CHARACTERIZATION OF KENAF BAST FIBRE FILLED POLY(BUTYLENE SUCCINATE) COMPOSITES: MECHANICAL, WATER ABSORPTION AND WEATHERING PROPERTIES.

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by

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A2.   Conference paper 2 – Study on mechanical and morphological of kenaf bast fibre filled biodegradable poly(butylene succinate) composite. National Symposium of Polymeric Material (NSPM 2007), 27th – 29th November 2007, Universiti Kuala Lumpur (UNIKL), Kuala Lumpur.

A3.   Conference paper 3 – Mechanical properties and water absorption of kenaf bast fibre filled biodegradable poly(butylene succinate) (PBS) composites. International Conference for Young Chemists 2008 (2nd ICYC 2008), 18th – 20th June 2008, Universiti Sains Malaysia, Pulau Pinang.

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A5.   Journal paper 2 – Natural weathering of kenaf bast fibre-filled poly(butylene succinate) composites: Effect of fibre loading and compatibiliser addition. Journal of Polymers and The Environment, *article in press*. (DOI: 10.1007/s10924-010-0272-2)

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LIST OF ABBREVIATIONS

AA   Acetic anhydride

ASTM   American Society for Testing and Materials

CMC   Ceramic matrix composites

DCP   Dicumyl peroxide

DMA   Dynamic mechanical analysis

EFB   Empty Fruit Bunch

FRIM   Forest Research Institute Malaysia

FTIR   Fourier transform infrared spectroscopy

HDPE   High-density polyethylene

KBF   Kenaf bast fibre

KOH   Kalium hydroxide

LDPE   Low-density polyethylene

LTN   Lembaga Tembakau Negara

MA   Maleic anhydride

MAPE   Maleated polyethylene

MaPO   Maleated polyolefin

MAPP   Maleated polypropylene

MFI   Melt flow index

MMC   Metal matrix composites

NaOH   Natrium hydroxide

PA   Phatalic anhydride

PBS   Poly (butylene succinate)

PBSA   Polybutylene succinate –co–adipate

PBSgMA	Maleated poly (butylene succinate)
PC	Polycarbonate
PE	Polyethylene
PESU	Polyethylene succinate
PESU-AD	Polyethylene succinate –co–adipate
PLA	Poly (lactic acid)
PMC	Polymer matrix composites
PP	Polypropylene
pPBSgMA	Purified maleated poly (butylene succinate)
PS	Polystyrene
SA	Succinic anhydride
SEM	Scanning electron microscopy
TAPPI	Technical Association of the Pulp and Paper Industry
TGA	Thermogravimetric analysis
UV	Ultraviolet
WPC	Wood plastic composites

LIST OF SYMBOLS

%	Percent
wt. %	Weight percentage
M_m	Equilibrium water content
°C	Degree celcius
T_m	Melting temperature
rpm	Rotation per minute
N	Normality
W_t	Water absorption at t time
W_1	Weight of dry specimen
W_2	Weight of the specimen after certain period of immersion
T_g	Glass transition temperature
E'	Storage modulus
E"	Loss modulus
Tan δ	Loss tangent
phr	Part per hundred resin
D_m	Time taken to achieve equilibrium
M_m	Equilibrium water content
G_d	Grafting degree
V	Volume of KOH/C_2H_5OH solution that was used for titration of grafted sample
V_0	Volume of KOH/C_2H_5OH solution that was used for titration of blank sample
M	Molar concentration of the KOH/C_2H_5OH solution

W	Weight of the pPBSgMA compatibilizer
ρ	Density
a	Apparent weight of specimens in air
b	Apparent weight of specimens in water
l	Average Fibre Length
d	Average Fibre Diameter
V_s	Volume of sample
V_c	Volume of empty, closed sample chamber
V_e	Volume of the expansion chamber
m	Weight of sample
P_s	Density of sample
ΔE_{ab}	Total colour change
L	Lightness
a	chromacity coordinates represent the red-green direction
b	chromacity coordinates represent the yellow-blue direction

PENCIRIAN KOMPOSIT POLI(BUTILENA SUKSINAT) TERISI GENTIAN KULIT KENAF: SIFAT MEKANIKAL, PENYERAPAN AIR DAN PENCUACAAN.

ABSTRAK

Pencirian komposit poli(butilena suksinat) (PBS) terisi gentian kulit kenaf (KBF) ini melibatkan beberapa peringkat kajian. Pertamanya, kesan pembebanan gentian (10 – 40 % berat) terhadap sifat fleksural dan hentaman komposit telah dikaji. Kekuatan fleksural komposit didapati meningkat dengan peningkatan pembebanan gentian sehingga mencapai nilai optimum pada 30 % berat gentian (wt. %) dengan peningkatan sebanyak 9.4 % sebelum menurun dengan pembebanan seterusnya. Selain itu, modulus fleksural komposit juga meningkat sebanyak 87.1 – 424 % dengan peningkatan pembebanan KBF dari 10 ke 40 wt. %. Ini menunjukkan penambahan KBF pada pembebanan 30 wt. % telah menjanjikan keseimbangan prestasi dan pemprosesan kepada komposit. Walau bagaimanapun sifat kekekuan KBF telah menyebabkan penurunan kekuatan hentaman komposit tersebut. Keduanya, kesan panjang gentian (5, 10, 15 dan 20 mm KBF) terhadap sifat mekanikal komposit telah dikaji pada pembebanan 30 wt. %. Komposit dengan panjang gentian 10 mm telah menunjukkan peningkatan kekuatan dan modulus fleksural yang tertinggi iaitu sebanyak 16.7 dan 3.6%. Manakala komposit dengan 15-mm dan 20-mm KBF yang menpunyai gentian relatif yang lebih panjang pula menunjukkan kekuatan fleksural dan hentaman yang lebih rendah kerana gentiannya telah mengalami kerosakan yang teruk akibat kenaan ricihan mekanikal yang tinggi semasa proses penyebatian. Ini telah dibuktikan dengan analisis panjang, diameter dan nisbah aspek gentian. Peringkat ketiga memfokuskan kepada penambahbaikan pelekatan antaramuka gentian-matrix dengan menggunakan agen penserasi "maleated" PBS (PBSgMA) tidak tertulen dan tertulen. Bagi penyediaan PBSgMA, kepekatan pemula DCP telah ditetapkan pada 1 phr

manakala kepekatan MA divariasikan kepada 3 – 10 phr. Peningkatan kekuatan fleksural dan hentaman yang optimum telah dipemerkan oleh komposit dengan penambahan 5 wt. % agen penserasi tidak tertulen dan tertulen pada kepekatan MA 5 phr. Walau bagaimanapun sifat mekanikal komposit dengan agen penserasi tidak tertulen sedikit rendah berbanding komposit dengan agen penserasi tertulen kerana ia mengandungi baki MA yang tidak bertindak balas yang mana boleh menghalang pembentukan ikatan sempurna antara matrik dan gentian. Peringkat terakhir melibatkan penilaian prestasi penyerapan air dan pencuacaan semulajadi ke atas komposit tanpa dan dengan agen penserasi tertulen. Peningkatan kandungan air pada keseimbangan (M_m) lebih kurang 2.49 hingga 12.5 % berat telah diperhatikan dengan peningkatan pembebanan gentian dari 10 hingga 40 wt. % bagi komposit tanpa agen penserasi. Ini adalah disebabkan oleh kehadiran lebih banyak KBF yang bersifat hidrofilik di dalam komposit tersebut. Sebaliknya M_m bagi komposit dengan agen penserasi tertulen pada kepekatan MA 3 – 7 phr lebih rendah berbanding komposit tanpa agen penserasi. Ini berkemungkinan disebabkan oleh pembentukan pelekatan antaramuka gentian-matrik yang baik dengan kehadiran agen penserasi. Kesan kemerosotan sifat komposit akibat penyerapan air telah dibuktikan dengan penurunan sifat fleksural dan degradasi struktur komposit selepas ia direndam selama 90 hari. Pendedahan kedua-dua komposit tanpa dan dengan agen penserasi kepada pencuacaan semulajadi untuk tempoh 6 bulan telah menurunkan sifat fleksuralnya kerana ia telah mengalami degradasi pengoksidaan foto dan termal yang teruk semasa pendedahan tersebut. Walau bagaimanapun penurunan sifat fleksural terhadap pencuacaan yang dialami oleh komposit dengan agen penserasi tertulen lebih tinggi berbanding komposit tanpa agen penserasi kerana ia mengandungi lebih banyak bilangan kumpulan kimia yang boleh mengalami pengoksidaan semasa pencuacaan. Degredasi pencuacaan terhadap spesimen juga telah dibuktikan dengan analisis FTIR, pemeriksaan SEM dan analisis perubahan warna.

CHARACTERIZATION OF KENAF BAST FIBRE FILLED POLY (BUTYLENE SUCCINATE) COMPOSITES: MECHANICAL, WATER ABSORPTION AND WEATHERING PROPERTIES.

ABSTRACT

Characterization of kenaf bast fibre (KBF) filled poly(butylene succinate) (PBS) composites in this study involved several stages. Firstly, the effect of KBF loadings (10 – 40 wt. %) on flexural and impact properties were investigated. The flexural strength of the composites increased with increasing fibre loadings up to 30 wt. % with the highest value of about 9.4 % before decreasing with a further increase in fibre loading. The flexural modulus of the composites increased about 87.1 – 424 % with increasing KBF loadings from 10 to 40 wt. %. This indicates that the addition of KBF at 30 wt. % loading had resulted in a balance of performance and processability of the composites. However, the stiff nature of the KBF resulted in the reduction of the composites' impact strength. Secondly, the effect of fibre length (5, 10, 15 and 20 mm KBF) on the mechanical properties was investigated at fibre loading of 30 wt. %. Composite with 10 mm KBF length showed the highest increment in flexural strength and modulus of about 16.7 and 3.6%, respectively. The inferior flexural and impact strength of the composites with 15 mm and 20 mm KBF length could be due to the relatively longer fibres that underwent severe fibre attrition as a result of high mechanical shearing during the compounding. This was proven by analysis of the fibre length, diameter and aspect ratio. Third stage focused on the improvement of fibre-matrix interfacial adhesion by an introduction of unpurified and purified maleated PBS compatibilisers. For preparation of PBSgMA, DCP initiator concentration was kept constant at 1 phr while MA concentration was varied from 3 - 10 phr. The optimum enhancements in flexural and impact strength

were observed in both composites with addition of 5 wt. % unpurified and purified compatibilisers at 5 phr MA concentration. The inferior mechanical properties of the composites with unpurified compatibilisers to those with purified compatibilisers probably due to the presence of unreacted MA in the unpurified compatibilisers which could restrict the formation of complete bridging between matrix and fibres. The last stage involved evaluation of water absorption and natural weathering performance on both the uncompatibilised and compatibilised PBS/KBF composites. Increment about 2.49 to 12.5 wt.% in equilibrium water content (M_m) were observed for uncompatibilised composites with increasing fibre loading from 10 to 40 wt. %. This was attributed to the presence of more hydrophilic KBF in the composites. On the contrary, the M_m for the composites with purified compatibilisers at concentrations of MA 3 – 7 phr were lower than that of uncompatibilised composite. This may be due to the formation of a good fibre-matrix interfacial adhesion with the presence of purified compatibiliser. The deteriorating impact of water on the composites was proven by reduction in the flexural properties and degradation of the composites' structure after exposed to 90 days water immersion. Exposure of both uncompatibilised and compatibilised composites to natural weathering for a period of 6 months resulted in a decrease of the flexural properties due to severe photo- and thermal-oxidation degradation during the exposure. However, the reduction in flexural properties upon natural weathering observed for the composites with purified compatibilisers was higher than the uncompatibilised composites due to the higher content of chemical groups of the former, which were more susceptible to undergo oxidation during weathering. The degradation of specimens upon weathering was also proven by FTIR analysis, SEM examination and colour change analysis.

CHAPTER 1 – INTRODUCTION

1.1   Problem statement

Incorporation of non-biodegradable fillers such as glass, carbon, mineral and metallic fillers/fibres in polymer composites makes it difficult to dispose and recycle the composites (Goda *et al.*, 2006). Due to this reason, people prefer to use natural fibres/fillers to substitute the conventional fillers/fibres in certain composite applications such as house hold products, construction panels and interior automotive parts (Huda *et al.*, 2006; Shibata & Fukumoto, 2006). Lignocellulosic materials such as henequen, hemp, sisal, kenaf, coir, jute, palm and wood in their natural condition have been widely used as fillers for thermosetting and thermoplastic composites (Franco & Gonzalez, 2005a). Lignocellulosic fibres also contribute to the composite with high specific stiffness and strength, a desirable fibre aspect ratio, biodegradability, renewable resources and a low cost per unit volume basis (Franco & Gonzalez, 2005a).

In the Malaysian scenario, kenaf plant is identified as a new potential crop due to it fast growing characteristic and low pests attack in comparison to other local crops (Jalaludin, 2001). Kenaf bast fibre (KBF) which is extracted from outer bark of kenaf plant has superior strength compared to other lignocellulosic fibres but lower in comparison to synthetic fibres (i.e. E-glass, Kevlar and carbon fibres) (Bismarck *et al.*, 2005). Aside from such as low density, less machine wear during processing, no health hazards and a high degree of flexibility, KBF in short fibre form is also easy to be moulded into a product using conventional thermoplastic processing such as extrusion, compression moulding and injection moulding (Zampaloni *et al.*, 2007). However, the incorporation of KBF into conventional polymer composites does not

promise fully-biodegradable characteristics because the matrix phase is not capable of undergoing biodegradation. To produce a fully-biodegradable composite, a combination of natural fibre as a reinforcement and biodegradable polymer matrix is needed.

Recently, biodegradable composites have been developed using a wide range of biodegradable plastics and one of the commercially available synthetic biodegradable polymer is poly (butylene succinate) (PBS). PBS is semi-crystalline aliphatic thermoplastic polyester produced via polycondensation reaction of 1,4-butanediol and succinic acid (Fujimaki, 1998). It has processability and physical properties similar to that of PE, a tensile strength between PE and PP, and stiffness between LDPE and HDPE (Fujimaki, 1998; Uesaka *et al.*, 2000). PBS has also been proven to undergo degradation during disposal in compost, moist soil, fresh water with activated sludge and sea water and the biodegradability of the PBS is very much depending on the polymer structure (Fujimaki, 1998). However, there is a lack of wide-scale adoption of the PBS by industry due to the high cost of the synthetic biodegradable polymers. In order to mitigate the impact of the high material cost, incorporating of low cost fillers such as starch, lignocellulosic fibres and waste flour are the great choice (Sen & Bhattacharya, 2000; Baiardo *et al.*, 2004). The incorporation of low cost filler raise a great potential for the PBS composites to be used in various applications such as house hold products, construction panels and interior automotive parts.

However, the different polarity between hydrophilic lignocellulosic fibres and hydrophobic polymer matrix results in the lack of fibre-matrix interfacial adhesion and thus lead to poor mechanical properties and dimensional stability of the composites (Mehta et al., 2006; Friedrich *et al.*, 2005). The interfacial adhesion could

be optimized by introduction of fibre surface chemical treatment and interfacial compatibiliser (Bledzki & Gassan, 1999). Previously, various surface treatments such as treatment with alkali, silanes and anhydrides; and combination of treatment such as alkali-silane and alkali-acetic anhydride were reported by several workers (Aziz & Ansell, 2004; Bledzki & Gassan, 1999; Demir *et al.*, 2006). However, the utilization of compatibiliser is more economical in comparison to the chemical treatments because it only required a small amount of compatibiliser to enhance the composite properties (Arbelaiz *et al.*, 2005). In contrast, the chemical treatments usually require a large quantity of solvent and this made it impractical for a large scale production.

From the previous studies, MA treatment either by direct treatment on the fibre surface or by the introduction of maleated polyolefin such as MAPP and MAPE has been proven to be successful in improving the fibre-matrix interfacial adhesion (Maldas & Kokta, 1995; Rozman *et al.*, 2003). In addition, a lot of attempts have been made by previous researchers to produce compatibiliser based on the polymer-grafted-maleic anhydride such as MAPP and MAPE (Qiu *et al.*, 2005; Zhu *et al.*, 2006) and PBSgMA (Mani *et al.*, 1999). Several studies were also reported that the addition of PBSgMA compatibiliser could improve the mechanical properties of the lignocellulosic materials/PBS composites (Sen *et al.*, 2002; Tserki *et al.*, 2006). In this presence study, PBS/KBF composites were added with unpurified and purified PBSgMA in order to investigate the effect of the purification process on compatibiliser performance. The use of lignocellulosic fiber-polymer composites in outdoor applications make it is necessary to examine the durability of the composites against natural weathering and water absorption because the composite products are usually exposed to solar degradation and moisture during service life (Tajvidi *et al.*,

2006; Zou *et al.*, 2008). There appears to be very least studies reported on PBS/KBF composite system and no study reported on the durability of composites compatibilised with PBSgMA upon exposure to hot and humid tropical climate natural weathering.

1.2   Research objectives

In this study, attempts were made to produce a fully biodegradable composite by incorporating of kenaf bast fibre (KBF) in poly (butylene succinate) (PBS) composite. There are four research objectives for this study:

(1) To investigate the effect of fibre loading (10, 20, 30 and 40 wt. %) on PBS/KBF composite properties. KBF with length of 5 mm was used in this study and the composites were compounded based on the predetermined parameters as outlined in Section 3.3.1. The aim of this study was to determine the optimum fibre loading where the PBS/KBF composite exhibited optimum value in mechanical properties.

(2) To observe the effect of fibre length (5, 10, 15 and 20 mm KBF) on the flexural and impact properties of PBS/KBF composites with 30 wt. % KBF loading. The effect of composites compounding on the final fibre length and diameter distributions and aspect ratio of the KBF were also carried out. Composite with optimum fibre length which obtained the highest mechanical properties was used in the next study on the effect of maleated compatibiliser addition.

(3) To investigate the effect of unpurified (PBSgMA) and purified (pPBSgMA) maleated PBS compatibilisers addition to the PBS/KBF composites mechanical properties. The fibre-matrix interfacial adhesion for the compatibilised composites was also proven by SEM examination. The comparison of mechanical properties between composites with unpurified and purified compatibilisers was also carried out to investigate the effect of the compatibiliser purification on its performance. Prior to composite preparation, the compatibilisers were characterized by FTIR analysis and titration acid groups derived from the anhydride functional groups to determine the grafting degree.

(4) To evaluate the performance of PBS/KBF composites against water absorption and natural weathering. Neat PBS and its composites; and selected purified PBSgMA compatibilised composites were chosen for this study. The effect of water absorption was determined by measuring the water uptake of the specimens upon 90 days water immersion. The deterioration impact of water during the immersion was also determined by measuring the percent of change and recovery on the specimens' flexural properties. The natural weathering study was carried out on the selected specimens for a maximum period of 6 months in order to investigate the durability of the specimens under warm and humid tropical climate of Malaysia. The effect of natural weathering on the flexural properties was examined for every 2 months for a total of 6 months exposure. The specimens' degradation upon weathering was also proven by FTIR analysis, SEM examination and colour change analysis.

CHAPTER 2 – LITERATURE REVIEW

2.1   Introduction

Applications for lignocellulosic fibre thermoplastic composites are gaining acceptance due to renewed interest in the environment. The trend toward "environmental friendly" and "biodegradability" is the driving force behind the increased utilization of lignocellulosic fibre polymer composites (Doan et al., 2006). In the automotive industry, weight reduction, improved mechanical properties, acoustic properties, recycle ability, and cost reduction are the dominant factors (Bismarck *et al.*, 2005). The main utilization of lignocellulosic fibre composites is in the production of interior automotive parts such as door, head liners, parcel shelves, seat backs, interior sunroof shields and headrests (Mueller and Krobjilowski, 2003; Clemon & Caulfield, 2005). The thermoplastic polymers are widely used due to its easiness to be processed into a product, capable of undergoing repeated cycles of softening and hardening and the process is reversible (Obewele, 2000).

2.2   Matrix

Matrix by definition is a continuous phase that filled free volume uncovered by filler. Matrix is divided into two major groups known as thermoset and thermoplastic. Generally, matrix acts as a glue to hold fillers/fibres together and protect the fillers/fibres from mechanical and environmental damage (American Composites Manufacturers Association, 2004). In composite system, matrix phase plays role as a medium to transfer stresses through the fibre-matrix interface to the reinforcement or filler. However, the applied stresses can only be transferred efficiently from the matrix to the dispersed phase if the composite system can obtain

a good fibre/filler-matrix interfacial adhesion (Franco & Gonzalez, 2005b). In case of natural fibre filled polymer composite, the incompatibility between the composite components resulted in poor stress transfer from the matrix phase to the incorporated filler (Khan & Bhattacharia, 2007). As a consequence, the composite will fail prematurely.

2.2.1 Thermoplastics

Based on the thermal or thermo-mechanical scheme, thermoplastic can be defined as polymer that softens and flows under an action of heat and pressure, and hardens upon cooling and assumes the shape of the mould (Obewele, 2000). Compounding thermoplastic with appropriate ingredients, can usually withstand several of these heating and cooling cycles without suffering any structural breakdown (Chanda & Roy, 2007). Among thermoplastics that are used as the matrix in reinforced plastics, the largest tonnage group is polyolefins, followed by nylon, polystyrene, thermoplastic polyesters, polyacetal, polycarbonate, and polysulfone (Obewele, 2000). The choices of thermoplastics are dictated by the type of application, the service environment, and the cost. Nowaday, new generation of thermoplastic which is known as biodegradable thermoplastic has been produced commercially due to its environmentally friendly properties (ExcelPlas Australia, 2002).

2.2.2 Biodegradable polymers

Biodegradable thermoplastic is the new interest recently. The biodegradable thermoplastics are widely produced due to growing awareness of the inter connectivity of global environmental factors, principles of sustainability, industrial

ecology, eco-efficiency, green chemistry and engineering are being integrated into the development of the next generation of materials, products, and processes (Friedrich *et al.*, 2005). The biodegradable thermoplastic can be produced from bio based resources like cellulose, soy protein and starch. However, some bio-based renewable resources were modified by addition of the biodegradable functional group such as PBS, PBSA, PSU and PLA (Fujimaki, 1998; Lee & Wang, 2006).

Non-biodegradable polymers are not incorporated into the carbon cycle and thus, increase the landfill capacity during the disposal (Kim *et al.*, 2000). The utilization of biodegradable materials is the best way to keep our world green. A lot of plastic wastes that made of polyolefins are disposed everyday, but they take hundred of years to be decomposed through the conventional way (Clarinval & Halleux, 2005). Due to the risen of environmental concern, a lot of biodegradable plastics are developed, one of them is poly(butylene succinate) (PBS). It has excellent biodegradability in the natural environment such as soil, lake, sea, and compost and has mechanical properties comparable with the general purpose thermoplastic such as PE,PP and PS (Lee *et al.*, 2005). In general, biodegradable polymers can be classified in terms of its degradation mechanisms i.e. biodegradable, compostable, hydro-biodegradable, photo-biodegradable and bioaerodable (ExcelPlas Australia, 2002). Biodegradable polymers are usually classified as environmentally biodegradable plastic because they degraded in combination of more than 1 mechanism. Normally, it decomposed into carbon dioxide, methane, water and inorganic compounds by enzymatic action of micro-organisms (ExcelPlas Australia, 2002).

2.2.3 Poly(butylene succinate) (PBS)

PBS is aliphatic polyester by structure and produced through polycondensation reaction of 1,4-butanediol and succinic acid (Fujimaki, 1998). Polycondensation reaction between glycol and aliphatic dicarboxylic produces different aliphatic polyester depending on types of glycol and aliphatic dicarboxylic that are used. According to Fujimaki (1998) several aliphatic polyesters were produced commercially such as polybutylene succinate (PBS), polybutylene succinate adipate (PBSU-AD), polyethylene succinate (PESU), polyethylene succinate adipate (PESU-AD). The unit structures of the aliphatic polyesters are shown in Figure 2.1.
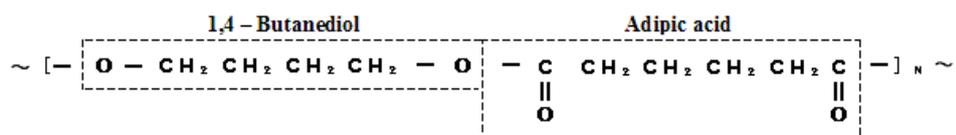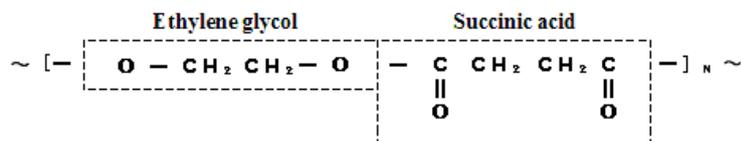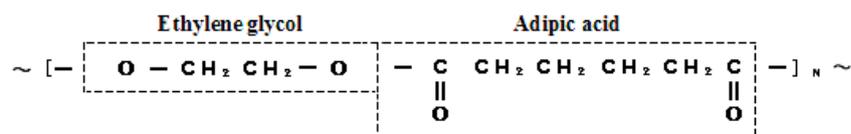
Figure 2.1: Unit structures of aliphatic polyesters (Fujimaki, 1998)

In the natural environment, PBS decomposes into water and carbon dioxide (Showa Highpolymer Co. Ltd, 2007). PBS has been used in various applications such as films, sheets, filaments, nonwoven fabrics, laminates, molded foam products and injection-molded products (Fujimaki., 1998). PBS with the trade name of Bionolle (Showa Highpolymer Co. Ltd, Japan) has been proven to be biodegradable in the natural environment and has awarded with "OK Compost" label from AIB-Vincotte (AVI), the Belgian Certification and Screening Body, as an indication of its capacity to decompose thoroughly in compost (Showa Highpolymer Co. Ltd, 2007). The scope of application fields for PBS is growing, and it is currently used in agriculture and fishery applications, civil engineering and construction; and for common household goods (Showa Highpolymer Co. Ltd, 2007). Showa Highpolymer is one of PBS manufacturer that is working to develop systems with lower cost and could give benefit to a wider segment of applications. PBS is friendly with nature because it has excellent biodegradability in soil, fresh water, sea water and compost (Fujimaki, 1998). The biodegradability of aliphatic polyesters is very much depending on their polymer structure and can be summarized as in Table 2.1.

Table 2.1: Relationship between polymer structures and biodegradability of aliphatic polyester (Fujimaki, 1998).

Biodegradability Test	Poly(butylene Succinate) (PBS)	Poly(butylene succinate-co-adipate) (PBSU.AD)	Poly(ethylene succinate) (PESU)
In hot compost	Normal	Rapid	Normal
In moist soil	Normal	Rapid	Normal
In the sea	Slow	Rapid	Slow
In water with activated sludge	Slow	Slow	Rapid

2.3   Fillers/fibres

In general, incorporation of filler is essential to modify properties of a composite such as physical properties, mechanical properties, flame/smoke, shrinkage control and weight management (Clemons & Caulfield, 2005). Filler not only reduce the cost of composite, but also frequently impart performance improvements that might not otherwise be achieved by the reinforcement or resin ingredients alone (Clemons & Caulfield, 2005). Filler can be defined as dispersed phase in composite materials and also can be defined as foreign constituent added to a matrix material that usually modified the properties of the composites (Tolinski, 2009).

Fibre reinforced composites can be classified into two main categories usually referred to short fibre and continuous fibre reinforced materials. Continuous reinforced materials often constitute of a layered or laminated structure. The woven and continuous fibre styles are typically available in a variety of forms, being pre-impregnated with the given matrix (resin), uni-directional tapes of various widths, plain weave, harness satins, braided, and stitched (Huang & Ramakrishna, 2002). The short fibres are typically employed in compression molding and sheet molding operations .They come in the form of flakes, chips, and random mat (which can also be made from a continuous fibre laid in random fashion until the desired thickness of the ply / laminate is achieved) (Huang & Ramakrishna, 2002).

2.3.1   Lignocellulosic based fibre/filler

Plants derived fibre such as jute, sisal, kenaf and hemp are traditionally used since the start of human kind. In A. D. 105 Ts'ai Lun of imperial court of China found a way to make paper sheets using mulberry fibre and other bast fibres along

with fish net, old rags, and hemp waste (Bismarck *et al.*, 2005). Nowadays, the utilization of plant fibres in plastic composites especially in automotive interior parts applications are widely commercialised. According to Bismarck *et al.* (2005) natural fibres can be classified into 3 major parts, vegetable (cellulose), animal (protein) and mineral fibres as shown in Figure 2.2.
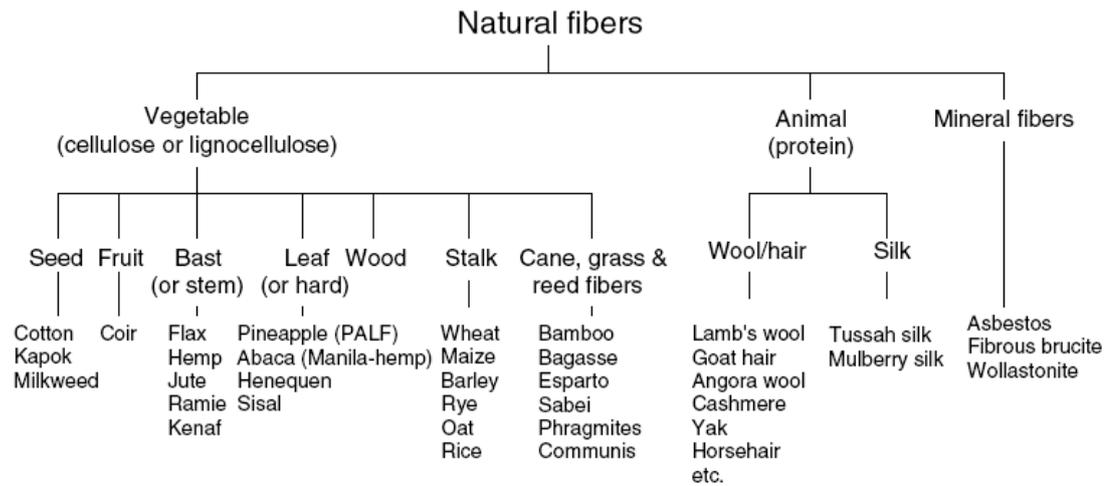
Figure 2.2: Classification of natural fibres (Bismarck *et al.*, 2005)

Recently, there has been a gaining of interest in the use of lignocellulosic fibres as reinforcements in plastic composites due to their outstanding mechanical performance and perceived environmental advantages. However, issues such as lack of established delivery channels, processing complications due to the low density of the fibres (feeding, metering, and bridging) and performance issues such as odor control are limiting the wider use of natural fibres as reinforcements in thermoplastics based composites (Clemons & Caulfield, 2005). Some plant fibres like industrial hemp, flax, kenaf, coir and henequen exhibit good mechanical properties, especially on a weight basis. This makes them competitive to glass fibres as reinforcement in certain composite applications (Van de Weyenberg *et al.*, 2006; Mehta *et al.*, 2006). Lately, composites filled natural fibre receive increasing

attention both by academia and industry due to the natural fibres properties; renewable, biodegradable, less abrasive to tooling, and less irritating to the skin and respiratory system (Bos *et al.*, 2006). Incorporation of natural fibres could also reduce the composite cost due to their low processing cost and abundantly available resources (Mutje *et al.*, 2007). Besides some other natural fibres such as empty fruit bunches (EFB), coir and wood fibre were reported to have good performance as filler in plastic composites (Abdul Khalil *et al.*, 2007; Geethamma *et al.*, 2005; Neagu *et al.*, 2005). However, fibre quality and agronomic aspects of the fibre, such as disease and lodging resistance should be improved (Van Dam, 2000). Other than that, the homogeneity of a batch in colour and lustre of the fibre is very important aspect, especially in textile application (Van Dam, 2000).

The incompatibility issue between natural fibre and polyolefin is a major drawback in producing good quality composites. Several techniques could be applied to overcome the incompatibility and the poor interfacial adhesion between natural fibre and polyolefin such as introduction of maleated polyolefin compatibiliser and fibre surface treatments/modifications (Bledzki & Gassan, 1999; Demir *et al.*, 2006; Qiu *et al.*, 2005). The strong interfacial bonding strength that is obtained by improving the compatibility between hydrophilic filler and hydrophobic polymer matrix enhances the physical, mechanical and thermal properties of the composites (Yang *et al.*, 2007). The hygroscopic nature of the natural fibres usually limits the use of the fibres in applications that involve exposure to atmosphere or contact with aqueous media (Najafi *et al.*, 2007). The poor resistance of the natural fibres to water absorption is expected to result in the undesirable effects to the mechanical properties and the dimensional stability of the composites (Espert *et al.*, 2004). According to Panthapulakkal & Sain (2007) the poor water resistant of the natural

fibre could be overcome by introducing physical and chemical fibre pre-treatment and incorporating of coupling agent. The fibre pre-treatment is expected to reduce the hydrophilicity of the fibre while the incorporation of coupling agent could help in improving the fibre-matrix interfacial adhesion.

2.3.2   Kenaf plant

Kenaf (*Hibiscus cannabinus L.*) is annual row corps from the Malvaceae family is a valuable native plants in Africa and India (Jalaludin, 2001). Nowadays, kenaf is widely cultivated in many parts of the world such as Europe, South America, Mexico, United States, Japan, China and India (Jalaludin, 2001). Kenaf also known as mesta (Bengal, India), palungi (Madras), decan hemp (Bombay), ambari (Taiwan), Java jute (Indonesia), pupoula de Sao Francisco (Brazil) and there are more than 129 common names for kenaf has been recognized (Jalaludin, 2001). Kenaf is woody-stemmed herbaceous dicotyledons plant grown in the tropics and subtropics, from the bast of whose stems fibres can be extracted (Rowell & Han, 1999). It requires less water to grow than jute and can adapt to a wider variety of soils and climates (Rowell & Han, 1999).

2.3.2.1 Growing & harvesting

Kenaf grows quickly, rising to heights of about 4 - 5m in a 5 – 6 month growing season and 25 - 35 mm in diameter at maturity and is ready to be harvested to get the fibre (Rowell & Han, 1999). There are several combinations of factors effecting the growth of kenaf plants such as rain fall, temperature, soil fertiliser and etc (Rowell & Han, 1999). Normally, kenaf plants are harvested at different times during the plant life cycle according to utilization of the fibre. For example in paper

and composites, kenaf are harvested at the end of the growing season, allowed to dry in the field and then processed into fibre (Rowell & Han, 1999). According to Rowell & Han (1999) the content of cellulose fibre is the highest during the maturity time and promising outstanding fibre strength, but in pulp application the kenaf is harvested before maturity to reduce the lignin content in the fibre.

2.3.2.2 Retting

After harvesting the kenaf plant, the fibre should be separated and extracted from woody tissue of the fibre crops. This retting process involves separation of technical fibre bundles from the central stem and loosening the fibres from the woody tissue (Bismarck *et al.*, 2005). There are several retting techniques can be adopted to extract the fibre and the techniques can be classified as in Figure 2.3.
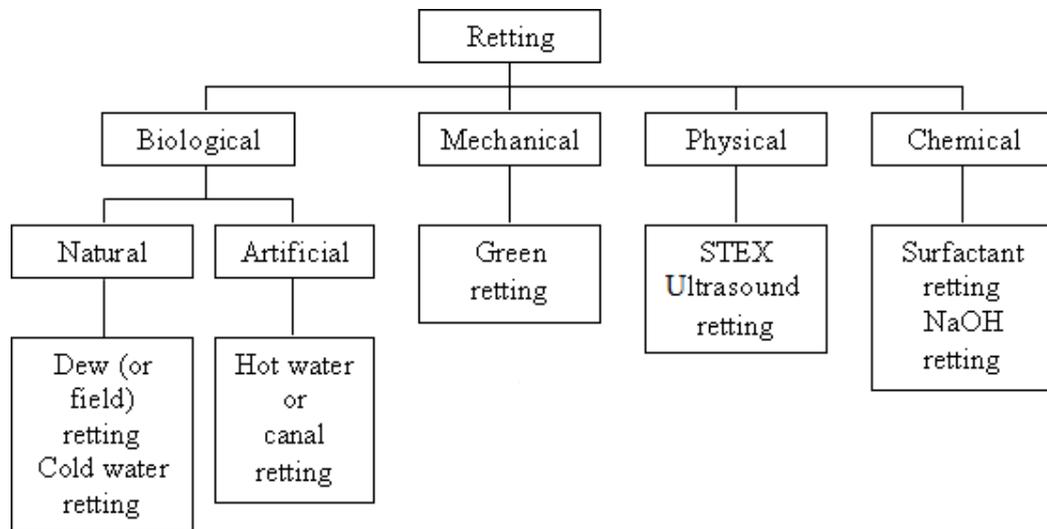
Figure 2.3: Classification of commercial retting techniques (Bismarck *et al.*, 2005).

From all these retting techniques discovered, the most common technique is dew or field retting, traditionally cold water retting and mechanical retting (Morrison *et al.*, 1999). Biological retting is much preferred because it produces superior fibre

quality (Morrison *et al.*, 1999). Dew retting by means of exposed the fibre bundle to the environment on the field until microorganisms separate the fibres from the cortex and xylem (Bismarck *et al.*, 2005). The degradation of the cortex primarily occurs due to the action of indigenous fungi. Mycelium grows on the carbohydrate-rich tissue, utilises the easily access pectin, and degrades the pectin in the phloem with excreted enzymes (Bismarck *et al.*, 2005). However, the retted fibre quality is highly depended on weather conditions, rainfall and humidity, sun hours, temperature, and the way the fibre crops are spread on the ground (Morrison *et al.*, 1999; Bismarck *et al.*, 2005).

Traditional cold-water retting is mainly used by fibre producers in Eastern Europe and the process utilises anaerobic bacteria that break down the pectin of plant straw bundles submerged in huge water tanks, ponds, hamlets or ditches, rivers, and vats (Bismarck *et al.*, 2005). The process takes between 7 and 14 days and depends on the water type, the temperature of the retting water, and bacterial inoculation (Bismarck *et al.*, 2005). The process produces high quality fibres, but it can cause environmental pollution due to unacceptable waste water of organic fermentation (Bismarck *et al.*, 2005). However, this retting process is still being practiced in certain countries such as India and Bangladesh due to low cost and produce good quality of retted fibre (Bismarck *et al.*, 2005). Mechanical or green retting is much simpler and more cost-effective alternative to separate the bast fibres from the plant straw or stem. The raw material for this procedure is either field dried but only slightly retted (2 to 3 days, but 10 days maximum) (Bismarck *et al.*, 2005). The bast fibres are separated from the woody part by mechanical means. However, the produced green fibres are much coarser and less fine as in comparison to dew retted or water retted fibres and unsuitable for textile application (Bismarck *et al.*, 2005).

2.3.2.3 Physical characterization

Physically, the kenaf plant can be recognized by large yellow flowers with crimson centre, 3-7 lobed palmate upper leaves and heart-shaped lower foliage (Idris, 2001). It also has bristly around 2 cm fruits (Idris, 2001). Generally, kenaf upper leaves have 5 lance-shaped lobes but some other varieties have a solid leaf shape especially for many hibiscus varieties (Idris, 2001). Kenaf stalk is green and round in shape and has tiny thorns on the outer surface (Rowell & Stout, 1998). The size of the stalk is very depending on its variety. However, the diameter of a kenaf stalk is around 3 cm and become smaller with the height of the stalk (Rowell & Stout, 1998). The kenaf stalk consists of 3 main parts; core, bast and inner bast as illustrated in Figure 2.4:
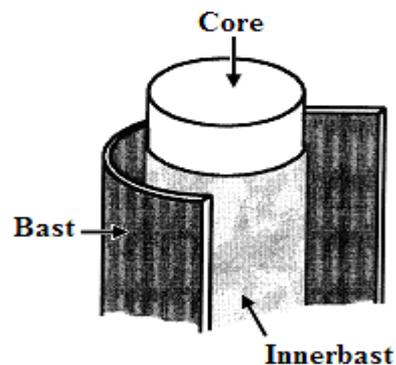
Figure 2.4: Parts of kenaf stalk (Nishimura *et al.*, 2002).

2.3.2.4 Chemical composition

Chemical composition and structure made-up of natural fibres vary greatly and depend on the resources and processing methods. Most plant fibres except for cotton are composed of cellulose, hemicelluloses, lignin, waxes, and some water-soluble compounds, where cellulose, hemicelluloses, and lignin are the major constituents (Bismarck *et al.*, 2005). However, the chemical contents are different

according to the variety, location of plantation, climates, irrigation and environmental aspects (Bismarck *et al.*, 2005). Chemical composition, moisture content, and microfibrillar angle of several vegetable fibres are shown in Table 2.2. Cellulose can be considered as the major component of natural fibre. It is a highly crystalline, linear polymer of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by β -1,4-glycosidic linkages with a degree of polymerization (n) of around 10,000 (Bismarck *et al.*, 2005). The structure of cellulose is illustrated in Figure 2.5. It is the main component providing the strength, stiffness, and structural stability to plants. Hemicelluloses are polysaccharides branched polymers containing 5 and 6 carbon sugars of varied chemical structure, the molecular weights are below the cellulose but still contribute as a structural component of wood (Bismarck *et al.*, 2005).

Table 2.2: Chemical composition, moisture content, and microfibrillar angle of lignocellulosic fibres (Bismarck *et al.*, 2005).

Fibre	Cellulose (wt. %)	Hemicellulose (wt. %)	Lignin (wt. %)	Pectin (wt. %)	Moisture Content (wt. %)	Waxes (wt. %)	Micro-fibrillar Angle (deg)
Flax	71	18.6-20.6	22	2.3	8-12	1.7	5-10
Hemp	70-74	17.9-22.4	3.7-5.7	0.9	6.2-12	0.8	2-6.2
Jute	61-71.5	13.6-20.4	12-13	0.2	12.5-13.7	0.5	8
Kenaf	45-57	21.5	8-13	3-5			
Ramie	68.6-76.2	13.1-16.7	0.6-0.7	1.9	7.5-17	0.3	7.5
Nettle	86				11-17		
Sisal	66-78	11-14	10-14	10	10-22	2	10-22
Henequen	77.6	4-8	13.1				
PALF	70-82		5-12.7		11.8		14
Banana	63-64	10	5		10-12		
Abaca	56-63		12-13	1	5-10		42
Oil palm EFB	65		19				
Oil palm mesocarp	60		11				46
Cotton	85-90	5.7		0-1	7.85-8.5	0.6	-
Coir	32-43	0.15-0.25	40-45	3-4	8		30-49
Cereal straw	38-45	15-31	12-20	8			
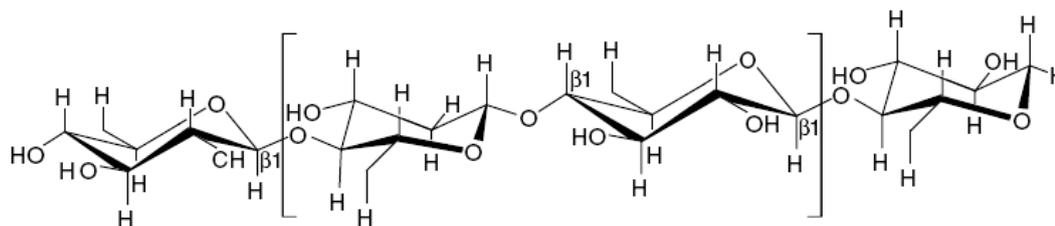
Figure 2.5: Probable structure of cellulose (Bismarck *et al.*, 2005).

Lignin is an amorphous, cross-linked polymer network consisting of an irregular array of variously bonded hydroxy-and methoxy-substituted phenyl propane units (Rowell & Han, 1999). The chemical structure varies depending on its source as well as the way in which they are combined. Lignin is less polar than cellulose and acts as a chemical adhesive within and between fibres, and the probable structure of lignin showed in Figure 2.6.
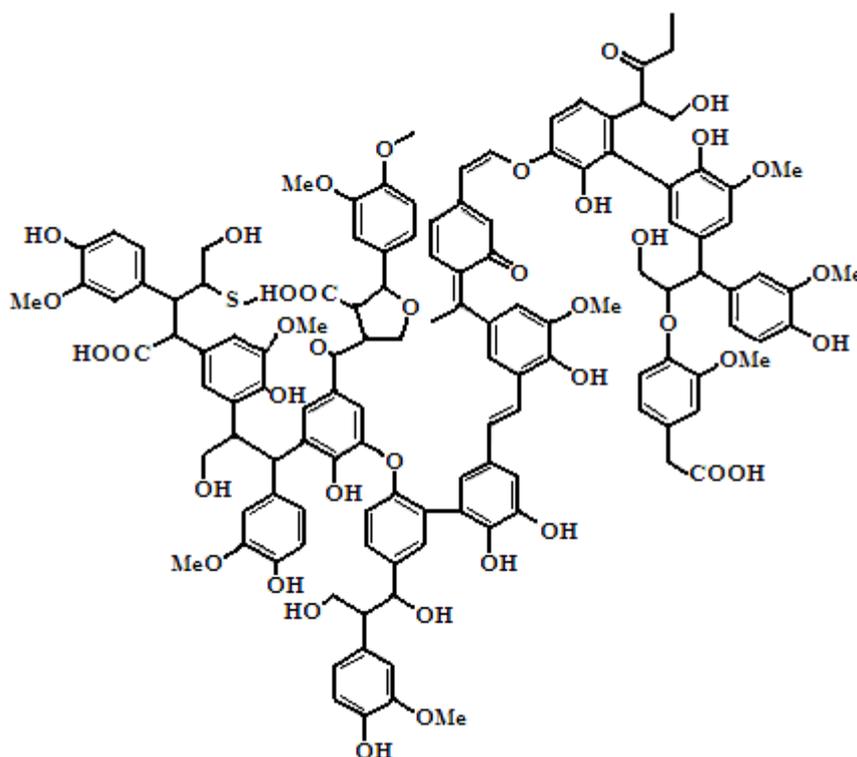
Figure 2.6: Probable structure of lignin adopted from pine kraft lignin structure
(Thielemans & Wool, 2005).

Pectins are complex polysaccharides, the main chains of which consist of a modified polymer of glucuronic acid and residues of rhamnose. Their side chains are rich in rhamnose, galactose, and arabinose sugars (Neto *et al.*, 1996). Pectins are important in non-wood fibres, especially bast fibres. The lignin, hemicelluloses, and pectins collectively function as matrix and adhesive, helping to hold together the cellulosic framework structure of the natural composite fibre (Neto *et al.*, 1996). Natural fibres including kenaf fibre also contain lesser amounts of additional extraneous components, including low molecular weight organic components (extractives) and inorganic matter (ash) (Neto *et al.*, 1996). Normally, the ash content in kenaf bast is about 7.3 – 9.2% and in kenaf core is about 4.2-6.0% (Neto *et al.*, 1996).

2.3.3 Kenaf bast fibre

Kenaf bast fibre can be extracted from outer bark of the kenaf stalk which has long fibre and high strength. The fibre was conventionally used for twines, cordage, and ropes, and now it is being explored for material use in apparels and non-woven composites (Parikh *et al.*, 2002).

2.3.3.1 Characterization of kenaf bast fibre

Physically, kenaf bast fibre is similar to jute fibre but in terms of fibre structure, kenaf bast fibre made-up of the rings of fibre cell bundles form a tubular mesh that encases the entire stem from top to bottom (Rowell & Stout, 1998). Two layers can usually be distinguished, connected together by lateral fibre bundles, so that the whole sheath is really a lattice in three dimensions (Rowell & Stout, 1998).

The cell bundles form links of the mesh, but each link extends only for a few centimeters before it divides or joins up with another link (Rowell & Stout, 1998).

Kenaf bast fibre also referred to the sheath extracted from the plant stems, whereas a single fibre is a bundle cells forming one of the links of the mesh (Rowell & Stout, 1998). Each cell is roughly polygonal in shape, with a central hole, or lumen, comprising about 10 % of the cell area of cross section. In longitudinal view, the fibre appears as overlapping of the cells along the length of the fibre. The cells are firmly attached to one another laterally, and the region at the interface of two cells is termed the middle lamella (Rowell & Stout, 1998). Separation of cells seen to be threadlike bodies ranging from 0.75 to 5 mm in length, which are referred to as ultimate cells (Rowell & Stout, 1998). A single fibre thus comprises a bundle of ultimate cells. Transverse selections of single fibres show that the numbers of ultimate cells in a bundle range from a minimum of 8 or 9 to a maximum of 20 – 25 and the single fibres are only about 1 - 7 mm long and about 10-30 microns wide (Rowell & Stout, 1998). Figure 2.7 shows the micrograph of kenaf fibre cross-section.
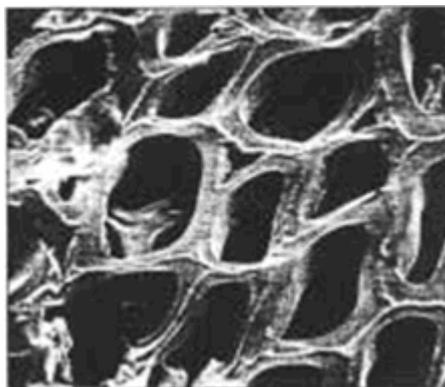

Figure 2.7: Kenaf bast fibre cross section (Zhang, 2003).
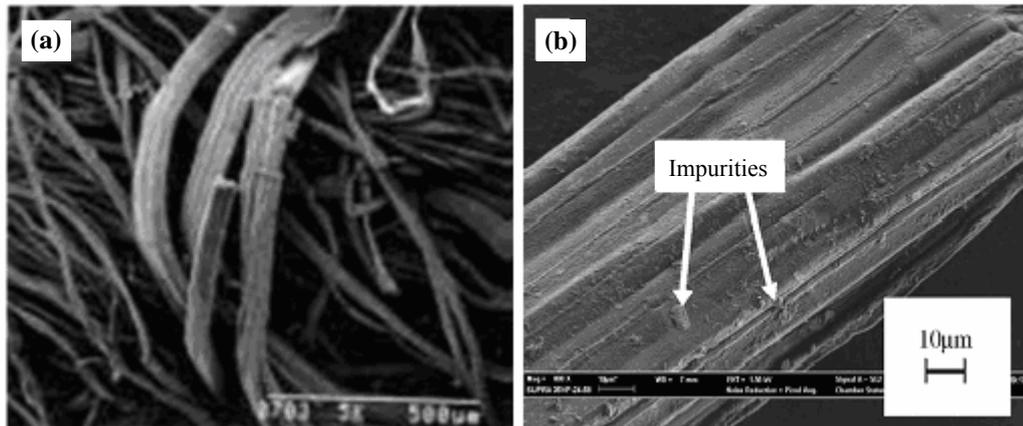
Figure 2.8: (a) Kenaf bast fibre in bundle form (Zhang, 2003), (b) Impurities on kenaf bast fibre surface (Edeerozey *et al.*, 2006).

Surface of kenaf bast fibre is coarse and clearly shows the presence of impurities on the fibre surface as shown in Figure 2.8 (b). The surface impurities originate from the residual of waxy epidermal tissue, adhesive pectin and hemicelluloses which adhere on the fibre surface (Herrera-Franco & Valadez-Gonzalez, 2005).

Physical and mechanical performances of kenaf bast fibre are very depending on species, a natural variability within species, and differences in climates and growing seasons (Clemons & Caulfield, 2005). According to a study reported by Ogbonnaya *et al.* (1997) the specific gravity of the kenaf stalk is not a variable factor for the first 6 weeks of growing but the increment in specific gravity of kenaf stalk start after 8th week of growing and gradually increases thereafter. The specific gravity of kenaf is adversely affected by water stress due to unfavourable carbon balance during drought, leading to the starvation of the plants and under-development of the cell wall (Ogbonnaya *et al.*, 1997). The mechanical performance of KBF is good but not as good as the synthetic fibres such as glass and carbon fibres. The balance of significant reinforcing potential at low cost and low density is part of the reason why they are attractive to industries like automotive manufacturing. From Table 2.3, the fibre length of kenaf is higher than sisal, jute, hardwood and softwood,

so it contributes to higher aspect ratio which promotes better interaction with matrix of composite system (Clemons & Caulfield, 2005). As shown in Table 2.4 tensile properties of kenaf bast fibre are outstanding compared to other natural fibres but slightly lower compared to synthetic fibres (i.e. E-glass, kevlar and carbon fibres).

Table 2.3: Dimensions of selected natural fibres (Clemons & Caulfield, 2005).

Fibre Type	Length (mm)		Width (μm)	
	Average	Range	Average	Range
Flax	33	9 – 70	19	5 – 38
Hemp	25	5 – 55	25	10 – 51
Kenaf	5	2 – 6	21	14 – 33
Sisal	3	1 – 8	20	8 – 41
Jute	2	2 – 5	20	10 – 25
Hardwood	1	-	-	15 – 45
Softwood	-	3 – 8	-	15 – 45

Table 2.4: Characteristic values for the density, diameter, and mechanical properties of natural and synthetic fibres (Bismarck *et al.*, 2005).

Fibre	Density (g cm^{-3})	Diameter (μm)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
Flax	1.5	40 – 600	345 – 1500	27.6	2.7 – 3.2
Hemp	1.47	25 – 500	690	70	1.6
Jute	1.3 – 1.49	25 – 200	393 – 800	13 – 26.5	1.16 – 1.5
Kenaf			930	53	1.6
Ramie	1.55	–	400 – 938	61.4 – 128	1.2 – 3.8
Nettle			650	38	1.7
Sisal	1.45	50 – 200	468 – 700	9.4 – 22	3-7
Hanequen					
PALF		20 – 80	413 – 1627	34.5 – 82.5	1.6
Abaca			430 – 760		
Oil palm EFB	0.7 – 1.55	150 – 500	248	3.2	25
Oil palm mesocarp			80	0.5	17
Cotton	1.5 – 1.6	12 – 38	287 – 800	55 – 12.6	7 – 8
Coir	1.15 – 1.46	100 – 460	131 – 220	4 – 6	15 – 40
E-glass	2.55	< 17	3400	73	2.5
Kevlar	1.44		3000	60	2.5 – 3.7
Carbon	1.78	5 – 7	3400[a] – 4800[b]	240[b] – 425[a]	1.4 – 1.8

[a] Ultra high modulus carbon fibres.
[b] Ultra high tenacity carbon fibres.

2.3.3.2 Utilization of kenaf bast fibre

Kenaf bast fibre is used traditionally for twine, cloth, rope, burlap, carpet felting and forage for animals. This bast fibre can be an alternative fibre for pulp and paper due to it superior quality of pulp than the commercial hardwood, and its paper has tear resistance comparable to that made of softwood pulps (Ayerza & Coates, 1996). Besides, kenaf bast pulps have two major benefits; (1) high yield and (2) low lignin content which is suitable as raw material for pulp and paper (Han *et al.*, 1999). Kenaf bast fibre also has been used as reinforcement for unsaturated polyester composites. Incorporation of alkali treated kenaf bast fibre in unsaturated polyester composite proven that it could enhance strength and rigidity of the composites (Aziz & Ansell, 2004). The composites have mechanical strength characteristics of glass-filled plastics but are less expensive and light in weight. In 1996 the utilization of kenaf for interior automotive panels was pioneered by Ford Company Limited in their car, Ford Mondeo (GM inside news.com, 2008).

In construction and housing industries kenaf/plastic composites are molded into lightweight panels and claimed to be suitable to replace wood and wood-based products in many applications. Examples of extruded profiles of kenaf thermoplastic products are shown in Figure 2.9. Kenaf bast fibre also has been used in production of lightweight laminate composites made from kenaf and polypropylene (PP) fibres for indoor panel applications (Shibata & Fukumoto, 2006). Besides, kenaf/thermoplastic composites are also suitable to be moulded into commercial food storage containers and virtually any other products which made of plastic. Non-food related packaging opportunities are also numerous, including bulk chemical and pharmaceutical packaging, parts packaging in the electrical and electronics industries, and disposable packaging for large consumer appliances (Shibata &

Fukumoto, 2006). Recently, kenaf and several other fibres i.e., flax, bamboo, pineapple, silk, sisal and jute, and ramie have been used as reinforcement for biodegradable composites due to advantages such as renewability, low density, and high specific strength (Ochi, 2008).
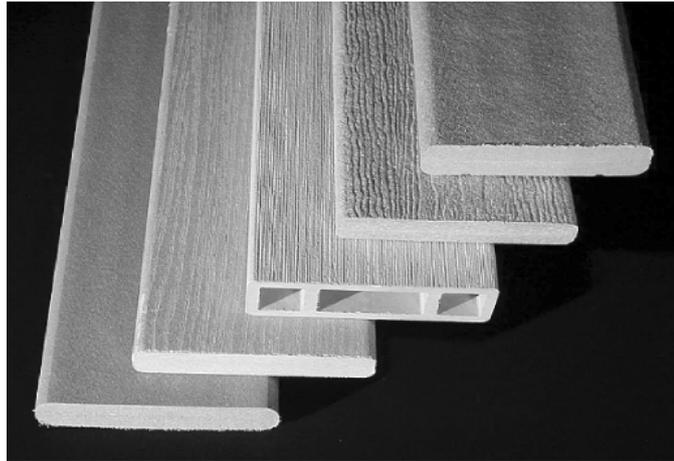

Figure 2.9: Extruded kenaf thermoplastic products.

2.4   Fibre-matrix interface

In general, interface is defined as a perfect two-dimensional (2-D) mathematical surface dividing into two distinguished phases or components (Jancar, 2003). In composite system, interface is defined as a surface formed by a common boundary of reinforcing fibre and matrix that are in contact with and maintains the bond in between for the transfer of loads (Kim & Mai, 1998). In contrast, interphase is defined as a geometrical surface of the classic fibre-matrix contact as well as the region of finite volume extending there from, where in the chemical, physical and mechanical properties vary either continuously or in a stepwise manner between those of the bulk fibre and matrix material (Kim & Mai, 1998). For the investigation purpose of stress transfer from the matrix to the reinforcement, all stress transfer phenomena are assumed to take place at the fibre-matrix interface and the stress