

**WATER ABSORPTION AND HYGROTHERMAL
AGING BEHAVIOR OF KENAF FIBER-
REINFORCED POLY(LACTIC ACID)
COMPOSITES**

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**WATER ABSORPTION AND HYGROTHERMAL AGING BEHAVIOR OF
KENAF FIBER-REINFORCED POLY(LACTIC ACID) COMPOSITES**

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘Water Absorption and Hygrothermal Aging Behavior of Kenaf Fiber-Reinforced Poly(lactic acid) Composites’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

ΔH_{cc}	Cold crystallization enthalpy
T_{cc}	Cold crystallization temperature
$^{\circ}\text{C}$	Degree Celsius
D	Diffusion coefficient
ΔH_c	Enthalpy of melt crystallization
ΔH_m°	Fusion enthalpy of the completely crystalline material
GPa	Giga pascal
T_g	Glass transition temperature
W_0	Initial weight of samples
kV	Kilovolt
MPa	Mega pascal
T_c	Melt crystallization temperature
ΔH_m	Melting enthalpy
T_m	Melting temperature
m^3	Metre cube
mg	Milligram
mm	Millimeter
M_w	Molecular weight
%	Percent
X_c	Percentage of crystallinity
cm^{-1}	Reciprocal centimeter
W_t	Samples weight after water absorption
s	Second
k	Slope of graph
L	Specimens thickness

t	Time
M_t	Water uptake at certain time
M_∞	Water uptake at equilibrium
w	Weight
wt %	Weight percentage

LIST OF ABBREVIATIONS

DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
KF	Kenaf fiber
MFI	Melt flow index
PLA	Poly(lactic acid)
PCL	Polycaprolactone
PEA	Polyesteramides
PET	Polyethylene terephthalate
PHA	Polyhydroxyalcanoate
PS	Polystyrene
SEM	Scanning electron microscopy

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ABSTRAK

Dalam kajian ini, tingkah laku penyerapan air, sifat mekanikal, haba dan morfologi komposit poli(asid laktik)/kenaf (PLA/KF) dengan saiz gentian berbeza telah dikaji. Komposit PLA/KF disediakan dengan menggunakan penyemperit skru tunggal dan kaedah pengacuan suntikan dan diikuti dengan penuaan higroterma pada 60 °C selama 4 minggu. Penyerapan air dan sifat mekanikal komposit PLA/KF dengan masa rendaman dilaporkan dan dibandingkan dengan PLA. Komposit PLA/KF menunjukkan peningkatan berat tepu dan pekali resapan yang lebih tinggi daripada PLA, yang menunjukkan bahawa penambahan gentian kenaf menyebabkan penyerapan air yang lebih tinggi disebabkan oleh sifat hidrofilik gentian tersebut. Kekuatan tegangan dan modulus tegangan menurun dengan teruk selepas penuaan. Komposit PLA/KF dengan gentian yang lebih besar mempunyai kekuatan tegangan dan modulus yang lebih tinggi daripada gentian yang lebih kecil kerana nisbah aspek yang lebih tinggi. Morfologi permukaan dan permukaan patah bagi komposit PLA dan PLA/KF yang kemas dengan masa rendaman berbeza diperhatikan dengan mengimbas mikroskop elektronik. Lompang dan keretakan ditemui yang disebabkan oleh kemerosotan PLA dan penyahikatan PLA dan kenaf. Spektrum FTIR menunjukkan bahawa bilangan kumpulan –OH dalam komposit PLA/KF selepas penuaan adalah lebih daripada komposit sebelum penuaan disebabkan oleh resapan molekul air ke dalam komposit. Tg dan Tm untuk komposit PLA/KF berkurangan selepas penuaan disebabkan oleh pengurangan berat molekul telah dianalisis dengan kalorimetri pengimbasan pembezaan.

WATER ABSORPTION AND HYGROTHERMAL AGING BEHAVIOR OF KENAF FIBER-REINFORCED POLY(LACTIC ACID) COMPOSITES

ABSTRACT

In the present study, the water absorption behaviour, mechanical, thermal and morphological properties of poly(lactic acid)/kenaf (PLA/KF) composites with different fiber size were investigated. PLA/KF composites were prepared by using single screw extruder and injection moulding method and followed by hygrothermal aging at 60 °C for 4 weeks. The water absorption and mechanical properties of the PLA/KF composites with immersion time were reported and compared to those of neat PLA. PLA/KF composites showed higher water uptake at equilibrium and diffusion coefficients than that of neat PLA, which indicated that the addition of kenaf fiber induced higher water absorption caused by the hydrophilic nature of the fibers. Tensile strength and tensile modulus severely decreased after aging. PLA/KF composite with larger fiber has higher tensile strength and modulus than that with smaller fiber due to its higher aspect ratio. The morphologies of surfaces and fractured surfaces of neat PLA and PLA/KF composites with different immersion time were observed by scanning electronic microscopy. The voids and micro-cracks were found which was due to the degradation of PLA and debonding of PLA and kenaf. FTIR spectrum showed that the number of –OH groups in PLA/KF composite after aging were more than composite before aging due to diffusion of water molecules into the composites. T_g and T_m for PLA/KF composites decrease after aging due to the reduction in molecular weight and plasticization effect of PLA were analysed by differential scanning calorimetry.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Recently, the research of biomass-based polymers has been given notable attention as to minimize the environmental impact of petroleum-based plastics as they do not undergo biodegradation in landfill or composting environment, resulting in serious environmental pollution. According to Darie et al. (2013), biomass-based plastics, e.g. polyhydroxybutyrate; chemosynthesis products, e.g. poly(lactic acid); and chemically modified natural products, e.g. esterified starch and cellulose acetate. Due to its excellent mechanical properties, possibility of utilization by composting as well as high availability in form of ready-to-use commercial grades, modified for different melt processing technologies, poly(lactic acid) (PLA) is a biodegradable polymer with the highest potential for industrial application (Barczewski et al., 2019).

However, PLA is more expensive and provides shorter service time in comparison to petroleum-based polymers due to its poor resistance to hydrolysis and thermal degradation. The inherent brittleness and low toughness of PLA are due to a low entanglement density limit its applications in niche markets (Choudhary et al., 2010). Incorporation of PLA with low-cost natural fillers such as kenaf may extend its application range and can also reduce the final products price. Kenaf fibers have recently received a lot of attention as a biomass-based additive (Kamarudin, 2018). Kenaf fibers are less abrasive toward processing machinery and tooling than inorganic-mineral fibers such as glass fiber, making them less hazardous to the production workers. Incorporating kenaf fibers into the PLA reduces specific weight per specific strength while improving PLA properties (Salim et al., 2020). However, this factor may also deteriorate the mechanical properties of the composite part over the time, especially

when expose to different environmental conditions such as heat and water moisture expose (Moudood et al., 2019).

The durability of PLA/natural fiber composites should be illustrated during their service life. Aging is a gradual, continuous process of nature change in chemical and physical. Natural aging tests are very representative because they allow for the replication of identical exposure conditions (Boubakri et al., 2009). However, they are time consuming and may take years to complete. Hygrothermal aging as a degradation process combines the effects of moisture and temperature, resulting in significant deterioration of mechanical and physical properties of materials (Yu et al., 2016). Generally, when polymer and its composites are immersed in hydrothermal environment, they tend to absorb water (Tham et al., 2014). Composites after moisture absorption degrade their physical, thermal and mechanical properties. As a result, materials engineers and researchers face a challenge in retaining the mechanical and thermal properties of hydrothermally conditioned composites (Nayak et al., 2016).

1.2 Problem Statement

In any application, material durability is an important consideration. Environmental exposure (e.g. heat and moisture exposure) degrades the natural fiber and polymer, which may deteriorate the mechanical properties or contribute to failure during actual service. Materials durability in terms of environmental exposure is measured by the changes in mechanical performance, thermal properties, morphological properties and appearances of material after underwent hygrothermal aging. According to Morton et al. (2003), the application of natural fiber composites to prospective outdoor applications such as decking and railing is limited by the moisture absorption of natural. Moisture absorption of natural fiber is a major concern because it

can cause dimensional changes of its composites, resulting in loss of interfacial integrity. Many factors influence the water absorption of composite materials, including temperature, fiber volume fraction, reinforcing fiber orientation, fiber permeability, exposed surface area, diffusivity, and the reaction between water and matrix (Islam et al., 2010). The influence of natural fiber degradation on the deterioration of biodegradable composite characteristics can be precisely determined using hygrothermal aging. There are few studies on the hygrothermal aging of PLA/natural fiber composites has been studied (Jiang et al. 2019; Hu et al., 2010).

In this research, PLA/kenaf composites (ratios 70/30 wt %) with different sizes of kenaf filler (50-100 mesh and pass through 100 mesh) will produce using single screw extruder and injection molding. The effect of hygrothermal aging on water absorption behavior, mechanical, thermal, microstructure and morphological properties of neat PLA and PLA/kenaf composites before and after hygrothermal aging (1 week, 2 weeks and 4 weeks) were investigated.

1.3 Objectives

There are 4 objectives of the study and summarized as follow:

1. To study the water absorption and hygrothermal aging behavior of neat PLA and PLA/kenaf composites.
2. To investigate the effect of hygrothermal aging on the mechanical properties of neat PLA and PLA/kenaf composites.
3. To investigate the effect of hygrothermal aging on the thermal properties of neat PLA and PLA/kenaf composites.
4. To investigate the morphological changes of neat PLA and PLA/kenaf composites resulted from the hygrothermal aging.

1.4 Scopes of research

In this study, the neat PLA specimens and PLA/kenaf composites with ratio of 70/30 with different sizes of kenaf fibers (50-100 mesh size and pass through 100 mesh size) were prepared using single screw extruder. Based on Hassan et al. (2020), 30 wt% is the optimum fiber volume that improved mechanical properties but decreased as more fiber volume incorporated, in which the findings are supported by Chen et al. (2015). Then, the pellets were then used for the preparation of dumbbell-shaped specimens for tensile test specimens through injection molding. After sample preparation, the specimens were underwent hygrothermal aging by immersed in 60 °C water bath tank for 4 weeks. To simulate the actual working environment of the possible applications, temperature at 60 °C was chosen in this research. The water absorption and hygrothermal aging behavior with immersion time of neat PLA/kenaf composites were analyzed. The mechanical characteristics of neat PLA and PLA/kenaf composites were characterized by tensile test. Next, the thermal properties of pure PLA and PLA/kenaf composites were investigated using DSC. Morphological properties of pure PLA and PLA/kenaf composites were then determined using SEM.

1.5 Thesis Organization

This thesis has five chapters:

CHAPTER 1 provides general information about the study including an introduction, problem statement, research objectives, scope of study and a structure of the thesis.

CHAPTER 2 covers general knowledge and relevant literature related to each polymer. It also includes general information on the polymer blends.

CHAPTER 3 gives the information of materials, polymer blend preparation in this study and the general description of the characterization methods used.

CHAPTER 4 presents the experimental result and discussion of the water absorption behavior, mechanical, thermal and morphological properties of PLA/kenaf composite.

CHAPTER 5 summarizes the conclusion of this study and recommendation for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradable polymer

According to Mohanty et al. (2002), one of the important efforts to reduce the environmental impact of petroleum-based plastics is the development of biodegradable polymers (Mohanty et al., 2002). Biodegradable polymers are polymers that undergoes deterioration of its properties, in term of physical and chemical besides a decrement of its molecular mass in a process called biodegradation. In this process, biodegradable polymers degrade into carbon dioxide, methane, water, inorganic compounds or biomass. In both aerobic and anaerobic conditions, this process is carried out by naturally occurring micro-organisms such as bacteria, fungi and algae (Luckachan & Pillai, 2011). Polymer biodegradation process takes place in two steps. The first step is polymers fragmented into species of lower molecular mass via abiotic chemical reactions (photo-degradation, oxidation and hydrolysis) or biotic reactions (degradation by microorganisms). The second step is the polymer fragments bio assimilation by microorganisms and their 7 mineralization (Vroman & Tighzert, 2009). Figure 2.1 shows the biodegradation mechanism of polymers under aerobic conditions (Mueller, 2006).

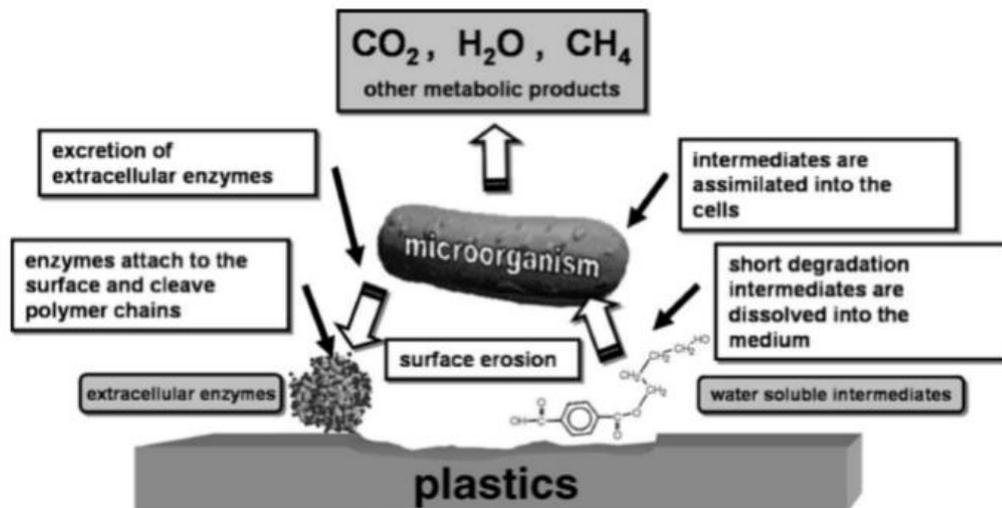


Figure 2.1: Scheme of general mechanism of enzymatic catalyzed hydrolytic polymer degradation (Mueller, 2006).

Biodegradable polymers are classified into two groups, based on whether they are made from natural or synthetic resins. Natural resins are naturally produced from biomass products and micro-organisms. They have excellent biocompatibility but exhibiting poor antigenicity and batch-to-batch variation. Example of natural resins produced from biomass products are polysaccharides (starch, cellulose, etc.), proteins (gelatin, wool, silk, etc.) and lipid (fats and oil). Polyhydroxyalcanoate (PHA) is the natural polyesters resin produced by plant or microorganisms. Synthetic resins are synthesized either through conventional synthesis from bio-derived monomers (renewable resources) or synthetic monomers. For instance, PLA are polyesters derived from bio-derived monomers. PLA is renewable because it is made from renewable agricultural feed stocks. Polycaprolactone (PCL) and polyestaramides (PEA) are examples of synthetic resins based on petrochemical products. Petroleum-based synthetic resin are non-renewable but are capable for tailor-making of mechanical properties according to the requirement (Doppalapudi et al., 2014). Figure 2.2 shows the classification of biodegradable polymers (Dinesh, 2016).

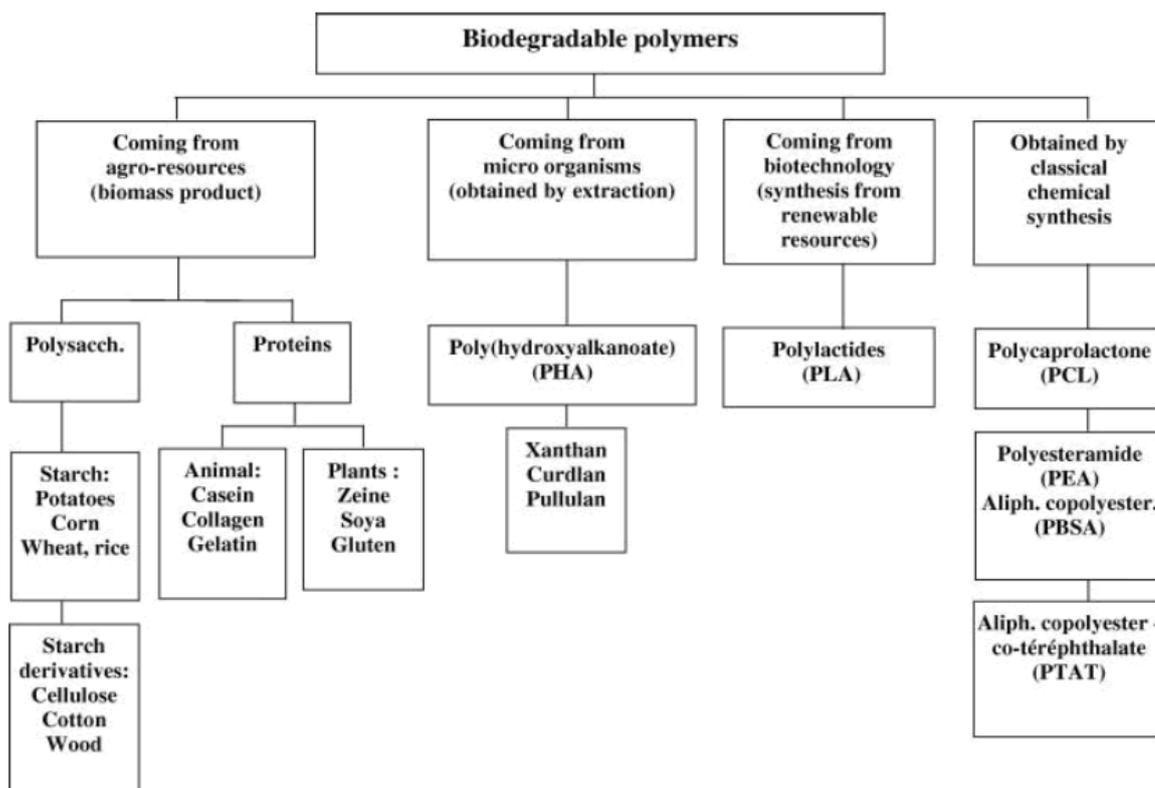


Figure 2.2: Classification of biodegradable polymers (Dinesh, 2016).

Polycondensation reactions and ring opening polymerization are used to synthesis biodegradable polymer (Vroman and Tighzert, 2009). There are various examples of biodegradable polymers and their potential applications. Products such as flexible packaging film, flushable sanitary articles, sheet and unwoven packaging, bottles, fishing nets and catering items (food cups, cutlery, trays and straws) can be produced from biodegradable polymers (Parth et al., 2011).

Compared to conventional petroleum-based polymers, the use of biodegradable polymers offers several important environmental benefits. Composts resulting from biodegradable polymers can increase the organic content of soil, water and nutrient retention. Next, the use of biodegradable polymer as a replacement for conventional polymers has the potential to reduce chemical inputs and also suppressing plant disease (Gautam, 2009). Products from biodegradable polymers such as plastics bags to be

thrown after use can increase the rate of organic waste degradation in landfills while reducing the landfill space usage and extending landfill life. Furthermore, the energy required for synthesis and manufacturing is generally much lower for most of the biodegradable polymers as compared to that of non-biodegradable polymers (Parth et al., 2011).

2.1.1 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) is a the member from the aliphatic polyesters family. It is frequently synthesised from α -hydroxy acids, e.g. polyglycolic acid or polymandelic acid (Taimur, 2018). PLA is growing in popularity in the industrial packaging field and the biocompatible or bio-absorbable medical device market. It is one of the biodegradable and renewable polymers that has great potential to substitute the petroleum-based synthetic polymers for many applications as it has many attractive and desirable properties. For instance, it has high strength and modulus, biodegradable and ease to process on standard plastic processing equipment (Farah et al., 2016). PLA is a thermoplastic which can be synthesized from bio-derived monomers extracted from a variety of materials including corn starch (Auras et al., 2005).

2.1.2 Synthesis of PLA

According to Suryanegara et al. (2009), PLA derived from natural resources can be synthesized via ring-opening polymerization or condensation polymerization of lactic acid monomer acquired from fermentation of dextrose from starch feedstocks. Lactic acid monomer ($C_3H_6O_3$) is a simple chiral molecule produced via fermentation. L-lactic acid and D-lactic acid are its two nantiomers. Both D- and L-enantiomers are produced in bacterial systems while the L-isomer is produced in humans and other mammals. Figure 2.3 shows chemical structure of stereoisomers of lactic acid (Yang et al., 2020).

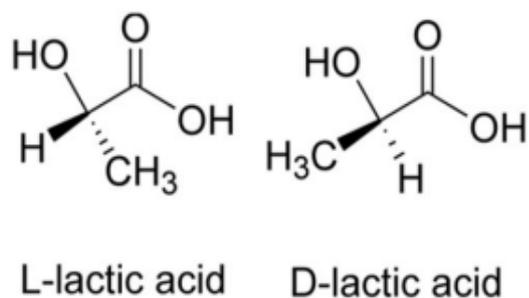


Figure 2.3: Two stereoisomers of lactic acid (Yang et al., 2020).

There are two ways to performed polymerization of lactic acid to high molecular weight PLA: direct condensation of lactic acid under high vacuum or ring-opening polymerization of the cyclic dimer intermediate (lactide) formed (Stefanial and Masek, 2021). In direct condensation, water produced from the condensation is removed under high vacuum and temperatures using solvent. Direct condensation forms a low or intermediate molecular weight polymer which will then be used to produce PLA of a range of molecular weights by reacting it with epoxides, peroxides or isocyanates. Direct condensation process needs to be conducted at temperature below 200°C to prevent the generation of entropically favored lactide monomer at temperatures above that (Taimur, 2018). Lactide, a cyclic intermediate dimer, is produced and purified by distillation in the solvent-free process. The catalytic ring-opening polymerization of lactide intermediate produces PLA with controlled molecular weight. Figure 2.4 shows the manufacturing process of the high molecular weight PLA (Yang et al., 2020).

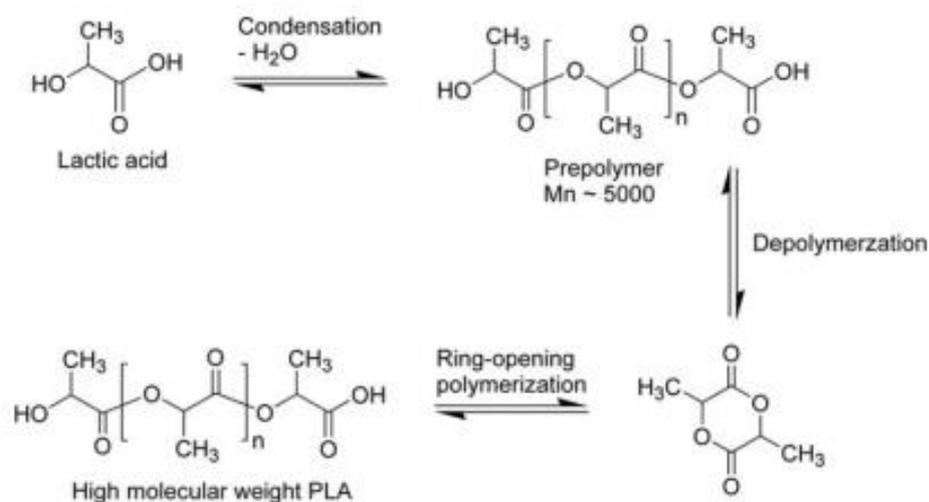


Figure 2.4: Manufacturing process of the high molecular weight PLA (Yang et al., 2020).

2.1.3 Properties of PLA

Table 2.1 shows the properties of PLA (Farah et al., 2016; Tamiur, 2018). PLA provides comparable mechanical, thermal, optical and barrier properties as compared with commercially available commodity polymers such as PP, PET and PS (Castro et al., 2016).

Table 2.1 Properties of PLA (Farah et al., 2016; Taimur, 2018).

Properties	Characteristics
Density (g/cm ³)	1.21-1.25
Glass transition temperature, T _g (°C)	45-60
Melting temperature, T _m (°C)	150-162
Moisture regain (%)	0.4-0.6
Heat resistance (°C)	110
Tensile strength (MPa)	21-60
Tensile modulus (GPa)	2.7-16
Elongation at break (%)	7
Crystallinity (%)	37

PLA is a thermoplastic polymer with high strength and high modulus. Farah et al. (2016) and Taimur (2018) reported that the tensile strength and tensile modulus of PLA are 21-60 MPa and 0.35-3.5 GPa respectively but has low elongation at break of about 7 %. In addition, Kang et al (2015) found that its tensile strength value can go up to 63.6 MPa. PLA has inherent brittleness at room temperature as it has glass transition temperature, T_g above room temperature.

According to Donald and Dimitris (2014), PLA is a semi-crystalline polymer with a T_g range of 45-60 °C and T_m in range of 150-162 °C, which requires processing temperatures in range of 185-190 °C. Heat resistant of PLA can withstand temperatures of 110 °C. By physically blending the polymer with PDLA (poly-D-lactide), the melting temperature can be increased by 40–50 °C and the heat deflection temperature can be increased from around 60 °C to as much as 190 °C.

However, PLA is found to be highly sensitive to heat and thus having poor thermal stability (Lim et al., 2008). PLA is hydrophobic in nature and has limited gas barrier capacity. It is extremely brittle, with elongation at break less than 10%. Pure PLA has some significant characteristic properties, such as weak thermal stability, low gas barrier properties, and low ductility and toughness are inadequate for many applications. Therefore, PLA is needed in order to compete with other flexible polymers (e.g. polypropylene, polyethylene) or fillers (e.g. kenaf fibers).

Hygrothermal degradation is an aging process that combines the effects of moisture and temperature, resulting in significant weight loss and reduction of mechanical properties (Chow et al, 2005). The moisture penetration (i.e., diffusion) mechanism becomes active only after the specific damage to the composites occurs as a result of exposure of the composite to a hot and moist environment (Mohd Ishak et al, 1994).

Before biodegradation can begin, the polymer must first be hydrolyzed at high temperatures (about 60 °C) to reduce the M_w . PLA degrades quickly and disintegrates within weeks to months in conditions of high temperature and high humidity, as in active compost. The primary degradation mechanism is a two-step process that starting with hydrolysis and is followed by bacterial attack on the fragmented residues. The high M_w polyester chains hydrolyze to lower M_w oligomers during the initial phases of degradation (Farah et al, 2016). Figure 2.5 shows the hydrolysis degradation of PLA (Valencia, 2019).

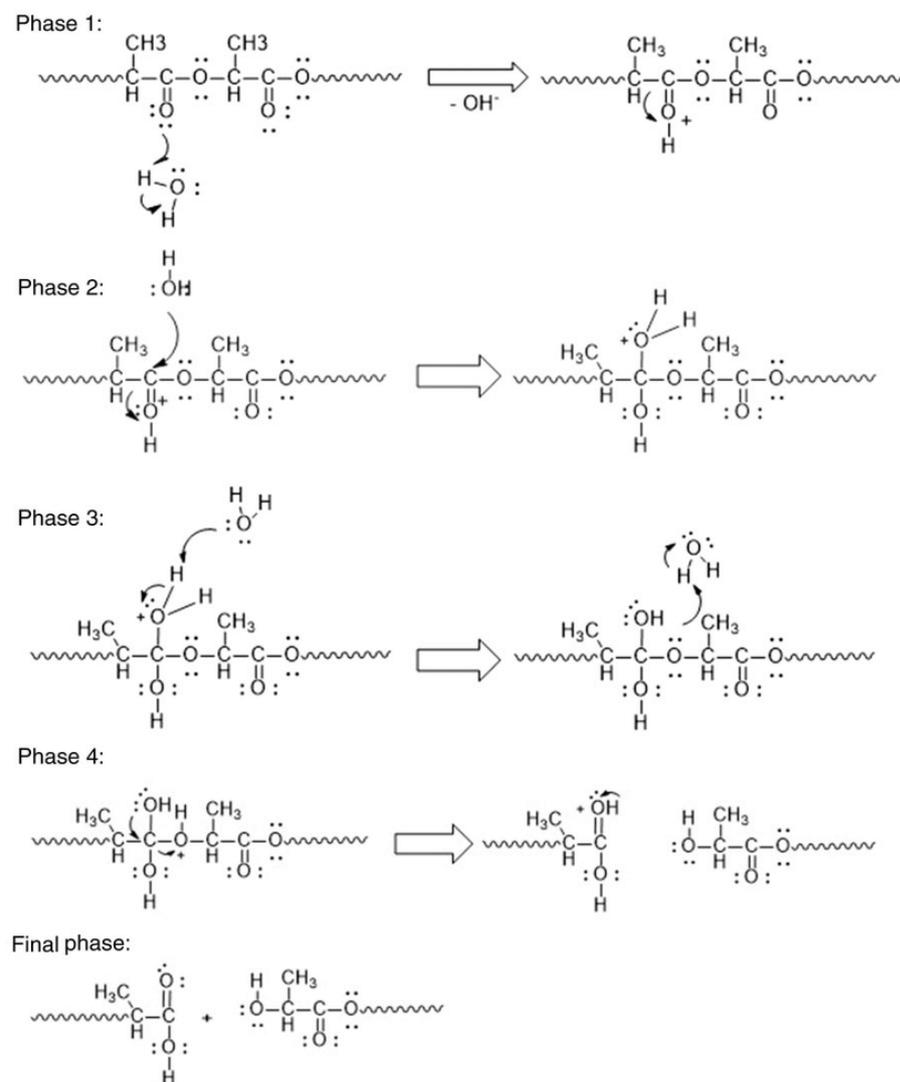


Figure 2.5: Hydrolysis degradation of PLA (Valencia, 2019).

PLA hydrolysis degradation is also dependent on several factors, such as M_w , crystallinity, purity, temperature, pH, presence of terminal carboxyl or hydroxyl groups, water permeability, and additives acting catalytically that may include enzymes, bacteria or inorganic fillers. PLA is very stable under normal use conditions and will retain its M_w and physical properties for years. This is exemplified by its increasing use in clothing and other long-lasting applications. High M_w PLA is also naturally resistant to bacterial and fungal growth, making it suitable for applications such as food packaging and sanitation. (Farah et al, 2016).

In engineering practical application, moisture absorption test are commonly used for quality control and to measure the degradation of composite materials quality (Lemana et al, 2008). As a result, accurate prediction of property changes with aging has significant scientific value and engineering applications. The method that provides aggressive conditions for material accelerated ageing tests is hygrothermal aging.

Biodegradable is one of the main advantage of PLA. Biodegradation is the nature's way for recycling PLA and this process occurs in two main steps. Primary degradation is the process which the polymer chain fragments as a result of hydrolysis or an oxidative reaction. The second step is ultimate biodegradation, which the microorganisms convert the low M_w chains formed into biomass, water and carbon monoxide at a high temperature of 58 °C and 50% of relative humidity. Biodegradation of PLA happens within two weeks and it will completely disappear by 3-4 weeks when composting together with other biomass (Meinander et al., 1997). PLA biodegradation is highly affected by temperature and moisture which promote its polymer chains hydrolysis and then rapid up the biodegradation rate. Figure 2.6 shows the proposed schematic mechanism of PLA biodegradation (Tanjung et al., 2020).

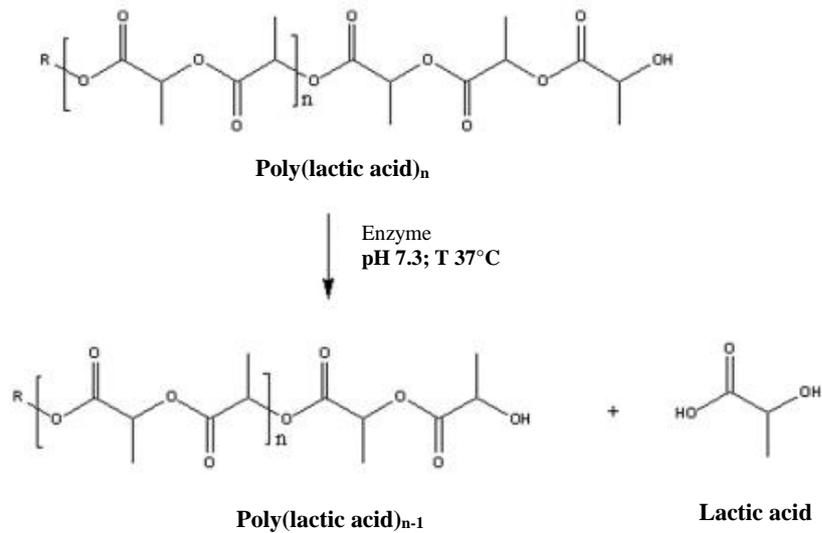


Figure 2.6: Proposed schematic mechanism of PLA biodegradation (Tanjung et al., 2020).

2.1.4 Application of PLA

PLA can be processed through most thermoplastic processing methods such as extrusion, injection molding and compression moulding, into broad range of applications. There are two main categories of PLA industrial applications, which are consumer durable products and consumer non-durable products. Consumer durable products are commodity products with a lifetime of more than three years, such as car components and medical products. On the other hand, consumer non-durable products can last up to three years. For example, short-term medical products, packaging and service ware (Castro et al., 2016).

PLA has been used in medical field such as those in medical equipment and implants items. The applications of PLA as medical implants include tissue growth, bone grafting and fracture fixation devices. PLA is suitable to be made into medical implants as lactic acid is naturally produced by the body and has no toxicity on humans. Furthermore, as it degrades over time into harmless lactic acid, the removal of implants is not required (Castro et al., 2016).

By spinning process, PLA can be extruded into fibers. PLA is fairly polar, so it can absorb moisture and is suitable for fiber applications. PLA textiles has wicking properties and breathability which makes it a comfortable material suitable for garment industries to manufacture products such as apparel and homeware. It also has wicking properties and the ability to absorb organic compounds. These properties make PLA a suitable candidate for wipes, feminine hygiene products and diapers (Taimur, 2018).

The use of PLA in packaging and serviceware has largely increased recently. For instance, it is used for compostable packaging materials include compost bags, food packaging, and disposable tableware due to its biodegradability (Taimur, 2018). PLA is used to produce bottles for water and juices but not those for carbonated beverages due to low barrier toward CO₂. PLA can also be used for agricultural applications to protect soils against erosion and plants against weeds, insects and birds (through mulch films), to cover greenhouse tunnels and to function as a drip irrigation tube. The most promising advantage of using PLA for plasticulture is that it is biodegradable after use (Castro et al., 2016).

2.2 Natural Fibers

Natural fibers are renewable resources since they are biodegradable, and manufacture of natural fibers consumes more energy. One significant disadvantage of natural as compared to synthetic production requires little time effort and energy but it is quietly costly to product. Natural fibers are non-uniformity, variety of dimensions and mechanical properties as compared to synthetic fibers (Bismarck et al., 2005). Hence, the primary task to be accomplished in order to improve natural fiber quality over synthetic fiber is to develop high performance natural fiber reinforced composites. Figure 2.7 shown the classification of natural fiber (Bismarck et al, 2005).

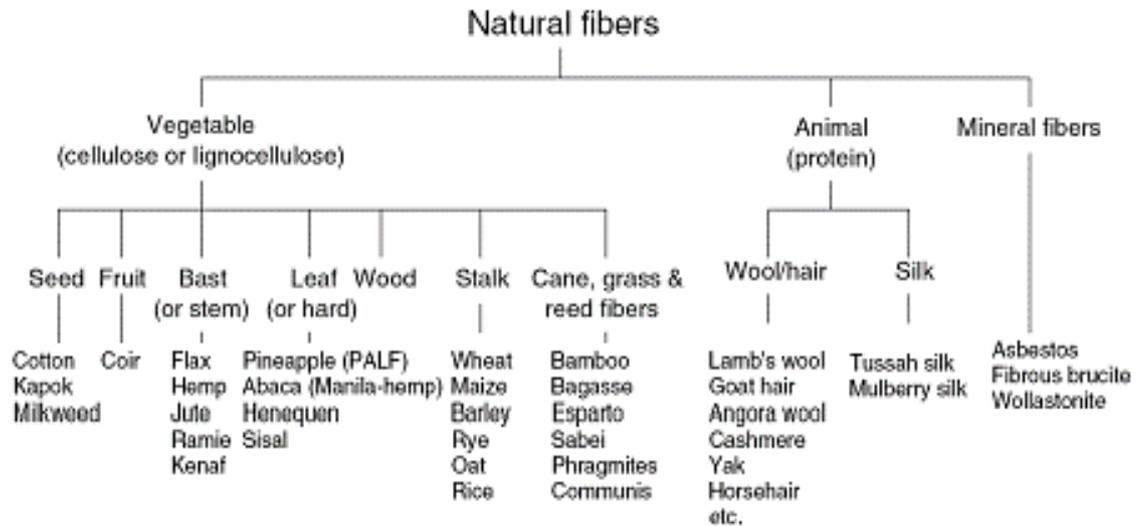


Figure 2.7: Classification of natural fiber (Bismarck et al, 2005).

According to Bismarck et al. (2005), natural fibres are polar and hydrophilic because they contain a large amount of hydroxyl (-OH) group. However, the majority of polymer matrices are hydrophobic in nature. Due to non-uniform fibre dispersion in the matrix and a poor fibre matrix interphase, the addition of hydrophilic natural fibres to hydrophobic polymers results in a composite with poor mechanical properties. This polarity also causes high moisture absorption in natural fiber-based composites, resulting in fibre swelling and void formation in the fibre matrix interphase. If the moisture in natural fiber is not removed, it will results in a porous product (Bismarck et al., 2005).

High moisture absorption might also cause mechanical properties deterioration and change in dimension stability. In general, these concerns are solved by fiber surface treatment or matrix modification. Otherwise, the main limitation in utilizing natural fiber is the limited thermal stability of natural fibers. They degrade when heated above 200 °C, limiting the number of polymer materials to be as matrix (Bismarck et al., 2005). Table 2.2 shown the characteristic values for the density, diameter and

mechanical properties of natural fibers and synthetic fibers (Ravi and Siva, 2017). As shown in Table 2.2 , characteristic values of kenaf fiber is outstanding compared to other natural fibers but lower compared to synthetic fibers, such as E-glass, Kevlar and carbon fibers.

Table 2.2: Characteristic values for the density, diameter and mechanical properties of natural fibers and synthetic fibers (Ravi and Siva, 2017).

Fiber	Density (gcm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Flax	1.5	345-1500	27.6	2.7-3.2
Hemp	1.47	690	70	1.6
Jute	1.3-1.49	393-800	13-26.5	1.16-1.5
Kenaf	1.2	295-1191	22-60	1.6
Ramie	1.55	400-938	61.4-12.8	1.2-3.8
Sisal	1.45	468-700	9.4-22	3.7
PALF	0.95	413-1627	34.5-82.5	1.6
Abaca	0.7-1.55	248	3.2	25
Cotton	1.5-1.6	287-800	5.5-12.6	7.8
Coir	1.15-1.46	131-220	4-6	15-40
E-glass	2.55	3400	73	2.5
Kevlar	1.44	3000	60	2.5-3.7
Carbon	1.78	3400 ^a -4800 ^b	240 ^a -425 ^b	1.4-1.8

^a = Ultra high modulus carbon fibers, ^b = Ultra high tenacity carbon fibers.

2.2.1 Kenaf Fiber

Kenaf is one of the most significant fiber crops in the world. It is obtained from the plant *Hibiscus cannabinus*, which can be grown optimal conditions (Mazharul, 2021). Kenaf fiber is well-known natural fibers that is used as reinforcement in polymer

matrix composites. It has the potential to replace synthetic fiber like glass fiber. The incorporation of kenaf fiber can provide mechanical properties comparable to synthetic fiber while having a lower density than traditional materials, result in lightweight and environmental friendly polymer composites, also known as green composites. Several factors can influence the performance of kenaf-reinforced polymer composites, including chemical treatment, fiber content, the part of the kenaf fiber used, fiber form, and water uptake. (Rozyanty et al., 2019). Figure 2.8 shows the photo of kenaf plant, components of a typical stalk in cross-section showing the bast and core, kenaf bast fiber and kenaf core fiber (Adole et al., 2019).

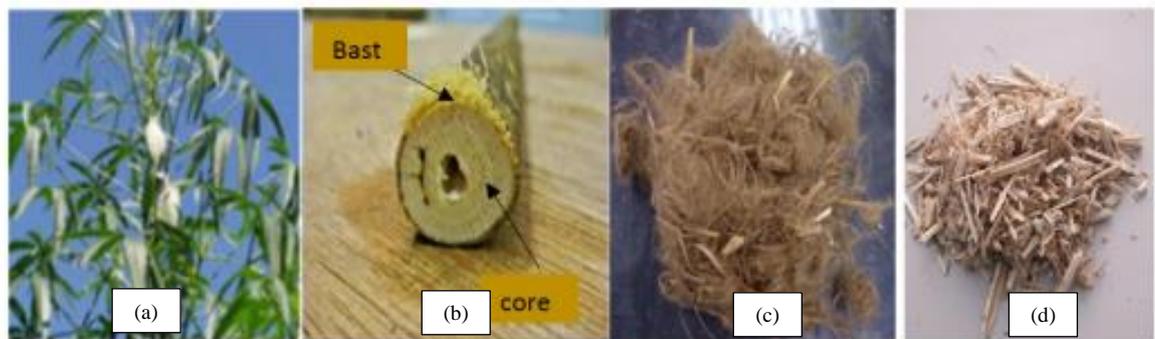


Figure 2.8: The photo of (a) kenaf plant, (b) cross-section of kenaf stalk, (c) kenaf bast fiber and (d) kenaf core fiber (Adole et al., 2019).

Ashori et al. (2006) has conducted research on both the bast fibre and the core fibre and concluded that the kenaf bast fibres were slender and longer, whereas the core fibres were much wider and shorter. The morphology and chemical properties of the bast and core fibres revealed that they were considerably different. Table 2.3 shows the chemical properties and compositions kenaf in percentages (Ashori et al., 2006).

Table 2.3: Chemical properties and compositions kenaf in percentages (Ashori et al., 2006).

	Bast	Whole	Core
Holo-cellulose	82.6	77.2	75.8
Cellulose	56.4	48.7	46.1
Hemi-cellulose	26.2	28.1	29.7
Lignin	14.7	19.9	22.1
Pentosan	13.5	19	20.7
E.B. Extract	2.7	2.3	2.2
1% NaOH Extract	14.5	17.3	20.6
Hot water	3.4	3.6	3.9
Ash	2.2	1.8	1.6

2.2.2 Properties of Kenaf Fiber

According to Mazharul (2021), kenaf fibers have a long staple, thus very fine and strong yarn can be spun. It can be either lightweight or heavyweight. Kenaf fiber has the same breaking strength with low-grade jute, but slightly weakened only when wet as it is hydrophobic. It can be either lightweight or heavyweight. Moreover, kenaf fiber has very low elasticity and it is fragile in nature. This fiber is capable of being chemically degraded. Table 2.4 show the mechanical properties of kenaf fiber respectively (Mazharul, 2021).

Table 2.4: Mechanical properties of kenaf fiber respectively (Mazharul, 2021).

Mechanical Properties	Characteristics
Density (g/cm ³)	1.2
Breaking strength (MPa)	100.64
Elastic modulus (GPa)	23
Yarn breaking load (N)	79
Tensile strength (MPa)	283-900
Elongation (%)	1.6
Moisture absorption (%)	8.3-17

According to Paridah et al. (2011), have remarkable mechanical properties that allow them to replace glass fibers as reinforcing elements in polymer composites. The physical and mechanical properties of kenaf fiber reinforced soy-based bio-composites are affected by fiber length, fiber content, and fiber orientation (Liu et al, 2007). This also includes the types of the fibers, whether they are long fibers, short fibers, or powder form. Besides, according to Nurazzin et al. (2021), the mechanical properties of the hybrid composites are significantly influenced by the aspect ratio of the kenaf fiber. To ensure good reinforcing efficiency in composites, particularly during tensile loads, the fiber length must be higher than the critical length. This allows shear forces at the fiber-matrix interface to be transmitted into the fibre from the matrix.

Transmission electron microscopy is an effective tool for studying the ultrastructure and morphology of kenaf fibre cell walls (Abdul et al., 2010). Figure 2.9 illustrate transverse sections of kenaf cell wall fibers composed of intercellular layers (primary and secondary wall-S1, S2, S3) and its core fibers showed great variability in size, shape and structure of the cell wall fibers.

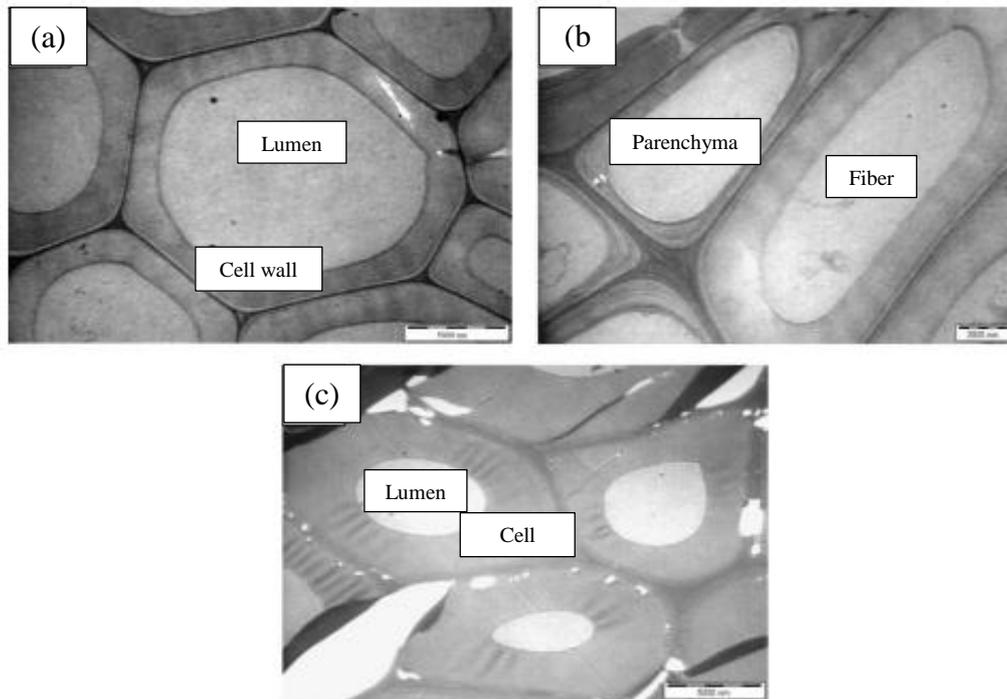


Figure 2.9: Transmission electron micrograph of ultra-thin section of kenaf fibers: (a) kenaf core fibers, (b) transverse section of core fibers, and (c) transverse section of kenaf bast fibers. Cell wall structure stained with uranyl acetate and lead citrate (Abdul et al., 2010).

2.2.3 Water absorption of Kenaf Fiber

According to Roger and Harry (2006), the ability of kenaf fibers to absorb moisture relies on the hydrophilic nature of the fibers itself. The cellulose and hemicellulose of kenaf fiber consists of a large number of hydroxyl (-OH) groups, which gives hydrophilic nature to kenaf fiber. Lignin is one of the components in natural fibres that are hydrophobic in nature and this cause decreased in water uptake effectively due to the hydrophobicity of lignin (Yang et al., 2019).

On the other hand, the cellulose and hemicellulose have a high amount of -OH groups, making them water accessible when the -OH groups are exposed (Nurazzi et al., 2021). However, the accessibility of the cellulose component is limited compared to hemicellulose, since cellulose is semi-crystalline. The crystalline region of the

cellulose is inaccessible to water molecules, but the amorphous region of the cellulose is accessible to water molecules (Mokhothu and John, 2015).

According to Nurazzi et al. (2021), the mechanism of water absorption of kenaf fibers starts with the water molecules penetrate and fill the space between microfibrils, which cause fibers swelling. The absorption of water by kenaf fibers can be in two states: (1) the water bound to the cell walls and middle lamella through the hydrogen bonds with $-OH$ groups and (2) free water filled into micro- and macropores of cell walls, then retained by capillary forces. The cellular cavities then reached the saturation point as it was completely filled by water molecules. Figure 2.10 shows the swelling process of kenaf fibers (Nurazzi et al., 2021).

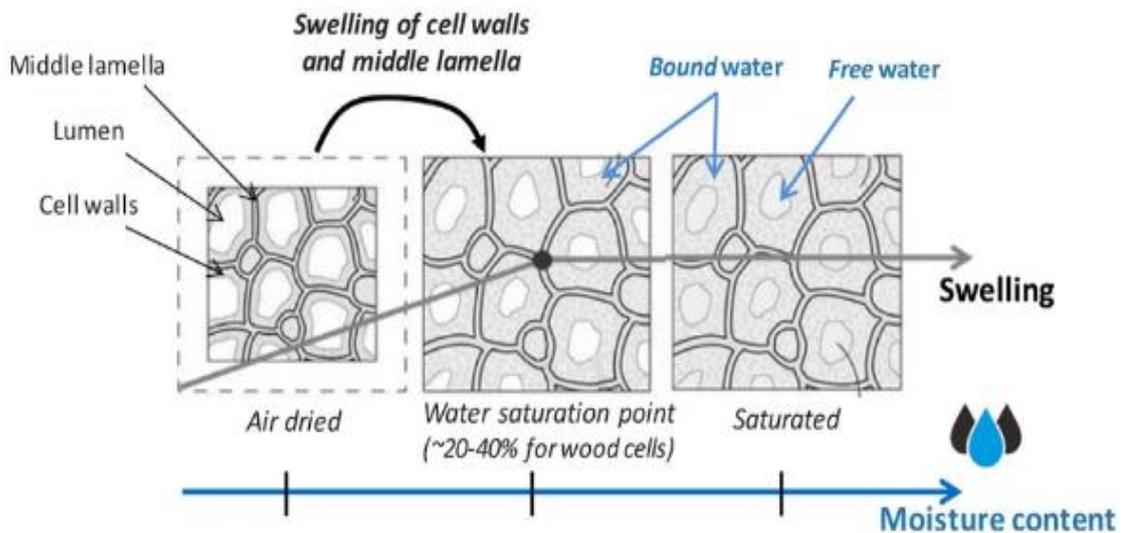


Figure 2.10: The swelling process of kenaf fiber (Nurazzi et al., 2021).

The swelling of fiber resulting in formation of cracks and debonding of the fiber-polymer interface as shown in Figure 2.11. This initiated when water-soluble materials on the fiber surface start to leach away, creating osmotic pressure pockets at the surface of the fibers (Mochane et al., 2019). In addition, the absorbed water molecules can act as a plasticizer, leading to regions of inefficient transfer and a deterioration in the mechanical characteristics of the composite (Nurazzi et al., 2021).

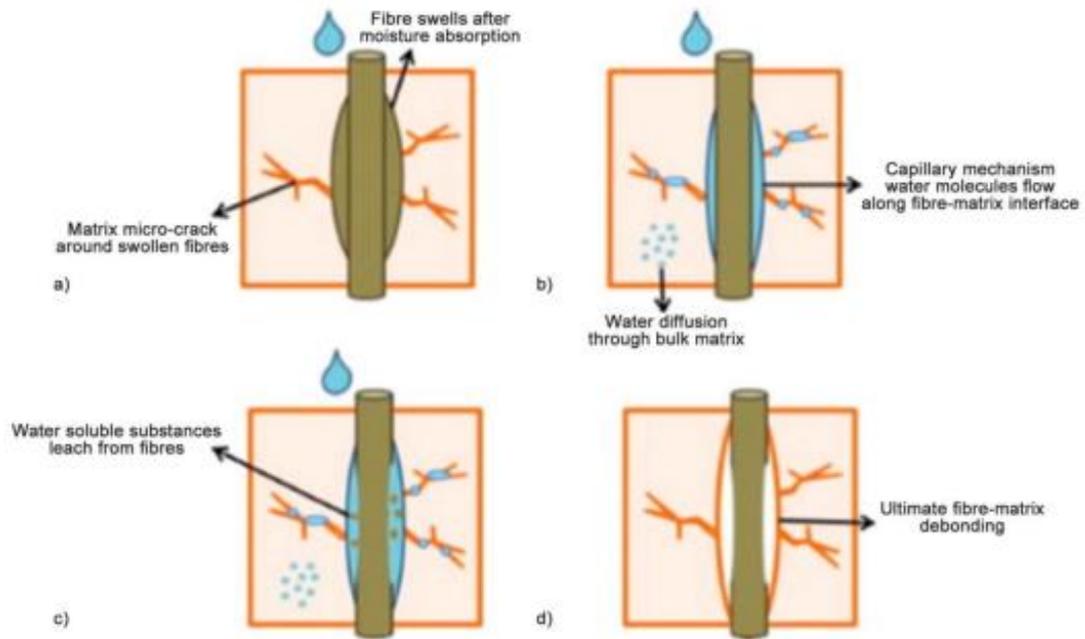


Figure 2.11: (a) Formation of micro-cracks due fiber swelling; (b) penetration and transport of water molecules through micro-cracks; (c) water soluble substance leaching; and (d) debonding of fiber-matrix interface (Mochane et al., 2019).

2.2.4 Applications of Kenaf Fiber-Reinforced Composites

Many scientists and researchers are currently attempting to manufacture structural elements, electrical components, automotive components, aircraft parts, and other products using natural vegetable fiber as reinforcements. Previously, Hafizah et al. (2014) had used kenaf fibre reinforced polymer laminates to strengthen reinforced concrete beams. The finding of other researchers reported improved mechanical performance for all strengthened beams, as well as an increase in maximum flexural strength of 40% fibre weight. An interior headliner model for an automobile has been produced using PLA/kenaf fibre content at 50% fiber weight with satisfy mechanical properties. In addition, Davoodi et al. (2010) used glass hybrid epoxy/kenaf composite for a passenger car bumper beam.