

Chapter 2

Literature Reviews

2.1 Introduction

Nowadays, the use of plastics has rapidly increased, which leads to an agglomeration of large amount of wastes. Decomposition of plastic wastes requires long time period, because these materials are highly resistant to environment influences, such as humidity or microbial attack. Therefore, the degradability of polymer in the natural environment has become an important topic to resolve the increasing pollution problems. Current mass-produced synthetic polymers are highly resistant to biological degradation, for example, polyethylene terephthalate (PET). PET, a thermoplastic aromatic polyester, is widely used in manufacturing of textile fibers, soft-drink bottles, photographic film and packaging films, as PET has excellent material properties. Owing to the increased awareness of environmental issues, recycling of PET has recently attracted great interest around the world. (Awaja, 2005) However, recycling of polymer is difficult or inexpedient due to technical and economic considerations. It would seem advisable to replace the synthetic plastics in mass use by some biodegradable plastic materials. Within the new group of degradable polymers, various types of aliphatic polyesters play a major role with respect to industrial relevance. (Müller R, 2001)

The field of biodegradable polymers is a fast growing area of polymer science because of the interest in such polymers for temporary surgical and pharmacological applications. Also, biopolymers offer a possible alternative to traditional non-biodegradable polymers in many applications. (Vert, 1992)

Poly(lactic acid) (PLA) is degradable aliphatic polyesters, which attracts increasing use in medical, industrial and agricultural applications. PLA has the advantage of being not only biodegradable but also renewable since its raw material, lactic acid (LA), is produced from microbial fermentation of biomass. (Södergård A, 2002) It is suitable for packaging applications, since PLA's glass transition temperature (T_g about 55-60°C) is above the service temperature. Additional benefits for packaging applications are good heat resistant ability and processability with standard plastic equipment.

2.2 Polymerization of lactic acid

Lactic acid (LA) is the basic building block for Poly(lactic acid) (PLA). It is highly water soluble, three-carbon chiral acid that is naturally occurring and most commonly found in L(-) form. PLA is a rigid thermoplastic polymer and can be either amorphous or semicrystalline, depending on its stereochemistry and its thermal history. Poly(L-lactic acid) or poly (D-lactic acid) is semicrystalline, but mixed form, poly(D,L-lactic acid), is amorphous. For semicrystalline PLA, the glass transition temperature (T_g) is 58°C and melting point (T_m) is 130-230°C (Mecerreyes, 1999). Figure 2.1 depicts the polymerization methods which are currently available for poly (lactic acid) (PLA) synthesis. Lactic acid is a hydroxy acid, having both a hydroxyl and a carboxyl group, which enables its polymerization directly via a polycondensation reaction into poly (lactic acid). This polycondensation is a reversible reaction, which is not easy to drive to completion because of the difficulty of removing water from the reaction that is very viscous melt. Polycondensation therefore produces low molecular weight oligomers,

which are unusable for many applications unless external linking agents are used to increase the molecular weight of the polymer. High molecular weight PLA, however, can be obtained from an azeotropic polycondensation where the water by product is removed from the reactor as an azeotropic mixture with the solvent, such as diphenyl ether, under reduced pressure (Ajioka, 1995; Enomoto, 1992). Alternatively, many researchers focus on ring-opening polymerization, which includes polycondensation of lactic acid, followed by a depolymerization into the dehydrated cyclic dimer, lactide, which can be ring-opening polymerized into high molar mass polymers. Tin(II)bis-2-ethylhexanoic acid or tin(II)octoate is preferred for the bulk polymerization of lactide at 180-210°C due to their solubility in molten lactide and high catalytic activity (Mecerreyes, 1999).

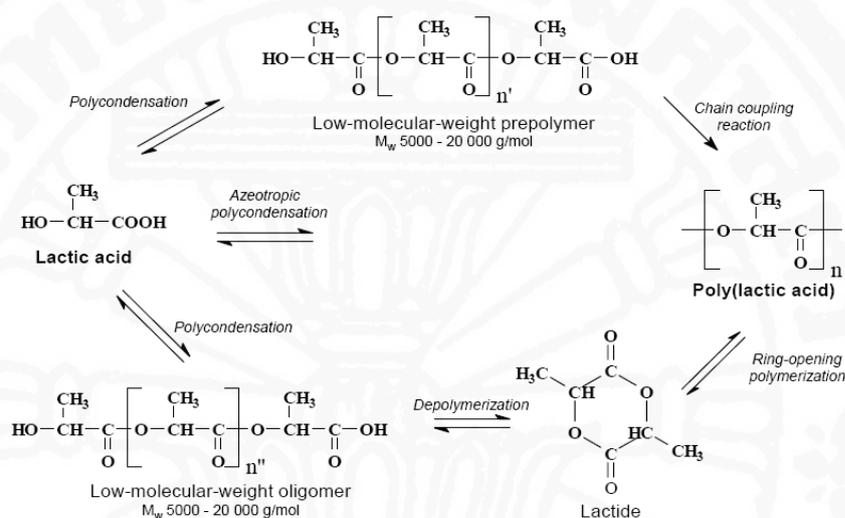


Figure 2.1 Overview polymerization methods of high-molecular weight poly(lactic acid) (Mecerreyes, 1999)

2.3 Copolymerization of poly (lactic acid)

Copolymerization of lactic acid or lactide with other monomers has been recognized as a valuable tool in modifying the properties of PLA homopolymer. Although PLA appears very versatile, in general the properties of PLA homopolymer can only be slightly modified by varying the molecular weight or crystallinity. Copolymerization provides materials with a wider range of properties. PLA copolymers present all the classical structures, namely random, diblock or multiblock, star, etc., with all the consequent variations in properties one can predict from such differences (Vert, 1995).

Various types of monomers have been shown to increase the glass transition temperature (T_g) of poly(lactic acids). Fukuzaki and co-workers (Imasaka, 1990; Fukuzaki, 1990) used α -hydroxy acids containing aromatic rings as the side groups or in the main chains to stiffen the oligomer chain. L-lactic acid was copolycondensed with aromatic hydroxy acids such as p-hydroxybenzoic acid, p-hydroxyphenylacetic acid, and p-3(hydroxyphenyl)propionic acid, or monomers having aromatic rings as side-group residues, e.g. DL-mandelic acid and L-3-phenyllactic acid. In lactide copolymerizations,

the incorporation of glycine and salicylic acid repeating units has increased the T_g (Helder, 1986; Supèr, 1994).

On the other hand, another modification approach is to lower T_g of PLA and improve its low temperature properties by increasing its flexibility. Copolymers of lactide and glycolide (GA) have found wide-spread use as biomedical materials due to an increase in hydrophilicity and enhanced degradation (Grijpma, 1990). In most case of copolymerizations of L-lactide, the length of crystallizable LA sequences is greatly reduced in comparison with homopolymerizations. It can therefore be expected that, as the amount of comonomer increases, the crystallinity and the melting temperature of the copolymer will be reduced. L-LA/GA copolymers in the composition range 25-65 wt.% GA are fully amorphous. Similarly, in stereocopolymers of L-lactide and D- or DL-lactide, the melting temperatures of the semicrystalline copolymers decrease as the content of D-units increases (Vert, 1986). This random incorporation of a small amount of lactide enantiomer of opposite configuration has been utilized in varying the degradation profile, but it has also been the most widely used method for improving PLA processability (Spinu, 1996; Kolstad, 1996). Copolymers of lactide and ϵ -caprolactone (CL) have a wide variety of mechanical properties, ranging from elastomeric to rigid, depending on the composition and the average sequence length (Grijpma, 1991). The chemical microstructure of these copolymers varies from random to diblock arrangement, depending on the polymerization and the type of initiator used. Transesterification, i.e., the exchange reaction of ester groups between different chains, generates the redistribution of sequences in the polyester chain, thus changing its microstructure (Bero, 1993). Lactic acid derivatives (Yin, 1999), other lactone (Abe, 1997; Fukuzaki, 1989) and ether lactone (Albertsson, 1992; Löfgren, 1995) monomers, as well as trimethylene carbonate (Buchholz, 1993; Storey, 1994) and its dimethyl derivatives (Schmidt, 1996) have also been widely studied as comonomers to obtain copolymers with versatile properties.

Modifications to the degradation kinetics of PLA, especially in drug release systems, have been of interest. The incorporation of flexible water soluble polyethers, such as poly(ethylene glycol) and poly(propylene glycol) or their respective monomers, to form random and block copolymers, enables variation of hydrophilicity, biodegradation rate, and of course the final mechanical properties (Chen, 1997; Stevels, 1996). In addition, poly(orthoester) and poly(anhydride) have been reported as bioerodible materials, and thus the PLA copolymers with corresponding monomers have shown surface erosion behavior (Zhu, 1997; Schwach-Abdellaoui, 1999).

On introduction of functional side groups by copolymerization, variation in the physical properties can be achieved. PLA copolymers with pendant side-chain amino groups of the lysine (Barrera, 1995; Hrkach, 1995) and di-hydroxyl (Chen, 1999) groups will provide a functional handle to attach bioactive molecules and to prepare graft copolymers. The free carboxylic acid groups, obtained from the copolymerization of malic acid (Kimura, 1993; Ouchi, 1989), can also be further functionalized to manipulate the material properties. These groups are thought to have a catalytic effect on the hydrolytic scission of the ester bonds, increasing the degradation rate. Copolymers with polydepsipeptides having pendant carboxyl and amino, or thiol groups have also been reported (In't Veld, 1992). In addition, Chen et al. have copolymerized a cyclic carbonate monomer, which has a cyclohexene group, with L-lactide to introduce C=C functional groups. This provides opportunities to introduce other functionalities or free radical crosslinking (Chen, 1998).

2.4 Polymerization of bis(hydroxyethyl) terephthalate

Poly(ethylene terephthalate) (PET) production process involves two different starting reactions. Esterification reaction is taken place where terephthalic acid (TPA) reacts with ethylene glycol (EG) at a temperature between 240-260°C. Trans-esterification reaction is then employed, where dimethyl terephthalate (DMT) reacted with EG at 150-220°C, as shown in Figure 2.2. Additionally, trans-esterification is the much preferred process due to easier purification. The product from these processes is bis(hydroxyethyl) terephthalate (BHET) which is then further polymerized to PET in successive the polycondensation process. PET has T_g at 69-115 °C and T_m at 265°C (Awaja F, 2005).

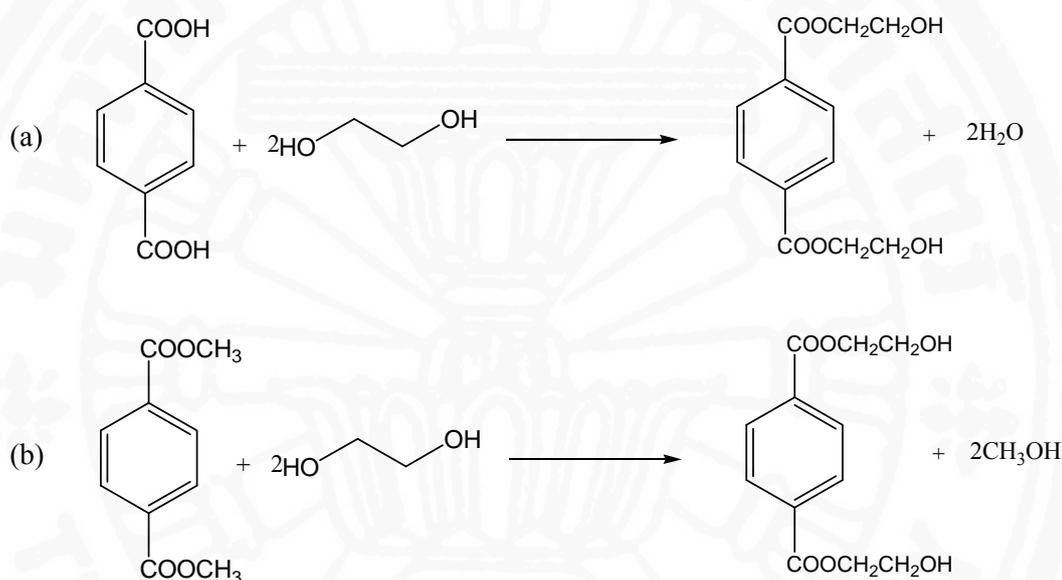


Figure 2.2 Different synthesis process of BHET starting from (a) terephthalic acid (TPA) and (b) dimethyl terephthalate (DMT)

2.5 Synthesis of PET-*co*-PLA copolymers

Given the good properties of each polymer, PET copolymerized with PLA could be interesting copolymer. Therefore, this copolyester is widely studied by many researchers. In recent years, PET-*co*-PLA was synthesized by *Olewnik et. al.* by melt reaction of L-lactic acid (LA) and BHET in the present of tin(II)chloride activated by *p*-toluene sulfonic at 180°C for 6 hours (Olewnik, 2007). The authors found that the copolyesters showed T_g at temperature higher than that of heat PLA, which reflects an insertion of terephthalate unit in the copolyester chain. The short sequence length of PET synthesized from low BHET content results in amorphous copolyester. The results indicated that PET-*co*-PLLA was amorphous when its composition was equimolar and exhibits a melting point only when PET block length was close to 9 monomer units. These melting temperatures were much lower than those of original PET, which also indicated an incorporation of aliphatic PLA units in PET chain.

2.6 Chain linking reactions

The way to achieve high molecular weight polyester is to conduct condensation oligomers with chain extenders. Chain extenders are usually bifunctional compounds that can increase the molecular weight of polymer. In polyester chains, hydroxyl end-group usually coexists with the carboxyl end-groups. Typical chain extenders for polyesters, which contain –OH and –COOH groups, are bisoxazolines, diisocyanates, diepoxides, dianhydrides and bisketeneacetals. Chain extenders can be classified according to polyester functional end-groups that they react with. The chain extenders that react with carboxyl end-group are effective, in addition to the chain length by reducing the overall carboxyl content leading to high hydrolytic and thermal stability which in turn maintains molecular weight during melt processing. (Awaja F, 2005) The higher number of COOH leads to obtain the lower molecular weight of polymer. The decrease of carboxyl end group will reduce the acid value leading to high thermal stability and reacting well with hydroxyl chain extender. An examples of carboxyl reactant chain extender is 2,2'-bis(2-oxazoline) (BOX) reacted with PLA (Tuominen J., 2000) and PET (Torres N.,2001). The other type of chain extenders is hydroxyl reactive chain extenders. Some examples of hydroxyl reactive chain extender are hexamathylene diisocyanate (HMDI) reacted with PLA, PET and 1,4-butane diisocyanate(BDI).(Tuominen J.,2003) Unspecific type of –OH or –COOH reactive chain extenders are isophorone diisocyanate(IPDI) (Kylmä J.,1997), diphenylmethane diisocyanate(MDI) and pyromellitic dianhydride(PMDA).(Tang X,2007)

The chain extending of polyesters can be conveniently and economically performed in an extruder if the reaction rate is high enough. 2,2'-bis(2-oxazoline) (BOX) was used as chain extender of recycled PET during processing in a twin-screw extruder and injection molding to improve mechanical properties.(Torres N.,2001) BOX is an effective chain coupling agent to obtain high molecular weights with a fast reaction rate of lactic acid oligomers. BOX can reduce acid value that leads to high thermal stability and molecular weight of carboxyl-terminated prepolymers, but does not react with aliphatic alcohol. (Tuominen J.,2002)

The increasing of MW of poly(lactic acid) (PLA) by diisocyanate is widely used. For example, the using of HMDI as a chain extender to synthesize high molecular weight PLA in direct polycondensation at 160°C under N₂ atmosphere.(Woo S.,1995) The chain extender reacted with hydroxyl terminal group of polymer in the final step. The highest molecular weight was obtained when antimony trioxide Sb₂O₃ was used (Mw = 76,000 g/mol). The excess amount of HMDI can react with the other end group (COOH) and react with the urethane group to form a branch, known as an allophanate reaction. The reaction of HMDI with PLA producing branch and crosslink structure decreased at lower reaction temperature. High MW PLA can be obtained if the reaction time and temperature increase, because of formation of branch structure.(Tuominen J.,2003)

The study of lactic acid oligomer has a hydroxyl group at one end of polymer chain and a carboxyl group at the other by chain extending reaction with HMDI and BOX in melt mixer at 150°C.(Tuominen J.,2003) The molecular weight increased slowly when using only HMDI with lactic acid oligomer (Mw from 13000 to 48000 g/mol) during the three hours reaction time and at the same time the acid value decreased from 11 to 7 mgKOH/g. Isocyanate groups thus reacted with carboxyl groups, but not fast enough to be used in the chain linking of lactic acid oligomers. In 30 minutes reaction time, an equimolar amount of BOX decreases the acid value from eleven to three mgKOH/g but slowly increases molecular weight (Mw from 20,000 to 35,000 g/mol). For using both chain extenders in sequential or simultaneous time with excess of BOX, it provided the

same molecular weight (Mw 300,000) which is quite higher than only one chain extender but longer time is required to reach high molecular weight for simultaneous experiments. When HMDI was allowed to react before addition of excess BOX, higher molecular weight polymer than that obtained when BOX was added first.

Torres N. et al. reported a method for chemical modification of virgin and recycled PET. The reaction of chain extension was carried out in a melt mixer by using various chain extenders to improve mechanical properties of PET. Preliminary tests showed that diisocyanates were more reactive toward the end groups of virgin PET than bis-oxazolines or diepoxides. Samples of modified virgin PET with diisocyanates possess molecular weight and intrinsic viscosity superior to those of virgin PET. They found that aliphatic diisocyanate (HMDI) provided higher MW than aromatic diisocyanate (MDI) at the same concentration of chain extender. The high of chain extender concentration and residence time leads to higher intrinsic viscosity and molecular weight polymer. Chemical modification of recycled PET by 0.9% wt of HMDI in melt mixer lead to an increase in the molecular weight (Mw) from 30,000 to 51,000 g/mol, the intrinsic viscosity from 0.6 to 0.84 dL/g, and mechanical properties, particularly the elongation at break, from 5 to 300% at 5 minutes of residence time. Modified polymers are still thermoplastic and uncrosslinked but discoloration occurred with diisocyanates. This method led to a recycled PET having an intrinsic viscosity, molecular weight, and mechanical properties close to those virgin PET. (Torres N.,2001)

2.7 Chemical structure characterization of PET-co-PLA copolyesters

Olewnik et. al. reported a method for characterization of PET-co-PLA copolyesters by using ^1H and ^{13}C NMR in order to confirm the incorporation of lactate units in PET chains. The authors found that copolyesters containing nearly equimolar terephthalate/lactate ratio were not completely random and present some block-copolymer character, while the microstructure of PET-rich copolyesters was a random one, due to longer PET sequence length. The latter exhibited a melting point close to 210 °C, while the other ones were amorphous. (Olewnik E. 2007)

Chemical structure of the copolyester are characterized in term of arrangement of lactate and terephthalate in the chain structure, which are reported by the degree of randomness, B, and the number- and weight-average block lengths of condensation copolymers (Tessier et. al.). When A and B represented two differences monomers, the content of connections of repeat units to both symmetrical (AA + BB) and unsymmetrical (AB) were established through an approach based on functional group probabilities. Several parameters introduced in the literatures to characterize the randomness in AA + BB condensation copolymers compared to B. A method for calculating functional group probabilities from the diad and triad number-fractions determined by NMR spectroscopy was described for poly(ethylene terephthalate)-poly(ϵ -capro-lactone) copolyesters. (Tessier M.,2003)