PREPARATION AND PROPERTIES OF IMPACT MODIFIED POLY(LACTIC ACID)/KENAF FIBER COMPOSITES

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PREPARATION AND PROPERTIES OF IMPACT MODIFIED POLY(LACTIC ACID)/KENAF FIBER COMPOSITES

by

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DEDICATIONS

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

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		Page
$\approx$	Almost equal to	1
wt%	Weight percentage	3
CO_2	Carbon dioxide	6
%	Percentage	9
$>$	More than	10
T_g	Glass transition temperature	12
T_m	Melting temperature	12
˚C	Degree Celsius	12
rpm	Rotation per minute	41
phr	Part per hundred part of resin	42
F_{max}	Maximum force in the force-deflection trace	50
a	Notch length	50
B	Specimen thickness	50
W	Specimen width	50
y	Geometrical correction factor	50
T_{cc}	Crystallization temperature	50
ΔH_m	Enthalpy of fusion	50
ΔH^*_m	Fusion enthalpy of fully crystalline PLA	50
E’	Storage modulus	51
δ	Tan delta	51
ΔH_c	Enthalpies of crystallization	59

LIST OF ABBREVIATION

DCP	Dicumyl peroxide
DOA	Bis(2-ethylhexyl) adipate
DP	Degree of polymerization
ENR	Epoxidised natural rubber
GTA	Glyceryl triacetate
i-PLA	Impact modified poly(lactic acid)
KF	Kenaf fibers
LLDPE	Linear low density polyethylene
MA	Maleic anhydride
MAPE	Maleic anhydride-modified polyethylene
MAPLA	Maleic anhydride-modified poly(lactic acid)
MAPO	Maleic anhydride-modified polyolefin
MAPP	Maleic anhydride-modified polypropylene
PBAT	Poly(butylene adipate-*co*-terephthalate)
PBS	Poly(butylene succinate)
PCL	Poly(ε-caprolactone)
PDLA	Poly(D-lactic acid)
PE	Polyethylene
PLA	Poly(lactic acid)
PLLA	Poly(L-lactic acid)
PP	Polypropylene
UV	Ultra violet

PENYEDIAAN DAN SIFAT-SIFAT KOMPOSIT TERUBAHSUAI HENTAMAN DARI POLI(LAKTIK ASID)/SERABUT KENAF

ABSTRAK

Penyediaan dan sifat-sifat komposit terubahsuai hentaman daripada poli(laktik asid) (PLA) dan gentian kenaf (KF) telah dikaji. Bahagian pertama dalam kajian ini melibatkan kesan pengubahsuaian hentaman terhadap sifat-sifat terma, mekanikal, morfologi dan juga biorosotan (pencuacaan semula jadi dan pengambusan tanah) PLA. Suhu peralihan kaca (T_g) PLA di dalam adunan tidak berubah secara ketara dengan penambahan pengubahsuai hentaman. Ketidakserasian adunan dapat dilihat daripada analisis dinamik mekanikal (DMA), di mana adunan menunjukkan dua nilai T_g yang berbeza yang merujuk kepada PLA dan pengubahsuai hentaman. Pemanjangan tahap putus dan kekuatan hentaman adunan meningkat dengan penambahan pengubahsuaian hentaman. Kajian morfologi melalui mikroskop imbasan elektron (SEM) menunjukkan pemisahan fasa yang menggambarkan ketidakserasian adunan PLA/pengubahsuai hentaman. PLA dengan 20 wt% pengubahsuai hentaman telah dipilih sebagai matriks dan ianya menunjukkan nilai kekuatan hentaman optimum meningkat 8 kali ganda berbanding PLA tulen. Bahagian kedua kajian ini adalah untuk menganalisa kesan penambahan 40 wt% serabut kenaf (KF) ke atas sifat-sifat mekanikal PLA termodifikasi hentaman (i-PLA). Nilai tegasan alah, pemanjangan tahap putus, kekuatan hentaman dan keliatan patahan berkurangan dengan penambahan 40 wt% KF. Apabila dibandingkan dengan komposit PLA/KF, komposit i-PLA/KF menunjukkan penurunan nilai tegasan alah dan modulus Young tetapi nilai pemanjangan tahap putus, kekuatan hentaman dan keliatan patahan lebih tinggi berbanding komposit PLA/KF. Komposit i-PLA/KF menunjukkan 55.5, 3.8, 78.1, 49.1 % lebih tinggi

bagi tegasan alah, modulus Young, kekuatan hentaman dan keliatan patah berbanding komposit PP/KF.

PREPARATION AND PROPERTIES OF IMPACT MODIFIED POLY(LACTIC ACID)/KENAF FIBER COMPOSITES

ABSTRACT

Preparation and properties of impact modified composites from poly(lactic acid) (PLA) and kenaf fiber (KF) was investigated. The first part of this study was to evaluate the effect of impact modifier on the thermal, mechanical and morphological properties as well as biodegradability (natural weathering and soil burial) of PLA. The glass transition temperature (T_g) of PLA in the blends did not significantly change with addition of impact modifier. From dynamic mechanical analysis (DMA), the immiscibility of the blends can be observed. The blends showed two distinct T_gs corresponding to PLA and the impact modifier. The elongation at break and notched impact strength of the blends increased with increasing impact modifier. Morphological study via scanning electron microscopy (SEM) showed the phase separation of the PLA/impact modifier blends, which indicated the immiscibility of the polymer blends. PLA with 20 wt% impact modifier was chosen as a matrix for the second part of this study as it showed the optimum notched impact strength increased 8-folds compared to pure PLA. The second part of this study was to evaluate the effect of 40 wt% KF on the mechanical properties of chosen impact modified PLA (i-PLA). The yield stress, elongation at break, notched impact and fracture toughness of i-PLA were decreased with addition of 40 wt% KF. As compared to PLA/KF composites, i-PLA/KF composites showed lower yield stress, Young’s modulus but higher elongation at break, notched impact strength and fracture toughness than that of PLA/KF composites. i-PLA/KF composites showed 55.5, 3.8, 78.1 and 49.1 % higher respectively for yield stress, Young’s modulus, notched impact strength and fracture toughness than PP/KF composites.

CHAPTER ONE

INTRODUCTION

1.1 Problem statement

Plastics have become an inseparable and integral part of our lives and also one of the greatest innovations of the millennium (Siddique et al., 2008). Plastics have been used in packaging, automotive and industrial applications, medical delivery systems, artificial implants and other healthcare applications, water desalination, flood prevention, preservation and distribution of food, housing, communication materials, security systems, and other uses (Siddique et al., 2008, Vaz et al., 2003). Plastics are one of the major polymer materials used in packaging where the main reasons why plastics have been chosen are low density, not susceptible to loss of strength when wet, fabrication capabilities, long life, light weight, transparency, and cheap. In addition, plastics have good mechanical properties (Siddique et al., 2008, Noda et al., 2001).

Currently the world depends on fossil fuels for plastics manufacture (~270 million metric tonnes of fossil fuels) (Suresh Kumar et al., 2004, Khardenavis et al., 2007) and since plastics are made using non-degradable polymers (based on fossil fuels), plastics do not degrade under normal environmental conditions, resulting in various forms of environmental pollutions particularly during incineration (Kim et al., 2006).

In recent years, there has been an increasing concern of the environmental problems caused by increasing number of applications and mass volume uses of plastics in part due to increasing number of world population (Limpan et al., 2010). So as a result, many efforts have been made to develop environmentally friendly and biodegradable polymers as an alternative replacement for traditional petroleum-based non biodegradable polymers (Avella et al., 2005, Lodha and Netravali, 2005, Khardenavis et al., 2007).

Poly(lactic acid) (PLA) is one of the most promising candidates for further development since it is not only biodegradable but is produced from non fossil renewable resources such as sugar beets or corn starch (Murariu et al., 2008a, Baiardo et al., 2003). PLA exhibits good mechanical strength, processability and biocompatibility, and so can be used as a replacement in the production of many products currently produced from petroleum-based polymers (Jiang et al., 2005, Byrne et al., 2009). PLA is a commercially feasible packaging polymer as a replacement for petroleum-based polymer applications such as meat packaging, milk cartons, and beverage bottles, which constitute a large part of typical household waste and the use of biodegradable PLA reduces the environmental impact associated with packaging disposal (Byrne et al., 2009).

A significant material issue limiting the broader adoption of PLA in packaging is its brittleness and thus poor impact strength. Due to this, cracking and tearing of the polymer can occur during processing where force is placed on the polymer during manufacturing. These problems can be solved by copolymerization or blending with an impact modifier in order to improve the impact strength of the brittle PLA (Murariu et al., 2008b, Byrne et al., 2009).

PLA is expensive; this high cost limits its commercial applications to some extent (Murariu et al., 2008a, Murariu et al., 2008c). Therefore, in response to the demand for extending PLA applications while reducing its production cost, PLA can be blended with plant fibers such as kenaf fiber to develop biodegradable composites. Biodegradable composites are best candidates for short term applications such as cosmetics packaging.

The mechanical properties of a composite depend among others on the fiber-matrix interaction. An adequate interaction would form interface that allows efficient stress transfer from the matrix to the fiber (Huneault and Li, 2007). Hydrophilic plant fibers are not compatible with hydrophobic polymers such as PLA resulting in poor mechanical properties (Plackett, 2004). This problem of poor fiber-matrix interaction can be improved with fiber treatment or with the use of appropriate compatibilizer (Kim et al., 2007a, Nakason et al., 2006). Compatibilizer, maleic anhydride grafted polymer has been widely studied and used. The anhydride functionality of maleic anhydride grafted polymer reacts with cellulosic fiber hydroxyl groups while the grafted polymer entangled and/or co-crystallizes with the bulk polymer chains of the bulk matrix. This results in efficient stress transfer from the matrix to the fiber (Seo and Kim, 2008).

1.2 Research objectives

1. To investigate the effect of an impact modifier (at several compositions) on the thermal, mechanical and morphological properties as well as biodegradability (natural weathering and soil burial) of poly(lactic acid) (PLA). The best PLA/impact modifier blend composition that showed a good balance of mechanical properties (strength vs toughness) was used as the matrix for the study on the biodegradable composite.

2. To prepare and characterize mechanical properties of the biodegradable composites made of impact modified poly(lactic acid) and kenaf fiber. In order to promote fiber-matrix interaction, maleated poly(lactic acid) was prepared and used as compatibilizer. The properties of biodegradable composites were compared with those of polypropylene/kenaf fiber composites. Fiber loading was 40 wt%.

CHAPTER TWO

LITERATURE REVIEW

2.1 Plastics and the environment

Since plastics have started been used in 1930, it has become one of the most important part in our daily life. Figure 2.1 shows clearly that the total global production of plastics grew from 1.5 million tons in 1950 to 245 million tons in 2006. In the past 20 years, the production and the use of plastics in the world has enormously increased, worsening the problem of the waste disposal (Avella et al., 2005).

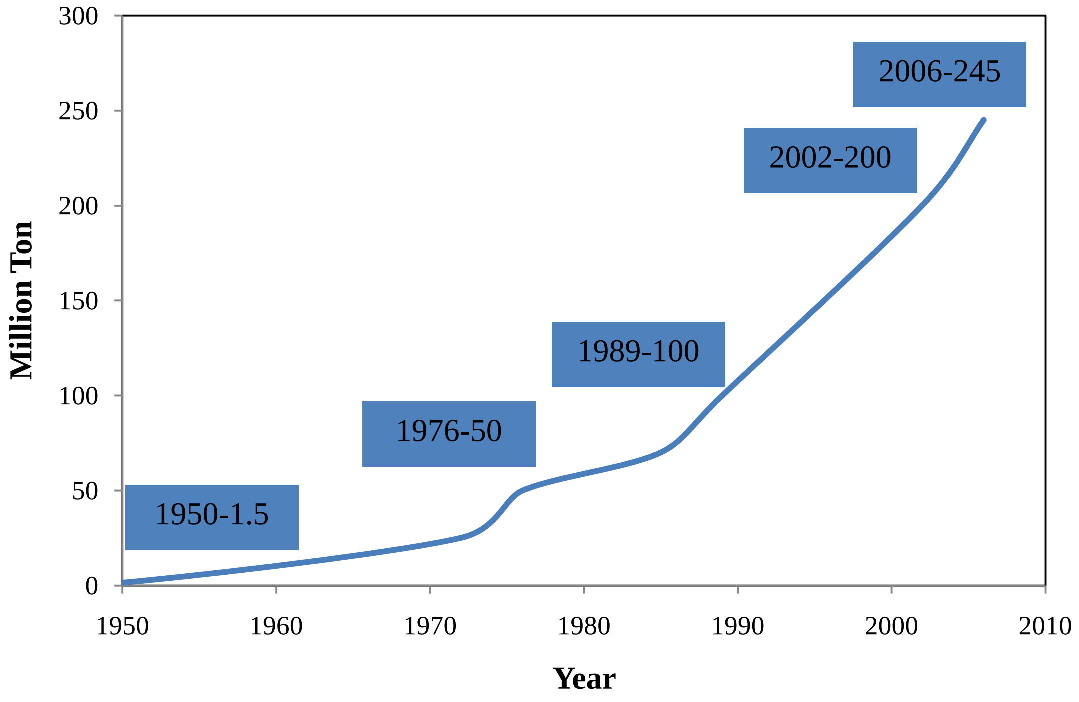

Figure 2.1 World Plastics Production since 1950 (Lopez et al., 2009)

Conventional polymers such as polypropylene (PP) and polyethylene (PE) persist for many years after disposal. Built for the long haul, these polymers seem inappropriate for applications in which plastics are used for short time periods and then disposed. Furthermore, plastics are often soiled by food and other biological substances, making physical recycling of these materials impractical and generally undesirable (Gross and Kalra, 2002). One major drawback of most polymers is the problem with their disposal. Since they may be resistive to degradation (depending on the polymer, additives, conditions etc), non-degradable polymers tend to accumulate in what is today's most popular disposal system, the landfill (Kyrikou and Briassoulis, 2007). The growing interest in environmental impact of discarded plastics has directed research on the development of plastics that degrade more rapidly in the environment, leading to a complete mineralization or bioassimilation of the plastics (Avella et al., 2005).

Some commercially successful biodegradable plastics are based on chemical synthesis like polyglycolic acid, polylactic acid, polycaprolactone, and polyvinyl alcohol. Others are products of microbial fermentations like polyesters and neutral polysaccharides or are prepared from chemically modified natural products like starch, cellulose, chitin or soy protein (El-Naggar and Farag, 2010).

2.2 Biodegradable polymers

Biodegradable polymers are an alternative replacement for traditional petroleum-based non biodegradable polymers. It decreases the waste disposal problems created by plastics waste that become crucial nowadays (Avella et al., 2005). Rising oil prices helped to stimulate early interest in biodegradables in the 1970s, and concerns over the dwindling availability of landfill sites, environmental regulations, and increasing oil prices are reviving interest in biodegradable materials today (Mohanty et al., 2005).

Biodegradable polymers may be defined as those which undergo microbially induced chain scission leading to photodegradation, oxidation, and hydrolysis, which can alter the polymer during the degradation process. Another definition states that biodegradable polymers are capable of undergoing decomposition primarily through enzymatic action of microorganisms in to carbon dioxide (CO_2), methane, inorganic compounds, or biomass in a specified period of time (Mohanty et al., 2002).

Figure 2.2 shows classification of biodegradable polymers and they are classified into four families. Except for petrochemical product family, which is of fossil origin, most biodegradable polymers are obtained from renewable resources or biomass. The biomass product family is agro based polymers obtained from biomass by fractionation. The microorganisms and biotechnology families are polyesters, obtained, respectively by fermentation from biomass or from genetically modified plants and by synthesis from monomers obtained from biomass. The petrochemical products family are also polyesters but totally synthesized by petrochemical process (John and Thomas, 2008). Blending two or more biodegradable polymers are also of interest to produce a new biopolymer designed for specific requirement (Mohanty et al., 2002).

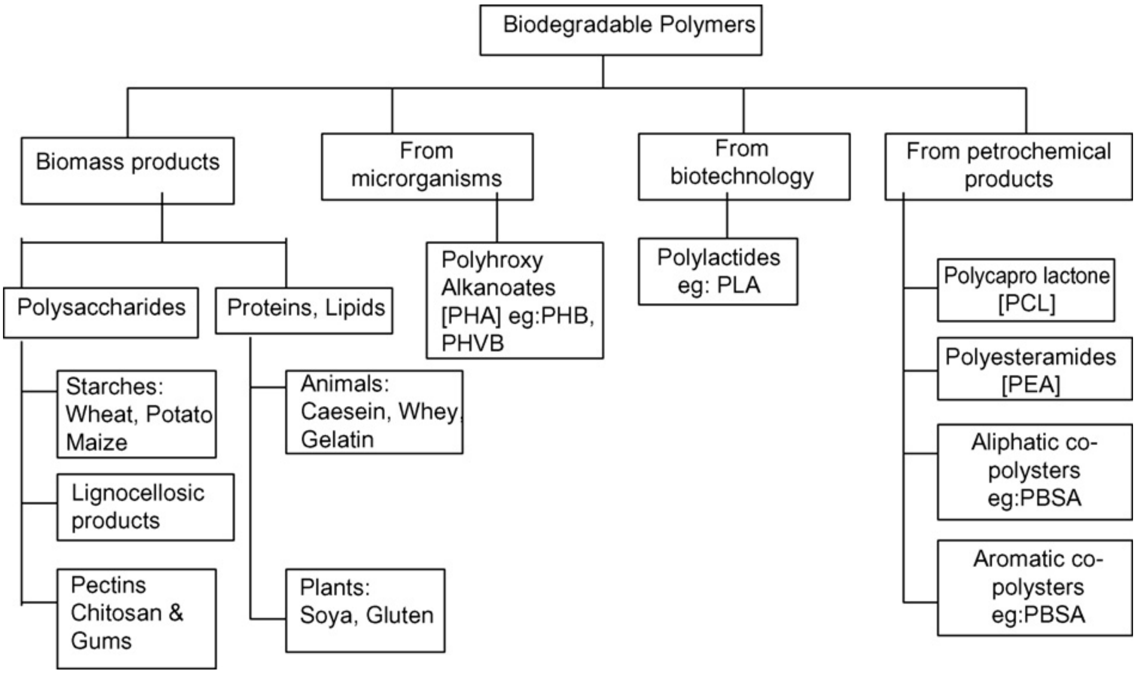

Figure 2.2 Classification of biodegradable polymers (Averous and Boquillon, 2004)

Biodegradability is not only a function of origin but also of its chemical structure and degrading environment. When a biodegradable material (neat polymer, blended product, or composite) is obtained completely from renewable resources, it may be termed as a green polymeric material. The life cycle of compostable biodegradable polymers is represented schematically in Figure 2.3.

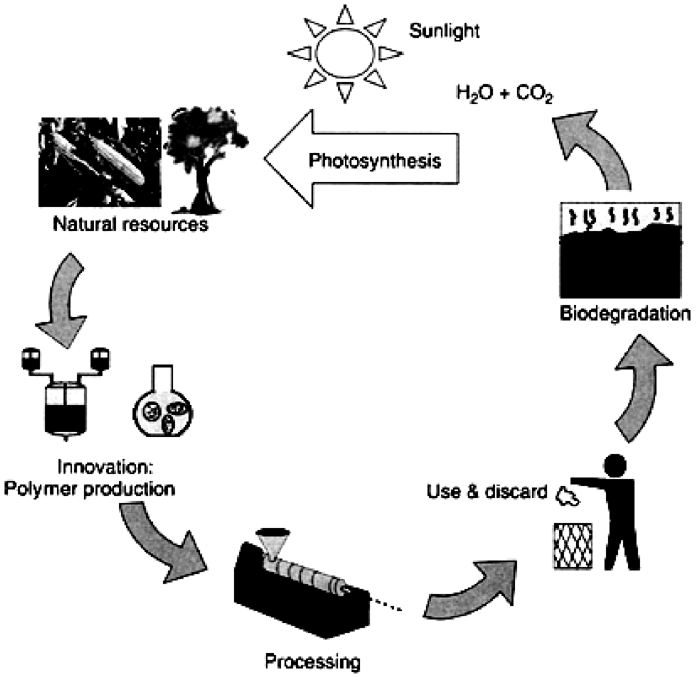

Figure 2.3 Life cycle of biodegradable polymers can maintain CO_2 balance in the environment (Mohanty et al., 2005)

2.3 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) belongs to the family of aliphatic polyesters commonly made from α-hydroxy acids, which include poly(glycolic acid) or poly(mandelic acid) (Agrawal et al., 2004, Soares, 2008). PLA is a rigid biodegradable thermoplastic, high-strength, high-modulus polymer that can be made from annually renewable resources to yield articles for use in industrial packaging, in the agricultural field, or for the bioabsorbable medical device market. It is easily processed like polyolefin plastics such as polypropylene (PP) and polyethylene (PE) by conventional processing methods such as injection molding, sheet extrusion, blow molding, thermoforming or fiber spinning (Oksman et al., 2003, Soares, 2008).

PLA is degraded by simple hydrolysis of the ester bond. This reaction occurs spontaneously and does not require the presence of catalytic enzymes. When disposed of properly, PLA will hydrolyze to harmless, natural products in about six months (compared to 500 to 1000 years for conventional plastics such as polystyrene and polyethylene). It could be a technical and economic solution for the problem of the eventual disposal of the very large amount of plastic packaging used in the world (Soares, 2008).

2.3.1 Production and synthesis of PLA

The basic building block for poly(lactic acid) is lactic acid. Lactic acid is one of the most important organic acids produced by lactic acid bacteria (LAB), discovered by Swedish scientist C.W. Scheele in 1780 from sour milk (Reddy et al., 2008). Lactic acid can be manufactured either by carbohydrate fermentation or chemical synthesis from petrochemical feedstock (Soares, 2008). The majority of the world's commercially produced lactic acid is made by the bacterial fermentation of carbohydrates, using homolactic organisms such as modified and optimized strains Lactobacilli, which exclusively form lactic acid. The various types of carbohydrates that can be utilized in the fermentation depend on the particular strain. In general, most of simple sugars obtained from agricultural by products can be used, including: (i) glucose, maltose, and dextrose from corn or potato starch; (ii) sucrose from cane or sugar beet; and (iii) lactose from cheese whey. Along with carbohydrates, the organisms require proteins and other complex nutrients. These requirements are very species-dependent, so it is typical to develop strains around the available nutrients, since these can add considerable cost to the process. High yield (up to 90% of weight of carbohydrate) commercial fermentation is usually conducted in a batch process, which takes three to six days to complete (Soares, 2008, Garlotta, 2001). The synthesis of lactic acid into high molecular weight poly(lactic acid) can follow three different routes of polymerization (Figure 2.4).

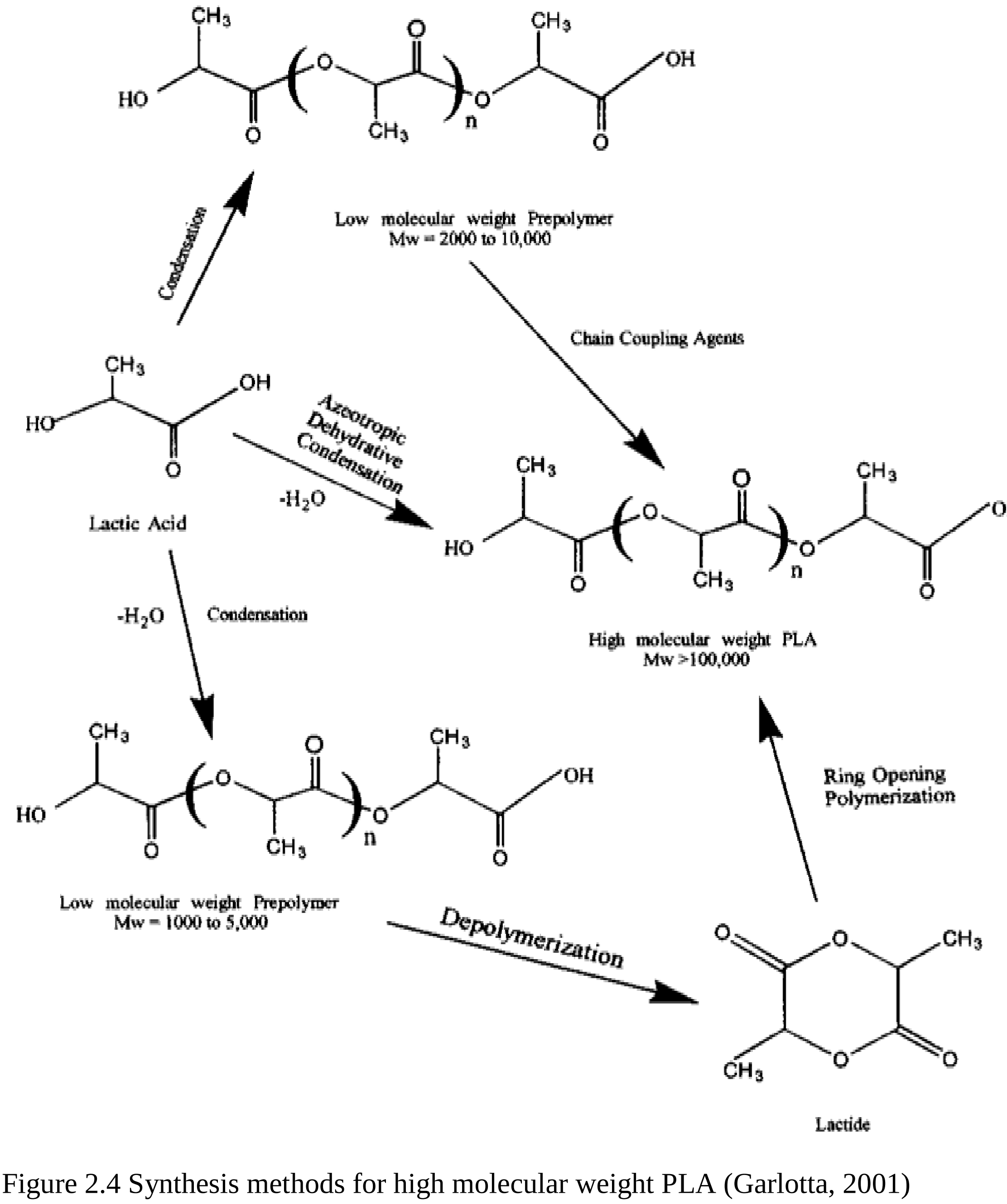

Figure 2.4 Synthesis methods for high molecular weight PLA (Garlotta, 2001)

First route by direct condensation of lactic acid, because the direct condensation route is an equilibrium reaction, difficulties of removing trace amounts of water in the late stages of polymerization generally limit the ultimate molecular weight achievable by this approach. The second route is to collect, purify and ring-open polymerize of the cyclic lactide dimer to yield high molecular weight PLA (>100,000). Ring opening polymerization was first demonstrated by Wallace Carothers in 1932 but significantly high molecular weights were obtained only with improved lactide purification techniques developed by DuPont in 1954. The third and most recent method yields higher molecular weights (>300,000) and is polymerization by azeotropic dehydration of lactic acid with a catalyst under high temperatures and reduced pressures. The residual catalysts can cause problems during further processing, such as unwanted degradation, or in the case of medical applications, catalyst toxicity (Lunt, 1998, Soares, 2008).

2.3.2 Morphological characterization

High molecular weight poly(lactic acid) is a colourless, glossy, stiff thermoplastic with properties similar to polystyrene (PS) (Kaplan, 1998). The amorphous PLA is soluble in most organic solvents such as tetrahydrofuran (THF), chlorinated solvents such as chloroform, benzene, and dioxane. Crystalline PLA is soluble in chlorinated solvents and benzene at elevated temperatures (Garlotta, 2001).

Lactic acid (2-hydroxy propionic acid) is the simplest hydroxyl acid with an asymmetric carbon atom and exists in two optically active configurations (Figure 2.5) (Gupta and Kumar, 2007, Soares, 2008). The L-isomer is produced in humans and other mammals, whereas both the D- and the L-enantiomers are produced in bacterial systems.

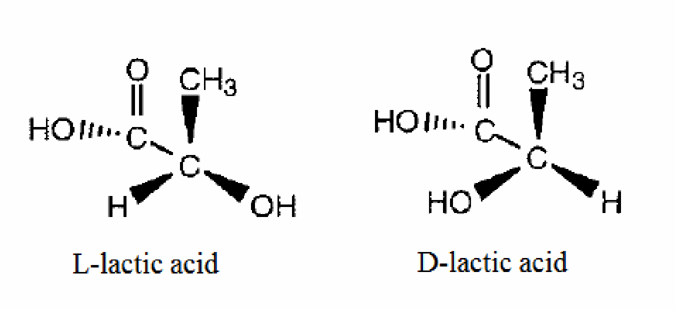

Figure 2.5 L- and D- enantiomers of lactic acid. Note the difference in location of the hydroxyl group in the chiral carbon (Soares, 2008)

Hence, when polymerized, poly(lactic acid) assumes two forms: poly(L-lactic), poly(D-lactic acid) (Figure 2.6). Both can coexist in the same chain, either in a random or in a block copolymer, poly(D,L-lactic acid). Poly(levo-lactic acid) and poly(dextro-lactic acid) are highly crystalline with identical chemical and physical properties, while poly(D,L-lactic acid) or poly(meso-lactic acid), a racemic polymer obtained from an equimolar mixture of D- and L-lactic acid, is amorphous, with weak mechanical properties. The involvement of D- and L- units in the sequences of PLLA and PDLA, gives a profound effect on their thermal and mechanical properties. Generally, the increased stereo-isomeric ratio decreases the crystallinity and accordingly the melting temperature is lower. On the other hand, a 1:1 polymer blend of PLLA and PDLA undergoes formation of a stereo complex that shows quite different properties from those of PLLA or PDLA (Urayama et al., 2002).

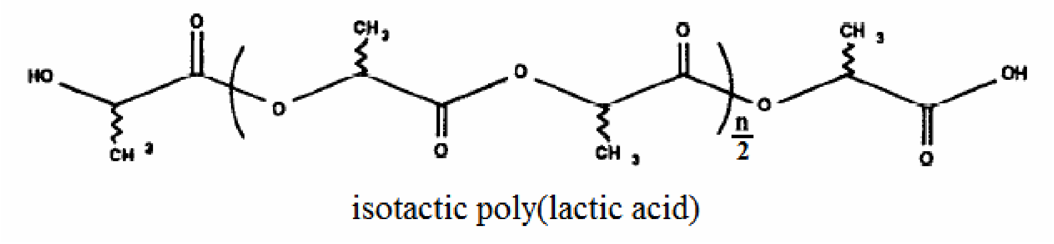

Figure 2.6 Isotactic poly(lactic acid). Either the L- or D- enantiomers yield stereoregular isotactic chains which are prone to stack in an ordered structure (Soares, 2008)

2.3.3 Mechanical and thermal properties of PLA

PLA is receiving commercial interest because its mechanical properties making it a good alternative to many currently used commodity polymers including polypropylene (PP), polyethylene (PE) and poly(ethylene terepthlate) (PET); unfortunately, PLA is rigid and brittle (Sawpan et al., 2009, Baiardo et al., 2003). The most common mechanical properties found in the literature for poly(lactic acid) are tensile strength, Young's modulus, and elongation at break following ASTM methods D638 or D882 (tensile tests for dumbbell shapes and thin films respectively). The mechanical behavior is highly dependent not only on gross quantities of poly(lactic acid) such as molecular weight and degree of crystallinity, but also its microstructure seems to play an extremely important role in the mechanisms of deformation. PLA has good mechanical properties, with tensile strength, Young's modulus and elongation at break in the range of 55 to 60 MPa, 3.2 to 3.7 GPa and 2.5% to 6%, respectively (Baiardo et al., 2003, Jiang et al., 2005, Soares, 2008). PLA is a partially crystalline polymer with a glass transition temperature (T_g) in the range of 55 to 65˚C and a melting temperature (T_m) around 160 to 170˚C (Baiardo et al., 2003, Li et al., 2009). PLA, however, is too stiff and brittle for room-temperature applications as its glass transition temperature (from 55 to 65˚C) is well above room temperature.

2.3.4 Limitations

A significant material issue limiting the broader adoption of PLA in packaging is its brittleness (with less than 10% elongation at break) and thus poor impact properties. Due to this, cracking and tearing of the polymer can occur during processes where force is placed on the polymer during manufacturing (Byrne et al., 2009, Murariu et al., 2008a), there is a general interest to formulate new grades with improved flexibility, ductility, higher impact properties and toughness, while the tensile strength performances are maintained at the optimal level required by a given application, which would eliminate the processing and handling deficiencies, precedes the possibility for widespread utilization and substitution for commodity plastics (Murariu et al., 2008b).

2.3.5 Toughen PLA

2.3.5.1 Copolymerizations

The brittleness of PLA can be modified by copolymerization of lactic acid with other monomers such as ε-caprolactone, glycolide, trimethylene carbonate, ethylene glycol, etc. (Jiang et al., 2005, Kricheldorf, 2001, Rasal et al., 2010). Jean et al. (2003) study the effect of copolymerization of lactic acid monomer with ε-caprolactone; with copolymerization both PLLA-PCL multiblock copolymers and PLLA-PCL-PLLA triblock copolymer were found to have good mechanical properties and to behave like thermoplastic elastomer. Hiljanen-Vainio et al. (1996) showed that racemic-PLA copolymer containing 1% caproyl units was hard and brittle; increasing the caproyl units by a few percent decreased the modulus and substantially increased the elongation. Nakayama et al. (2007) synthesized multiblock poly(L-lactide)-co-poly(ε-caprolactone) with elongation at break three times higher than pure PLLA.

The application of PLA in the field of commodity plastics requires a dramatic reduction in the costs of this polymer, as well as reliable and controllable technical processes. Because none of the aforementioned PLA copolymers are commercially available at this time, blending with different polymers and plasticizers is probably the most extensively used methodology to improve PLA mechanical properties (Jiang et al., 2005).

2.3.5.2 Blending with polymers

Blending PLA with other polymers (biodegradable and non-biodegradable) provides a more-practical and economic way of toughening PLA. Blending PLA with other polymers can substantially modify the mechanical and thermal properties, degradation rate, and permeability (Rasal et al., 2010, Jiang et al., 2005). The blending of PLA with polymers to improve impact strength has however been widely reported. For example the impact strength of PLA has been improved through blending with poly-ε-caprolactone (Semba et al., 2007), starch (Martin and Avérous, 2001), poly(ethylene oxide) (Heald et al., 2002) and poly(hydroxyl butyrate) (Rychter et al., 2006). Most of these blends are immiscible and compatibilizers are needed to improve their compatibility. For example PLA and starch are two promising candidates for biodegradable polymer blends. However, hydrophobic PLA and hydrophilic starch are thermodynamically immiscible leading to poor adhesion between the two components, resulting in poor and irreproducible performance. Two approaches are usually used to improve blend compatibilization (Ajji and Utracki, 1996). The first approach is to introduce a third component into the polymer system, reducing the interfacial energy, improving dispersion, and consequently enhancing adhesion between binary polymer phases. A block copolymer, for instance, is often used. The second method is reactive blending. In principle, this approach promotes chemical reactions between the two polymers in a molten state, often by introducing either a reactive third component with appropriate functional groups or a catalyst. The second approach is generally more economical than the first (Zhang and Sun, 2004a). However, although the impact strength is improved due to blending with these polymers, there is a related reduction in tensile strength (Martin and Avérous, 2001). Jiang et al. (2005) study the effect of blending of poly(lactic acid) (PLA) with poly(butylene adipate-*co*-terephthalate)

(PBAT) and found that impact strength was increased from 2.6 kJ/m^2 for neat PLA to 4.4 kJ/m^2 for PLA-20 % PBAT. Figure 2.7 shows micrographs of impact-fractured surfaces of blends with different PBAT contents. Micrographs of the impact-fractured surfaces show more evidences of ductile fractures as more and longer fibrils can be observed from the surfaces with the increase in PBAT content. Coupled with this improvement in the impact strength, however, there is an associated reduction in tensile strength and modulus of the PLA/PBAT blends with increasing PBAT content. Tensile strength decreased by 25% from 63 (neat PLA) to 47 MPa (20% PBAT) while modulus decreased by 24% from 3.4 (neat PLA) to 2.6 GPa (20% PBAT).

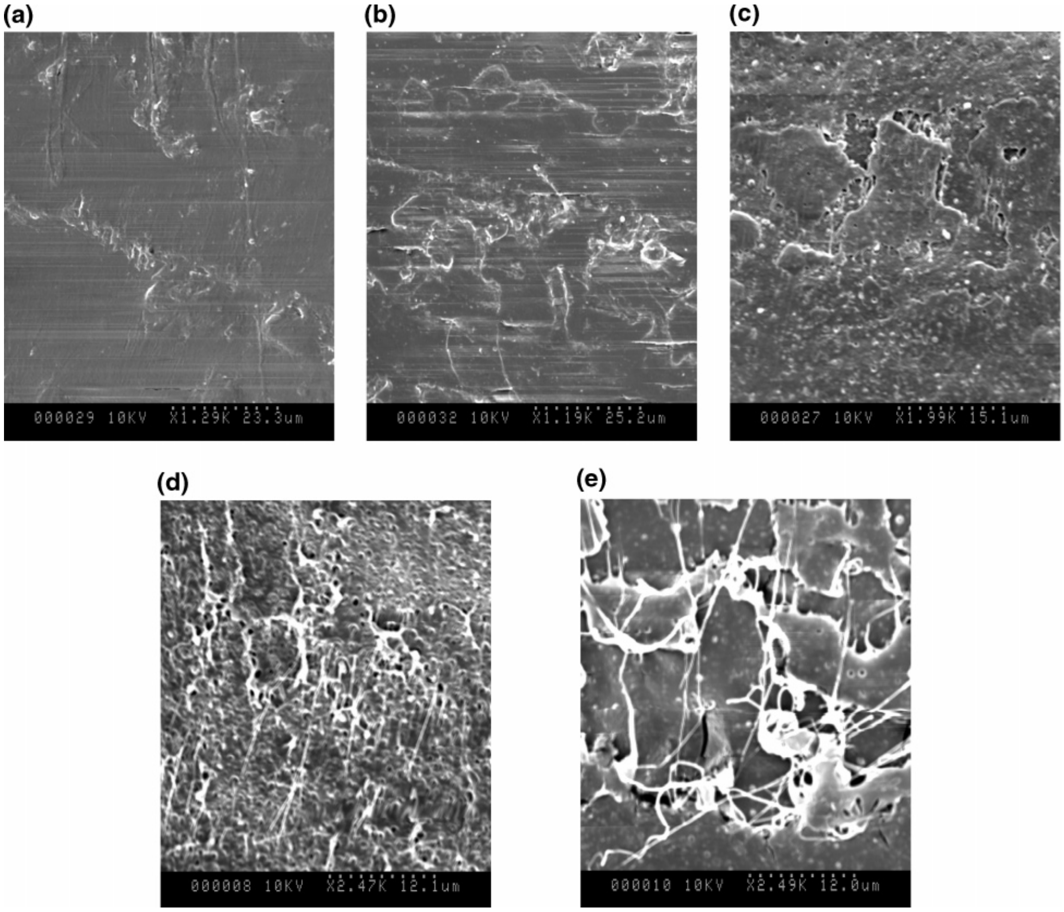

Figure 2.7 SEM pictures of the impact-fractured surfaces of blends with different PBAT contents. (a) Neat PLA, (b) 5% PBAT, (c) 10% PBAT, (d) 15% PBAT and (e) 20% PBAT (Jiang et al., 2005)

2.3.5.3 Blending with plasticizers

A large number of investigations have been made to improve PLA properties via plasticization but due to a great number of variables, e.g. nature of PLA matrix, type, and optimal percentage of plasticizer, thermal stability at the processing temperature, etc., unfortunately sometimes poor mechanical properties have been reported. In this context, it is important to note that unsuitable choice of the plasticizer can lead to PLA mixture that is not miscible, to migration of the plasticizer, to degradation of the polyester matrix and/or of the plasticizer along processing, etc. Typically, amounts from 10 to 20 wt% plasticizers are required to provide a substantial reduction of the glass transition temperature (T_g) of the PLA matrix and affect mechanical properties (Murariu et al., 2008b). The preferred plasticizer for PLA can be any biodegradable product, sufficiently non-volatile, with a relatively low molecular weight to produce a desired decrease in Young's modulus and increase in impact strength. It is well known that the monomer, lactide itself, is considered as one of the best plasticizers for PLA (Jacobsen and Fritz, 1999), but it has the disadvantage to migrate very rapidly to the polymer surface. Excessive volatility can lead to fouling of the process equipment, which is observed when PLA with high content of lactide is processed. The addition of plasticisers to PLA has been widely reported, with the most common studied including glucose monoesters and partial fatty acid esters (Jacobsen and Fritz, 1999), lactic acid oligomers (Martin and Avérous, 2001), glycerol esters (Oksman et al., 2003, Ljungberg et al., 2003), citrates (Ljungberg et al., 2003, Baiardo et al., 2003, Ljungberg and Wesslén, 2005), citrate oligoesters (Ljungberg and Wesslén, 2005), citrate oligomers (Ljungberg and Wesslén, 2003) and even higher molecular weight plasticizers like poly(ethylene glycol) (Baiardo et al., 2003, Paul et al., 2003, Hu et al., 2003), poly(propylene glycol) (Kulinski et al., 2006), etc.

These plasticisers have been shown to be effective in reducing the brittle behavior of PLA. Coupled with this improvement in the mechanical properties, however there is an associated reduction in glass transition temperature (T_g). As the glass transition temperature of PLA is low, in the range of 55 to 65°C, any reduction limits the application of the polymer further (Baiardo et al., 2003, Byrne et al., 2009). Murariu et al. (2008b) reduced the PLA brittle behavior and improved its ductility, by selecting three plasticizers, bis(2-ethylhexyl) adipate (DOA), glyceryl triacetate (GTA), and tributyl O-acetylcitrate (TBAC). The increase in (DOA) plasticizer fraction up to 20% leads to a surprisingly 11-fold increase of impact strength (Izod), while the fracture is characterized by a ‘‘hinge break’’, where 20% of GTA results in a sample that do not initiate any breakage with respect to neat PLA and PLA-20% TBAC.

In general, it has been accepted that the addition of a reasonable amount of plasticizer (e.g. 15–20 wt%) into PLA matrix leads to improved flexibility properties whereas for smaller percentages, especially up to 10 wt%, some ‘‘antiplasticizing’’ effects in relation to the mechanical properties can be recorded (Jacobsen and Fritz, 1999). On the other hand, the choice of plasticizer used as a modifier for PLA is limited by the legislative or technical requirements of the application (Ljungberg and Wesslén, 2005) and in this context its selection becomes more difficult. The nature of the plasticizer can strongly influence the final properties of the products, where the impact and/or crystallization properties are required to be higher than a critical value (e.g. in injection-molded parts, plastic containers, fibers, films, etc.).

2.3.6 Toughening mechanisms

Several studies have reported occurrence of various energy-dissipative mechanisms locally in a stressed specimen before catastrophic crack development (Li and Shimizu, 2007, Jiang et al., 2005, Yin et al., 2009). Mechanisms such as crazing, cavitation, bond rupture, crack growth, plastic and viscoelastic deformations, etc., relieve stresses and consequently reduce the stored elastic energy. High strength and toughness therefore, result primarily from special combination of these mechanisms that retard or arrest the growth of cracks (Smith, 1971).

Using fractured surfaces of notched Izod impact tested samples as a means of differentiating brittle to ductile fractures, previous studies reported noticeable whitening only occurs at the origin of the notched tip for brittle fracture, while ductile fracture involves all of the material around the fractured surface in stress whitening and forms a yielding zone (Yin et al., 2009). Rubber modification provides an effective method to improve the impact strength of a rigid polymer matrix (brittle to ductile transition). The main role of the dispersed rubber particles is to induce an overall deformation mechanism, rather than a localised one (Loyens and Groeninckx, 2003). In rubber-toughened plastic systems, two types of cavitation induced by impact or tensile tests are discerned, which includes internal cavitation in the rubber domains for the blends with strong interfacial adhesion and debonding cavitation between the interfaces with insufficient interfacial adhesion (Li and Shimizu, 2007). The dispersed rubber particles are likely to cavitate and/or debond upon the application of a load. The voiding of the rubber phase leads to a relief of the triaxial stress state ahead of the notch or crack, thus creating a stress state beneficial for the initiation of multiple matrix shear yielding (Loyens and Groeninckx, 2003).

The criteria for rubber cavitation have been studied by Dompas and Groeninckx (1994) and also by Lazerri and Bucknall (1993). The cavitation ability of the rubber particles was found to depend on the volume strain imposed upon sample loading. Figure 2.8 illustrates the different steps involved during the event of rubber cavitation.

The model explains the increasing resistance against cavitation with decreasing rubber particle size.

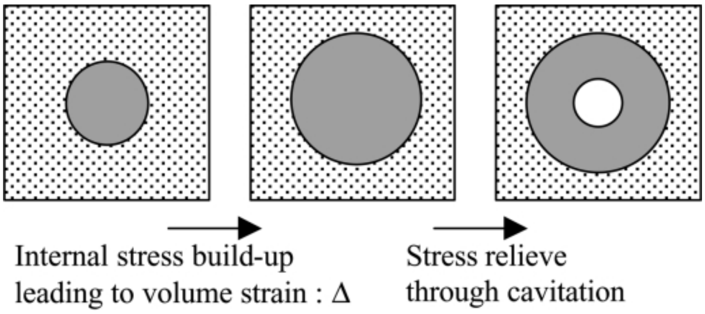

Figure 2.8 Schematic presentation of the steps involved in rubber cavitation (Loyens and Groeninckx, 2003)

Bucknall et al. (2000) have developed a dynamic mechanical thermal spectroscopic technique (DMTS) that allows investigating cavitation as a separate process during the early stages of deformation in the absence of shear yielding. Generally, the mechanisms causing the damage during brittle fracture have been prescribed as mainly crazing or microcracks (leading to stress whitening) and cavitation (Liang and Li, 2000). Crazing, cavitation, shear banding, crack bridging, and shear yielding reportedly occur as important energy dissipation processes involved in the impact fracture of toughened polymer systems (Jiang et al., 2005).

PLA has strength and modulus comparable to those of commercially available engineering polymers. However, PLA exhibits brittle fracture behavior, especially under impact loading conditions, and therefore, it is important to examine the fracture behavior using PLA specimens that are notched or cracked (Arakawa et al., 2006). Only a few experimental studies examining the fracture behavior of PLA have been published (Arakawa et al., 2006). Park et al. (2004) studied effect of annealing on the fracture toughness of poly(lactic acid), Park et al. (2006) studied effect of crystallinity and loading-rate on mode I fracture behavior of poly(lactic acid) and Arakawa et al. (2006) studied the tensile fracture behavior of a biodegradable polymer, poly(lactic acid).

2.3.7 Degradation of PLA

PLA can be completely degraded under compost conditions. Although it has a hydrophobic characteristic (non-water soluble), microbes in marine environments can degrade it into water and carbon dioxide (Briassoulis, 2004), and hydrolyzes more promptly than polyhydroxyalkanoates in anaerobic condition (Moura, 2006). The first step of PLA degradation does not require microbial action and is characterized by the cleavage of the ester linkages to lactic acid by a temperature and humidity-enhanced process (Figure 2.9) (Agarwal et al., 1998, Lunt, 1998, Ho and Pometto III, 1999). Then lactic acid is biodegraded by microbes into carbon dioxide, methane, and water (Sinclair, 1996). The complete degradation of PLA by hydrolysis in the environment takes from several months to two years in a composting condition depending on its molecular weight, moisture and temperature, which is relatively fast compared to 500 to 1,000 years for petroleum-based plastics such as polystyrene and polyethylene (Datta et al., 1995).

The biodegradability of PLA depends on the environment to which it is exposed. Suyama et al. (1998) reported that 39 bacterial strains of class Firmicutes and Proteobacteria isolated from soil environment were capable of degrading aliphatic polyesters such as poly(hydroxyl butyrate) (PHB), poly(ε-caprolactone) (PCL) and poly(butylene succinate) (PBS), but no PLA-degrading bacteria were found. These results showed that PLA-degrading microorganisms are not widely distributed in the natural environment and thus, PLA is less susceptible to microbial attack in the natural environment than other microbial and synthetic aliphatic polyesters. It was also found out that among the 41 genera (105 strains) of actinomycetes from the type culture, the PLA degraders phylogenetically belonged to Pseudonocardiaceae family and related genera, including the genera of Amycolatopsis, Lentzea, Kibdelosporangium, Streptoalloteichus, and Saccharothrix (Suyama et al., 1998, Tokiwa and Calabia, 2007). Out of 14 fungal strains tested, only two strains of F. moniliforme and one strain of Penicillium roqueforti could assimilate lactic acid and racemic oligomer products of PLA but no degradation was observed on PLA (Tokiwa and Calabia, 2006, Tokiwa and Calabia, 2007).

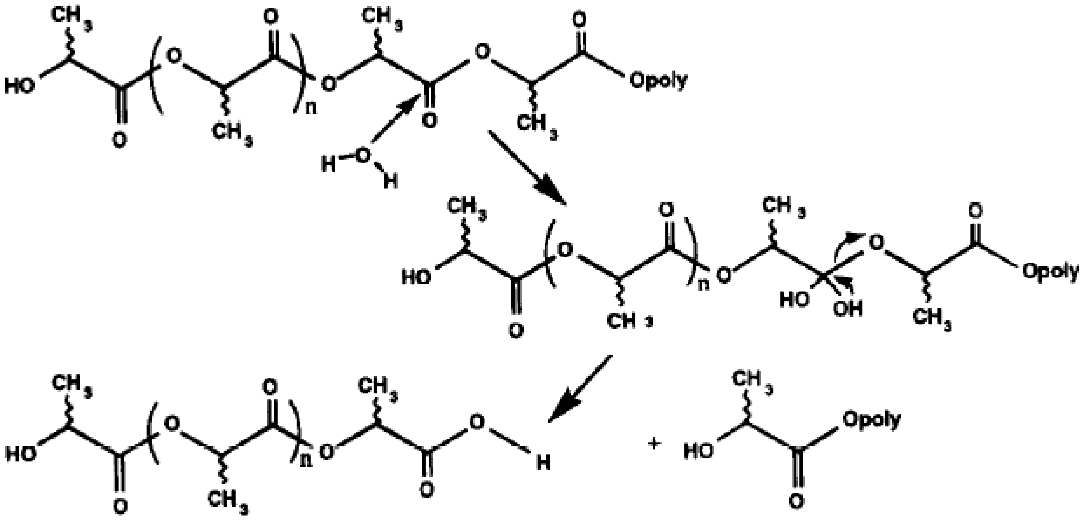

Figure 2.9 Hydrolytic degradation in PLA (Lunt, 1998)

2.3.7.1 Natural weathering

Natural weathering or environmental degradation is an acceptable method of acquiring data about material performance under the influence of atmospheric factors such as temperature, humidity, and solar radiation or UV radiation, as well as seasonal variations and environmental pollutants. It represents the overall effects of the factors as well as the interplay of those parameters (Ismail and Awang, 2008). As the outdoor applications of plastics become more widespread (e.g., disposable plates, cups, cutlery, and drinking straws; agricultural mulch films; packaging bags and films; containers for liquid foods; loose fill packaging; and golf tees) it is important to have an understanding of weathering effects on their material properties (Ghorpade et al., 2001). The durability of its products against weathering, particularly UV light becomes of concern.

UV exposure can cause changes in the surface chemistry of the materials, also known as photodegradation, photodegradation results in a serious deterioration in mechanical properties, and color change during service life making the products aesthetically unappealing (Matuana et al., 2001). There are a few reports on UV degradation of PLA. Ho and Pometto III. (1999) and Lee et al. (1989) described separately action of UV and relative humidity (RH) on PLA. Zaidi et al. (2010) investigated the degradation of polylactide (PLA)/Cloisite 30B nanocomposites under natural weathering as a function of clay loading (1, 3 and 5 wt%) for up to 130 days, The results showed that the photo-oxidation mechanism of PLA was not modified in the presence of Cloisite 30B, but only the degradation rates were accelerated. The decrease of the weight-average molecular weight, and the number-average molecular weight associated with an enhanced polydispersity of the nanocomposite samples indicated that chain scission was the most prominent phenomenon in natural weathering. The thermal degradation of the PLA was faster in the presence of clay. Finally, the weathering effect on the morphology of exposed samples observed by SEM revealed that the fractured surfaces exhibited many voids and cracks, these defects were much more pronounced for the PLA nanocomposites.

2.3.7.2 Soil burial

The degradation of PLA has been studied several years ago, but understanding on this subject is still inadequate. This is clearly evidenced by lack of information on the mechanisms involved and the microorganisms associated with the degradation. Polymers are degraded in the soil by the action of a wide variety of microorganisms. Therefore, the ecological and taxonomic studies on the abundance and diversity of polymer-degrading microorganisms in the different environment are necessary because they are responsible for the degradation of plastic materials (Tokiwa and Calabia, 2006). In general, polymer degradation takes place through the scission of the main chains or side chains of polymers. Different degradation mechanisms whether chemical or biological can be involved in the degradation of biodegradable polymers. A combination of these mechanisms can also happen at some stage of degradation.

The rates of biodegradation of polymers are influenced by several factors including molar mass, chemical structure, stereochemistry, hydrophilic/hydrophobic balance and chain mobility (Rizzarelli et al., 2004). Lately, crystallinity has been singled out as the factor that affects mostly enzymatic degradation of polymers (Nagata et al., 1998, Montaudo and Rizzarelli, 2000). Several reports showed that the crystalline part of the PLA was more resistant to degradation than the amorphous part, and the rate of degradation decreases with an increase in crystallinity (Tsuji and Miyauchi, 2001). Calmon et al. (1999) found that PLA films had weight losses varying from 0 to 100% after burial in soil for 2 years depending on PLA type and location. Osawa et al. (2000) found that the molecular weight of PLA in PLA/starch 70/30 moldings decreased by about 60% after burial in soil for 45 days versus 10% for PLA alone.

2.3.8 Applications of PLA

There have been an increasing number of studies on the use of high molecular weight PLA in the biomedical field such as drug delivery systems, including fertility and cancer control and surgical repair materials such as fracture pins and sutures (Sheth et al., 1997, Arakawa et al., 2006). PLA is a commercially feasible packaging polymer as a replacement for petroleum based polymers application such as meat packaging, milk cartons, beverage bottles and cosmetic containers which constitute a large part of typical household waste and the use of biodegradable PLA reduces the environmental impact associated with packaging disposal (Butterwick and Lowe, 2009, Park et al., 2006, Byrne et al., 2009). Figure 2.10 shows some application of PLA in packaging industry.

Figure 2.10 PLA as packaging materials