SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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THE EFFECT OF VARIOUS COMPATIBILIZERS ON PROPERTIES OF MENGKUANG LEAF FIBRE FILLED POLY(LACTIC ACID) COMPOSITE

By

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DECLARATION

I hereby declare that I have conducted, complete the research work and written the dissertations entitled **“Effect of Various Compatibilizers on Properties of Mengkuang Leaf Fibre Filled Poly(lactic acid) Composite”.** I also declare that it has not been previously submitted for the award or any degree or diploma or other similar title of this for any other examining body of University.

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile-Butadiene-Styrene
ASTM	American Society for Testing and Materials
DSC	Differential Scanning Calorimetry
EBA-GMA	Ethylene-n-Butylacrylate-Glycidyl methacrylate
EMA-GMA	Ethylene Methyl Acrylate-Glycidyl Methacrylate
EVA	Ethylene Vinyl Acetate
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
IM	Impact Modifier
LA	Lactic Acid
LDI	Lysine-Based Diisocyanate
LDPE	Low Density Polyethylene
LLDPE	Linear Low-Density Polyethylene
MA-g-SEBS	Maleic Anhydride Grafted Styrene Ethylene Butylenes Styrene
MaPO	Maleic Peroxides
MLF	Mengkuang Leaf Fibre
NPCC	Nano-Calcium Carbonate
NR	Natural Rubber
OBC	Olefin Block Copolymer
PA6	Polyamide 6
PBS	Polybutylene Succinate
PCL	Poly(Caprolactone)
PDLLA	Poly(DL-Lactide)
PE	Polyethylene
PEG	Polyethylene Glycol

PEgAA	Polyethylene Grafted with Acrylic Acid
PEgMA	Polyethylene Grafted with Maleic Anhydride
PET	Poly (Ethylene Terephthalate)
PGA	Polyglycolic Acid
PHA	Polyhydroxyalkanoates
PHBHHx	Poly(3-Hydroxybutyrate-Co-3-Hydroxyhexanoate)
PLA	Poly(Lactic Acid)
PLLA	Poly-L-Lactide
PP	Polypropylene
PS	Polystyrene
PVA	Poly (Vinyl Alcohol)
PVC	Polyvinyl Chloride
SEBS-g-MA	Styrene Butadiene Butylene Styrene Grafted Maleic Anhydride
TPE	Thermoplastic Elastomer

LIST OF SYMBOLS

T_m	Melting point
T_g	Glass transition temperature
T_{cc}	Cold crystallization temperature
χ_c	Degree of crystallinity
ΔH_m	Enthalpy of melting
ΔH_c	Enthalpy of crystallinity
ΔH_f	Enthapy of fusion
W_{PLA}	Weight fraction of PLA

KESAN BAHAN PENGSERASI YANG BERLAINAN TERHADAP SIFAT POLI(ASID LAKTIC)/SERAT DAUN MENGKUANG (PLA/MLF) KOMPOSIT

ABSTRAK

Poli (asid laktik)/serat daun mengkuang (PLA/MLF) komposit telah disediakan dengan menggunakan penyebatian leburan. Poli (etilena-ko-metil akrilat-ko-glycidil methaktilat (EMA-GMA) dan stirena-b-etilena/butilena-b-stirena tercantum maleik anhidrida (SEBS-g-MA) digunakan sebagai bahan pengserasi dalam komposit PLA/MLF untuk meningkatkan sifat komposit. Pada peringkat pertama, kajian ini memberi tumpuan kepada sumbangan komposisi yang berbeza (10, 20, 30, dan 40% berat) MLF di dalam PLA. Penilaian dilakukan melalui ujian tegangan, analisa termal oleh kalorimetri pengimbasan perbezaan (DSC), analisis morfologi oleh mikroskop imbasan elektron (SEM), dan spektroskopi inframerah (FTIR). Pemanjangan pada takat putus, modulus, dan kekuatan tegangan komposit PLA/MLF berkurang dengan ketara berbanding dengan PLA tulen. Darjah kehabluran komposit PLA/MLF berkurang sedikit dengan penambahan MLF. Berdasarkan termogram DSC, komposit PLA/MLF menunjukkan kehadiran puncak lebur bimodal akibat mekanisme penghabluran semula yang berlaku semasa pemanasan. Pemerhatian melalui SEM menunjukkan interaksi yang lemah antara komponen dan penyebaran pengisi yang lemah. Di peringkat kedua, EMA-GMA diperkenalkan untuk meningkatkan sifat-sifat komposit PLA/MLF. Namun, pengurangan kekuatan mekanik yang serupa telah diperhatikan, mencadangkan bahawa EMA-GMA tidak dapat bertindak sebagai bahan pengserasi yang baik dalam komposit PLA/MLF. Darjah penghabluran PLA/MLF berkurang dengan kehadiran EMA-GMA. Permukaan patah juga diperhatikan mempunyai aglomerasi. Di peringkat ketiga, SEBS-g-MA diperkenalkan sebagai bahan pengserasi. Kehadiran SEBS-g-MA juga tidak dapat meningkatkan sifat-sifat tegangan komposit. Sifat-sifat yang lebih baik telah diperhatikan dalam sistem dengan EMA-GMA berbanding SEBS-g-MA.

THE EFFECT OF VARIOUS COMPATIBILIZERS ON PROPERTIES OF MENGKUANG LEAF FIBRE FILLED POLY (LACTIC ACID) COMPOSITE

ABSTRACT

Poly (lactic acid)/mengkuang leaves fibres (PLA/MLF) polymer composites were prepared by melt compounding technique. Ethylene methyl acrylate-glycidyl methacrylate (EMA-GMA) and styrene butadiene butylene styrene grafted maleic anhydride (SEBS-g-MA) were used as compatibilizers in PLA/MLF composites to enhance the properties of the composites. In the first stage, the study focused on the contribution of different compositions (10, 20, 30, and 40 wt. %) of MLF in PLA. The evaluation was performed through tensile test, thermal analysis by differential scanning calorimetry (DSC), morphological analysis by scanning electron microscope (SEM), and chemical interaction study by fourier transform infrared (FTIR) testing. The percentage elongation, modulus, and tensile strength of PLA/MLF composites decreased significantly in comparison with pure PLA. Degree of crystallinity of PLA/MLF composite slightly reduced with the incorporation of MLF. Based on the DSC thermogram, PLA/MLF composites show the presence of bimodal melting peaks due to melt-recrystallization mechanism that might happen during heating. SEM observation indicated poor interaction between components and poor dispersion of the filler. In the second stage, EMA-GMA was introduced to improve the properties of PLA/MLF composites. However, similar trend of reduction in mechanical strength was observed, suggesting that EMA-GMA could not act as a good compatibilizer in PLA/MLF composites. Degree of crystallinity of PLA/MLF reduced in the presence of EMA-GMA. Fracture surface also observed to have agglomeration. In the third stage, SEBS-g-MA was introduced as a compatibilizer. The presence of SEBS-g-MA also could not improve tensile properties of the composite. However, better properties were observed in the system with EMA-GMA compared with SEBS-g-MA.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

The wide and extensive use of plastic materials resulted in million tons of plastic wastes in the landfill sites each year globally. Conventional plastics will take a long time to degrade, thus it had drastically increased the ecological problems. This problem does not seem to come to an end since the consumption and global production of plastics have continued to rise. Plastic waste disposal problems have existed over decades but there are still lack of successful methods to solve it. Besides, continuously increasing of crude oil prices during the past few decades and shortage of fossil resources have increase the need to find an alternative way to replace it with some renewable resources. New rules and regulations have forced manufacturers to use more environmentally and harmless materials. This problem had emerged concern and attention from the people all over the world. Thus, many solutions have been suggested and developed such as the development of biodegradable materials.

Biodegradable polymers and biopolymers have been in the focus of academic research since these materials are expected to solve this issue. Biopolymers are differed from biodegradable polymers in terms of it is persistent to microbial degradation even though it also produced by bacteria. The definition of biopolymers is a polymer that is biodegradable or has bio-based content or both. Bio-based polymers may be biodegradable or non-biodegradable, depending on their composition or structure or the environment where they are placed(Mohanty et al., 2005). Bio-based content is the fraction of the carbon content (new carbon content from agriculture resources or biological material versus fossil carbon content). Polythioester is one of the example of a non-biodegradable biopolymers because of their persistent to microbial degradation(Steinbüchel, 2005).

Another advantage of biopolymers that made it attractive is its potential to reduce the carbon dioxide quantities in the atmosphere by cutting the emissions of carbon. This is because the use of biopolymers such as PLA which currently produced from plants that used carbon dioxide from the air and turns it into starch that can be processed into plastic (PLA)(Numata and Kaplan, 2011). Thus, biopolymers which sourced from renewable resources will reduce the dependence on petroleum. For an instance, poly(lactic) acid (PLA) is a biodegradable biopolymers that has been used widely in engineering and biomedical applications, domestic applications and also agricultural applications(Sin, 2012). D. Bondeson and K. Oksman (2006) had studied the mechanical properties of cellulose whisker/polylactic acid nanocomposites(Oksman et al., 2006) and the effect of polyvinyl alcohol in polylactic acid/cellulose whisker nanocomposites(Bondeson and Oksman, 2007).

A biodegradable polymer is a high molecular weight polymer that degrades as an action of microorganisms and/or enzymes. In other word, it can be defined as an event which takes place through the action of enzymes and/or chemical decomposition associated with living organisms and their secretion products(Albertsson, 2004). Biodegradable polymers are broadly classified into two main categories: (1) natural and (2) synthetic. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources. The examples of biodegradable polymers are poly (vinyl alcohol) (PVA), poly(lactic acid) (PLA), and polyhydroxyalkanoates (PHA)(Mohanty et al., 2000). There are many biodegradable polymers that have been produced along with microorganisms and enzymes capable of degrading them have been identified. For an instance, production of green polyethylene (PE), polyvinyl chloride (PVC), and other green plastics. Besides, biodegradable polymers such as cellulose, chitin, starch, polyhydroxyalkanoates (PHAs), polylactide, poly(ε-caprolactone), collagen, and other polypeptides have been synthesized. Biodegradable material is very useful for tissue engineering field. For an instance, poly(lactides) and poly(glycolides) has been discovered extensively to be used as orthopedic devices(Middleton and Tipton, 2000). Besides, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) and poly(DL-lactide) (PDLLA) blends aimed to prepare a soft and elastic biomaterial for use in nerve generation. PHBHHx is a family of PHA(Gao et al., 2006).

Other examples of biodegradable polymers are polyglycolic acid (PGA), polybutylene succinate (PBS) and poly(ε-caprolactone), polybutylene succinate terephthalate, and many more. Recently, technological advancements have substantially improved the properties of some bio-based polymers, such as heat resistant poylactic acid (PLA), enabling a wider range of applications(Sangeetha et al., 2016b). R. Mat Taib and coworkers (2014) had investigated the incorporation of poly(lactic acid) (PLA) with Kenaf bast fiber composites toughened with an impact modifier to improve the flexibility of PLA. The impact modifier used was ethylene acrylate copolymer impact modifier (IM)(Taib et al., 2014).

Among all other biodegradable plastics, PLA is the most extensively researched and utilized biodegradable and renewable thermoplastic polyester, with a potential to replace conventional petrochemical-based polymers. PLA is currently the most widely used biodegradable polymer in many industrial applications due to its good mechanical properties, processability, and biocompatibility. Biocompatibility is considered as the most eye-catching aspect of PLA, especially with respect to biomedical applications. A biocompatible material should not produce toxic or carcinogenic effects in local issues.

Nevertheless, PLA is marketed for biomedical applications such as medical implants, sutures, and drug delivery systems(Sin et al., 2013) and commodity applications such as disposable cutlery and cups, plastic bags, and food packaging(Demirbas, 2007).

Moreover, PLA is recycleable, compostable and its production also consumes les carbon dioxide. PLA is renewable and is produced from lactic acid obtained through microbial fermentation of renewable resources such as corn starch making it a sustainable alternative to petrochemical-based plastics products. These sustainability and eco-friendly characteristics make PLA an attractive biopolymer. PLA has properties that are comparable to many commodity polymers (e.g., polypropylene, polyethylene, polyvinyl chloride, and polystyrene) such as high stiffness, clarity, gloss, and UV stability. PLA also has better thermal processability compared to other biopolymers, such as poly(hydroxyl alkanoates) (PHAs), poly(ethylene glycol) (PEG), poly(caprolactone) (PCL), etc(Sangeetha et al., 2016a).

It is the most promising material for the productions of environment friendly, high performance products. It is proven to be superior to conventional plastics in terms of energy consumption and carbon dioxide emission in life cycle analysis. Commercial availability of PLA for industrial applications is satisfactory and the polymer is the only biodegradable polymer based on natural resources that is produced with a capacity over 140,000 tons per year. Although its tensile strength and elastic modulus are quite comparable to poly (ethylene terephthalate) (PET), the poor toughness, low glass transition temperature (55-65ºC)(Khuenkeao et al., 2016), and inherent brittleness(Lunt, 1998) had limits its use for wide range of applications. Other main limitations are its relatively high price, poor thermal resistance (low heat deflection temperature) and limited gas barrier properties. Besides, the low impact strength and less heat tolerance of the material makes it inadequate for more demanding applications. PLA is a very brittle material with very less elongation at break (less than 10%).(Nagarajan et al., 2016) PLA is relatively hydrophobic and is chemically inert with no reactive side-chain groups making its surface and bulk modifications difficult(Oksman et al., 2003).

In such a scenario, several strategies have been put forward to improve the material properties of PLA. The brittleness of PLA can be modified via several approaches: (1) copolymerization of lactic acid with other monomers, such as α-caprolactone and (2) by blending PLA with a second polymer or a plasticizer. Extensive efforts have been made to modify the brittleness of PLA via the first approach. Nevertheless, none of these PLA copolymers are commercially available in the market. Blending PLA with other flexible biodegradable or non-biodegradable polymers present a more practical and economic way of toughening the material. To overcome the toughness problems, a lot of researches were conducted on copolymerization, plasticization, and blending of PLA with other copolymers to improve the flexibility of PLA. In recent times, maleated rubbers like maleic anhydride grafted styrene ethylene butylenes styrene (MA-g-SEBS) were found to serve well as toughening agent for polymer blends and nanocomposites. Blending PLA with other polymers is the most viable methodology for toughening PLA(Rasal et al., 2010).

On the other hand, at 2.2 US$/kg (Taib et al., 2014), PLA is seen as an expensive polymer as compared to traditional major petroleum-based plastics. Thus, to reduce the cost and at the same time improving the range of PLA properties, many studies have been conducted on PLA with various natural fibers such as kenaf (Taib et al., 2014) and jute(Plackett et al., 2003a). Natural fibers have been considered as fillers and reinforcing materials for thermoplastics and thermosets (Taib et al., 2014). There are many publication on PLA composites with natural fibers such as kenaf (Ochi, 2008), abaca(Bledzki et al., 2009), chicken feather(Cheng et al., 2009), cotton(Graupner, 2008), bamboo(Porras and Maranon, 2012), and jute. In many of these research, the addition of natural fibres help in achieving the required properties.

Natural fibres are of interest because of their advantages such as renewability, biodegradability, low density, processability, and good mechanical properties(Taib et al., 2014). The main drawback of using natural fibers is the lack of adhesion with hydrophobic polymer matrices, which results in poor composite properties. This make it quite not suitable for some potential application such as automotive components. However, the adhesion between the two composites components can be improved with physical and chemical modification of either or both materials or by using coupling agent such as silane coupling agent, lysine-based diisocyanate (LDI) (Lee and Wang, 2006), maleated peroxides(MaPO)(Keener et al., 2004), etc.

Most of the research reported the addition of coupling agent in polymer composites has increases its properties(Lee and Wang, 2006). However, different coupling agent will work differently in different system. The effectiveness of coupling agent commonly is affected by its composition in polymer composites. The impact performance or toughness of a composite can be improved in several ways: i) increase the matrix toughness; ii) optimize the fiber-matrix interface; iii) optimize the filler-related properties such as filler content, particle size, and dispersion; iv) aspect ratio and orientation distributions also play a role in toughness of composites containing more fibrous materials(Oksman and Clemons, 1997, Taib et al., 2014).

A conventional approach to improve the impact performance of a composite is to incorporate an impact modifier within the matrix as part of the formulation prior to compounding. Another possible approach to improve the toughness of PLA is to use a suitable plasticizer such as triacetin and polyethylene glycol (PEG)(Rasal et al., 2010).

One of the interesting natural fibers is mengkuang leaf fiber(MLF). In recent study, mengkuang leaf fiber (MLF) has been used as a filler in natural rubber blended with EVA.(Hashim et al., 2017) The effect of different blending sequences and fiber loadings from 10 to 40 parts by weight per hundred parts of resin on the torque development, tensile properties, thermal degradation and morphology of EVA/NR/MLF composites was studied. F. Hashim and coworkers(Hashim et al., 2017) reported that the properties of developed composites are influenced by the amount of the MLF. From the research, the increase in MLF loading resulted in an increase in stabilization torque value and the Young's modulus, but a decrease in the tensile strength, the elongation at break, and the thermal stability of the composites. As MLF loading increased, fibres in the matrix showed frequent fibre pull-out and holes, because of poor adhesion between the fibre and the matrix(Hashim et al., 2017).

Biodegradable composites are prepared by combining biodegradable polymers such as polylactic acid (PLA) and polybutylene succinate (PBS) with natural fibres or fillers such as kenaf(Ochi, 2008), jute(Hu et al., 2010) and wood flour(Shah et al., 2008). To the best of our knowledge, there is no research has been conducted on the use of MLFs as fillers in virgin PLA or PLA blend with compatibilizer. Therefore, in this research, mengkuang leaf fiber (MLF) is used as natural fillers to reduce the cost of virgin PLA and at the same time expected to slightly maintain the properties of PLA.

Based on previous research, the mechanical strength might be dropped slightly but the leaves are believed to have strong fibres because they were used for making ropes(Hashim et al., 2017). Meanwhile, ethylene methyl acrylate-glycidyl methacrylate (EMA-GMA) and styrene butadiene butylene styrene grafted maleic anhydride (SEBS-g-MA) are used as compatibilizers for PLA because of high impact strength and good heat resistance as compared with other elastomeric materials.

1.2 Problem Statement

In PLA filled natural fibres with the primary aim to reduce the cost of PLA by replacing the weight of PLA with natural fibre, the reduction in mechanical properties are normally reported(Bax and Müssig, 2008). A few researchers (Bledzki et al., 2009, Mukherjee and Kao, 2011) reported that the reduction of mechanical properties due to weak interfacial adhesion between filler and PLA and also compatibilizers.

One of the efforts that can be done to enhance the properties of PLA/MLF composites is by the addition of compatibilizer. A good compatibilizer could act as a bridge between PLA and filler thus could improve the properties of the composites by increasing interfacial adhesion/interaction. However, it should be noted that different compatibilizers could act differently in different systems. A compatibilizer which can act as effective compatibilizer in one composite system might not be useful in another composite. Hence, the effect of different compatibilizers towards PLA/MLF composites should be studied. Some research have mentioned the ability of styrene butadiene butylene styrene grafted maleic anhydride (SEBS-g-MA) to increase the mechanical properties and impact properties of PLA composites(Chow et al., 2012).

In polymer composites, the properties of composites are very much affected by filler content, chemical treatment, and the interaction between matrix and fiber. There are many publications on PLA composites with natural fibers such as kenaf(Taib et al., 2014), flax(Bax and Müssig, 2008), sisal(Li et al., 2011), oil palm(Harmaen et al., 2013), coconut(Wu, 2009), and wood(Shah et al., 2008). For an instance, the addition of flax fibre in PLA has been found to increase the composite strength and stiffness(Bax and Müssig, 2008). However, R. Mat Taib and coworkers (Taib et al., 2014) reported that the addition of kenaf fibres reduced the tensile strength of PLA by 47%. This proved the poor interaction between PLA and kenaf fibres composite due to lack of adhesion between kenaf fibre and hydrophobic polymer matrices of PLA. Bax and Müssig (2008) also reported the decrease in mechanical properties of PLA with the addition of flax fibre(Bax and Müssig, 2008). According to the experiment, with increasing weight fraction of flax fibre, the impact strength of PLA/flax composites were reduced.

In PLA filled natural fibre composites, it is very crucial to study the effect of filler content and compatibilizer on tensile, impact strength and toughness. The morphological, mechanical, and thermal properties studies also important to understand the strength and rigidity of the composites, and the fractured surface.

1.3 Research Objectives

One of the most important aspects of materials development in thermoplastics engineering is to achieve a good combination of mechanical properties (i.e. stiffness, strength and toughness), possible process ability and at a moderate cost. The main objectives of this study are stated as below:

i. To investigate the effect of various compositions of MLF on tensile, thermal and morphological properties of PLA composites.
ii. To examine the effect of different amounts of compatibilizers, ethylene methyl acrylate-glycidyl methacrylate (EMA-GMA) and styrene butadiene butylene styrene grafted maleic anhydride (SEBS-g-MA) as a compatibilizer on tensile, thermal and morphological properties of PLA/MLF composites.
iii. To compare the tensile, thermal, and morphological properties of different compatibilizers used in PLA/MLF composites.

To achieve the objectives, PLA is mixed with MLF at different compositions (10wt% - 40wt%) and the properties of the composites was examined to obtain the optimum composition of MLF in PLA. The optimum composition was selected based on the highest value in tensile testing and observation of fracture surface by using SEM. Then, the blend of PLA with the optimum composition of MLF is mixed with different compositions (5wt% - 20wt%) of ethylene methyl acrylate-glycidyl methacrylate (EMA-GMA) and its properties will be evaluated. Another compatibilizer which is styrene butadiene butylene styrene grafted maleic anhydride (SEBS-g-MA) also mixed with PLA/MLF composites to study the effect of different amounts of the compatibilizer (10 wt. % to 40 wt. % based on the weight of MLF) in PLA. The amount of MA used in SEBS-g-MA is 1.0 - 1.2 % as stated in Table 3.3. The mechanical, thermal, and morphological properties of the above blends are investigated and the properties will be compared with virgin PLA. FTIR was also used to analyse the possible chemical interactions among components by indicating the functional groups present.

1.4 Thesis Outline

Chapter 1 comprised of a brief introduction on the background of poly (lactic acid) (PLA) composites and natural fibres. The issues related to PLA composites and the recent methods used in improving the properties were highlighted. The objectives and scope of research were stated clearly.

Chapter 2 consists of detailed literature review on the background theories adopted in this research. Numerous published research works on the development of PLA composites with the addition of compatibilizer were well-documented. Besides, the recent advances related to PLA/natural fibres from publications were summarized.

Chapter 3 provides the basic information of the materials used in this research, the sample preparation techniques, and the characterization methods.

Chapter 4 presents the result and discussion of this research. The findings on the tensile properties of PLA/MLF composites were reported and analysed. In the second part of the chapter, a EMA-GMA was introduced as a compatibilizer in PLA/MLF polymer composites. Various compositions of EMA-GMA used in the composite were discussed and examined. Second compatibilizer was introduced with different compositions to compare the effect of different compatibilizer in PLA/MLF polymer composites.

Chapter 5 summarized the significant findings in this study. Suggestion for future recommendations were also introduced.

CHAPTER 2

LITERATURE REVIEW

2.1 Poly(lactic) acid (PLA)

Biodegradable and biopolymers have been in the focus of academic research because of the emerging concern over energy crisis and environment problems. Biopolymers are said to have better properties compared to commodity polymers. The chemical structure of biopolymers opens possibilities to reactive modification. Thus, most biopolymers and their blends are applied successfully. The growing concern on the impact of the non-degradable plastic materials on the environment has forced manufacturers to use harmless materials such as biodegradable polymers for their products(Sangeetha et al., 2016a).

Polymers made up of renewable resources are expected to gain a lot of attention nowadays as petroleum resources become less secure. Hence, polymers made up of renewable resources are expected to replace the position of the petroleum based plastics in the current scenario of oil scarcity. The use of polymer blends or composites able to bring out revolution in so many fields such as automobile, pharmaceutical, and packaging industry. The revolution is due the enhancement of the properties made by the combination of biodegradable polymers with other polymers by improving the molecular interactions and molecular bonding.(Sangeetha et al., 2016a) For an instance, Zhang et al. (2009) prepared blends of polylactic acid with thermoplastic acetylated starch (ATPS) via melt mixing method. It was found that the impact strength increased thrice with increase in percentage of acetylated starch (40 wt%) than that of pure PLA(Zhang et al., 2009). Besides, Su et al. (2009) used glycidyl methacrylate (GMA) grafted POE (mPOE) as a toughening agent for of PLA. The uncompatibilized PLA/POE (85/15) blend exhibited impact strength of only 19.4 J/m^2. The impact strength was increased seven times that of neat PLA with the use of compatibilizer(Su et al., 2009). Taib et al. (2014) melt blended PLA using varying amounts of 0 to 50 (wt%) ethylene acrylate copolymer impact modifier. A significant increase in the elongation at break was observed at 10 wt% impact modifier(Taib et al., 2014).

Biopolymers are natural-based polymers which derived from natural resources and is fully renewable as a part of the ecosystem. The biopolymers were also termed as organic polymer derived from living organisms which are biodegradable(Sangeetha et al., 2016a). Figure 2.1 shows the synthesis of biopolymers from renewable feedstocks.

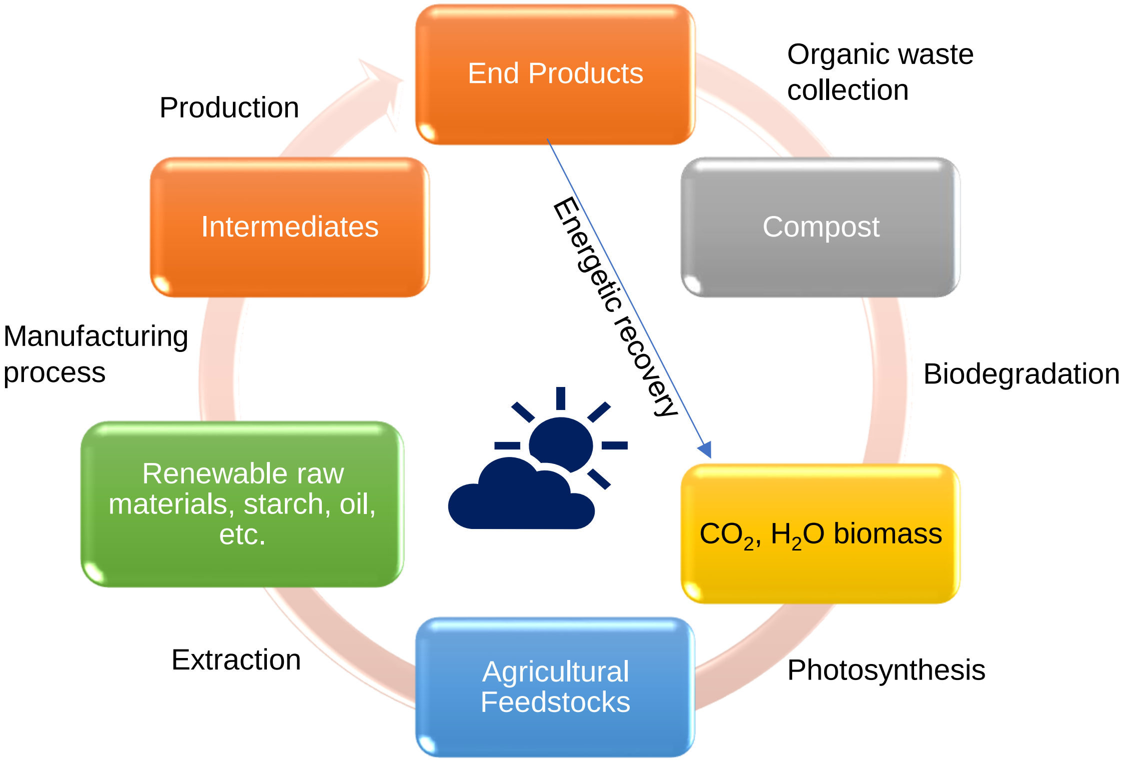
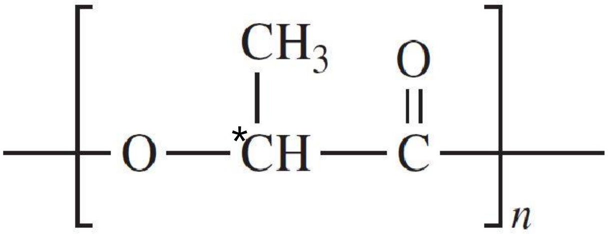


Figure 2.1: Synthesis of biopolymers from renewable feedstocks(Mohanty et al., 2005).

Among all of others biodegradable polymers, poly (lactic acid) (PLA) is currently the most widely used in many industrial applications. PLA has high stiffness, gloss, clarity and UV stability properties that are comparable to many commodity polymers such as polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), and polystyrene (PS). Beside its relatively high tensile strength and modulus compared to other thermoplastics such as polyethylene terephthalate (PET), polypropylene (PP), the low impact strength and less heat tolerance of the material makes it inadequate for more demanding application(Nagarajan et al., 2016).

The gifted feedstock for production of PLA is lactic acid (2-hydroxy propionic acid), which contains a chiral centre. Lactic acid (LA) can be produced by fermentation from renewable resources, such as cane molasses, corn, potato, and beet sugar. The structural formula of PLA is shown in Figure 2.2 below. It is a chiral polymer in which molecules containing asymmetric carbon atoms have a helical orientation. The two optical isomers of PLA are PLLA and PDLA. The crystal structure of PLA is based on an orthorhombic-base-centered unit cell that contains two 10/3 helical chains arranged along the c-axis. PLA shows hexagonal packing(Sangeetha et al., 2016a).



$$-\left[O-\overset{\overset{CH_3}{|}}{{}^{*}CH}-\overset{\overset{O}{\|}}{C}- \right]_n-$$

Figure 2.2: Structural formula of poly (lactic acid) (PLA) (Sangeetha et al., 2016a)

2.1.1 Physical and Chemical Properties

The properties of PLA were affected by the presence of chiral centre in its structure. Due to the chiral nature of lactic acid, several distinct forms of polylactide exist: poly-L-lactide (PLLA) is the product resulting from polymerization of L, L-lactide (also known as L-lactide). PLLA has a crystallinity of around 37%, a glass transition temperature 60-65°C, a melting temperature 173-178°C. the surface energy of a PLA made up of 92% L-lactide and 8% meson-lactide was found to be 49 mJ/m^2, with dispersive and polar components of 37 and 11 mJ/m^2, respectively, which indicates a relatively hydrophobic structure compared with that of other biopolyesters(Sangeetha et al., 2016a).

The best solvent for PLA is chloroform. Other solvents are chlorinated or fluorinated organic compounds, dioxane, dioxolane, and furan. Among non-solvents, the most relative compounds are water, alcohols and alkanes(Schwach et al., 1994).

2.1.2 Barrier Properties

The barrier properties of PLA are good since it has been used widely in packaging applications. The carbon dioxide permeability coefficients for PLA polymers are lower than that of polystyrene (PS) at 25 °C. Meanwhile, the 0% relative humidity (RH) is higher than polyethylene terephthalate (PET). Diffusion will take place through the amorphous regions of a polymer. Therefore, the increase in the extent of crystallization will result to decrease in permeability(Lunt, 1998).

2.1.3 Crystallinity and Thermal Properties

The properties of PLA depend on its molecular characteristics such as spherulite size, crystallinity, degree of chain orientation, and morphology. PLA can be totally amorphous or semi-crystalline (up to 40% crystalline). The crystallization kinetics of PLA is found to be slow and exhibits comparatively same properties as PET. The rate of crystallization increases with a decrease in the molecular weight and it depends on the copolymer composition(Drumright et al., 2000).

According to Lunt (1998), the crystallization kinetics were affected by the composition of the polymer itself(Lunt, 1998). The level of crystallinity developed affects the polymer melting point. The crystallization of amorphous PLA can be started by annealing it temperature in between 75 °C until melting point. PLA copolymer that has undergo crystallization by annealing usually produces two melting peaks. Normally, PLA have glass temperature (T_g) in between 50 to 80 °C, and melting temperature (T_m) ranges from 130 to 180 °C(Sangeetha et al., 2016a).

2.1.4 Modification of Poly(lactic) acid (PLA)

To reduce the brittleness of the PLA materials, many strategies have been developed, including grafting, polymer blending, and the use of plasticizers. Over the past several years, extensive efforts have been made to surmount the brittleness of PLA. The most commonly used strategy was blending with flexible polymers(Sangeetha et al., 2016a). Various flexible polymers ranged from commercially available ones like linear low-density polyethylene (LLDPE), thermoplastic polyolefin, hydrogenated styrene-butadiene-styrene block copolymer (SEBS), polyamide elastomer, polyurethane, acrylonitrile-butadiene-styrene (ABS), ethylene-n-butylacrylate-glycidyl methacrylate (EBA-GMA), poly(butylenessuccinate-co-adipate), poly(β-hydroxybutyrate-co-β-hydroxyvalerat), to those experimentally synthesized species such as epoxidized natural rubber, glycidyl methacrylate grafted poly(ethylene octane) and polymerized soybean oil, have been employed as tougheners for PLA(Sangeetha et al., 2016a, Wu and Zhang, 2017).

In polymer blends, good interfacial adhesion is needed to achieve high impact strength since poor interface would easily result in premature interfacial failure and hence rapid and catastrophic crack propagation through the whole material. However, most polymer blends are thermodynamically immiscible due to the low entropy of mixing which result a sharp interface between the two phases result. Therefore, copolymers premade or formed in-situ has been widely employed to compatibilized two immiscible polymers(Sangeetha et al., 2016a). Ideally, the copolymer resides at the interface, resulting in decreased interfacial tension, smaller dispersed droplets, greater interfacial adhesion and increased energy transfer efficiency. Based on the recent study, relatively high contents of elastomeric phase are commonly demanded to trigger the brittle-to-ductile transition. It is reported that the interfacial compatibilization between PLA and olefin block copolymer (OBC) could be achieved through adding EMA-GMA as a compatibilizer(Wu and Zhang, 2017).

Meanwhile, PLA seen as a costly polymer when compared with petroleum based plastics. One of the approaches to decrease the cost while at the same time expanding the scope of PLA properties is to mix PLA with various filler especially natural fibres(Sangeetha et al., 2016a). Natural fibres are considered as fillers and strengthening materials for various polymer matrices. Natural fibres possess advantages such as sustainability, low thickness, non-abrasiveness amid preparing, high mechanical properties and more vitally, biodegradability. The primary downside of utilizing natural fibres is the absence of bond with hydrophobic polymer matrices, which brings about poor composite properties(Taib et al., 2014).

The attachment between the two composite parts can be enhanced with physical and chemical alteration of either or the two materials or utilizing compatibilizers. There are numerous research on PLA composites with natural fibres, for example, kenaf, flax, sisal, oil palm, coconut, and wood. In many these studies, the expansion of regular filaments has been found to expand composite strength and stiffness. The impact strength, however, is radically lessened to a value much lower than the virgin PLA. PLA/natural fibre composites, hence, are not reasonable for some potential applications that require great low-temperature effect and high-impact performance, for example, car parts(Taib et al., 2014).

Given the current environmental concerns, there is interest in the development of green thermoplastic elastomic (TPE) composites. One of the ways to meet this challenge is by introducing natural fibers into rubber-modified thermoplastic composites. Natural fibers possess many advantages, such as sustainability, recyclability, low density, and biodegradability. However, rapid developments of natural fiber thermoplastic composites are limited, because of the strong hydrophobic nature of the natural fibers, which causes poor adhesion between the matrix and the fiber. The concept of using bio-based materials reflects the increasing number of publications on the utilization of natural fibers such as jute, kenaf, sisal, pineapple leaf, bamboo, empty fruit bunch, and wood.

Biodegradable composites are prepared by combining biodegradable polymers such as polylactic acid (PLA) and styrene-etylene-butylene-styrene grafted maleic anhydride (SEBS-g-MA) with natural fibre or filler such as mengkuang leaves (MLF). To the best of our knowledge, there is no research have been conducted on the use of MLFs as fillers in PLA/SEBS-g-MA blends. Within this framework, an investigation will be carried out on the potential use of MLF as filler in PLA/SEBS-g-MA thermoplastic elastomers. The objective of the present work is to study the effects of various compositions of SEBS-g-MA as a compatibilizer for PLA/MLF polymer composites.

2.2 Natural fibre filled PLA composite

In recent years, there has been a lot of research and innovations in the natural fibre composites area. The growing interest on natural fibre composite is due to the advantages of these materials compared to the others. Natural fibres have long been considered as fillers or reinforcing materials for thermoplastic materials. Natural fibre composites have potential to replace synthetic fibres reinforced plastics at lower production cost and with improved sustainability(Mukherjee and Kao, 2011).

The mechanical performance of natural fibre composites is affected by many factors, such as fibre selection including the type, harvesting time, treatment and fibre content, matrix selection, interfacial strength, fibre dispersion and orientation, porosity and the composite manufacturing process itself. Although natural fibre composites have many advantages, they also possess a few disadvantages. Among the advantages of natural fibre composites are low density, high specific strength and stiffness, can be produced at lower cost than synthetic fibre, low hazard manufacturing process, give less abrasive damage to processing equipment and lastly less emission of toxic fumes when subjected to heat. However, the drawbacks are having high moisture absorption which result to swelling, have lower durability, lower impact strength, and have a variable properties(Hashim et al., 2017).

Table 2.1 shows the properties of some natural fibres and main type of glass fibre (E-glass). It can be seen that Ramie, Flax, and Hemp have the highest tensile strength and Young's Modulus as compared to jute, sisal, cotton, coir, silk, feather, wool and E-glass(Mohanty et al., 2000).

Table 2.1: Mechanical properties of natural and synthetic fibres(Mohanty et al., 2000).

Fibre	**Density (g/cm3)**	**Length (mm)**	**Failure strain (%)**	**Tensile Strength (MPa)**	**Stiffness/Young's modulus (GPa)**
Ramie	1.5	900-1200	2.0-3.8	400-938	44-128
Flax	1.5	5-900	1.2-3.2	345-1830	27-80
Hemp	1.5	5-55	1.6	550-1110	58-70
Jute	1.3-1.5	1.5-120	1.5-1.8	393-800	10-55
Sisal	1.3-1.5	900	2.0-2.5	507-855	9.4-28
Cotton	1.5-1.6	10-60	3.0-10	287-800	5.5-13
Coir	1.2	20-150	15-30	131-220	4-6
Silk	1.3	Continuous	15-60	100-1500	5-25
Feather	0.9	10-30	6.9	100-203	3-10
Wool	1.3	38-152	13.2-35	50-315	2.3-5
E-glass	2.5	Continuous	2.5	2000-3000	70

2.2.1 Introduction to Natural Fibres

Blending PLA with natural fibres is seen to be the most effective way to reduce the cost of production. According to Taib et. al. (2014), PLA is seen to be an expensive polymer as compared to traditional major petroleum-based plastics at market price 2.2 US/kg(Taib et al., 2014). Several attempts have been made to replace glass fibre with natural fibre to reduce the cost while improving the properties of composites. Recently, many automotive components such as car bumper used natural fibre(Taib et al., 2014).

The properties of natural fibres depend on their composition(Fuqua et al., 2012) as could be seen in Table 2.2. The major component of plant fibres is cellulose, which is a natural hydrophilic polymer composed of 1,4-β-bonded anhydroglucose units. These hydroxyl groups form intramolecular hydrogen bonds inside the macromolecule itself and among other cellulose macromolecules as well as with hydroxyl groups from the air. Wood is the most common commercial natural resource that contains cellulose(Shah et al., 2008). However, several natural fibres such as cotton, flax(Bax and Müssig, 2008), hemp, jute(Plackett et al., 2003b), and sisal and mengkuang leaf also contain a large amount of cellulose(Hashim et al., 2017).

The other major components of natural fibres are hemicelluloses and lignin. Hemicellulose is a branched multiple polysaccharide polymer composed of different types of sugars including glucose, galactose, arabinose, xylose, and mannose. Meanwhile, lignin is a highly crosslinked phenolic polymer. Both hemicellulose and lignin are amorphous polymers, whereas cellulose is a semi-crystalline polymer(Bledzki et al., 2009). Table 2.2 shows the structural parameters and chemical compositions of natural fibres. Different types are compared with different compositions of lignin, cellulose, hemicellulose, pectin and wax. The moisture content for different type of fibres were also stated.

Table 2.2: Chemical composition and structural parameters of some natural fibres(Fuqua et al., 2012).

Type of fibre	**cellulose**	**lignin**	**hemicellulose**	**pectin**	**wax**	**Moisture content**
Jute	61-71.5	12-13	13.6-20.4	0.2	0.5	12.6
Flax	71	2.2	18.6-20.6	2.3	1.7	10.0
Hemp	70.2-74.4	3.7-5.7	17.9-22.4	0.9	0.8	10.8
Ramie	68.6-76.2	0.6-0.7	13.1-16.7	1.9	0.3	8.0
Kenaf	31-39	15-19	21.5	-	-	-
Sisal	67-78	8.0-11.0	10.0-14.2	10.0	2.0	11.0
Henequen	77.6	13.1	4-8	-	-	-
Cotton	82.7	-	5.7	-	0.6	-
Coir	36-43	41-45	0.15 – 0.25	3 – 4	-	8.0

2.2.1.1 Mengkuang Leaf Fibres (MLF)

Mengkuang is the Malaysian name for Pandanus tectorius, also known as screw pine, which is a plant belonging to the Pandanaceae family. This family has about 600 known species. These species grow along mangroves and in local jungles. They are varying in size. The fruits can be eaten, and the leaves can be used for weaving. Moreover, the leaves yield strong fibres that are used for making rope and weaving hats and mats(Hashim et al., 2017).

2.3 Effects of poly (ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EMA-GMA) as a compatibilizer

In many of the research, EMA-GMA has been widely used as a compatibilizer in PLA. Melo and coworkers (Mélo et al., 2014) reported that the epoxy groups of EMA-GMA react with either hydroxyl or carbonyl groups of PLA resulting a good impact strength of the polymer composite. Meanwhile, Agrawal et. al. (2010) studied the influence of reactive compatibilizers on the rheometrical and mechanical properties of polyamide 6/low density polyethylene (PA6/LDPE) and polyamide 6/high density polyethylene (PA6/HDPE) blends(Agrawal et al., 2010). Polyethylene grafted with maleic anhydride (PEgMA), polyethylene grafted with acrylic acid (PEgAA), and ethylene-methyl acrylate-glycidyl methacrylate (EMA-GMA) were used as compatibilizers. EMA-GMA shows an impressive result as a compatibilizer in the blends. Hence, the effort to improve the properties of PLA/MLF composites have been continued in this study by using EMA-GMA as a compatibilizer and the outcomes were observed.

2.4 Effects of styrene butadiene butylene styrene grafted maleic anhydride (SEBS-g-MA) as a compatibilizer

Another compatibilizer was introduced to compare the properties between the two compatibilizers. Recent studies by Sangeetha and co-workers (2016) used SEBS-g-MA as a toughening agent in PLA(Sangeetha et al., 2016b). From the research, SEBS-g-MA could give an amazing increment to the properties of PLA. On the other hand, Chow et. al. (2012) studied the effect of SEBS-g-MAH on the properties of injection moulded PLA/nano-calcium carbonate composites(Chow et al., 2012). It is reported that the elongation at break and impact strength of the composite was enhanced and the thermal stability was improved with the addition of SEBS-g-MAH.