3.3.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was employed to characterize the residues of char and mass changes of KF and KFM-UPE composites before and after alkali treatment. The scans were carried out using dry solid fibers. The samples between 3 and 5 mg were placed in ceramic crucibles under nitrogen flowing at 50 ml/min from temperature between 25 to 600 °C at a rate of 10 °C/min. The measurements were made using a Mettler Toledo TGA/DSC2 to yield the decomposition temperature, mass loss and maximum decomposition peak. TGA and DTG data were normalised to indicate trend changes in thermal stability in terms of percentage weight loss and first derivative weight loss as function of temperature.

3.3.5 Field Emission Scanning Electron Microscopy

Field Emission Scanning Electron Microscopy (FESEM) from Zeiss Supra 35VP provided an excellent technique for examination of surface morphology of fibers and fracture surfaces of NFPCs. Fiber-matrix interfacial interaction that occurred after treatment of the fibers were examined. In this study, FESEM was operated at an acceleration voltage of 10 kV and a magnification ranged from ×100 to ×500 was used to collect FESEM images of the fracture surfaces of the tensile specimens. Cleaning and polishing were done on the fracture surfaces of KFM-UPE composites. For all tensile fracture surface specimens were prepared in dimension of 6 mm×6 mm×3 mm, the selected composite fracture surface was fixed on the stub using conductive tape to avoid charging effect by FESEM. In Figure 3.4, the samples were coated with gold by a plasma sputtering apparatus to make them conductive before FESEM evaluation. The overall process of the preparation and characterization of KFM-UPE composite was presented in Figure 3.5.

Figure 3.4: Sample preparation for FESEM.



Note:
Stage 1: Material preparation (Process based on experimental setup including collecting and cutting followed by chemical treatment for KFM)
Stage 2: Fabricating the KFM-UPE composites with initiator and accelerator for resin (100:2:1).
Stage 3: Analysis, evaluation and comparison of the obtained experimental data.

Figure 3.5: Overall Process of Preparation and Characterization of KFM-UPE Biocomposite

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared Spectroscopy Analysis

4.1.1 FTIR Analysis of Kenaf Fiber

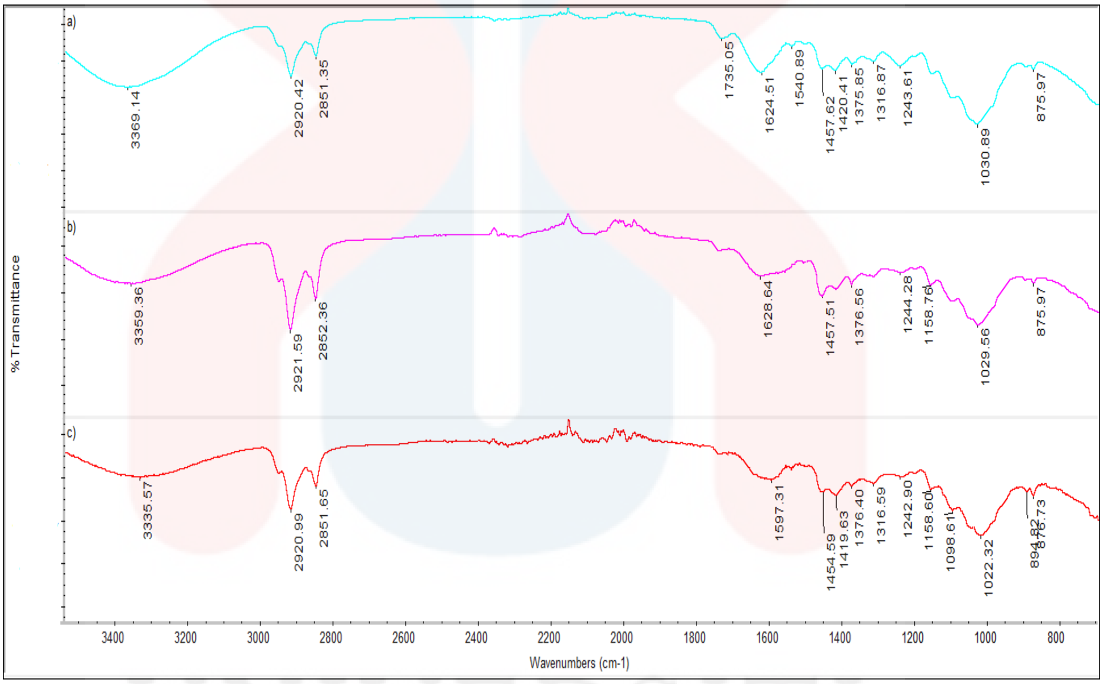


Figure 4.1: FTIR spectra of kenaf fiber (a) raw and with NaOH treatment in (b) 3 hours, (c) 6 hours.

Figure 4.1 presents FTIR spectra of untreated and alkali treated kenaf fiber (KF) for 3 h and 6 h. A broad absorption band at 3369.14 cm^{-1} is due to O-H stretching vibrations of cellulose and hemicelluloses. The region 3500–2500 cm^{-1} for the untreated and treated kenaf fibers is related to OH and CH_2 groups. The peaks located at 2920.42 cm^{-1} and 2851.35 cm^{-1} are attributed to CH and CH_2 groups, respectively (Khalil *et al.*, 2013). The band at 2851.35 cm^{-1} corresponds to CH_2 and CH_3 stretching vibrations that contains a functional group of alkanes (cellulose and lignin) and carboxylic acids. As for alkali-treated kenaf fibers, the 3369.14 cm^{-1} band assigned to the OH group decreased after this peak (Punyamurthy *et al.*, 2012). This disappearance is a consequence of the hemicelluloses are removed from the fiber and the formation of ionic carboxylates in the incompletely extracted samples, in which instance the corresponding peak appears at lower frequencies (1597.31 cm^{-1}).

The absorption band at 1735.05 cm^{-1} is due to carbonyl groups (C=O) stretching and vibration of acetyl groups of hemicelluloses, but this band can no longer be observed in alkali-treated kenaf fibers. This peak characterizes the hemicellulose, pectin and waxes present in the fibers before treatment. However, the intensity of the absorption band at around 1735.05 cm^{-1}, which corresponds to C=O stretching is found to depend on alkali treatment. The C=O stretching in alkali-treated kenaf fibers is significantly higher than that of untreated kenaf fibers. This is due to a process between the hydroxyl (OH) groups of the kenaf fibers and the sodium group with sodium hydroxide. In alkali treated fibers curve the intensity of C=O stretching was less intense due to the removal of (non-cellulosic impurities) such as pectin and hemicellulose from the surface by absence of carbohydrates (Dwivedi & Mehta, 2011).

The large peak observed at 1624.51 cm^{-1} for untreated kenaf fibers can be associated to the presence of lignin, assigned to aromatic vibration of benzene ring in lignin and is confirmed by the peak at around 700 cm^{-1}. The spectrum of treated kenaf fibers is distinguishable from that of untreated kenaf fibers, by the observed increase at 1457.51 cm^{-1} and 875.97 cm^{-1} are due to the in-plane CH_2 symmetric bending of the assigned to the symmetric ring vibration contribution. It is observed that the peak at 1243.61 cm^{-1} disappears in alkali-treated kenaf fibers. Alkaline treatment removes the waxy epidermal tissue, adhesive pectins and hemicelluloses that bind fiber bundles to each other. It can thus be summarized that the NaOH chemical treatments remove most of the lignin and hemicellulose components, which help to improve the mechanical properties of KFM-UPE composites.

The peak located at 1243.61 cm^{-1} appeared to decrease as soaking time increased. The intensity of transmission peak at 1243.61 cm^{-1} assigned to the C-O stretching vibration of the acetyl group in the lignin component, separated into two smaller peaks at 1260 cm^{-1} and 1230 cm^{-1}. The first one corresponds to vibrations in the guaiacyl structure of lignin and the second to the syringyl structure (Fengel & Wegener, 1984). The change of intensities at this peak after treatment indicates the removal of lignin after alkali treatment. The peak at 1030.89 cm^{-1} reflects the carbohydrate backbone of cellulose and the C-C ring breathing. The absorption band at 1375.85 cm^{-1} is owing to CH_2 bending in lignin whereas the broad peak at 1030.89 cm^{-1} is due to C-O stretching bond structure from the functional group of alcohol (cellulose, hemicellulose and lignin). As for untreated kenaf fibers, the small peak observed at 875.97 cm^{-1} is attributed to C-H “oop” bond structure of the functional group of aromatic (lignin). Similarly, there is a reduction in the intensity of the bands at 875.97 cm^{-1} as compared with treated fibers. The results obtained such that disappearing of smell from the kenaf fibers similar to Garside and Wyeth (2013).

By comparing with 6 h treatment, there was reduced in the intensity of the bands at 1098.61 cm^{-1} characterized as the C-O streching band structure of the functional group of alcohol due to immersion time in NaOH solution. There was combination of two different peak band of 894.82 cm^{-1} to 876.73 cm^{-1} to form a single peak 875.97 cm^{-1} after 3 h treatment. The 6 h treatment caused the breaking of certain bond stucture in functional groups that contain free hydroxyl bonded structure in the KF. A small peak at 1316.59 cm^{-1} for the 6 h NaOH-treated and 1316.87 cm^{-1} for the untreated was due to decrease in functional group alkanes in the 3 h NaOH-treated KF.

Table 4.1: Peak positions of the infrared spectra of kenaf fiber (Marcovich *et al.*, 2005).

Assignment	Untreated kenaf fiber (wavenumber, cm^{-1})	Treated kenaf fiber (wavenumber, cm^{-1})
Hydroxyl group and bonded OH stretching	3369.14	3359.36, 3335.57
C-H stretching, O-H stretching – Alkanes (CH; CH2; CH3), Carboxylic Acids	2920.42	2921.59, 2920.99
C-H stretching, O-H stretching – Alkanes (CH; CH2; CH3), Carboxylic Acids	2851.35	2852.36, 2851.65
C=O stretching (carboxylic acids and esters)	1735.05	-
C-H bending – Alkanes (hemicellulose and pectin)	1243.61	-
C-O stretching – Alcohol (cellulose; hemicellulose; lignin), Carboxylic Acids, Esters, Ethers	1030.89	1098.61 1029.56, 1022.32
C-H “oop” – Aromatic (lignin)	700	-

4.2 Thermogravimetric Analysis

4.2.1 Thermal Stability of Kenaf Fiber

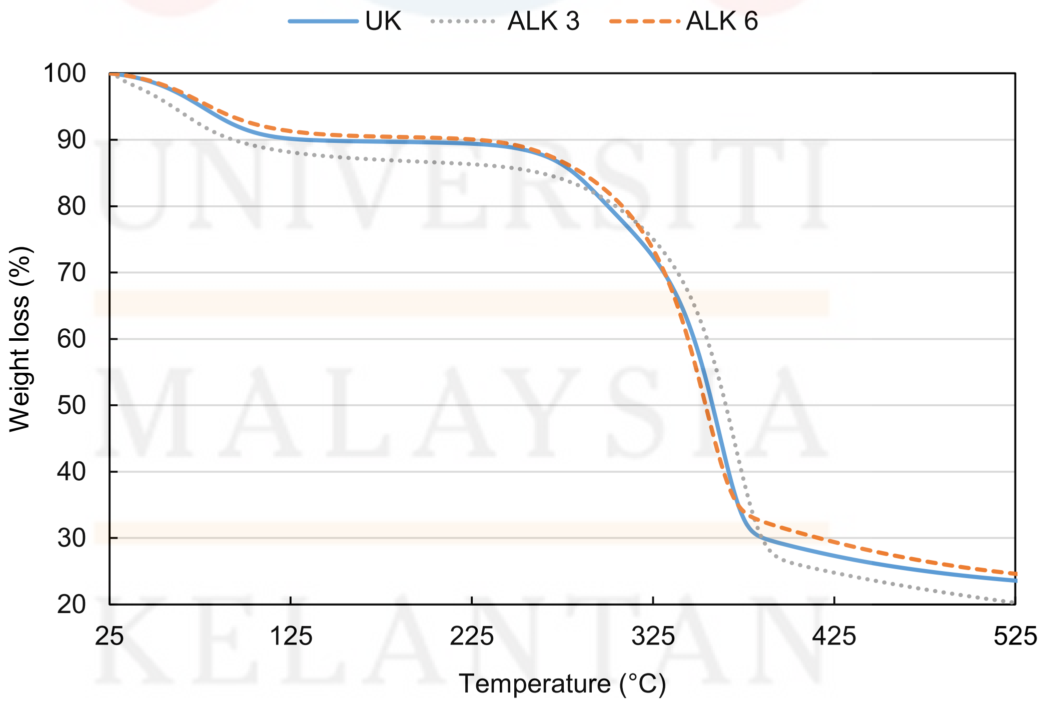
The thermal stability of kenaf fiber, UPE matrix and KFM-UPE composites was studied by TGA under nitrogen in the 25 to 600 °C range. As with kenaf fiber, the thermal degradation occurred in a two stage process where the first stage was associated to the degradation of hemicellulose between 220 and 280 °C. The degradation of lignin occurred between 280 and 300 °C was associated to the second stage (Garside & Wyeth, 2013).

Table 4.2: Thermal degradation and char residue data of kenaf fiber by TGA.

Sample code	$T_{initial}$ (°C)	R_{1peak} (%/min)/T_{1peak} (°C)	R_{2peak} (%/min)/T_{2peak} (°C)	Char residue (%)	
				450 °C	600 °C
UK	220	0.027/70	0.19/359	27.6	24.0
ALK 3	210	0.026/64	0.25/369	38.5	33.5
ALK 6	200	0.022/70	0.12/348	29.4	24.8

In the case of untreated kenaf fiber (UK), thermal degradation started at around 220 °C. The region between 250 and 480 °C was associated with the decomposition of cellulose, lignin, and hemicellulose. As illustrated in Table 4.2.1, the peak degradation temperature of alkalized kenaf fiber shifted to 369 and 348 °C were for 3 h and 6 h as compared to raw fiber peak temperature of 359 °C. Most of the cellulose was decomposed by thermal depolymerization of hemicellulose and the cleavage of the glycosidic linkage of cellulose at 350 °C. Hemicelluloses generally degraded more quickly than lignin and celluloses due to the presence of acetyl groups. Hemicelluloses tended to decompose between 180 °C and 350 °C while the decomposition of lignin could occur at the entire temperature range up to 900 °C (Alwani *et al.*, 2013). The dehydration and degradation of lignin occurred at 40–210 °C and maximum percentage of cellulose was found to decompose at 380 °C.

(a)



(b)

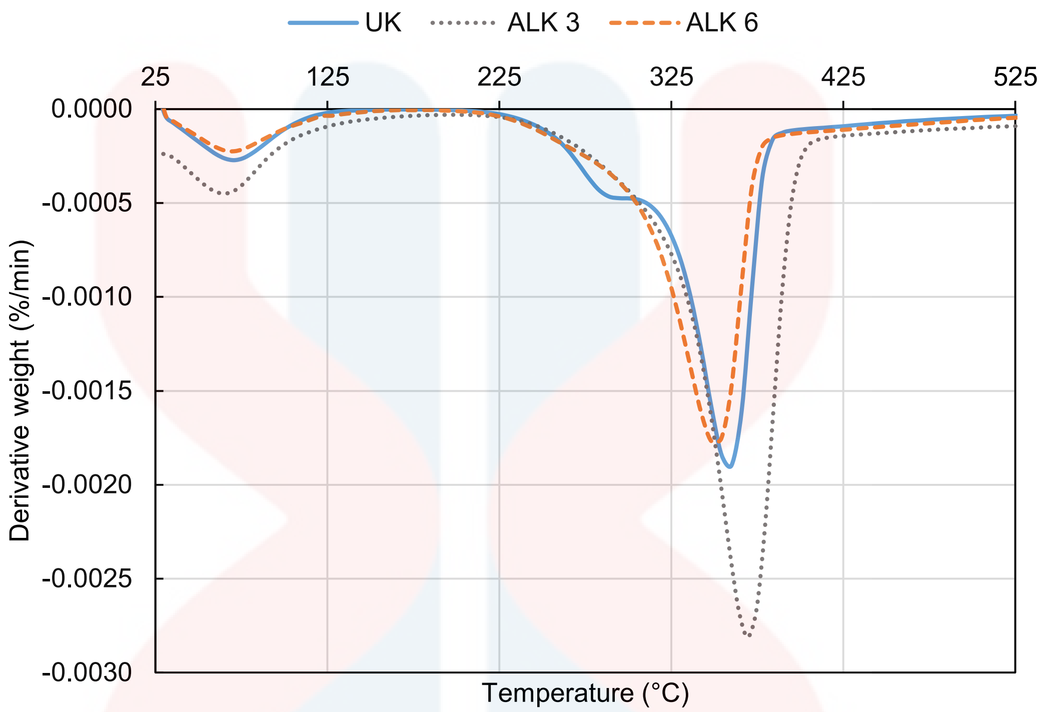


Figure 4.2: (a) Thermogravimetric analysis (TGA) and (b) derivative thermogravimetric analysis (DTG) for KFM after alkali treatment in different soaking times.

Furthermore, Figure 4.2a presented the curves of alkalized kenaf fiber must move to the right which suggested there was significant trend of increasing thermal stability. The increase in thermal stability after 6% NaOH treatment can be attributed to the removal of the amorphous structure of hemicellulose which was more aware of heat than other crystalline cellulosic components. Table 4.2 indicated that degradation for UK at 220°C was 62.57% of mass change and completed at 500 °C. However, ALK 3 indicated degradation at 210°C was 65.31% of mass change whereas ALK 6 indicated degradation at 200°C was 64.41% of mass change and completed at 500 °C. After treatment, fibers moved the initial decomposition temperature to 370 °C compared to raw fiber decomposition temperature of 356 °C (Arrakhiz *et al.*, 2012).

Figure 4.2b depicted derivative thermogravimetric curves (DTG) of untreated and alkalized kenaf fiber. Most specimens revealed that two distinct stages of the fiber's decomposition profiles. The first stage, started at 220 °C, clearly indicating noncombustible gas, such as H_2O, CO_2, formic and acetic acids, alkanes and other hydrocarbon derivatives caused hemicellulose degradation (Azwa *et al.*, 2013; Seki *et al.*, 2013). In Table 4.2, the second stage occurred between 348 and 359 °C at the maximum degradation temperature of kenaf fibers. The finding provided evidence that thermal degradation of cellulose occurred between 290 and 360 °C (Azwa *et al.*, 2013). A wider peak of lignin can be counted, which presented degradation temperature from 280 °C to 500 °C (Alvarez & Vázquez, 2004).

As shown in Table 4.2, the char residues of KFM without 6% NaOH treatment were 27.6 wt % at 450 °C and 24.0 wt % at 600 °C, whereas those of 6% NaOH treatment in 3 h were 38.1 and 33.5 wt %, whereas 6 h were 29.4 and 24.8 wt %, respectively. Therefore, the number of residues left after the composites were degraded which reduced the percentage of weight at 500 °C. There was little residue left for UPE resin due to the absent char. At the end of combustion, this char decomposed and the residue stopped existing at 500 °C which was understood as unreacted carbon. In a different study, some authors accepted the fact that char left at 500 °C is due to the removal of lignin through alkalization (Haameem *et al.*, 2015). In engineering applications, the first Differential Thermal Analysis (DTA) peak has an important discovery on maximum degradation peaks at higher temperatures which equal to the initial decomposition of the composite material (Monteiro *et al.*, 2012). The percentage of weight loss was higher and derivative weight loss was lower for treated fibers which was attributed to excellent thermal stability.

4.2.2 Thermal Stability of KFM-UPE Composites

In Figure 4.3a, TGA curves of neat UPE and KFM-UPE composites presented the existence of only one main mass-loss region, always located between 320 and 370 °C. The degradation temperature of the neat UPE was observed at 378 °C. Thus, this region of composites increased to 384 °C can be attributed to the thermal decomposition of neat UPE. The curves indicated that the first weight loss was observed between 50 and 175 °C, which corresponded generally to a loss of water in the composites accounting for about 2% loss in weight (Nguyen *et al.*, 1981).

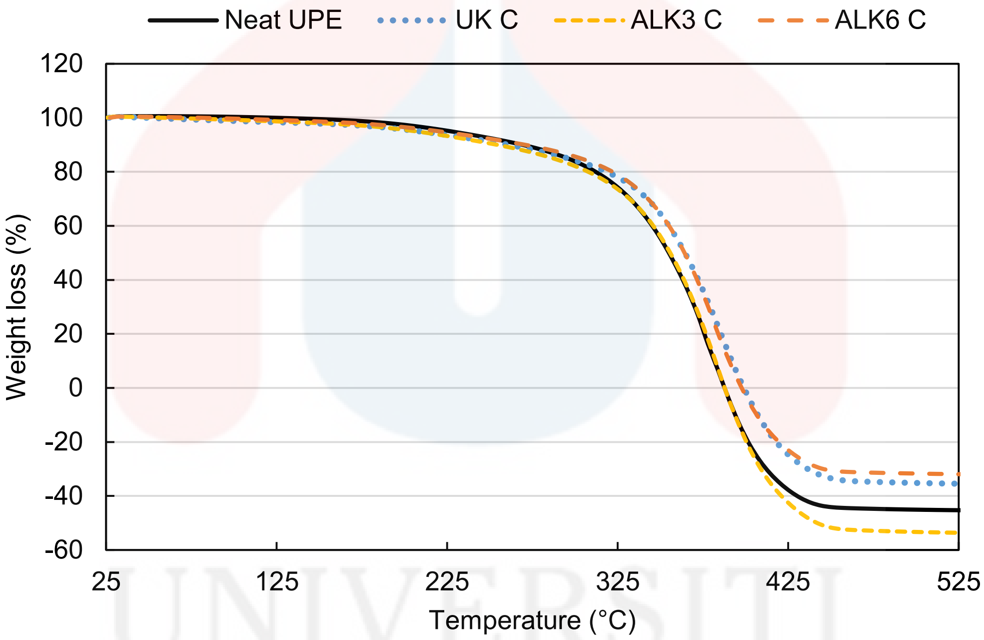


Figure 4.3 (a): TGA for KFM after alkali treatment in different soaking times .

As illustrated in Figure 4.3a, it can be seen that only one degradation stage of the decomposition profiles of composites, which indicated that NaOH treatment reduced the hemicellulose content of kenaf fiber. However, as a composite, this region with NaOH treatment in 3 h decomposed at a slightly lower temperature than NaOH treatment in 6 h and untreated ones. In contrast, the study by the author indicated that the large quantity in reduction of hemicelluloses and lignin from NaOH treatment of optimum immersion time increased thermal stability (Pickering, 2008).

On the other hand, it appears from Table 4.3 that neat UPE and NaOH treated composites had the same initial decomposition temperature (150 °C), which was slightly less than the untreated composites (170 °C) of KFM. Compared to untreated composites starting from 384 °C, the last degradation temperature for NaOH treated composites moved to higher temperature range 473—485 °C accounting to about 50% loss in weight. At this point, it clearly proved that untreated composites degraded fastly was due to the weak bonding between fiber and matrix than other composites and degraded slowly was due to higher cellulose content in the KFM.

Table 4.3: Thermal degradation and char residue data of kenaf/UPE composite by TGA.

Sample code	$T_{initial}$ (°C)	R_{peak} (%/min)/T_{peak} (°C)	Char residue (%)	
			450 °C	600 °C
Neat UPE	150	0.2957/378	44.2	45.6
UK C	170	0.2598/384	33.9	36.0
ALK3 C	150	0.3111/483	52.5	54.3
ALK6 C	150	0.2853/475	31.1	32.5

From the data in Figure 4.3a, it is apparent that this peak of composites must move to a higher temperature of 384 °C, revealing there has been marked rise in the thermal stability because of lower initial decomposition temperature against untreated composites. The treated composites also indicated a slight decrease in the decomposition temperature compared to the neat UPE. This decrease can be explained by ester bond (C-O) formed in the KFM-UPE composites and intermolecular hydrogen bonding during dispersion of the fiber in the matrix (Arrakhiz *et al.*, 2012). After alkali treatment, therefore, it was sensible to contact with humidity or oxygen. As ester bond apparently formed in the matrix, polymer chains of neat UPE was not able to break in the same conditions. The hot-pressing technique made friction between kenaf fiber and neat UPE and it was possible for polymer chains to induce a decrease in thermal stability when breakage between each other (Pickering, 2008).

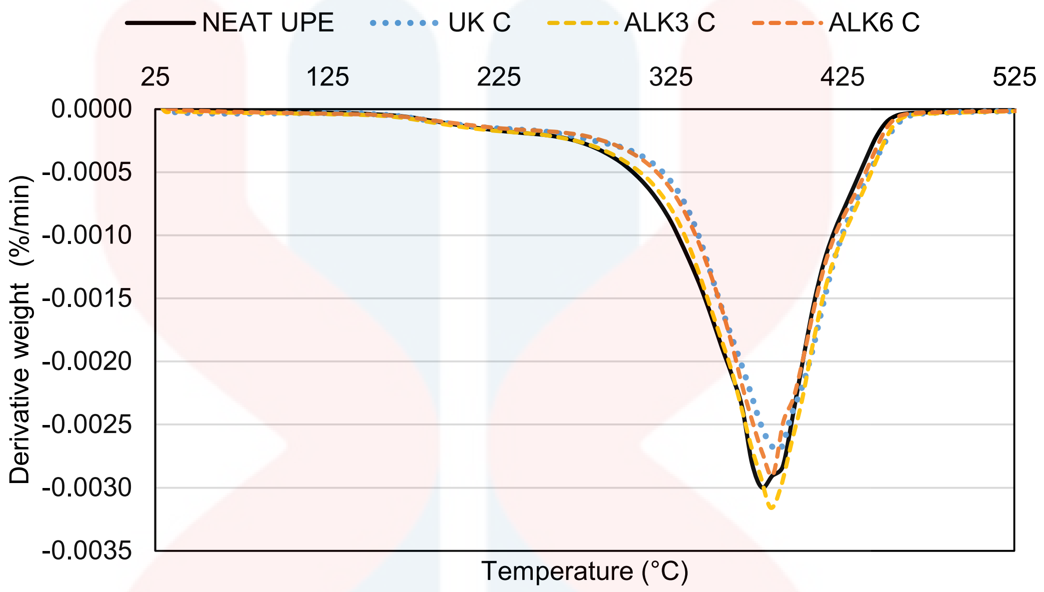


Figure 4.3 (b): DTG for KFM-UPE composites after alkali treatment in different soaking times.

From the data in Figure 4.3b, it is apparent that DTG made downward shift in temperature of degradation when KFM was incorporated in the matrix, going from UK C to ALK3 C and ALK6 C which were between 320 and 325 °C, suggesting there was significant trend of increasing thermal stability. Table 4.3 provided that degradation for untreated fiber at 170°C was 62.57% of mass change and completed at 500 °C. However, ALK3 C indicated degradation at 150°C was 44.57% of mass change whereas ALK6 C was 64.41% of mass change and completed at 500 °C. In case of treated composite of KFM, degradation started earlier was attributed to fiber-matrix adhesion in the KFM-UPE composites. The char residues of composites without NaOH treatment were 33.9 wt % at 450°C and 36.0 wt % at 600°C, whereas those of NaOH treatment in 3 h were 52.5 and 54.3 wt %, and 6 h were 31.1 and 32.5 wt %, respectively. The percentage of weight loss was higher and derivative weight loss was lower for treated composites, accounting for higher thermal stability compared to untreated composites. The treated KFM-UPE was stable below 170 °C due to enhanced interfacial interaction between KFM and UPE resin with alkali treatment.

4.3 Mechanical Properties of KFM-UPE Composites

4.3.1 Tensile and Flexural Strength

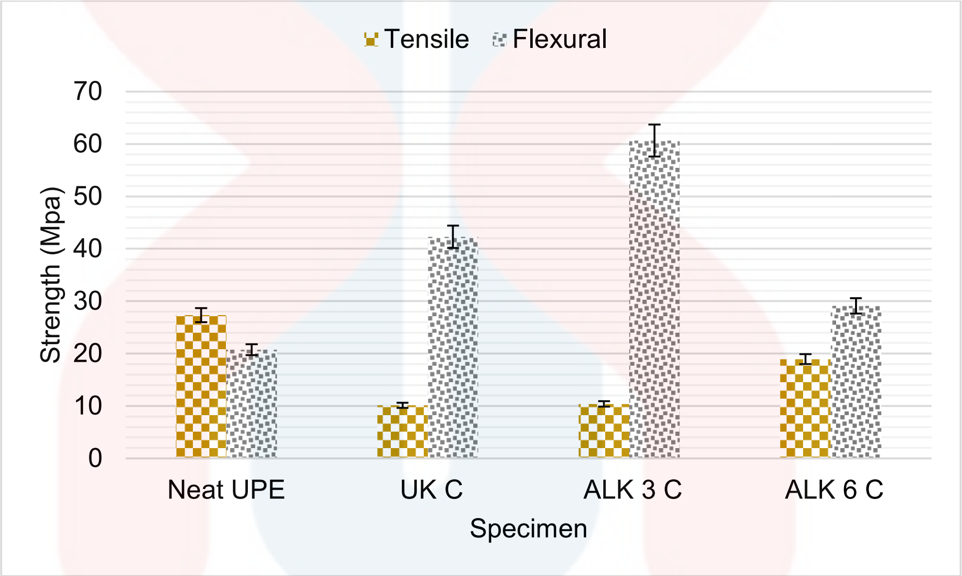


Figure 4.4: Tensile and flexural strength for neat UPE and KFM-UPE composites.

Figure 4.4 shows the measured average tensile strength of three specimens involved neat UPE, untreated and alkali treated KFM-UPE composites. The tensile strength decreased from neat UPE with highest (27.34 MPa) tensile strength, treated composites in 6 h (18.94 MPa), treated composites in 3 h (10.4 MPa), and while untreated composites shows the least (10.13 MPa) tensile strength.

The tensile strength of composites depicted in Figure 4.4 revealed that there has been marked rise by the increasing of immersion time at the same fiber content which was consistent with the finding of Edeerozey *et al.* (2007). Tensile strength of UK C was 2.6% and 46.6% lower than that of ALK3 C and ALK6 C, respectively. Tensile strength of neat UPE demonstrated a strength increase of almost 62.9%, 62%

and 30.7% than that of UK C, ALK3 C and ALK6 C, respectively. This study indicated that the interface between fiber and matrix was related to the load share from the matrix to the fiber, which contributed to the tensile strength. For good interfacial adhesion, the value of tensile strength of neat UPE was high (Rokbi *et al.*, 2011). The present findings also suggested that when MEKP was added to enhance the fiber-matrix adhesion, the loading force can transfer from the low-strength matrix to high-strength fiber. The increase in tensile properties for 6% NaOH-treated fiber composite was due to greater fiber–matrix interaction and physical bonding, because physical bonding also increased after alkali treatment due to the dipolar interactions between fiber and matrix (Rout *et al.*, 2001). Salmah *et al.* (2013) agreed that the increase of tensile strength due to removal of cementing materials and increased surface roughness.

Figure 4.4 shows the measured average bending strength of three specimens involved neat UPE, untreated and alkali treated KFM-UPE composites. Alkali treated composites in 3 h displayed highest (60.64 MPa) bending strength, untreated composites (42.29 MPa), alkali treated composites in 6 h (29.10 MPa) and while neat UPE showed the least (20.74 MPa).

The bending strength of composites as depicted in Figure 4.4 reduced by the increasing of immersion time at the same fiber content. Flexural strength of ALK6 C was 31.2% and 52% lower than that of UK C and ALK3 C, respectively. Tensile strength of ALK3 C demonstrated a strength increase of almost 30.3%, 65.8% and 52% than that of UK C, neat UPE and ALK6 C, respectively. In comparison between the composites at the immersion time from 3 h to 6 h, the bending strength of composites in 3 h of treatment was 52% higher than that of treatment in 6 h. Neat UPE suffered a loss of ductility and become stiffer but brittle due to the decrement of bending strength because of chain-scission. The trend observed in bending strength was similar to that found in bending modulus. The flexural strength of the composite increased linearly with immersion time and increased many higher than corresponding tensile strength obtained in experiment. Thus, KFM-UPE composites can withstand bending forces better than tensile stress compared to other composites.

This finding highlighted that the flexural strength was increased with increasing bonding surface area because of better adhesion between fiber and matrix. As the immersion time increased, the bonding surface area increased and hence bending strength decreased. Due to insufficient amount of bonding between matrix and fiber, the loads were not effectively be transferred from one end to another and hence there was reduction in bending strength of the composite. When the bonding between the fiber and the matrix was increased, a bending strength increased and strong bonding transferred loads from one end to another resulting in the increase in flexural strength of the composite, whereas when the percentage of fiber exceeded the require percentage, then the surface area increased. The enhancement was due to migration of lignin and the opening up of the fiber bundles. This was attributed to better fiber-matrix adhesion and resulted in low defects in the final composite (Prasad & Sain, 2003). Among the plausible explanations for these findings was that the weight percentage of the matrix decreased, therefore the bonding strength decreased, and loads could not be effectively transferred from one part to another resulting in the decrease in the flexural strength of the composites. Another reason for the reduction in flexural strength was because increasing the NaOH concentration solution can disturb the matrix continuity and reduction in bonding strength between neat UPE and the fiber (Mahjoub *et al.*, 2014).

The ultimate tensile strength is a maximum stress value obtained on a stress strain curve by dividing the maximum load on a material by the initial cross section of the test specimen. When reaching the ultimate tensile strength (UTS), the specimen tends to resulting changes in length beyond while the cross-section of the specimens becomes thinner. Yield strength is the maximum stress that can be applied without permanent deformation of the composites in this study while elasticity concerns the below the point relationship between stress and strain for non-permanent deformation .

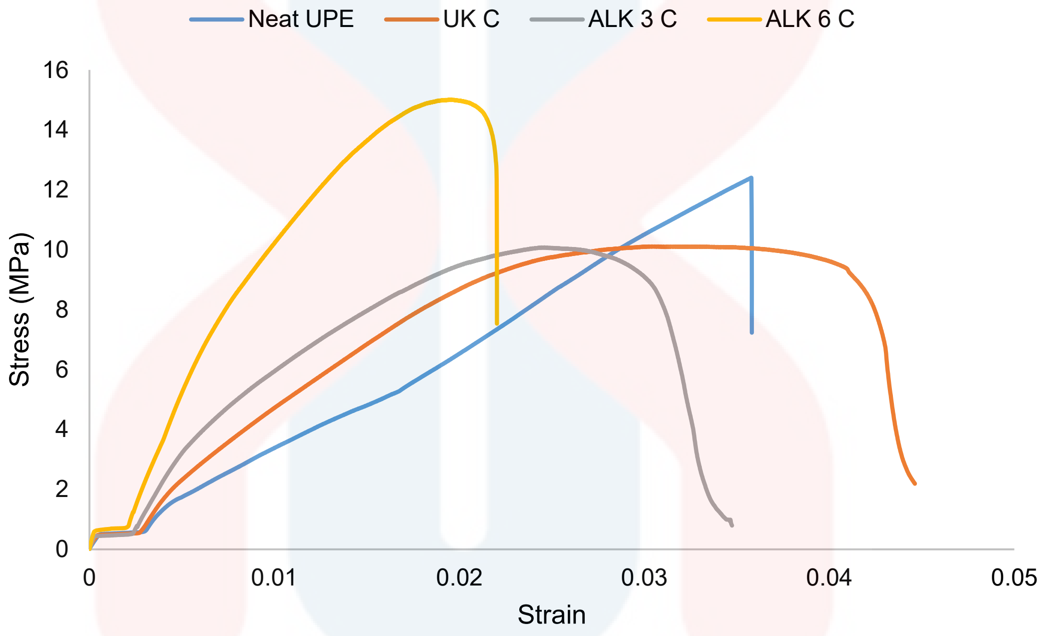


Figure 4.5: Tensile stress-strain diagram of neat UPE and KFM-UPE composites.

Figure 4.5 presented the stress strain diagram of neat UPE and all composites tested. ALK6 C displayed highest (15 MPa) maximum stress, neat UPE (12.3 MPa), UK C (10.1 MPa) while ALK3 C showed the least (10 MPa) maximum stress. ALK6 C was most brittle among neat UPE and other composites while UK C was least brittle. ALK6 C experienced very little plastic deformation before fracture. However, UK C experienced significant deformation before it eventually broke. It was noted that ALK6 C had highest yield strengths compared to other composites. On the other hand, there was a clear trend of decreasing maximum strain of treated composites compared to untreated ones because treated composites had best tensile strength, exactly correct flexibility and best resistance on the composite to the applied load (Satyanarayana *et* *al.*, 1990). Neat UPE displayed highest (0.036) maximum strain, UK C (0.033), ALK3 C (0.025) and while ALK6 C showed the least (0.019). ALK3 C showed fewer strain accounting for high bonding between fiber and matrix, which was attributed to the resin had low elongation at break (Prasad & Rao, 2011).

4.3.2 Tensile and Flexural Modulus

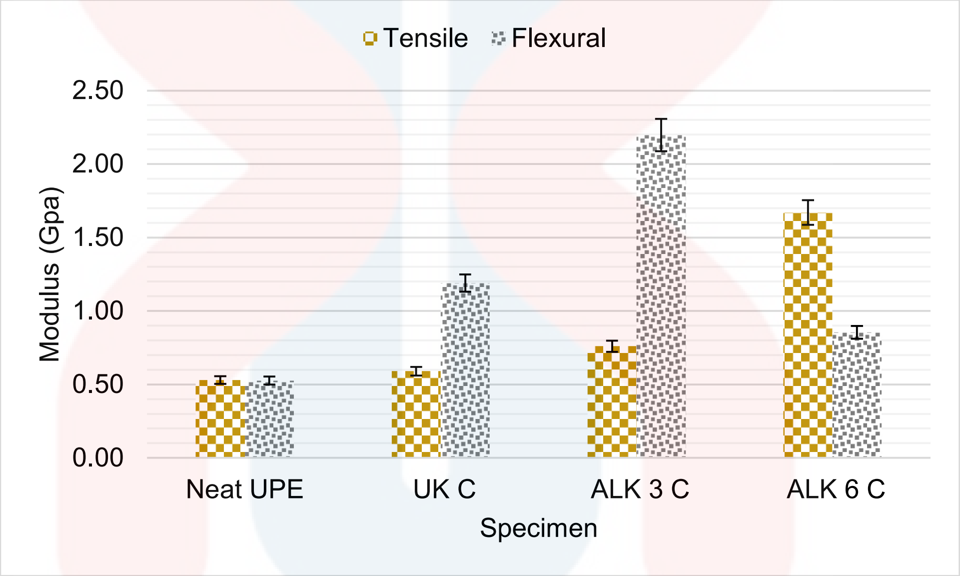


Figure 4.6: Tensile and flexural modulus for neat UPE and KFM-UPE composites.

As illustrated in Figure 4.6, the measured average tensile modulus of three specimens involved neat UPE, untreated and alkali treated KFM-UPE composites. The tensile modulus decreased from treated composites in 6 h with highest (1.67GPa) tensile modulus, treated composites in 3 h (0.76GPa), untreated composites (0.59GPa), and while neat UPE shows the least (0.53GPa) tensile modulus.

Figure 4.6 presented the tensile modulus of composites with 0 h, 3 h and 6 h of 6% alkali solution. It can be observed that the tensile modulus was reduced by the increasing of immersion time at the same fiber content. Tensile modulus of UK C was 22.4% and 64.7% lower than that of ALK3 C and ALK6 C, respectively. Tensile modulus of ALK6 C demonstrated a modulus increase of almost 64.7%, 68.3% and

54.5% than that of UK C, neat UPE and ALK3 C, respectively.

In consideration of the effect of alkali treatment on the tensile modulus from 3 h to 6 h, the results obtained the tensile modulus of composites in 3 h of treatment is 54.5% higher than that of treatment in 6 h. Due to better stiffness, values of KFM-UPE composites are much higher than neat UPE. For KFM-UPE composites, the findings suggested that the tensile modulus must not be higher or equivalent to neat UPE. In contrast, this higher value of tensile modulus was influenced by the fibers that support the stress from the matrix. The presence of KFM in UPE resin effectively enhanced the tensile modulus of UPE resin which was double as greater than that of neat UPE. According to Liu *et al.* (2009), the tensile modulus of a NFPC depended on the modulus of the fiber and the matrix. Consistent with findings by Edeerozey *et al.* (2007), the present finding found that the 6% alkali solution with 3 h immersion time was the best treatment condition in terms of tensile properties.

In Figure 4.6, the measured average bending modulus of three specimens involved neat UPE, untreated and alkali treated KFM-UPE composites. Alkali treated composites in 3 h displayed highest (2.20GPa), untreated composites (1.19GPa), alkali treated composites in 6 h (0.85GPa) while neat UPE showed the least (0.53GPa) bending modulus.

Figure 4.6 presented the bending modulus of composites with 0 h, 3 h and 6 h of 6% alkali solution. It can be observed that the bending modulus was enhanced by the increasing of immersion time at the same fiber content. The treatment of kenaf fibers with 6% NaOH solution at room temperature for 3 h greatly increased the flexural strength and slightly increased the flexural modulus (Lai *et al.*, 2008). The strengths and moduli of the KFM-UPE composites were highly attributed to the treatment conditions. There was, however an initial decrease in the Young’s modulus from ALK6 C was 61.4% and 45.9% with ALK3 C and UK C, respectively. This can be attributed to the high bending stress in the composite material. After that, there was a continual increase in the Young's modulus up to ALK3 C which recorded the highest value. ALK3 C demonstrated a bending modulus increase of almost 45.9%, 75.9% and 61.4% than that of UK C, neat UPE and ALK6 C, respectively. The trend observed in bending strength was similar to that found in bending modulus in neat UPE.

In consideration of the effect of alkali treatment on the bending modulus from 3 h to 6 h, the results obtained was the bending modulus of composites in 3 h of treatment that was 61.4% higher than that of treatment in 6 h, because of the low interaction and poor dispersion of the fiber in matrix. Another reason was a good stress transfer from the matrix to the incorporated fiber as bending modulus was higher for treated composites to those of untreated composites (Mehta *et al.*, 2006). Consistent with findings (Asri & Abdul Khalil, 2002) and (Arib, 2003), this study found that the flexural modulus and elastic modulus of the composite material exhibited the same values. The results showed that surface modification by alkali treatment has less influence on flexural properties compared to tensile properties. This can be explained that the flexural failure mode usually showed little or no fiber pull-out (Liu *et al.*, 2009), because applied force was perpendicular to reinforced fibers of the composite specimens in flexural test. Modulus of elasticity is an indication of the relative stiffness of composites. As shown in Figure 4.5, the slope of the elastic region of the stress-strain curve described the modulus of the specimens.

From the data in Figure 4.6, it is apparent that untreated composites recorded a maximum deflection of about 6.5E-6 N/m2, composites treated with 3 h recorded a maximum deflection of about 7E-6 N/m2 and while composites treated with 6 h recorded a maximum deflection of about 5.5E-6 N/m2. As flexural modulus increased the strength of the composite material increased, so the maximum deflection decreased. Thus, composites treated with 3 h recorded the highest flexural modulus values. Highest maximum deflection is due to the strong bonds between the two phases.

4.3.3 Tensile and Flexural Elongation at Break

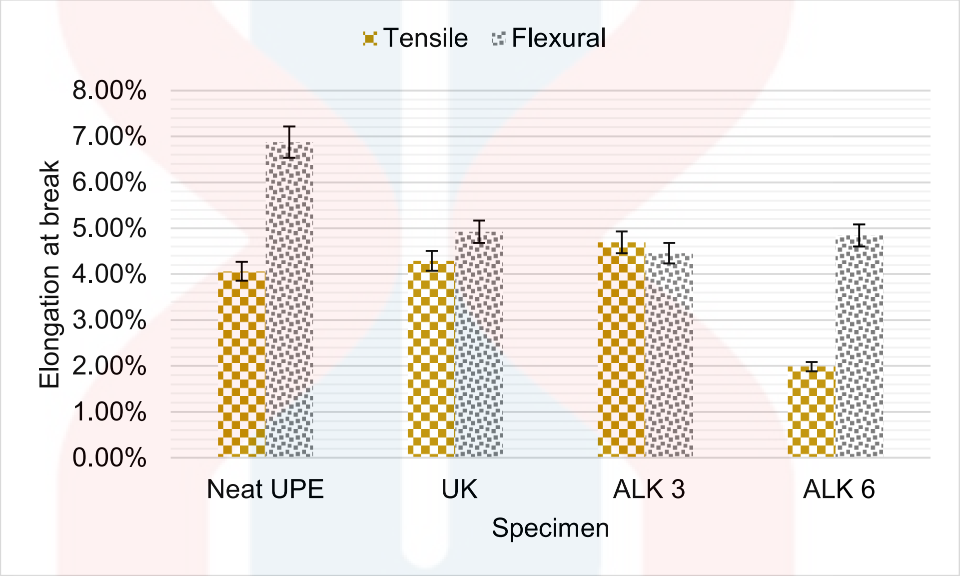


Figure 4.7: Tensile and flexural elongation at break for neat UPE and KFM-UPE composites.

Figure 4.7 shows the measured average tensile elongation at break of three specimens involved neat UPE, untreated and alkali treated KFM-UPE composites. The tensile elongation at break decreased from treated composites in 3 h with highest (4.69%) elongation at break, untreated composites (4.29%), neat UPE (4.06%), and while treated composites in 6 h shows the least (1.99%). This figure also shows the measured flexural elongation at break of neat UPE, untreated and alkali treated KFM-UPE composites.

The flexural elongation at break decreased from treated composites in 6 h with highest (6.88%) elongation at break, treated composites in 3 h (4.92%), untreated composites (4.84%), and while neat UPE shows the least (4.45%). The results revealed that the increasing of immersion time at the same fiber content decreases the elongation at break of the composite because KF and UPE resin are rather stiff and brittle. Thus, the composites had lower elasticity than neat UPE can be expected. The breakage of the composite material started from the interface between two phases. When the immersion time increased, the breakage of the composite material increased. The percent elongation at break of the composites ended lower than that of the matrix. This affected composites because of low fracture strain and the poor adhesion between the matrix and the fibers (Chumsamrong *et al.*, 2005).

Elongation at break of KF happened higher than that of UPE resin can explain the fracture of UPE resin before tensile failure of KF. Salmah *et al.* (2013) agreed well with the results obtained from the elongation at break of those treated composites if fewer than untreated composites exhibited high modulus of elasticity through the enhanced fiber wettability by the surface treatment of KFM using 6% NaOH solution. Furthermore, the decrease in essential elongation at break was due to the loading of KF can eliminate structural integrity of UPE resin. Treated composites of shorter immersion time produced fast breakage can mean improved fiber–matrix adhesion compared to untreated composites. Another reason for the results obtained was the progressive decrease on the elongation at break can be attributed to a reduction in deformability of the rigid interface between fibers and matrix.

4.4 Field Emission Scanning Electron Microscopy

4.4.1 Morphological Analysis of KFM-UPE Biocomposites

A high-resolution Field Emission Scanning Electron Micrograph (FESEM) micrograph of the kenaf fiber is shown in Figure 4.8a where it can be observed that physical structure of kenaf fiber is tubular with a circular section. Enlargement of a single fiber shows that it is composed of microfibers with an external diameter averaging 40 µm. Microfibers are therefore responsible for higher breaking strength, higher initial modulus and fewer extensibility. Such structure enhances better interfacial adhesion by increasing the specific contact area between fiber and matrix, promotes friction between them, thus higher mechanical properties of the resultant composites can be expected.

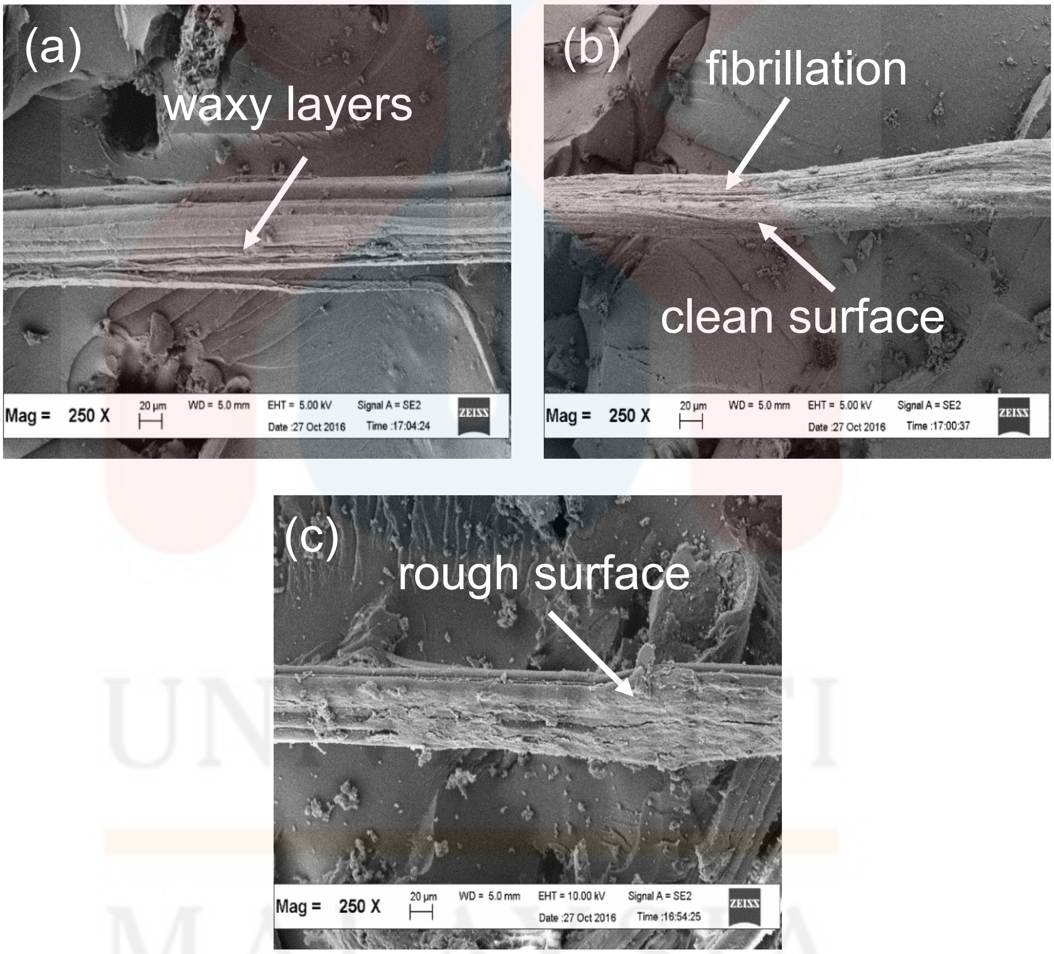


Figure 4.8: FE-SEM of (a) untreated KF, (b) 3 h NaOH-treated KF and (c) 6 h NaOH-treated KF.

From Figure 4.8a, the presence of wax, oil and surface impurities covering fiber surface on untreated KFM can be observed, on the contrary, 6% NaOH treatment most effectively removed these impurities, resulting in cleaner fiber surface. In addition, this groove-like structures on treated KFM due to the removal of cementing materials such as hemicellulose and lignin from the interfibrillar region reflected the findings of Ariawan *et al.* (2015). Thus, the morphological examinations of samples depicted in Figure 4.8b can provide a strong evidence of good adhesion between the matrix and the fiber due to the surface wetting of the UPE resin on the treated composites was greater than that of the untreated composites (Aziz & Ansell, 2004).

In general, the development of rough surfaces in fibers was a desired effect since this was seen that the interfacial bonding between fiber and matrix can show good performance and most studies examined enhancement of mechanical properties when KFM were used as reinforcements in UPE composites which was consistent with the finding of Li *et al.* (2007). Better fiber pre-impregnation from hot-pressing method allowed better fiber wetting and thus enhanced the mechanical interlocking between KF and UPE resin. Figure 4.8c illustrated the rough surface on treated KFM was increased with increase of immersion time by 6 % NaOH treatment which proved the existence of good adhesion which also increased mechanical interlocking with UPE resin. Likewise, the rough surface of the fiber provided a wider surface area for composite matrix . The presence of bundles in the untreated KFM reinforcing the resin limited the effective surface area. When the soaking time increased to 6 h, the cell was exposed and much particles was clearly removed, thus the roughness of fiber surface increased. In alkali-treated condition, most remaining cuticle material must able to expose lignin on the fiber surface (Prasad *et al.*, 1983). However, the micrograph in Figure 4.8b shows that 3 h treated KF fiber surface is smoother than that of 6 h treated KF fiber surface. Rough surface of 6 h treated KF can also due to the removal of all globular particles, waxes, cuticles and other plant impurities deposited on the fiber surface. This rougher surface yielded both rigidity of KFM under stress and bonding reaction and exposed hydroxyl groups on the matrix surface, so that favored the dissolution of hemicelluloses within the interfibrillar region when treated with alkali for longer durations (Sudhakara *et al.*, 2013).

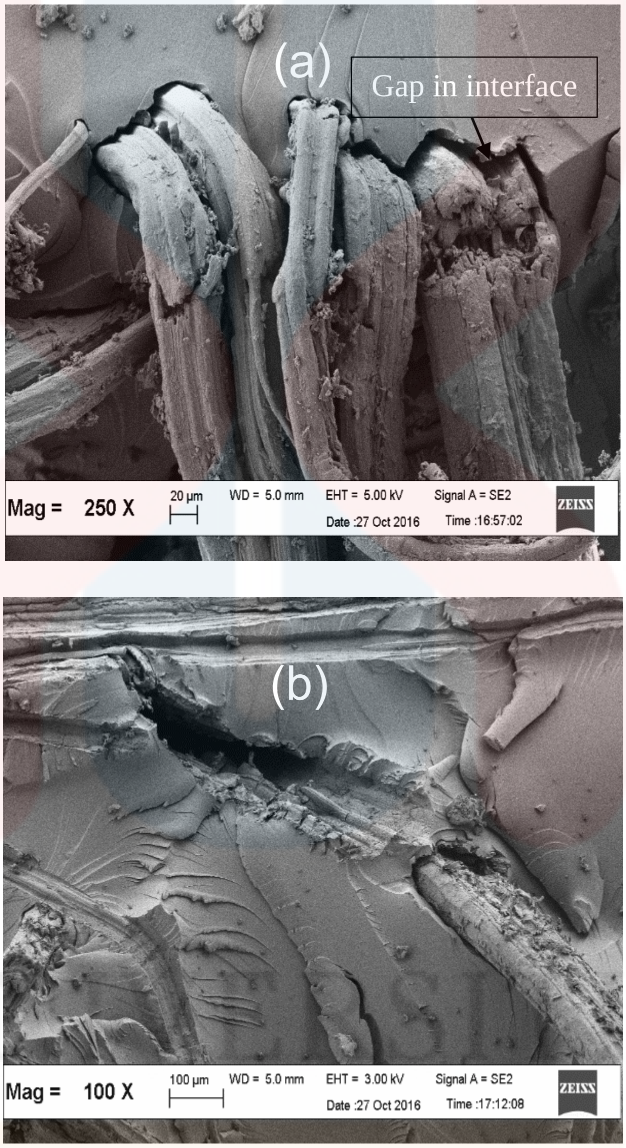


Figure 4.9: FE-SEM micrograph of (a) tensile fracture specimen and (b) fiber pull out.

The failure morphology of the composites following the alkali treatment used for the experiment was examined through FESEM. From Figure 4.9a-b, this found the fiber fracture and pull out from the specimen and also the dislocation of fibers. The application of the load resulted fracture took place in the specimen (Naveenkumar *et al.*, 2015). Thus, this observation clearly indicated poor adhesion and interaction between KF and UPE resin during tensile loading on the surface at x250 magnification depicted in Figure 4.9a. Some holes and extruding fibers featured on fracture surface were due to fiber pull-out failures, indicating that the most of the untreated fibers have come out without breaking during the shear failure, resulted in high degree of pull out. KFM consisted of random fiber orientation can be clearly seen that the fracture surface was rough (Shibata *et al.*, 2008). From Figure 4.9b, the number of holes from the pulled out fiber of the composite with 3 h treatment was less than of the composite with 6 h treatment. Wong *et al.* (2010) reported that this was due to the reduced surface area of the fibers while fibers could not absorb enough fracture energy. On the other hand, FESEM observations indicated that there was a considerable difference in the fiber-matrix interaction between 3 h and 6 h of giving treatment. Some gaps between fiber and matrix were clearly found for 6 h NaOH-treated composites which were responsible for the low mechanical properties. Meanwhile, 3 h NaOH-treated composites showed better fiber-matrix adhesion and gaps between fiber and matrix were not observed which were responsible for higher mechanical properties.

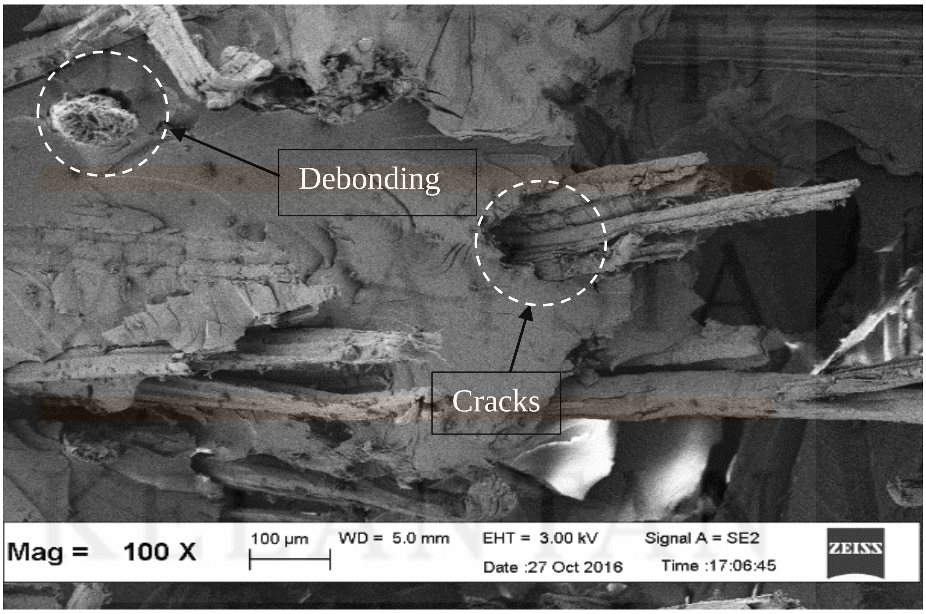


Figure 4.10: Fiber-matrix debonding

As cracks propagated between the fiber-matrix interfaces, matrix separation happened around the KF because of debonding, resulting in fiber pull-out due to greater extent of delamination depicted in Figure 4.9b . Hydrophilic KF attracted water molecules into the untreated composites and also caused fiber-matrix debonding. KF provided stiffness to the composite but fiber-matrix debonding due to hydrophobic UPE resin caused the tensile stress can transfer failures from the matrix to the fiber. This can be proven by the cracks that appeared on the surface of KFM-UPE specimens and FESEM image on the surface at x100 magnification depicted in Figure 4.10. Valadez-Gonzalez *et al.* (1999) agreed well with that of a poor interface because of the incompatibility between hydrophilic fiber and hydrophobic matrix.

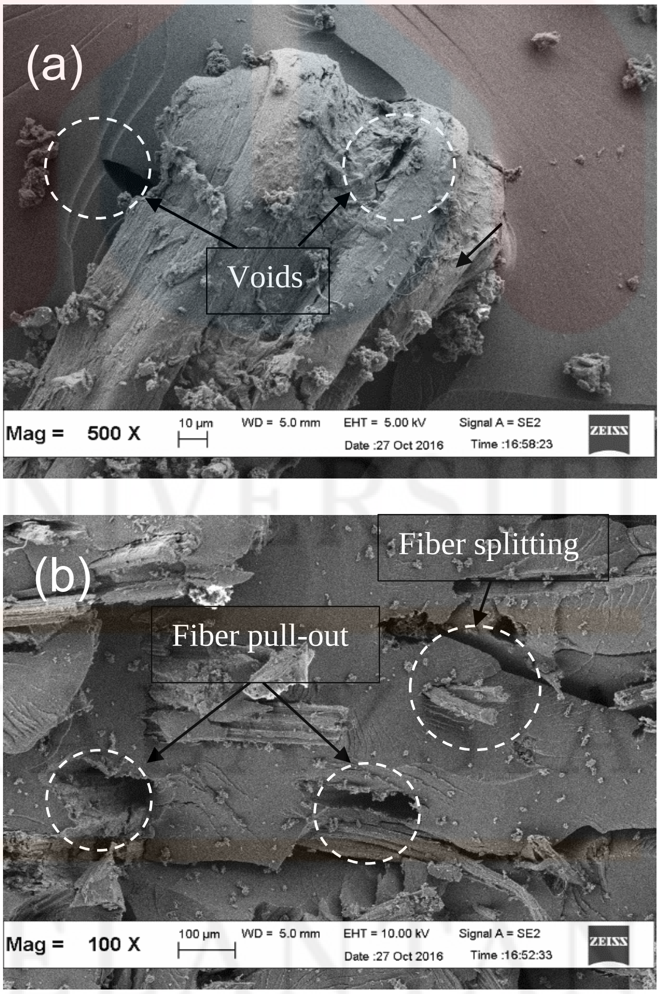


Figure 4.11: FE-SEM micrograph of (a) fully impregnated resin and (b) voids into fracture surface.

Figure 4.11a shows the FESEM micrographs obtained from giving treatment that featured the interfibrillar voids between entangled fibers. On other hand, Figure 4.6a shows UPE resin was fully impregnated into these voids and a lower extent of fiber pull-out with more fiber breakage, which confirmed better fiber-matrix adhesion, also indicates fibers were carrying higher load share than matrix (Ku *et al.*, 2011). The interface quality has an influential act on the load share when most load must transfer from matrix to the reinforcement through the interface. In contrast to Ku *et al.* (2011), Faruk *et al.* (2012) argued that the void was found at certain area of the fractured surface because of low tensile strength and modulus.

Cao *et al.* (2006) reported the fibers within the untreated fibers were packed together but splits were observed following the treatment. At higher soaking time takes place, it can be seen that most of the fiber split the fiber bundles into individual bundles of last fibers depicted in Figure 4.11b. Fiber fibrillation can be observed for NaOH-treated composites which attributed to optimum tensile strength by increasing immersion time from 3 h to 6 h. Fibrillation enhanced the tensile strength because significant stress can propagate through the fiber and break the untreated fiber bundle down into smaller ones by dissolution of the hemicellulose, thus increased the effective surface area available for contact with the matrix (He *et al.*, 2016). Unfortunately, the tensile strength for the composites with longer immersion time than 6 h could not enough due to the fiber damages, eventually causing tensile strength reduction explained this phenomenon. Moreover, Haameem *et al.* (2015) observed less fiber damage, suggesting less effective energy dissipation which improved the tensile strength. Similarly, Nishino *et al.* (2003) found that this could provide more anchorage for the matrix, and hence improve the tensile strength of the biocomposite.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study set out to fabricate KFM-UPE composites using hand lay-up and compression moulding techniques. The present study was designed to determine the effect of NaOH chemical treatment on mechanical and thermal properties of KFM-UPE composites. The following conclusions can be drawn from the present study.

FTIR study has identified the optimum alkali immersion time for 6% NaOH treatment to detect changes of functional group in alkali-treated kenaf fiber. This experiment confirmed that the hemicellulose, pectin and waxes present in the fibers before treatment at 1735.05 cm^{-1}, but this band can no longer be observed in alkali-treated kenaf fiber. The results of FESEM investigation show that better interfacial interaction between UPE resins and KF. 6% NaOH treatment most effectively removed these impurities, resulting in cleaner fiber surface. Taken together, these findings suggest a role for optimum alkali immersion time in promoting mechanical interlocking via interfaces. TGA study has confirmed the findings of Ariawan *et al.* (2015) which found that the increase in thermal stability after 6% NaOH treatment attributed to the removal of the amorphous structure of hemicellulose which was more aware of heat than other crystalline cellulosic components. Taken together, these results suggest that the treated composites have higher thermal stability compared to untreated composites. The contribution of this study has been to confirm 3 h treatment showed best results to a significant enhancement of mechanical performance such as tensile and flexural properties of KFM-UPE biocomposites. The current data highlight the importance of treated KFM-UPE biocomposites have the highest tensile strength (18.9MPa); modulus (1.67GPa); elongation at break (4.69%) while highest flexural strength (60.6MPa); modulus (2.2GPa); elongation at break (6.88%).

This study was limited by the absence of DSC experiment to study the melting temperature about the processing temperature of UPE resins when KFM-UPE biocomposites are fabricated. It is unfortunate that the study did not include new chemical treatments such as DIH-HEA and surface acetylation. Notwithstanding the relatively limited sample, this work offers valuable insights into FESEM investigation that has been confirmed by FTIR study and mechanical tests.

5.2 Recommendations

These findings provide the following insights for future research:

i) The introduction of improved compounding technology and new chemical fiber pretreatments such as DIH-HEA and surface acetylation can overcome hydrophilic character of natural fiber.

ii) Computer software is used to predict the properties of the natural fiber plastic composites, for example, Solidworks.

iii) Control of processing parameters such as temperature, pressure, time is requirement to manufacture good composites. The stainless steel mould must avoid moisture as well as natural fiber must repeat hours to dry.

iv) Average reading of test specimens must repeat three to seven times. Accurate readings eliminate standard error of measurement so that data trends can be nearly visible.

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