THE EFFECT OF OIL PALM EMPTY FRUIT BUNCH (EFB) LOADING, GLYCEROL ADDITION AND ANHYDRIDE MODIFICATION ON THE PROPERTIES OF POLYLACTIC ACID (PLA) BIOCOMPOSITE

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by

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TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

%	Percentage
Mpa	Megapascal
˚C	Degree Celsius
μm	Micrometer
GPa	Gigapascal
mm	Millimeter
T_g	Glass transition temperature
T_m	Melting temperature
ppm	Part per million
g	Gram
min	Minute
g/cm^3	Gram/cubic centimeter
rpm	Revolution per minute
psi	Pressure (pounds per square inch)
kN	KiloNewton
mm/min	Millimeter per minute
kg	Kilogram
J	Joule
ρ	Density
mg	Milligram
kV	KiloVolt
cm^{-1}	Reciprocal centime (wavenumber)

LIST OF ABBREVIATIONS

3D	3-Dimensional
AA	Acrylic Acid
AIBN	Azobisisobutyronitrile
Bio-PA	Bio-polyamide
Bio-PE	Bio-polyethylene
Bio-PP	Bio-polypropylene
BPO	Benzoyl peroxide
C=C	Carbon-carbon double bond
CI	Crystallinity Index
CPC	Cottonseed Protein Concentrate
DAS	Dialdehyde starch
DCP	Dicumyl Peroxide
EFB	Empty Fruit Bunch
EVO	Epoxidized Vegetable Oil
FRC	Fibre Reinforced Composite
FTIR	Fourier-Transform Infra-Red
GMS	Glycerol Monostearate
HDPE	High Density Polyethylene

IAh	Itaconic anhydride
KBr	Potassium Bromide
MAh	Maleic anhydride
MAh-g-PE	Maleic anhydride grafted polyethylene
MAh-g-PP	Maleic anhydride grafted polypropylene
MCC	Microcrystalline cellulose
NaOH	Sodium hydroxide
$NaClO_2$	Sodium chlorite
Na_2CO_3	Sodium carbonate
OH	Hydroxide (hydroxyl)
PA	Polyamide
PBS	Polybutylene succinate
PBSA	Polybutylene succinate-co-adipate
PE	Polyethylene
PEG	Poly(ethylene glycol)
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxy butyrate
PHBV	Poly(hydroxybutyrate-co-hydroxy valerate)
PHV	Polyhydroxy valerate
PLA	Poly(lactic acid)

POSS	Polyhedral oligomeric silsesquioxane
PP	Polypropylene
PPC	Poly(propylene carbonate)
PU	Polyurethane
PVA	Poly(vinyl alcohol)
QIAh	Itaconic anhydride with hydroquinone
QMAh	Maleic anhydride with hydroquinone
R&D	Research & Development
ROP	Ring opening polymerization
SAh	Succinic anhydride
SDG	Sustainable Development Goal
SEM	Scanning Electron Microscopy
TBF	Treated banana fibres
WA	Water absorption
XRD	X-ray diffraction

KESAN PENAMBAHAN TANDAN BUAH KELAPA SAWIT KOSONG (EFB), PENAMBAHAN GLISEROL DAN PENGUBAHSUAIAN ANHIDRIDA TERHADAP SIFAT-SIFAT BIOKOMPOSIT ASID POLILAKTIK (PLA)

ABSTRAK

Kajian ini bertujuan untuk mencipta biokomposit yang diperkuat dengan tandan buah kelapa sawit (EFB) dalam asid polilaktik (PLA). Pada masa yang sama, biokomposit PLA/EFB ditambah dengan gliserol, iaitu sejenis pemplastik, untuk mengkaji kesan gliseol dalam PLA/EFB. Pada peringkat akhir kajian ini, 20% EFB (PLA/20%EFB) telah dirawat dengan sebatian anhidrida (anhidrida maleik MAh, anhidrida suksinik SAh, dan anhidrida itakonik IAh) pada peratusan yang berbeza sebelum dimasukkan ke dalam PLA untuk meningkatkan keserasian antara PLA dengan EFB. Hidrokuinon telah ditambah semasa rawatan EFB, untuk mengelakkan pembukaan ikatan C=C (kumpulan tak tepu), dan kesan penambahan hidrokuinon diperhatikan. Berdasarkan hasilnya, penambahan EFB dan gliserol ke dalam PLA telah mengurangkan sifat mekanikal, terutamanya disebabkan oleh ketidakserasian antara PLA, EFB degan gliserol. Pada peringkat kemudian, melalui pemerhatian analisis morfologi, antara muka PLA dengan EFB telah bertambah baik, dan mikrograf SEM menunjukkan pengagihan dan kebasahan EFB yang dirawat secara berkesan dalam matriks. Biokomposit dengan EFB yang dirawat menunjukkan peningkatan ketara sebanyak 54.41% (SAh-EFB), 93.70% (MAh dengan hidrokuinon-EFB), dan 128.35% (IAh dengan hidrokuinon-EFB) dalam modulus tengangan. Penyerapan air meningkat dengan pertambahan EFB dan gliserol kerana sifat hidrofilik bahan tersebut, namun ia dapat dikurangkan melalui rawatan anhidrida, terutamanya dengan penambahan hidrokuinon. Selain itu, terdapat juga peningkatan dalam sifat lenturan,

tetapi dengan pengurangan sedikit dalam kekuatan impak. Walau bagaimanapun, ujian terma dan XRD menunjukkan perubahan yang tidak signifikan. Hasil kajian ini membuktikan bahawa adalah wajar untuk merawat EFB menggunakan sebatian anhidrida dalam kajian ini untuk meningkatkan sifat antara muka antara EFB dan matriks PLA.

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ABSTRACT

This study aimed to develop biomass-reinforced biocomposites by using empty fruit bunch (EFB) as reinforcement materials in PLA. At the same time, PLA/EFB composite was added with glycerol, which was a plasticizer to study the effect of glycerol in these biocomposites. In the later stage of this study, 20% EFB (PLA/20%EFB) was further treated with different anhydride compounds (maleic anhydride MAh, succinic anhydride SAh and itaconic anhydride IAh) at different percentages before incorporating into PLA to improve the compatibility between PLA and EFB. Owing to the unsaturated group of MAh and IAh, hydroquinone was added to prevent the opening of C=C during the treatment of EFB, and therefore the effect of hydroquinone addition was observed. From the results, incorporating EFB and glycerol addition to PLA had lowered its mechanical properties. The reduction in properties was mostly due to the incompatibility between PLA, EFB and glycerol. In later stage, through observation via the morphological analysis, the interfacial between the PLA and EFB was improved, and SEM micrographs show the improved distribution and effective wetting of treated EFB within the matrix. Biocomposites with treated EFB exhibited remarkable improvements of 54.41% (SAh-EFB), 93.70% (MAh with hydroquinone-EFB), and 128.35% (IAh with hydroquinone-EFB) in tensile modulus. The presence of hydroquinone in preventing C=C opening of MAh and IAh also show improvement compared to treated EFB without hydroquinone. Water absorption increased with EFB and glycerol loading due to the hydrophilic

nature of the fillers, but was mitigated through anhydride treatment, especially with hydroquinone inclusion. In addition, there were also improvements in flexural properties, but with a slight reduction in impact strength. However, thermal and XRD testing of the biocomposites show insignificant changes in the properties. These results proved that it was feasible for treating EFB using anhydride compounds in this study to enhance the interface properties between the EFB and PLA.

CHAPTER 1

INTRODUCTION

Most of the plastics used by the community today are made from fossil fuel based chemical, and the non-degradable nature of plastics had created a huge problem to the earth. Since plastics have been developed, there will be expected amount of 4725 million tons of plastics have been produced until year 2050, and among these large amount of plastics, most of them are not recycled and left in the environment (Dokl et al., 2024). The usage of fossil fuel based chemical also led to the depletion of natural resources in the future. Among different approaches to reduce and solve the issues brought by plastics, most of the industry has agreed on material replacement, i.e., replacing of fossil fuel-based chemical with bio-resources derived materials that could preserve the non-renewable natural resources, while improving the degradability of the bio-resources derived plastics. In other words, sustainability is the main target in recent research and development (R&D) for a green future. There are few bio-based derived polymers such as polylactic acid (PLA), polyhydroxyvalerate (PHV), and polyhydroxyalkanoates (PHA) which have been developed in the early 21st century, and nowadays, there are some bio-based polymeric materials have been commercialized in the market. The common materials used for synthesizing bio-based polymer are vegetable oil, cellulose, and starch. These bio-based polymeric materials made plastics are also known as bioplastics (Ibrahim et al., 2021).

Polylactic acid is one of the sustainable material replacements for fossil fuel based chemical plastics, and its distinctive properties made it one of the best materials for bioplastics synthesising. although PLA is well-known for its biodegradability, sustainability, and high tensile strength. PLA has the cons of low flexibility, brittleness, poor heat stability, low impact strength, poor barrier properties, and slow

crystallization rate (Rozman et al., 2000). These poor properties of PLA have limited its application in various industries, for instance, there are underutilization of PLA in food packaging, as its high gas and water permeability could not prevent rotten of food efficiently (Krishnan et al., 2016).

The application of bioplastics in various industries had a positive impact on the plastic waste issues, however, replacement of bioplastics had faced difficulty in heavy workload working condition. This situation is due to the inferior properties of bioplastics as compared to conventional plastics, and several research have reported that, bioplastics need extra costs to achieve comparable mechanical properties to conventional plastics (Bilo et al., 2018; Othman et al., 2020). Therefore, bioplastics has been reinforced by various low cost materials, especially renewable resources. Among various renewable resources used for bioplastics reinforcement, starch and natural fibre are widely used (Babalola & Olorunnisola, 2019), as they are abundant in nature. Oil palm empty fruit bunch has been selected as the reinforcement agent for the bioplastics in this study. *Elaies guineensis* or oil palm is planted extensively for oil production especially in South-East Asia Countries such as Malaysia, Indonesia, and Thailand, and is originated from West and Central Africa. In Malaysia, the plantation of oil palm tree has reached 5.67 million hectares, while the total exports of palm oil and its related products were recorded 24.72 million tonnes in year 2022 (Kadir, 2022). Oil palm empty fruit bunch (EFB) is the by-product of the extraction of palm oil from the oil palm FFB. It contains a marvellous number of fibres, making it could be applied in various industries. Also, EFB is a popular fibre to be used in papermaking and as reinforcing material in composites due to its high fibre content.

In this study, the approach used for resolving the issue is using different chemical anhydride for the treatment of fibres which could improve the interfacial

adhesion between the materials within the matrix, and at the same time increasing the mechanical properties. Instead of acid compounds, anhydride compounds are chosen as chemical reagents for the EFB treatment, because of the higher chemical reactivity behaviour of anhydride compounds compare to acid compounds that tend to react with hydroxyl groups of EFB, forming covalent bonding with the fibres that could improve the adhesion between fibres and polymer matrix. In addition, this could reduce side reactions that possibly alter the EFB chemical structure, such as acid hydrolysis if acid is used as coupling agent that might degrade the fibres properties. Anhydride compounds, namely maleic anhydride (MAh), succinic anhydride (SAh) and itaconic anhydride (IAh) are chosen as the coupling agent for the issue mentioned, but there are limited studies using these chemicals as fibre treatment in bioplastics. These anhydrides serve as coupling agents to enhance fibre–matrix interactions through possible covalent bonding with the hydroxyl groups of EFB. In addition, hydroquinone is added during MAh and IAh treatments to preserve the carbon–carbon double bond (C=C) and avoid radical-induced degradation of the coupling agents. Also, prevention of opening of the C=C could help in preserving the completeness of the anhydride compounds, preventing other unnecessary reactions that influenced the efficiency of fibres treatment. In common treatment of fibres using MAh and IAh, hydroquinone is added to prevent radical reactions that causing the opening of C=C. Therefore, to address the mentioned issue, treatment of EFB using MAh and IAh has separated into two variations, which are, one with addition of hydroquinone and the other without it.

In general, PLA would be used as the polymeric matrices, and oil palm EFB as reinforcement. EFB is a bio-waste that largely produced annually in Malaysia. Utilization of EFB to reinforce PLA could help in continuous development of the industry, but addition of lignocellulosic fibres might weaken the performances of the

PLA due to the incompatibility of PLA with fibres. PLA/EFB composite will be plasticised using glycerol as the plasticiser to enhance its flexibility and also reduce the brittleness. As a widely used plasticizer glycerol will interact with the polymer matrix, could improve its ductility, that widen the application of the biocomposites. Also, the use of the compatibilizer (MAh, SAh and IAh) is explored to enhance the fibre-matrix interactions. These chemical treatments can facilitate bonding between the EFB and PLA through promoting covalent or hydrogen bonding via the hydroxyl groups from the fibres. This is to strengthen the compatibility between PLA and EFB, ensuring an improved interfacial properties biocomposites with improved physical and mechanical performances. Additionally, MAh and IAh consist of carbon-carbon double bond, and during treatment of EFB using MAh and IAh without addition of hydroquinone, there might be other unnecessary side reactions occurred, which could affect the performance of the coupling agents. Thus, EFB treatment using MAh and IAh is further added with hydroquinone to prevent C=C bond opening (premature radical polymerisation of C=C), and the different of the composites' performances treated with MAh and IAh before and after addition of hydroquinone will be investigated. In addition, the water absorption of the composites will be investigated too.

Despite various studies on fibre-reinforced PLA, there remains a research gap on systematically comparing these three anhydride treatments and the effect of hydroquinone inclusion. Additionally, limited studies address how these treatments influence not only the mechanical properties but also the water absorption of the composites. Therefore, this study is needed to evaluate and optimise chemical treatment of EFB for improving compatibility with PLA, while also exploring how hydroquinone influences the efficiency of MAh and IAh treatments. The novelty of

this study lies in the direct comparison of three different anhydrides in combination with hydroquinone to enhance both interfacial bonding and water resistance in PLA/EFB composites.

The general aim of this research study is to investigate the utilization and effect of oil palm empty fruit bunch (EFB) in reinforcing polylactic acid (PLA), with the effect of glycerol addition as plasticiser and the chemical treatment of EFB.

To achieve this aim, the specific objectives of this project are:

i) To study the properties of PLA/EFB biocomposites at different loading of EFB and glycerol.
ii) To investigate the effect of hydroquinone addition on the treatment of EFB using anhydride compounds.
iii) To compare the performance and water absorption of PLA/EFB biocomposites prepared from different anhydride treated EFB, with and without hydroquinone.

CHAPTER 2

LITERATURE REVIEW

2.1 Bioplastics

Conventional plastics not only causing exhaustion of fossil fuel, but it also releases greenhouse gases and other waste pollutants during processing of the materials, which later led to environmental pollution including global warming, not to mention how plastic wastes damaging the environment. The rising of awareness on exhaustion of fossil fuel guided the industry to search for alternative material for synthesizing conventional plastics, and therefore bioplastics which used different renewable resources have been developed. Bioplastic is defined as plastic material which partly or completely synthesis by renewable resources. In current development of bioplastics, there are three classifications of bioplastics, which are biodegradable bioplastics, non-biodegradable bioplastics, and biodegradable petrochemical plastics (such as poly(vinyl alcohol) (PVA), and poly(butylene succinate) (PBS) which are biodegradable in certain conditions) (Rosenboom et al., 2022). However, indeed bioplastics resolve the non-renewable resources depletion issue, but some bioplastics are also not biodegradable and its production might causes environmental pollution such as bio-polyethylene (Bio-PE), bio-polypropylene (Bio-PP), and bio-polyamide (Bio-PA) (Atiwesh et al., 2021). In recent development of bioplastics, the trend of materials selection tends to those abundant in nature, and reusable wastes, such as starch, cellulose, plant oil, etc. (Klein et al., 2019).

Bioplastics usually synthesized by these three common methods, which are, bacterial polyester fermentation through using of natural polymer (PLA, PHA, PHV, PHB, etc.), chemical polymerization using chemical such as polybutylene succinate PBS, and polyglycolic acid, and use of natural polymer (starch, cellulose, protein, etc.)

(*Handbook of Bioplastics and Biocomposites Engineering Applications*, 2011). These commercialized bioplastics now have partly replaced conventional plastics in various industrial applications. As aforementioned, nature of bioplastics such as low heat stability, brittleness, high water uptake, low chemical and mechanical properties have limited the usage of bioplastics. Reinforcement of bioplastics has become one of the promising methods to produce a high-performance bioplastic in order to reduce the usage of conventional plastics.

Materials used for bioplastics reinforcement usually have two types, which are synthetic materials, and natural or biomass resources. The common synthetic materials used for bioplastics reinforcement are synthetic fibres such as carbon or glass fibre. However, some synthetic materials such as synthetic glass fibre could reduce the biodegradability of bioplastics which make the environmental pollution even worse (Folino et al., 2020; Yang et al., 2014). For the sustainability goal in the industry, using of renewable natural and biomass resources is one of the keys. The example of the resources are cellulose, chitosan, fibre, and clay, and studies have shown that these materials could strengthen the mechanical properties of bioplastics, while improving the biodegradability with minimum cost. These materials are abundant in nature, and some of them could be found as agriculture industry waste. Either synthetic or renewable natural and biomass resources could give promising result in bioplastics reinforcement, nevertheless, the degradability of the reinforced bioplastics varies depending on the interaction and compatibility between the reinforcing materials with the bioplastics.

2.1.1 Polylactic acid

Polylactic acid (PLA) is a bio-based aliphatic polyester which is a biodegradable and recyclable polymer. Polylactic acid is a thermoplastic synthesis from monomer named lactic acid that can be obtained from renewable resources, for example, sugarcane, starch, corn, food waste and some other biomass. The monomer unit of PLA is lactic acid, and polymerization of lactic acid will form PLA, the chemical structure of PLA is shown in Figure 2.1. PLA is well-known for its good mechanical properties, compatibility, and the biodegradability. These advantages of PLA make it a suitable material as a replacement for conventional plastics, in the applications of food packaging, construction, automotive, biomedical, and agriculture industries (Kong et al., 2023).

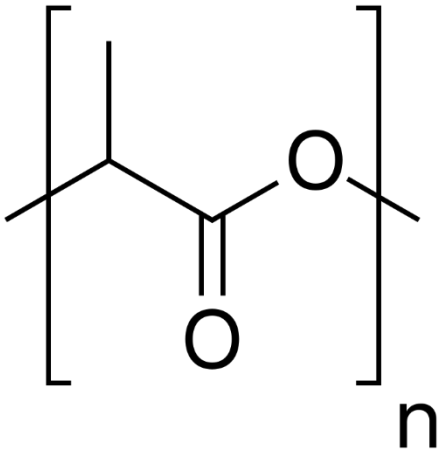

Figure 2.1: Chemical structure of PLA.

The common methods to produce PLA include, azeotropic dehydrative condensation, direct condensation polymerization, and lactide formation polymerization (García Ibarra et al., 2016). Azeotropic dehydrative condensation is a method using glycols and dibasic acids as solvents at high temperature with the azeotropic distillation to produce PLA with high molecular weight, but there will be solvents with catalysts left at the end of reaction (Ren, 2010). Another method is the

lactide formation polymerization, which also known as the ring-opening polymerization (ROP) in the industry. This method could produce high molecular weight PLA with three main types of radical initiators mechanisms, including insertion/coordination, cation and anion use. This method starts with the condensing of lactic acid, condensed water, mesolactic acid, followed by the low molecular weight polymer removal, recrystallization for getting high molecular weight pure lactide, and the addition of the three initiators to induce the polymerization (Chen et al., 2006). Direct condensation method is a two steps method, that involve carboxyl and hydroxyl groups dehydration condensation in first step, followed by the addition of coupling agents and esterification adjuvants to modify the PLA and also amplify the polymer chain. This method produce low impurities PLA that further require flammable solvents to increase the purities, which then making this method is less preferable in the industry (Chen et al., 2006).

However, application of PLA is limited due to its brittleness (low flexibility) although having good mechanical properties. In other words, properties of PLA including flexibility, stiffness, thermal stability, production cost, impact strength have to be modified and improved, to extend the applications of PLA in various industries. Polymer blending technique is one of the common methods used for PLA bioplastics modification. Blending PLA with other polymers could have the complementary advantages of both polymers to reinforce the bioplastics, for example, PLA often blends with PHA and PBS, which later could produce bioplastics with both PLA and PHA/PBS advantages. Besides, adding filler to reinforcing the PLA bioplastics is another regular technique to resolve the weakness of PLA. Renewable natural filler which is abundant in nature is a popular choice, and some of the examples of filler used are, fibres, cellulose, clay, and starch (Kong et al., 2023).

2.2 Reinforcing materials

The reinforcement of bioplastics is important to overcome the shortcomings of the bioplastics to be applied in different industries. The mechanical, chemical and thermal properties are the determining factors for the bioplastics to be widely applied in the industries and to replace the conventional plastics. There are varieties of reinforcing materials available. Different materials used as reinforcing agents in the bioplastics would have different effects on different bioplastics. Therefore, choosing of the reinforcing materials in the bioplastics is vital to maximize the effectiveness of the reinforcement. There are two major types of reinforcing materials, which are synthetic materials and natural resources. Both of the reinforcing material types provide promising effect on the bioplastics.

2.2.1 Synthetic materials

There are varieties of synthetic materials have been used as the reinforcing materials for bioplastics, these materials include carbon fibre, glass fibre, and polypropylene. There are studies on these materials showed that it could give promising improvements on the properties of bioplastics. Glass fibre is a synthetic fibre made from numerous amounts of fine glasses which is a silica-based material. It has the advantages of low density, relatively lower cost, high chemical resistance, and high strength, but it is high in stiffness which made it brittle. A study incorporated glass fibre in poly(4-hydroxy-L-proline) amide (PA) and poly(4-hydroxy-L-proline) ester (PE) bioplastics to study the flexural properties of this fibre reinforced composite (FRC) (Väkiparta et al., 2004). In the study, glass fibre reinforced PA achieved the highest flexural strength (888 MPa) among different recipes of glass fibre reinforced PA and PE. The results showed that the strength of the FRC would increase with the percentages of fibres within the biocomposites, and the orientation or position of the

glass fibre is vital in the fibre loading process within the bioplastics, as placing of the fibre on the tension side of the bioplastics would provide greatest reinforcement effect. Chen et al. (2009) used glass fibre as reinforcement for poly(propylene carbonate) (PPC) at the 10% addition of glass fibre up to 40% with 10% interval (Weifeng et al., 2009). The tensile strength of the composite has reached maximum at 20% glass fibre addition (29.75 MPa), which are 71.77% increment compared to pure PPC. At the same time, the thermal stability of the composite also has been improved compared to pure PPC as the degradation temperature increase with the addition of glass fibre (290.8 ˚C at 0% increase to 296.7 ˚C at 40% glass fibre loaded). Nevertheless, the rigidity of the composite increase as more glass fibres are loaded. There is also study using biodegradable glass fibre as the reinforcement for PVA (Zhu et al., 2022). The study reported that the composite have improved performance on the biocompatibility and mechanical properties, where the hydrogen bonding occurred among the PVA with the glass fibre, which then successfully lead to higher crystallinity of the composite. The compressive strength of the composite was increased 92.78% from 0.22 MPa of pure PVA to 3.05 MPa of 15% glass fibre incorporated PVA. The behaviour of the addition of glass fibre is similar to the few studies mentioned above, where the properties increment will reach threshold after a certain degree of addition (15% - 20%). Among these studies on glass fibre reinforced bioplastics, the biodegradability of the composites is seldom reported, but there are few studies on lignocellulosic fibre reinforced bioplastics stated that, using glass fibre in reinforcing bioplastics could lead to environmental issues (Folino et al., 2020; Yang et al., 2014).

Carbon fibre is a strong material with light weight made from carbon atoms, and due to its superior properties, it commonly used in industry to produce high strength products with lower weight. For instance, there were many automotive frames

used carbon fibre. However, the cons of carbon fibre include high production cost, and non-biodegradable which then results in sustainability and environmental pollution issues (Pimenta & Pinho, 2011). Another study used recycled carbon fibre to reinforce the PLA, and the result showed that the mechanical properties of the PLA are increased with the recycled carbon fibre loaded (Chen et al., 2013). The tensile modulus and strength of the composite compared to pure PLA increased 438% and 73% respectively from 0% to 30% fibre loading, whilst the flexural modulus and strength showed the similar behaviour, where it increased 400% and 53% respectively. However, there was a minor impact on the thermal properties of the PLA. In the study by Tey et al. (2020) on 3D printing of carbon fibre reinforced PLA composite, it showed that loading of carbon fibre will improve the mechanical properties of pure PLA, where it increase 175.3% and 180.5% for the tensile strength and Young's modulus respectively. This proved the workability of incorporation of the carbon fibre in brittle bioplastics such as PLA could help in increase the flexibility of the bioplastics, making it suitable to be used in 3D printing. Reddy et al. (2013) studies the effect of addition of different carbon fibre content and length in poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) (Reddy et al., 2012). As the summary of the study, the tensile and flexural strength of the composite increased with the carbon fibre and also the carbon fibre length (60 μm to 150 μm). The increment in the tensile strength is expected, as incorporation of fibre could help in distributing the applied load and extra load is required to break the bridge or the bond between the fibre with the polymer matrix. Longer fibre length would increase the tensile strength is due to its higher aspect ratio which assist in sustaining higher stress. This directly increases the maximum stress of the composite could be resist, and thus increase in the mechanical strength. The study also reported the increment of heat deflection temperature of the composite was increased by 32%

compared to pure PHBV. The maximum loading of the carbon fibre content was 30% as reported by Reddy et al. (2013), after this loading content, the composite's strength dropped.

Polypropylene (PP) is a thermoplastic polymer which is known for its high tensile strength, high thermal and chemical properties, and low weight. In recent development in bioplastics industry, there is biodegradable PP (Bio-PP) which could be used for bioplastics product manufacturing. Bio-PP could be manufactured through butylene dehydration of bio-isobutanol from glycose followed by polymerization process, but the research on the process of manufacturing of Bio-PP is limited, maing Bio-PP is less preferred in the market (Siracusa & Blanco, 2020). There is study using PP as reinforcing material for starch/chitosan based bioplastics by Jangong et al. (2019) (Jangong et al., 2019). PP is incorporated in the starch/chitosan based bioplastics, and it increase the mechanical strength of the bioplastics at optimum conditions. At appropriate condition, the composite show improved biodegradability where the composite have degraded more than 95% in 28 days. These studies showed that using synthetic materials as reinforcement materials would not have huge influence on the biodegradability of the bioplastics. To put in another way, synthetic materials give promising results in reinforcing the bioplastics, and the biodegradability of the reinforced bioplastics would varies based on the matrix interaction and also the compatibility of the major materials.

2.2.2 Natural resources

Indeed synthetic materials could provide significant positive reinforcement effect on the bioplastics, and it would not greatly influence the biodegradability. However, not all the available synthetic materials in reinforcing bioplastics are sustainable. Towards green industry in accordance with the sustainable development

goals (SDG), it is important in using sustainable materials in the industry to achieve the SDG. Natural resources are environmentally friendly, and most of them are sustainable, which made them suitable to be used as reinforcing materials in bioplastics. There are varieties of natural resources have been applied in reinforcing bioplastics in the market such as, cellulosic fibre (for instance, jute fibre, sisal fibre, Kenaf fibre, oil palm empty fruit bunch), clay, chitosan, and cellulose.

Clay is a type of fine grained natural soil material available in the Earth, which has the size of less than 0.002 mm in diameter. It is one of the abundant materials available to be used as polymer reinforcement. There are varieties of clay, such as bentonite clay, ball clay, and kaolin clay. There are wide range of applications for clay, for instance, clay for arts and crafts, agriculture use, construction materials, pottery and ceramics production as shown in Figure 2.2. In a research, modified kaolin (metakaolin) is used in starch-based bioplastics, the results showed there are improvements in the properties of the bioplastics, which the water permeability and absorption of the composites were dropped as the pores of the starch macromolecules chain were reduced by interaction between the clay molecules and the starch (Meite et al., 2021). In addition, the biodegradability of the composite was increased by 22% compared to pure starch-based bioplastics due to the development of fungi which then increased the bacteria activities. A study on interaction between clay and polymer by Gao (2004) stated that, using nano-sized filler (clay) would promote interfacial interaction between the bioplastics polymer matrix with the clay, that could results in better properties reinforcement (Gao, 2004). Harunsyah et al. (2021) prepared nano-particles clay reinforced cassava starch-based bioplastics plasticised with glycerol, and the results showed that the tensile strength of the composite increased with the loading of nano-clay, but after a certain limit, the tensile strength diminished as there will be

more space inside the matrix (Harunsyah et al., 2018). However, the addition of glycerol (plasticiser) influence the reinforcing effect of the nano-clay within the matrix negatively, as plasticiser increased the chain mobility in the matrix, which allowed the chain to slide between them with ease, resulting in reduction of tensile strength.

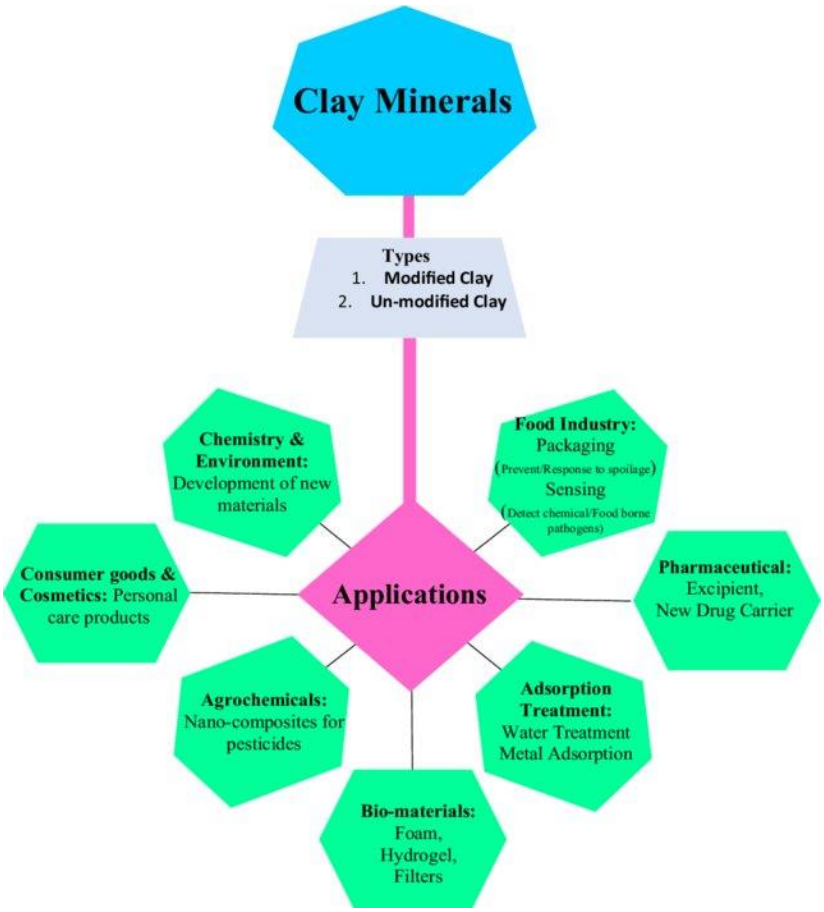

Figure 2.2: Applications of clay; Source: (Awasthi et al., 2019).

Chitosan is a natural polymer derived from chitin, which could be found in fungi, algae, and shells of crabs or shrimps. In other words, chitosan is an environmentally friendly material which can be found abundantly in the nature. It has a wide range of applications in different industries, for example, one of the materials in drug delivery systems, tissue engineering, food preservative and wound dressings. A study by Chandra et al. (2023), reinforced lignocellulosic plant based (such as banana, mango and hibiscus) with chitosan showed that the chitosan reinforced bioplastics have better mechanical properties, lower water permeability and higher

thermal stability, which having 257 ± 1.3 ˚C melting temperature (Chandra et al., 2023). Furthermore, the average mass loss of these bioplastics were 35.67% after 15 days, which indicates the biodegradability leading to less environmental impact. Chitosan is blended as reinforcing materials in the starch-based bioplastics to overcome its shortcomings, including, brittleness, hydrophilic nature and high water sensitivity (Tan et al., 2022). The loading of chitosan up to 20 wt.% could increase the tensile strength by 34.45% (from 3.86 MPa to 5.19 MPa) which is because of the increment of hydrogen bonding within the matrix between NH_3^+ from chitosan and OH^- from starch. Nevertheless, addition of chitosan also results in the decreased of the flexibility, and lower crystallinity index that lead to lower degradation temperature (worse thermal stability). Furthermore, the composite showed slower biodegradation rate than pure starch-based bioplastics, due to the antimicrobial property of chitosan (Tan et al., 2022).

Cellulose is one of the most abundant organic polymers in nature, it is a polysaccharide which is made up of glucose, as shown in Figure 2.3. It could be found in the cell walls of plants, such as cottons, bamboo, sisal, etc. As it is a natural resource, it is sustainable and biodegradable, which makes it one of the best options for reinforcing bioplastics. Pratama et al. (2019) blended cellulose as reinforcing materials in starch-based bioplastics, and it can be noted that the tensile strength of the composite with added cellulose is higher than pure starch bioplastics, the best formulation of the composite is 8:2 ; starch : cellulose (Pratama et al., 2020). Moreover, the biodegradability rate of the composite increases with the loading of cellulose compared to pure starch-based bioplastics.

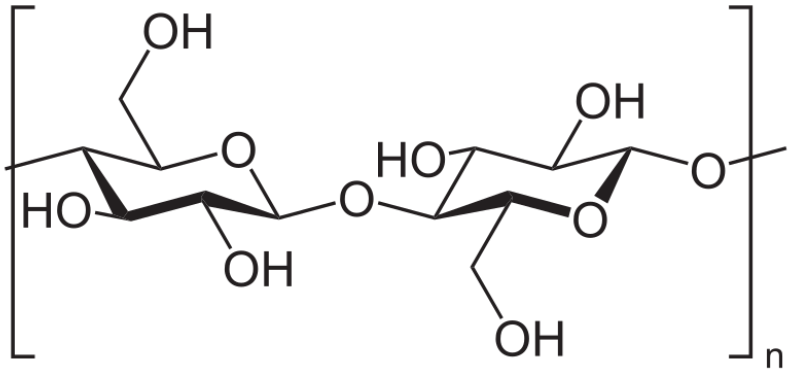

Figure 2.3: Chemical structure of cellulose.

Microcrystalline cellulose (MCC) is one of the commonly cellulose forms used in industry. MCC is derivative of cellulose, which is composed of tiny, packed and highly crystalline particles. It is in the form of white powder, which is odourless and tasteless. Lubis et al. (2018) extracted MCC from sugar palm fibres to be used for reinforcement of avocado seed starch bioplastics (Lubis et al., 2018). The tensile strength of the bioplastics increased as the MCC content increased, which was due to the increase in the amount of intermolecular hydrogen bonding between the MCC and starch. On the other hand, the elongation at break value of the bioplastics diminished with the loading of MCC, the bioplastics have reduced 81.74% at a 40 w.t%. loading of MCC Another study using MCC to reinforce cassava starch bioplastics reported increment in physical, mechanical, and thermal properties of the bioplastics after reinforcement by MCC (Abdullah et al., 2020). The hydrophobicity of the bioplastics is increased due to the increment of water contact angle by the loading of MCC, and the moisture content of the bioplastics is improved with higher content of MCC in the bioplastics because of the free volume within the matrix for water uptake is reduced by the addition of foreign material (MCC). The tensile strength and Young's modulus show increment as the addition of MCC because of the increasing of crystallinity, and inherent adhesion between the starch and MCC which have similarity in chemical structure (Ma et al., 2008). In addition, the thermal stability of the MCC reinforced

bioplastics is slightly increased compared to pure bioplastics because the MCC has higher thermal degradation temperature than starch. Nonetheless, the addition of MCC reduced the elongation at break due to the occurring of stress concentrations, which is the general trend for all reinforcement in bioplastics (Abdullah et al., 2020).

2.3 Lignocellulosic fibre reinforced bioplastics

Both of the synthetic and natural materials give promising results in reinforcing bioplastics, and the use of synthetic materials in reinforcing bioplastics did not affect the biodegradability of the polymer. However, usage of unsustainable materials should be minimised to lower down any environmental issues brought by these materials. In other words, using sustainable materials in reinforcing bioplastics is important in preserving and protecting the environment, which is one of the Sustainable Development Goals (SDG). Lignocellulosic fibres are one of the popular options among the various natural materials that suitable for reinforcing bioplastics. Lignocellulosic fibres are the natural fibres derived from varieties of plant sources, including agricultural wastes, and the major components in the fibres are cellulose, hemicellulose, and lignin. Thus, these fibres are renewable resources and abundant in nature, which is sustainable. The common lignocellulosic fibres used in reinforcing bioplastics are sisal fibres, hemp fibres, bagasse, rice straw, oil palm empty fruit bunch fibres, etc. The sources of these fibres are shown in Figure 2.4.

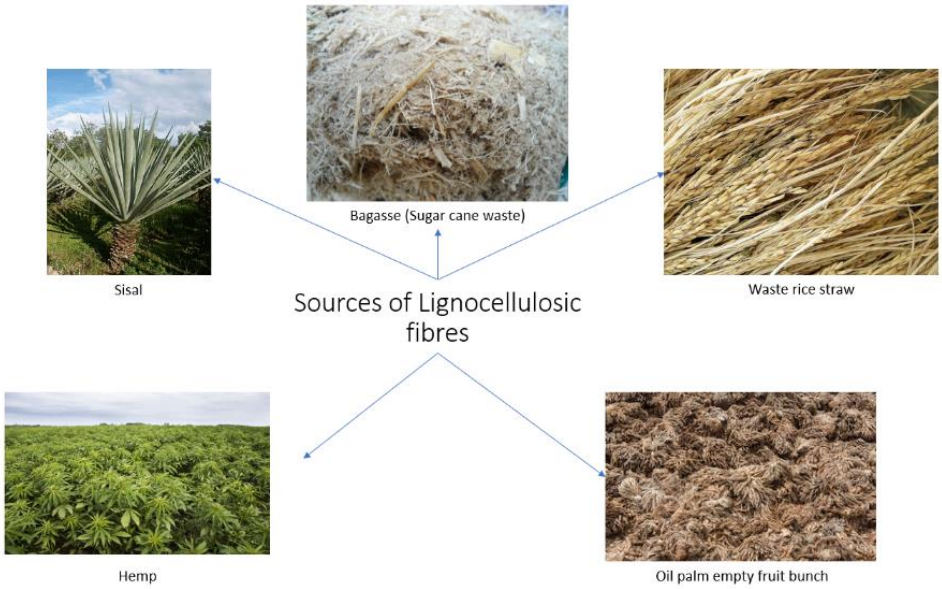

Figure 2.4: Sources of lignocellulosic fibres

Sisal fibre is derived from the Agave sisalana plant, which is a common plantation in Mexico and tropical countries. The fibres are extracted from the long leaves of the plant, and sisal fibres are well-known for their durability and strength, making them suitable for various applications, for instance, textile (bags, clothing, hats), paper making, ropes, and in composites as reinforcing material. In year 2013, Ranjan et al. (2013) used banana and sisal fibre to reinforce the PLA hybrid composite, and it used sodium hydroxide (NaOH) to eliminate and degrade hemicellulose, waxes and lignin (Ranjan et al., 2013). The results shown that mechanical properties, including tensile, flexural and impact strength are significantly improved with the addition of the fibres into PLA. In addition, alkaline treatment on the banana sisal fibres showed higher value in those mechanical strength compared to banana sisal fibres loaded PLA and pure PLA. Also, the interfacial interaction between the PLA and fibre is improved through the fibre treatment, through observation from Scanning Electron Microscopy (SEM). Study of sisal fibres used in protein-based bioplastics (cottonseed protein concentrate, CPC) as reinforcement showed that, there are lack of cross-linking between fibres and polymers although the addition of fibres indeed

strengthens the mechanical properties of the composites (Yue et al., 2020). Therefore, it further incorporated dialdehyde starch (DAS) to promote cross-linking within the matrix. At 5% loading of the sisal fibres into the CPC, the Young's modulus achieved 5 times improvement compared to pure CPC. Furthermore, at optimum concentration of DAS and sisal fibres, the interface between protein and fibres has a strong adhesion through the cross-linking properties of the DAS. This further leads to enhancement in thermal stability, water resistance and mechanical properties. In improving the interfacial interaction within the matrix, the loading percentage of fibres should be reduced as excessive fibres will tend to compact, making the composite easier to failure (Yue et al., 2020).

Hemp or *Cannabis sativa* (scientific name) has varieties of applications, such as, textile, papermaking, ropes and others. Hemp is a plant grown in temperate countries, for example, Canada, United States, and China. Hemp fibres referred to those fibres extracted from the stalk of the hemp plant. Hemp fibres are well-known for their versatility, strength, and durability. Due to its superior properties, it has been used as reinforcing materials for plastics since early 2000. Alao et al. (2023) used flame retardant additives and alkaline treated hemp fibre as reinforcement for PLA to study the thermal properties and water absorption ability of the composite. The hemp fibre was treated with NaOH solution and sprayed with the flame retardant (Palanot Oy fire retardant). The results showed that the composite exhibit better flame inhibition ability compared to pure hemp fibre reinforced PLA. Nevertheless, the water absorption of the composite is higher comparatively as nature of fibre tends to adsorb moisture, and the flame retardant used in the composite also exhibit hydrophilicity. On the other hand, Ahmed et. al (2023) used hemp and flax fibres to reinforce biopolymer produced by acrylic acid (AA), MAh, citric acid (CA) and glycerol (Shebaz Ahmed et

al., 2023). The fibre reinforced composite is prepared in the form of laminate to test the mechanical properties. Through mechanical testing, including tensile and flexural testing of the composite compared to fibre reinforced epoxy resin, there is 27% and 30% decrement in tensile strength and flexural strength respectively, which indicates that, at same reinforcing conditions, conventional plastics are much 'stronger' compared to the biopolymer. Hemp and coir fibre were used as filler (reinforcing materials) for Bio-PP ,and this study showed that the combination between hemp and coir fibre at the ratio of 1:3 gives highest value in both tensile strength and Young's modulus compared to pure Bio-PP, 608 MPa and 48.25 GPa respectively compared to Bio-PP of 512 MPa for tensile strength, and 43 GPa for Young's modulus (Sathish et al., 2021). Also, the elongation of the composite is enhanced along with the increment in strength, making the composite suitable for biomedical applications, such as bone and joint fixtures.

Bagasse is a by-product left after sugarcane have been processed to extract their juice for sugar production. After sugarcane is extracted, the fibrous materials left out is the bagasse. As an agricultural waste, it could be utilized as resources for papermaking, biofuel or fibre composite products making, and it contains a generous number of fibres, making it a good reinforcing material for polymer. In a study, bagasse is used as reinforcement for PLA/soy protein composite, which the bagasse is treated with NaOH before loaded into the composite (Boontima et al., 2014). The mechanical properties of the composite were tested, where the Young's modulus and tensile strength of the composites at 15% bagasse loading were increased by 53% and 51% respectively compared to pure PLA. Similarly, the impact and flexural strength of the composites were increased by 52% and 113% respectively at 15% bagasse loading. The impurities on bagasse's surface could be removed by alkaline treatment

which could reduce the fibre size which then lower the stress concentration and improve the dispersion of fibre within the matrix, leading to the decrement of the amount of crack during mechanical testing. However, there is also occurrence of fibre loading issue in polymer, which the water absorption of composite will increased as more voids are produced when more fibres are loaded, that allow more penetration of water. In addition, hydrophilicity of the fibres also contribute to increment of water absorption of the composite. Another study on bagasse fibre reinforced PLA by A. Bartos et al. (2021), investigated the effect of short and long bagasse fibre in reinforcing PLA. The loading of bagasse fibre indeed increased the Young's modulus of PLA, where the long bagasse fibre gives better effect than short fibre. Nevertheless, there is only minor improvement in tensile strength, but reduction of elongation of the composite (Bartos et al., 2021). In his study, the composite is added with malleated PLA coupling agent, but the study reported that, the interfacial adhesion between bagasse fibre and PLA is good, and the coupling agent did not function much in the composite. On the other hand, Aranda-Garcia et al. (2015) studied the effects of bagasse fibre incorporation in starch/PLA composite on water absorption and thermomechanical properties (Aranda-García et al., 2015). The impact strength and water absorption of the composite decrease as bagasse fibre is loading in. While the strength and modulus of tensile and flexural showed increment due to the hydrogen bonding between the fibre and the polymer matrix. The storage modulus (E'), increased as increment of bagasse fibre up to 15%. In addition, bagasse fibre loaded composite on heating to 160 ˚C has high resistance against the temperature as E' has lower degradation rate, because of the fibre contributing more hydrogen bonding and rigidity to resist against high temperatures (Aranda-García et al., 2015).

Rice straw is the by-product of rice plants after the grains have been harvested. Rice straw consists of large number of fibres which could be used for various purposes. As an agricultural by-product, rice straw are utilized as much as possible to avoid wastage of materials. Similar to other types of lignocellulosic fibres mentioned before, rice straw fibres could also be applied in papermaking and textiles industries. The effect of cellulose fibre derived from rice straw as reinforcement for starch-PVA biocomposite films was studied which aims to apply in food packaging industry (Sharma et al., 2022). Cellulose fibres isolated from the rice straw was further mixed with the biocomposites through solution casting method. Through thermal analysis, the biocomposite film with 30% rice straw fibre loading has improved the composite thermal stability which is approximately 13% increment. The water contact angle of the film with 25% fibre loading is 64.6 ± 5.8˚, which is higher than the pure film with 56 ± 5.04˚. At the same conditions, the antioxidant activity of the film has reached highest value of 20.04 ± 2%. However, excessive addition of fibre will cause increment in water vapour permeability due to the hydroxyl groups from the fibre. Rice straw cellulose microfibres was incorporated in thermoplastic corn starch films as reinforcement, and the results showed that at 3% fibres loading, the film was more rigid and harder to be broke, but the elongation of the film was decreased about 53% comparatively (Freitas et al., 2021). As the composite film was aimed to apply as food packaging, the water vapor permeability and oxygen permeability were studied, and at 3% fibres loading, the film has decrease in water vapor and oxygen permeability, which is around 15% and 30% respectively, that made the film more suitable for food packaging (Freitas et al., 2021). Chitosan extracted from shrimp for bioplastic film making, and rice straw fibre (and nanosized rice straw fibre, nanofibers) as reinforcement were used to study the feasibility of the film in food packaging

applications (Elhussieny et al., 2020). The film with 25% nanofibers added showed highest yield strength and Young's modulus at around 23 MPa and 1200 MPa respectively where the pure chitosan film is at around 19 MPa and 1050 MPa respectively only. The enhancement effect is because of the addition of the nanofiber formed 3-D networks within the matrix. However, the in-soil degradation rate for pure film is 75 days, but for the composite with different fibres loading is at 100 days. This indicates that the addition of fibre within a bioplastic might reduce the biodegradation rate.

2.4 EFB reinforced PLA

Empty fruit bunch (EFB) is a fibrous by-product from the palm oil industry, which is also a low cost resource for sustainable reinforcement The oil palm plant is one of the most versatile plants, extensively harvested for its palm oil, which is used in various industries, such as, food, cosmetics and biodiesel production. Other than palm oil, other parts of the plant, such as the kernel shells and fronds, could be applied in energy production, animal feed or as organic fertilizers. The other parts of oil palm plant which could be utilized are shown in Figure 2.5. Beyond these sub-products, EFB stands out with its high cellulose content, making it suitable as a reinforcement material for bioplastics composite due to its excellent mechanical properties. Additionally, utilizing EFB addresses the waste management issue in the palm oil industry, promoting the circular economy by transforming the agricultural residues into value-added products.