SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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EFFECT OF RECYCLING ON THE MECHANICAL PROPERTIES OF POLYLACTIC ACID (PLA)/IMPACT MODIFIER BLEND

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written dissertation entitled **“Effect of Recycling on the Mechanical Properties of Polylactic Acid (PLA)/Impact Modifier Blend”**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar tittle of this for any other examining body or university.

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LIST OF ABBREVIATIONS

ASTM	American Standard Testing Method
CSIM	Core Shell Impact Modifier
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermo-gravimetric
MFI	Melt Flow Index
PET	Polyethylene Terephthalate
PLA	Polylactic Acid
PP	Polypropylene
TGA	Thermogravimetric Analysis

LIST OF SYMBOLS

α	Perfect crystalline phase
α’ or β	Imperfect crystalline phase
^{o} C	Temperature
ΔH_c	Enthalpy of crystallization
ΔH_{cc}	Enthalpy of cold crystallization
$\Delta H°_f$	Heat of fusion of 100 % crystalline material
ΔH_m	Heat of fusion of sample
M_n	Number average molecular weight
M_w	Molecular weight
T_c	Crystallization temperature
T_{cc}	Cold crystallization temperature
T_g	Glass transition temperature
$T_{1/2}$	Crystallization halftime
T_m	Melting temperature
W_f	Weight fraction of CSIM
X_c	Degree of crystallinity

KESAN KITARAN SEMULA TERHADAP SIFAT-SIFAT MEKANIKAL POLILAKTIK ASID (PLA)/CAMPURAN PENGUBAHSUAI IMPAK

ABSTRAK

Kajian terhadap kesan kitar semula pada sifat-sifat mekanikal polilaktik asid (PLA)/campuran pengubahsuai impak telah dijalankan bagi mengkaji dan menganalisis kesan kitaran semula terhadap sifat-sifat mekanikal dan haba PLA. PLA telah disediakan dengan menggunakan proses penyemperitan diikuti oleh acuan suntikan. Sifat-sifat PLA dan campuran PLA dengan pengubahsuai impak telah disifatkan dengan ujian tegangan, ujian impak, analisis aliran cairan (MFI), pengimbasan perbezaan kalorimeter (DSC), dan analisis termogravimetri (TGA). Hasil yang ditunjukkan oleh kadar aliran leburan menunjukkan penurunan dalam kelikatan PLA apabila bilangan kitaran semula meningkat. Selain itu, suhu penguraian terma PLA berkurangan dengan penambahan bilangan kitaran semula oleh kerana degradasi terma dan berat molekul yang berkurang termasuk rintangan haba PLA yang semakin lemah. Analisis DSC menunjukkan sedikit penurunan dalam suhu peralihan kaca (T_g) untuk PLA dan PLA campuran dengan pengubahsuai impak apabila dikitar semula. Gabungan PLA dengan pengubahsuai impak sebahagiannya serasi untuk PLA dan menyampaikan fasa bergetah untuk PLA seterusnya meningkatkan pergerakan rantaian fleksibiliti PLA. Oleh itu, PLA akan berubah fasa bergetah pada suhu yang lebih rendah dan disebabkan itu, T_g akan lebih rendah jika dibandingkan dengan PLA tulen. Walau bagaimanapun, tahap penghabluran PLA campuran dengan pengubahsuai impak ternyata lebih tinggi untuk dibandingkan dengan PLA tulen disebabkan oleh pengurangan entalpi pelakuran PLA.

EFFECT OF RECYCLING ON THE MECHANICAL PROPERTIES OF POLYLACTIC ACID (PLA)/IMPACT MODIFIER BLEND

ABSTRACT

The research on the effect of recycling on the mechanical properties of polylactic acid (PLA)/impact modifier blend was conducted to study and investigated the influenced of recycling on the mechanical and thermal properties of PLA. PLA were prepared using extrusion process followed by injection molding. The properties of PLA and PLA blend with an impact modifier were characterized by tensile test, impact test, melt flow analysis (MFI), differential scanning calorimetry (DSC) analysis, and thermogravimetric analysis (TGA). Recycling PLA slightly reduced the mechanical properties and the increasing trend shown by melt flow rate indicates the decreased in viscosity of PLA as the number of recycling increased. Besides, the thermal decomposition temperature of PLA decreased as the number of recycling increased due to thermal degradation and reduced the molecular weight including weakening the thermal resistance of PLA. DSC analysis shows slightly decreased in glass transition temperature (T_g) for PLA and PLA blends upon recycling. Incorporation of PLA with an impact modifier is partially compatible to PLA and imparts the rubbery phase to PLA thus increase the flexibility chain movement of PLA. Thus, PLA changed a rubbery phase at the lower temperature and hence the T_g will be lower than pure PLA. Nevertheless, the degree of crystallinity of PLA blend with an impact modifier literally higher as to compare with pure PLA due to the reduction of enthalpy of fusion of PLA.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymers are composed of smaller units called monomer that are bonded together. Polymers can be synthetic and natural macromolecules. Natural polymer occurs in nature and can be extracted. Examples of naturally occurring polymers are silk, wool, DNA, cellulose, and proteins. Synthetic polymers are human-made and derived from petroleum oil. They are made by scientists and engineers. Examples of synthetic polymers include nylon, polyethylene, polyester, and epoxy. Synthetic polymers have been developed for durability and resistance to all forms of degradation (Kyrikou & Briassoulis, 2007).

Mostly manufactured polymers are thermoplastics. Thermoplastics are materials that can be heated and reformed over and over again. This behavior allows for easy processing and facilitates recycling. The other group, the thermosets, cannot be re-melted. Once these polymers are formed, reheating will cause the material to ultimately degrade, but not melt. A thermoplastic, is a plastic which becomes pliable above a specific temperature and returns to a solid state upon cooling. Most thermoplastics have a high molecular weight. The polymolecules chains associate through intermolecular forces, which permits thermoplastics to be remolded because the intermolecular interactions increase upon cooling and restore the bulk properties (Larson, 2015).

Thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process. Thermosets often do not melt, but break down and do not reform upon cooling. The physical properties of a thermoplastic change drastically without an associated phase change above its glass transition temperature, T_g, and below its melting point, T_m. Most thermoplastics are rubbery due to alternating rigid crystalline and elastic amorphous regions within this temperature range, approximating random coils (Sin *et al.,* 2007).

Besides that, some thermoplastics do not fully crystallize when it is above T_g, retaining some, or all of their amorphous characteristics. Amorphous plastics are used when high optical clarity is necessary. Amorphous plastics are less resistant to chemical attack and environmental stress cracking because they lack a crystalline structure (Larson, 2015). Brittleness can be decreased with the addition of plasticizers, which increases the mobility of amorphous chain segments to effectively lower T_g. Modification of the polymer through copolymerization or through the addition of non-reactive side chains to monomers before polymerization can also lower T_g (Larson, 2015).

In recent years, biodegradable polymer has been focused due to their obvious environment friendly property comparing to non-biodegradable or slowly degradable synthetic petrochemical based polymeric material. This attention also come up from the fact that some of these biodegradable polymers can be bio-based while the conventional plastics are petrol based (Larson, 2015).

According to Chow and Teoh (2015), PLA is one of the most important biodegradable polymers since PLA can be produced from renewable resources. PLA has good mechanical properties (i.e., high strength and modulus), a high degree of crystallinity, good bio-compatibility, and excellent biodegradability. This material has a high tensile strength (50–70 MPa) and elastic modulus (3-4 GPa) and this make it possible to replaced conventional polymers in numerous applications, such as packaging, extruded products, and thermoformed containers.

Polylactic acid (PLA) also is one of the most promising candidates for wide range future applications due to its multiple benefits, such as biodegradability, high degree of transparency, prominent mechanical performance and comparable processing properties to commonly used thermoplastics. The rate of composting PLA in industrial facilities is much higher in comparison to the composting rate of PLA at home. Polylactic acid is a versatile polymer made from renewable agricultural raw materials, which are fermented to lactic acid. The lactic acid is then via a cyclic dilactone, lactide, ring opening polymerized to the wanted polylactic acid. The polymer is modified by certain means, which enhance the temperature stability of the polymer and reduce the residual monomer content (Bijarimi *et al.,* 2012).

According to Song *et al.,* (2014), the brittleness and poor thermal stability restricted its more application in general plastics. This limit the application of PLA and a lot of researches had been carried out to overcome the limitation of the properties of PLA. One of the common method for improving the toughness of PLA is melt blending. Although some interesting results have been reported on toughening PLA, there are still some problems occur in the blending. For example, some blends were immiscible, and compatibilizers were needed to increase compatibility to access the desired mechanical properties. Furthermore, the elongation at break was so low as to limit the other potential applications of PLA, and the high toughening modifier content increased the cost of the blends.

In addition, some PLA blend improved impact strength at the expense of reducing the strength and modulus. The practical and economical ways of toughening the material are blending PLA with other flexible biodegradable and non-biodegradable polymers. Some of these blends were found to be immiscible, resulting in poor mechanical properties and need compatibilizers to enhance their compatibility (Mat Taib *et al.,* 2012; Afrifah & Matuana, 2010). Recently, with the environmental concern and growing cost of traditional petroleum-based material, PLA has been used for the replacement of traditional petroleum-based material such as polyethylene terephthalate (PETE), polystyrene (PS), and polypropylene (PP) (Song *et al.,* 2014).

The resulting polylactic acid can be processed similarly as poly(olefins) and other thermoplastics although the thermal stability could be better. Reinforcing with fibers is one possibility to enhance thermal stability. Polylactide polymers are stiff and brittle materials, and it is, therefore necessary to use plasticizers to improve the elongation and impact properties. The polylactide is fully biodegradable. The degradation occurs by hydrolysis to lactic acid, which is metabolized by micro-organisms of water and carbon monoxide. By composting together with other bio-mass the biodegradation occurs within two weeks, and the material has fully disappeared within 3–4 weeks (Shih *et al.,* 2010).

1.2 Problem Statement

In recent years, there is rapid growing of interest in biodegradable plastic derived from renewable biopolymers. Biodegradable plastic commercially available for applications such as disposable plates, cutlery, cup, and drinking straws; agricultural mulch films; packaging bags and films; containers for liquid foods; loose fill packaging; and golf tees. PLA is one on the examples of biodegradable plastics that has some weakness such brittleness, low toughness, and softening at low temperatures and relatively higher cost (Ge *et al.,* 2011).

Thermoplastics contribute to the total plastic consumption by 80 % roughly, and are used for typical plastics applications such as packaging (Dewil *et al.,* 2006). Plastics are found in appliances, furniture, casings of lead-acid batteries, and other products. Increasing cost and decreasing space of landfills are forcing considerations of alternative options for plastic solid waste (PSW) disposal (Zia *et al.,* 2007). Years of research, study and testing have resulted in number of treatment, recycling and recovery methods for PSW that can be economically and environmentally viable (Howard, 2002).

Recycling processes could be allocated to four major categories which is re-extrusion (primary), mechanical (secondary), chemical (tertiary) and energy recovery (quaternary). Each method provides a unique set of advantages that make it particularly beneficial for specific locations, applications or requirements. Mechanical recycling (i.e. secondary or material recycling) involves physical treatment, whilst chemical recycling and treatment (i.e. tertiary encompassing feedstock recycling) produces feedstock chemicals for the chemical industry. Energy recovery involves complete or partial oxidation of the material producing heat, power and/or gaseous fuels, oils and chars besides by-products that must be disposed of, such as ash (Mastellone, 1999).

PLA is one of the material that can produce the best properties such as impact strength and toughness almost the same with other commodity plastics. Besides, it helps to reduce the green house emission. PLA is biodegradable and it will break down into its constituent part carbon dioxide and water in a controlled composting environment within three months. However, practically it will take longer time to compost in landfill. PLA macromolecules were packed tightly which no light and oxygen were presence to assist any degradation process. Research analyst estimate that PLA bottle could take anywhere from 100 to 1,000 years to decompose in a landfill (Elizabeth Royte, 2006).

Recycling of PLA is important as the costing for this material is expensive. In this way, the PLA waste should be reduced. The effect on the properties of the PLA upon recycling should be observed on how the recycling process influence it. Besides, PLA has some weakness such as stiffness with low deformation at break and lower impact strength (Balakrishnan *et al.,* 2012; H Zhang *et al.,* 2013). In addition, the elongation at break was low as to limit other potential application of PLA, and the high toughening modifier content increased the cost of the blends (Meng *et al.,* 2011). Furthermore, some PLA blends improved impact strength at the expense of reducing the strength and modulus (Ge *et al.,* 2011). Therefore, a more economic and effective impact modifier for PLA is needed (Song *et al.,* 2014).

Recycled plastic is not perfect, however, as it still requires significant amounts of water and energy for production, when compared to other resources. The perception of plastic as being easily recyclable will further add to the problem, as consumers feel comfortable using more, but do not dispose of products in the correct manner. Despite these disadvantages, recycled plastic has great potentials as an eco-friendly resource. Instead of contributing to the contamination of oceans and the expansion of landfills, dispose of your plastics carefully, and allow them to be transformed into fantastic eco-friendly products. Recycled PLA is slightly reduced the properties thus it may be use the recycled PLA in order to produce new product with different applications which is literally more simple and eco-friendly (Scaffaro *et al.,* 2011).

Some of potential product that can be produced from recycled PLA including flower pots, seed pots, mini chairs and table, and staircase. Recycled plastic is a far better option than wood or steel in the environment as these have a relatively short life span. Recycled PLA, on the other hand, will outlast most materials by many years. Rotting and splintering is not an issue as the plastic doesn’t absorb water, and there’s no need to paint because it doesn’t lose its color (Scaffaro *et al.,* 2011).

1.3 Objectives

i. To prepare blends of PLA with an impact modifier.

ii. To determine the effect of recycling on the thermal and mechanical properties of the blends.

1.4 Significant of Work

In this project, pure PLA and PLA blended with an impact modifier were recycled for three times. The impact modifier was mixed with PLA using a single extruder. The effect of recycling on the mechanical and thermal properties of PLA was evaluated by several testing and analysis including tensile test, impact test, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) analysis. The thermal degradation effect on the viscosity of PLA was also determined by using Melt Flow Index (MFI).

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradability of Plastic

Biodegradable plastics are derived from renewable biomass sources, such as corn starch. Polycaprolactone (PCL), and poly (butylene succinate) (PBS) can be degraded by microorganisms even they are petroleum based. Besides that, poly (hydroxybutyrate) (PHB), poly (lactide) (PLA) and starch blends are produced from biomass or renewable sources, so that they are biodegradable. Acetyl cellulose (ACC) is either biodegradable or non-biodegradable, depending on the degree of acetylation. ACC's with a low acetylation can be degraded, while those with high substitution ratio are non-biodegradable (Tokiwa *et al.,* 2009).

Biodegradability is becoming important for single used plastic items in packaging, hygiene and agricultural applications where a limited lifetime may represent an intrinsic added value feature. A biodegradability plastic is defined as a degradable plastic in which the degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi, and algae. Biodegradable polymers breakdown in physiological environments by micromolecular chain scission into smaller fragments, and ultimately into simple stable and end products (Gupta *et al.,* 2007). Carbon dioxide is produced if oxygen is present the biotic degradation that occurs is aerobic degradation. If there is no oxygen available, the biotic degradation is anaerobic degradation, and methane is produced instead of carbon dioxide (Kyrikou & Briassoulis, 2007).

The process of degradation is affected by several factors such as the combination of polymer structures, numerous enzymes produced by micro-organisms, and variable reaction conditions which make it difficult to define biodegradation in general terms. Chemical reactions that take place during biodegradation can be classified into two groups; those based on oxidation and those based on hydrolysis. These reactions can occur either simultaneously or successively.

Biodegradation of polymer has two steps which are fragmentation and mineralization. Generally, decompositions begin with fragmentation, means the material that exposed to living or non-living factors undergoes a chemical decomposition of the polymer and therefore decomposes mechanically (fragments). The second phase is a necessary step that characterized this process as biodegradation since the partially degraded polymers (fragments) are metabolized into end products (Krzan, 2012).

There are other cases (oxo-degradable materials) where the material undergoes a quick fragmentation. The process of degradation in OXO-treated plastic is an oxidative chain scission that is catalyzed by metal salts leading to oxygenated (hydroxylated and carboxy lated) shorter-chain molecules. OXO plastics are designed so that they will not degrade deep in the landfill and generate methane which is a powerful greenhouse gas in anaerobic conditions. OXO-biodegradable products do not degrade immediately in an open environment because they are stabilized to give the product a useful service-life. Moreover, if the OXO-biodegradable products exposed to the environment, they will degrade only little much quicker than natural waste such as twigs and straw but much more quickly than ordinary plastic, the degradation and biodegradation will take place in nature (X. Ren, 2002).

The degradation process for OXO-biodegradable products is influenced by heat and UV light but the mineralization stage is slow, which means that the relatively inert microparticles of the plastics material remain and have a poor susceptibility to biodegradation (Krzan, 2012). Mineralization is the conversion of biodegradable material or biomass into gases (carbon dioxide, methane, and nitrogen), water, salts, mineral, and residual biomass. Mineralization process is completed when all the biodegradable materials or biomass is consumed and all the carbon converted to carbon dioxide (Krzan, 2012).

2.1.1 Advantages and Disadvantages of Biodegradable Plastics

The main advantage of biodegradable plastics applies to environmental properties when it comes to the handling of waste plastics and the effects of their decomposition to the environment. When biodegradable plastics decompose biologically, the resulting natural components do not affect the environment in any harmful way. Besides, non-biodegradable plastic does not release any harmful substances, they are relatively durable and dangerous as it may cause blockage of the sewage system and to animals. Biodegradable plastics decompose more quickly, however this negative effect is not altogether removed, which means that biodegradable plastics must not be dumped in the natural environment (Gupta *et al.,* 2007). However, if non-biodegradable plastics do make their way there by error, they will cause less damage than biodegradable plastics.

The advantages of biodegradable plastics are that they decompose into natural substances and do not require separate collection, sorting, recycling, or any other final waste solution as is the case with non-biodegradable plastics. Biodegradable plastics are not foreign to the natural environment like ordinary plastics, whose influence can only be diminished but not eliminated. But despite these advantages, they need to be collected, usually together with biological waste, and processed aerobically or anaerobically (Shih *et al.,* 2010).

The more common method is the aerobic process of composting. Compostable plastics are customized for industrial composting that differs from the domestic composting in temperature; the temperature of industrial composting is higher which means that degradation happens more quickly (Shih *et al.,* 2010). If biodegradable plastics are not collected together with organic waste and are processed with mixed waste, it is harder to take advantage of their biodegradability.

2.1.2 Environmental Problems

Biodegradable plastics may serve as a solution to the over-loaded landfills by diverting part of bulky volume plastics to other means of waste management, and to littering of disposable plastic products which are otherwise difficult to recycle. Biodegradable plastics of renewable resources origin contribute to sustainable development and help to preserve the non-renewable resources. The development of law and policy, the advance of technology and in waste management, adoption of economic and market-based instruments generated many new challenges in the decisions making a process to waste management (X. Ren, 2002).

Problems that are expected to be solved by biodegradable plastics generally include the increasing pressure on landfill. It is hoped that biodegradable plastics would divert part of bulky plastic wastes from landfills. Eliminating the cost involved in removing the collection bags before entering compost facilities from facilitating organic waste management (Brine & Thompson, 2010).

Recycling of plastics is not usually economically favourable since the cost is high hauling the lightweight and high volumes plastic waste to the recyclers. Cost and environmental impacts of cleaning the highly contaminated foodservice products are also significant. Moreover, littering of difficult-to-recycle products, for instance, foodservice disposables, has led to excessive environmental and visual pollution, which is of alarming concern particularly in some emerging economies, such as China. Biodegradable plastics of renewable sources will contribute to a more sustainable society by conserving the non-renewable resources, the fossil fuel (X. Ren, 2002).

As defined by the United Nations Environmental Program (UNEP), wastes are managed in a manner which will protect human health and the environment against the adverse effects by taking all practical steps. The hierarchy of Four-R, namely Reduces, Reuse, Recycle, and Recovery of the energy content should be followed by sound waste management of non-recyclable before final disposal. Figure 2.1 illustrates the municipal waste management.

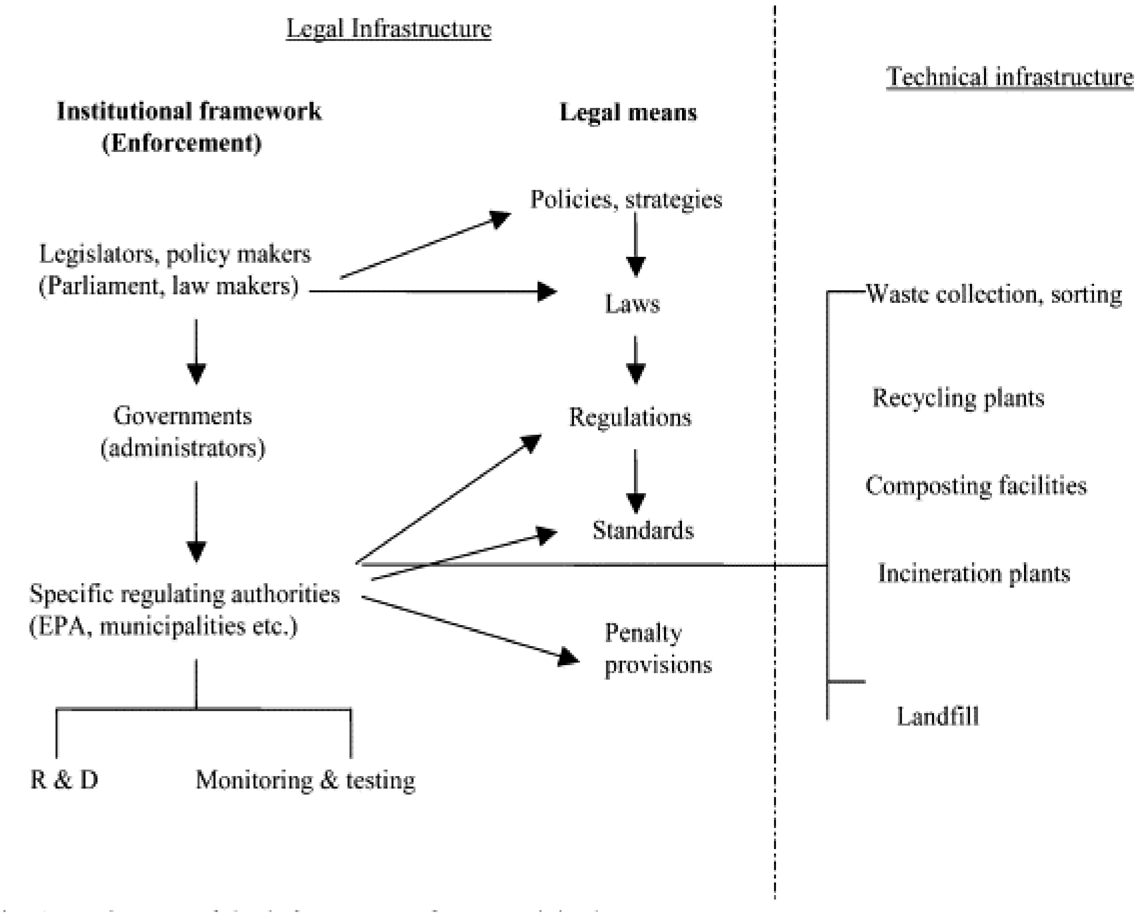

Figure 2.1: Diagram of the infrastructure for a municipal waste management (Vroman & Tighzert, 2009)

Generally, biodegradable plastics is driven by the situation under which plastic products are difficult or non-recyclable in an economically way. Essentially, biodegradable plastics are not created for material recycling. Thermoplastics can be recycled more readily than thermosets. Thermoplastics may be reshaped by heating and are usually used to produce parts by various polymer processing techniques such as injection molding, compression molding, and extrusion (Peters, 2007). Thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process. Moreover, thermosets do not melt, but decompose and do not reform upon cooling.

The common plastic recycling process involves reheating, during which biodegradable plastics will usually decompose and make further processing impossible. Mixing of biodegradable plastics in the feedstock of recycling will thus damage the process and the quality of recycled products. Furthermore, products made of biodegradable plastics should be labeled as such, so that they can be sorted out from recyclables. It is evident that clear labeling and identification of materials, necessary for an effective sorting, will become more important after biodegradable plastics are widely adopted. It would be necessary for policy makers as well as the industry itself to prepare for the change in advance (Shih *et al.,* 2010).

2.1.3 Plastic Waste Treatment and Management

Mostly waste treatment technology for biodegradable plastics is composting. Internationally accepted definitions for biodegradable plastics are all based on their compost ability. The success of biodegradable plastics will be decided by the availability of composting/digestion facilities.

In contrast to composting as an aerobic treatment process of organic wastes, gasification, an anaerobic process using existing sewage treatment facility or controlled landfill, has gained attention recently in some European countries. Europe is one of the few regions that attaches such importance to composting that EU is preparing a new Directive dedicated to composting (X. Ren, 2002).

Photochemically degradable plastics which found their application mostly in agriculture, the polymer chains are attached at the existing functional groups or with the help of sensitizing additives (aromatic/ heavy metal compounds) under the influence of sunlight

(UV radiation). There is still dispute about whether biological degradation follows, in addition to the concern about heavy metal contaminants. Therefore, they are not suitable for recovery by composting (Vroman & Tighzert, 2009).

There are new challenges on integrated waste management from biodegradable plastics such as clear labeling, source separation to sound operation of composting, and application of compost. Biodegradable plastics can achieve the objective of reducing pressure on landfill with fragmented regulations and standards at work. However, biodegradable plastics cannot solve the littering problem either, if not worsen them (X. Ren, 2002).

In addition, it is more suitable to influence people’s behavior through education and market-based instruments to improve the waste management system. Biodegradable plastics of renewable origin more comparable with conventional plastics in energy consumption, performance, cost, and also depends on the scale of production, thus successful commercialization of biodegradable plastics by the technology advancement in the field (X. Ren, 2002).

2.2 Polylactic Acid (PLA)

Polylactic acid (PLA) has caught the attention of polymer scientist as a potential biopolymer to substitute the fossil fuel-based plastics. PLA is biodegradable and has wide applications in biomedical field due to its biocompatibility characteristics. PLA is produced from lactic acid, that is itself derived from the fermentation of corn or sugar beets. PLA provide the major advantage of entering in the natural cycle, implying its return to the biomass due to its biodegradation ability. Recent studies on PLA had proven that the biopolymer has good mechanical properties, thermal plasticity, and biocompatibility, thus being a promising polymer for various end-use applications (Balakrishnan *et al.,* 2012).

Figure 2.2 shows the life cycle of PLA. All agricultural raw materials such as sugar or corn can be used as basic materials for PLA production. Moreover, waste organic materials from the agricultural production can also be used. These basic materials will be transferred to bacterial fermentation process into lactic acid, means the basic chemical needed for PLA production. This lactic acid then transferred into lactide, the cyclic dimer of lactic acid through a combined process of oligomerization and cyclization (Balakrishnan *et al.*, 2012). Recent research in life cycle assessments (LCA) have focused on developing PLA to find its place among traditional commodity polymers for various applications in the agricultural sector and in the packaging field. Generally, PLA can be processed like all other thermoplastic polymers with extrusion, injection molding, blow molding or fiber spinning processes into useful products (Inkinen *et al.,* 2011).

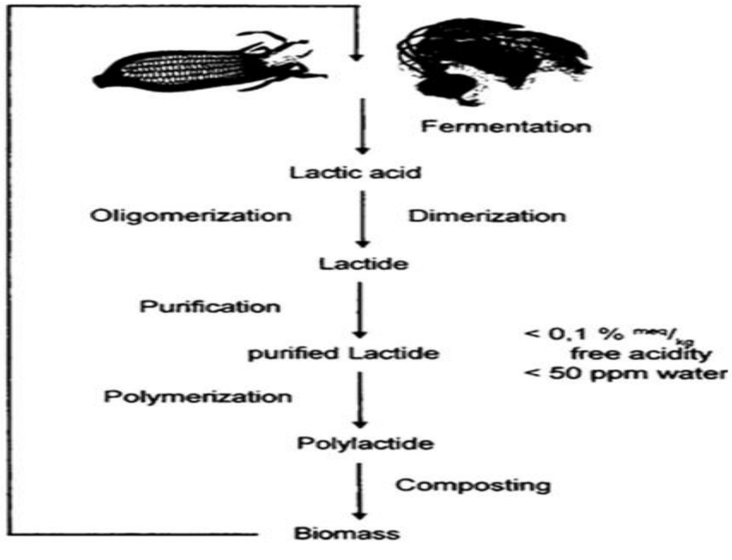

Figure 2.2: Lifecycle of polylactic acid (PLA) (Balakrishnan *et al.,* 2012)

The PLA products also can be recycled after use for the second time. They can even be hydrolyzed back into lactic acid, which is the basic monomer (Anderson *et al.,* 2003). The recycled lactic acid can be re-introduced into the polymerization process of PLA and the last possibility is to introduce PLA into the natural life cycle of all biomass where it degrades into carbon dioxide and water. Thus, the diversity of PLA becomes obvious as it can be recycled and decomposed like all other organic matter. In addition, if burned in an incineration plant or introduced into a classical waste management system, it will do no harm (Balakrishnan *et al.,* 2012).

PLA is also well known for its applications in the biomedical field. It has been used for more than 20 years for surgical devices such as sutures or clips. These biomedical applications have been extended to controlled drug delivery systems and larger parts such as screws for fracture fixation. PLA is highly accepted in the biomedical field, due to its excellent mechanical properties combined with its biocompatibility and its ability to degrade both in vivo and in vitro. Due to its high glass transition temperature of 55 °C and a melting temperature around 170 ºC, PLA is a stiff and brittle polymer. However, the crystallinity of PLA depends on the type of monomer used in polymerization due to the stereo isometric nature of lactic acid (L-levo and D-dextro-lactic acid) (Raquez *et al.,* 2013).

PLA has been utilized as biodegradable plastics for short-term use, such as rigid packaging containers, flexible packaging films, cold drink cups, cutlery, apparel and staple fibers, bottles, injection and extrusion mold, coatings, and so on. All of them can be degraded under industrial composting conditions. In the late 1990s, the bio-based nature of PLA was highlighted and its production as a bio-based polymer started. In this case, the newly developed polymers ought to have high performances and long-life utilities that can compete with those of the ordinary engineering plastics (Jacobsen & Fritz, 1999). There are many types of bio-based polymers are now under development, and several PLA types are also developed as promising alternatives to commercial commodities.

2.2.1 Properties of PLA

Properties of PLA depend on its component isomers, processing temperature, annealing time and molecular weight (M_w). The stereochemistry and thermal history have direct influence on PLA crystallinity. The rate of crystallinity is very important where crystallinity indicate the amount of crystalline region in the polymer with respect to amorphous content. The properties including hardness, modulus, tensile strength, stiffness, crease and melting points are affected by crystallinity. Clearly, crystallinity plays the important role in properties requirement (Farah *et al.,* 2016).

Physical properties such as density, heat capacity, and mechanical and rheological properties of PLA are dependent on the T_g of the PLA. T_g is one of the most important parameters for amorphous PLA, since dramatic changes in polymer chain mobility take place at and above T_g. For semi-crystalline PLA, both T_g and T_m are important physical parameters for predicting PLA behavior. The melting enthalpy estimated for an enantiopure PLA of 100 % crystallinity (ΔH°_m) is 93 J/g; it is the value that commonly referred to in the literature although higher values (up to 148 J/g) also have been reported. The T_m and degree of crystallinity are depended on the molar mass, thermal history and purity of the polymer (Farah *et al.,* 2016).

Generally, after several months of exposure to moisture, PLA degrades primarily by hydrolysis. PLA degradation occurs in two stages (Farah *et al.,* 2016). First, random non-enzymatic chain scission of the ester groups leads to a reduction in M_w. In the second stage, the M_w is reduced until the lactic acid and low M_w oligomers are naturally metabolized by microorganisms to yield carbon dioxide and water. The polymer degradation rate is determined by polymer reactivity with water and catalysts. Polymer degradation will be affected by any factor which affects the reactivity and the accessibility, such as particle size and shape, temperature, moisture, crystallinity, percentage isomer, residual lactic acid concentration, M_w, water diffusion and metal impurities from the catalyst (Brine & Thompson, 2010).

The M_w is important as it gives impact on the properties of polymers such as degradation, mechanical strength, and solubility. PLA with High M_w has a complete resorption time of two to eight years. This prolonged existence in vivo in some organs may lead to inflammation and infection. Thus, production of low M_w PLA is desirable as it provides a shorter degradation rate. The degradation rate of low M_w PLA (60,000 g/mol) and found that the implants able to maintain mechanical properties over period of times usually required for bone fracture healing (Brine & Thompson, 2010). Low M_w PLAs have a weak retarding effect which had been used for drug delivery. They degrade by hydrolysis relatively fast into lactic acid, which reduces the risk of material accumulation in tissue (Signori *et al.,* 2009).

The PLA barrier properties are one of the most important properties in food packaging. Generally, it is the polymer barrier or permeability performance against the transfer of gases, water vapor, and aroma molecules. Gas permeation properties of PLA (L: D ratio 96:4) and it can be seen clearly that polymer chain branching and small changed in L: D stereochemical content have no effect on permeation properties, however, film crystallinity profoundly impacted the permeation of the mentioned gases. For example, CH_4 permeation is 4.5 times lower than that of the other films due to higher crystallinity of biaxially oriented PLA film. Recent studies show that the water vapor transmission rate (WVTR) of crystalline and amorphous PLA in 6, 25, and 49 °C was reported as 27, 82, and

333 g/m^2 per day for the crystalline form and 54, 172, and 1100 g/m^2 per day for the amorphous form, respectively. He reported activation energies of 5 and − 0.1 kJ/mol for amorphous and crystalline PLA, respectively (Farah *et al.,* 2016).

The effects of D-lactide content, degree of crystallinity, and M_w of PLA films on WVTR were studied. Increasing crystallinity from 0 % to 20 % would decrease the WVTR of PLA films, while leveled off for crystallinity exceeding 30 %, so they suggested this change due to the higher resistance of restricted amorphous regions to water vapor permeation compared with that of the free amorphous regions. They also concluded that changes in M_n of PLA films in the range of 9×10^4 to 5×10^5 g/mol and D-lactide unit content of PLA films in the range of 0 % to 50 % have insignificant effects on their WVTR values (Farah *et al.,* 2016).

Oriented PLA (OPLA) was investigated with PET and oriented polystyrene (OPS) with physical, mechanical, and barrier properties. In terms of water vapor barrier, PET gave the best performance, followed by OPS and OPLA. PET showed the lowest oxygen permeability coefficients, followed by OPLA in the case of oxygen barrier properties, and OPS showed very poor oxygen barrier performance. According to these results, the barrier properties of PLA are remarkable and better than those of OPS (Masutani & Kimura, 2014). In addition, PLA is suitable for packaging a wide range of food applications. A very important property is the water content or water uptake of the biopolymer resin. PLA resins were tested and they were found to be situated near 0.5 %.

Furthermore, physical properties are important; one must know the dimensions, size, and weight requirements for a desired part or product. For example, if used by a surgeon, it must be light enough to handle precisely as implementation of material also becomes much easier and less hazardous when lighter. Density can also be a very important design parameter since elevated density values imply high transportation costs (e.g. light car parts reduce energy consumption). Density is often used for the calculation of ‘specific properties’, i.e. dividing mechanical properties by the appropriate density (Signori *et al.,* 2009).

The mechanical properties of lactic acid-based polymers can be varied to a large ranged from soft and elastic plastics to stiff and high strength materials. Semi-crystalline PLA is preferred over the amorphous polymer when higher mechanical properties are desired. Semi-crystalline PLA has an approximate tensile modulus of 3 GPa, the tensile strength of 50–70 MPa, the flexural modulus of 5 GPa, flexural strength of 100 MPa, and an elongation at break of about 4 %. Different from thermal properties, the mechanical properties and crystallization behavior of PLA are very dependent on the Mw and stereo chemical makeup of the backbone. For example, it has been shown that tensile modulus of PLLA increases by a factor of 2 when the Mw is raised from 50 to 100 kDa, and tensile strengths of 15.5, 80 and 150 MPa, for varying the M_w from 50 over 150 to 200 kDa respectively (Farah *et al.,* 2016).

On the other hand, the stereo chemical makeup is very easily controlled by the polymerization with D-lactide, L-lactide, D, L-lactide, or meso-lactide, to form random or block stereo-copolymers, while the Mw is directly controlled by the addition of hydroxylic compounds (i.e., lactic acid, water, alcohols). The ability to control the stereochemical architecture allows precise control over the speed and degree of crystallinity, the mechanical properties, and the processing temperatures of the material (Harris & Lee, 2008).

2.2.2 Crystallinity of PLA

Poly (lactic acid) (PLA) is a compostable polymer that can be derived completely from renewable resources. The repeating chemical structure of PLA is shown in Figure 2.3. Annual crops, such as corn and sugar beets, are currently utilized as feedstock in the commercial production of PLA resin. PLA is an aliphatic polyester thermoplastic with high strength and stiffness, but low in impact strength. These properties are significantly affected by the morphology, which can be controlled stereo-chemically to yield semi-crystalline or amorphous forms. Degradation of PLA occurs primarily through hydrolysis of the ester bond, and is highly dependent on temperature, moisture, microbial environment, morphology, as well as thickness and geometry (Inkinen *et al.,* 2011).

Homo-polymer PLA can be processed into fibres, textiles, films, and moulded objects with standard polymer processing equipment. Its initial uses were for medical and dental applications due to its biocompatibility and biodegradability. Applications range from sutures to drug delivery systems. More recently, however, its usage has extended to packaging materials for food and consumer goods; applications in which the polymer film is typically discarded after use. These applications utilize the amorphous form of PLA and take advantage of its ability to decompose relatively quickly in landfill or compost environments. Films, blow moulding, and paper coating (for water resistance) are processing methods that have been commercialized for the packaging industry. Fibre and textile applications have also been investigated and commercialized to a limited extent. Clothing and upholstery for office furniture are available in Japan, while bedding and linen applications are the sole commercial textile applications in the US. Other than the early medical applications, injection moulded applications that require high mechanical and durability requirements have not yet been reported (Signori *et al.,* 2009).

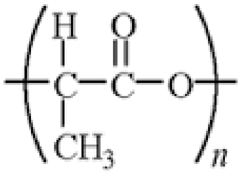

Figure 2.3: Repeat unit of the chemical structure of poly (lactic acid) (Harris & Lee, 2008)

Only limited research on injection moulded PLA for structural parts, such as those found in auto motive applications, exists in the literature. Although PLA can have good mechanical properties, its use in structural applications demands tight tolerances, good impact performance, and high durability; properties that current materials lack. Improvements in mechanical properties need to be made, while pre-serving the overall stability of the material before more widespread use is possible. This can be achieved through control of the polymer crystallinity, by using optimum processing parameters, and/or changes in the formulation of the material. Thus, an understanding of the crystallization behaviour and its effects on physical properties and performance is essential.

It is well known that PLA crystallinity can play a significant role in the mechanical and durability performance in rigid moulded applications. An increase in the polymer's overall crystallinity can lead to improvements in stiffness, strength, heat deflection temperature and chemical resistance. However, obtaining a highly crystalline, injection moulded article of PLA remains difficult, due to the slow crystallization rate. The crystallization halftime, $t_{1/2}$, of a pure sample of PLA is reported in the literature to be in the range of 17–45 min, depending on crystallization temperature, stereochemistry, and molecular weight, whereas polypropylene homo-polymers have half times that can be faster by an order of magnitude at similar degrees of undercooling. To obtain a component with sufficient crystallinity to maximize physical property enhancements during injection moulding, the cycle time would be extremely long or a post-annealing step would have to be added. Since a typical injection moulding cycle time is 60–90 s, this would be impractical and economically unrealistic for high volume automotive use (Harris & Lee, 2008).

Crystallization behaviour has been found to depend on the stereochemistry of PLA (Yang *et al.,* 2008). Two optically active forms of lactic acid exist: L-lactic acid and D-lactic acid. Lactic acid derived from petrochemical feed stock results in a racemic mixture of D- and L-isomers, while optically pure lactic acid can be selectively produced through fermentation with suitable micro-organisms. These can be synthesized to form various copolymers (poly (DL-lactic acid), PDLLA), homo-polymers (poly (L-lactic acid), PLLA and poly (D-lactic acid), PDLA), or blends, each with unique properties.

2.2.3 Toughening of PLA

Poly (lactic acid) (PLA) is a biodegradable plastic that can be produced from renewable resources. Packaging materials and hygiene product are example application from PLA due to their properties of good mechanical properties and processing as well as biocompatibility. However, according to Ljungberg and Wesslen (2002), the brittleness and thermal instability is the major disadvantages of PLA. Packaging materials as well as diapers require flexible polymer films, and in industry production line, there are no tolerance for film cracking or tearing when subjected to force during manufacturing.

One main task will be to modify these properties in such a way that PLA is able to compete with other more flexible commodity polymers such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) or polyvinyl chloride (PVC). Previous researchers had used plasticizers to enhance PLA’s elongation at break and reduce its brittleness. The introduction of plasticizers such as polyethylene glycol (PEG), glucose