



CHAPTER II

LITERATURE REVIEW

2.1 Reactive Extrusion

Reactive extrusion (REX) is a polymer processing technique that mainly involves the use of an extruder as a chemical reactor. Polymerization and other chemical reactions associated with polymers are carried out in situ, while processing is in progress. Therefore, REX differs from conventional polymer manufacturing methods, where synthesis is a separate operation and the extruder serves only as a processing aid. REX is receiving increased attention as a commercial technique because of its several advantages, which include lower cost and versatility. This entry includes various aspects of REX, as well as a discussion of interpenetrating polymer networks, which are some of the products of REX operations. The basic advantages of reactive extrusion are (L. P. B. M. Janssen, 2004):

- Constant throughput, which can operate as a continuous reactor
- High process flexibility
- No solvents, or only limited use of solvents
- Devolatilization of the reaction product in the extruder makes it possible to remove or recycle unreacted components
- Production of new materials

However, there are some restrictions to the use of extruders as polymerization reactors as well as to the type of extruder to be used.

- This is an economically feasible process; therefore, the resident time needed for the reaction should be short.
- In scale-up procedure, thermal inhomogeneities and fluctuating throughput may occur.

2.2.1 Main reactions in reactive extrusion

2.2.1.1 *Bulk polymerizations*

These are polymerization reactions of monomer or low molecularweight prepolymer either by addition reactions (chain reactions) or condensation reactions (step reactions) to form highly viscous material leading to the limitation of mixing and heat transfer.

2.2.1.2 *Graft and functionalizing reactions*

In grafting reactions, the chains of monomer units are connected to the polymer main chains. But in functionalizing reactions, the single units of monomer are chemically bonded to the polymer backbone. As a result of longer side chains, the viscosity of polymer during grafting reactions is higher than that of during functionalizing reactions.

Transesterification of EVA in an extruder was studied in 1994, by P.J. Kim *et al.*, using a modular intermeshing corotating twin-screw extruder with different screw configurations. The transesterification agent and catalyst used were 1-hexadecanol and dibutyl tin dilaurate (DBTDL), respectively. All the barrel section temperatures were set at 170°C. The reaction proceeded at various screw speeds and feed rates. The results showed that the conversion was increased by reducing screw speed and feed rate, as well as increasing the number of left-handed screw elements and kneading disc blocks, which increased resident time within the extruder and enhanced the conversion up to 31.8%.

2.2.1.3 *Interchain copolymerizations*

This is the reaction to form copolymer between two or more polymers with reactive groups. The combination of two or more different polymers also form graft copolymer. On the contrary to the normal grafting reactions, no monomers are used in this reaction.

In 2000, S. Jacobsen *et al.*, studied the single-step reactive extrusion of PLLA in a corotating twin-screw extruder with a collaboration of an equimolar complex catalyst of stannous octoate and triphenylphosphine. The resulting polymer from the single-step reactive extrusion can be used directly for any processing technology without any additional treatments. As compared with the bulk polymerization reaction in glass ampoule, the single-step reactive extrusion had a

higher conversion, due to mixing elements and high shear forces had an advantage in dispersing the materials. But lower in molecular weight, because of the contact of lactide with humid air throughout feeding. MWDs for both cases were narrow, owing to the use of triphenylphosphine, as a cocatalyst, and the use of ULTRANOX 626, as a stabilizer. Balancing of mass flow rate and screw speed was important, as well as extruder head pressure, because they had an effect on conversion, molecular weight, and MWD of polymer.

2.2.1.4 Coupling or branching reactions

These reactions involve polyfunctional coupling agents, in order to increase molecular weight of homopolymers by coupling with the polymeric chains.

2.2.1.5 Degradation reactions

These reactions result in lower molecular weight polymers which can be achieved by simple shear heating or addition of chemical substances such as peroxide. Degradation often occurs together with a narrowing of the molecular weight distribution.

2.3 Polylactide or Polylactic Acid (PLA)

Polylactic acid or polylactide (PLA) is a biodegradable, thermoplastic, aliphatic polyester derived from renewable resources, such as corn starch or other starch-rich substances like maize, sugar or wheat.

Lactic acid can be produced by bacterial fermentation. However, lactic acid cannot be directly polymerized to a useful product, because each polymerization reaction generates one molecule of water, the presence of which degrades the forming polymer chain to the point that only very low molecular weights are observed. Instead, lactic acid is oligomerized and then catalytically dimerized to make the cyclic lactide monomer. Although dimerization also generates water, it can be separated prior to polymerization.

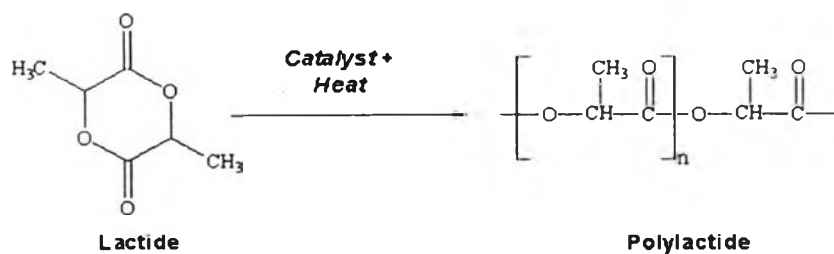
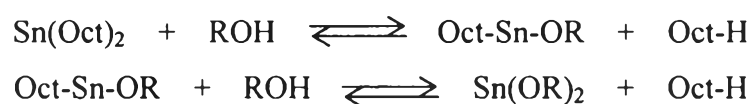


Figure 2.1 Polymerization of lactide. (<http://www.wikipedia.com>)

PLA of high molecular weight is produced from the lactide monomer by ring-opening polymerization using most commonly a stannous octoate catalyst, but for laboratory demonstrations tin(II) chloride is often employed. The catalyst is generally used for bulk polymerization for lactide because of its solubility in lactide, catalytic activity and racemization of the polymer has low rate. This catalyst promises good reaction rate, conversion of greater than 90%, low levels of racemization, that is less than 1% and providing higher molecular weight polymer. (Y.J Du *et al.*, 1995)

One of the accepted mechanisms suggesting in case of stannous octoate is coordination-insertion which the real catalyst is stannous alkoxide. If water remains in the initiating system of alcohol/stannous octoate, it will convert tin(II) alkoxide into less reactive species resulting in slower polymerization. (X. Zhang *et al.*, 2003)



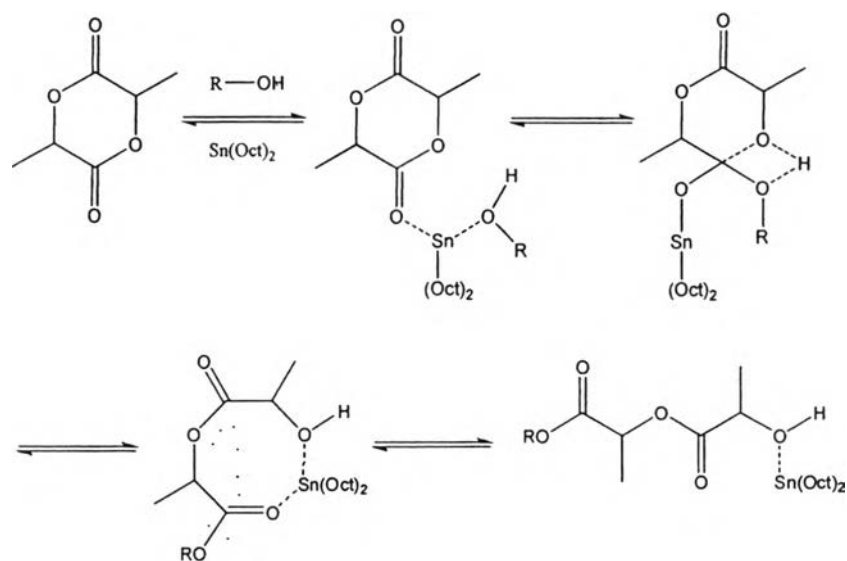


Figure 2.2 Generalized coordination–insertion mechanism of lactide to PLA;
R = growing polymer chain (V.M. Singh et al., 2008).

PLA of high molecular weight is either amorphous or semicrystalline at room temperature depending on the amounts of L, D and meso-lactide in the polymer and on thermal history. The presence of both meso and D-lactide reduce the percent crystallinity; PLA resins with more than 93% L-lactic acid are semicrystalline while PLA resins with 50-93% L-lactic acid are amorphous. (Vishesh M. Singh, 2008)

PLA has good water barrier properties and it can be biodegradable within 4-5 weeks by heat, humidity and microorganisms and it has become a significant commercial bioplastic. Its clarity makes it useful for recyclable and biodegradable packaging, such as bottles, yogurt cups, and candy wrappers. It has also been used for food service ware, lawn and food waste bags, coatings for paper and cardboard, and fibers-for clothing, carpets, sheets and towels, and wall coverings. In biomedical applications, it is used for sutures, prosthetic materials, and materials for drug delivery. (http://www.greenplastics.com/reference/index.php?title=Polylactic_acid)

2.3.1 Literature Survey

A large number of researches in poly(L-lactide) (PLLA), poly(DL-lactide) (PDLA) and copolymer of polylactide have been carried out since Kulkarni

et al., applied poly(L-lactide) (PLLA) plates and screws for fixation of fractured bones, in 1996. PLA with different in molecular weights were used for different applications.

Suong-Hyu Hyon *et al.*, (1997) studied the synthesis of polylactides with different molecular weights via ring-opening polymerization at 130°C for 72 h with stannous octoate as catalyst, which provides higher molecular weight than by polycondensation reaction. The effects of catalyst concentration and reaction time over monomer conversion and viscosity average molecular weight (M_v), and the effect of reaction time and temperature over M_v were also studied. The results showed maximum in monomer conversion and M_v (around 50×10^4) at catalyst concentration of 0.05 wt%. Since the molecular weight is closely related to the trace amount of water present in the polymerization. The water molecules will disappear more quickly with the increasing in catalyst concentration, which brings about the increasing in molecular weight. At initial reaction time, the monomer conversion and M_v tended to increase with time until monomer conversion reached 80%, both of monomer conversion and M_v decreased after this maximum point. This incident obviously occurred at higher temperature due to the thermal depolymerization of PLA.

The effect of hydroxyl and carboxylic substances over lactide polymerization in the present of stannous octoate was studied by X. Zang *et al.* Stannous alkoxide, the product of reaction between stannous octoate and alcohol, was an initiator of polymerization of lactide (coordination-insertion). The present of alcohol in the system affected the polymerization by ways of initiation formation, chain transfer and transesterification. As well as carboxylic acid, which affected to the polymerization by deactivation reaction. The results showed that the existing of alcohol increased PLLA polymerization rate. On the contrary, carboxylic acid decreased the polymerization rate of PLLA. The final molecular weight of PLLA was more sensitive to alcohol concentration and the present of both alcohol and carboxylic acid substances resulted in lower polymer molecular weight than that of only one substance. The polymerization induction period was found at high carboxylic acid concentration, due to decreasing in polymer chain growth rate at early reaction state caused by deactivation reaction.

In 2002, R.F. Storey *et al.*, studied kinetics and mechanism of stannous octoate as a catalyst in bulk polymerization of ϵ -Caprolactone at 130°C, varying the amount and structure of initiating alcohols. The alcohols used were 1-butanol, ethylene glycol (EG), and 1,3-propanediol (PD). H^1 NMR showed that induction period observed in bulk polymerization of ϵ -Caprolactone, catalyzed by stannous octoate (SO), which was a result of strong interaction between diols and stannous octoate. Stannous octoate preferentially interacted with diols such as EG, presented in the reaction, leading to the initial rate lag, which caused by the formation of more stable, inactive stannous alkoxides. Chain propagation will get back to the normal rate when all free diols were consumed. The rate of polymerization was affected by catalyst concentration and concentration of water added to the polymerization. Water acted as a catalyst deactivator, reducing the concentration of active chain.

In 2004, Y. Liu *et al.*, studied the synthesis and characterization of a brush-like copolymer of polylactide grafted onto chitosan. A brush-like poly(DL)-lactide can be grafted onto the chitosan backbone by using triethylaluminium as a catalyst in toluene at 70°C with various molar ratio of lactide to chitosan (2:1, 5:1, 6:1, 10:1, 20:1 and 40:1). The results from FTIR and H-NMR showed that the grafting percentage and the amount of lactide being introduced to the chitosan increase with increasing the ratio of lactide to chitosan.

$$\text{Grafting percentage (\%)} = \frac{\text{graft copolymer (g)} - \text{chitosan (g)}}{\text{chitosan (g)}} \times 100$$

Thermal properties of grafted copolymer from DSC curve indicated that the samples with feeding ratio more than 10:1 have decreasing in T_m because of the polylactide chains decrease the intermolecular interaction of hydrogen bonds along the chitosan chains and the flexibility of polylactide chains help in plasticized the chitosan chains. For the results of WAXS patterns of the various feeding ratio compared to chitosan reveal that the samples with feeding ratio more than 10:1 (grafting percentage more than 338%) have almost the same d-spacing (very similar packing mode).

In 2009, W. Yuanliang *et al.*, studied the Synthesis and characterization of a biodegradable thermoplastic shape memory polymer of poly(urethane-urea) shape memory polymer (PUU SMP) based on poly(DL-lactic acid) (PDLLA) Diols. The FTIR results confirmed the formation of PDLLA-PUU SMP from the N-H stretching vibration peaks at 3328 cm^{-1} , N-H bending vibration and carbonyl stretching vibration peaks at 1577 and 1617 cm^{-1} , respectively, in urethane amide and urea amide. The addition of hexamethylene diisocyanate (HDI) with butanediamine (BDA) as a chain extender resulted in the higher T_g of PDLLA-PUU SMP by more than 20°C ($T_g = 38.8^\circ\text{C}$) compared with that of PDLLA as presented in DSC thermogram because of both rigid urethane and rigid urea groups, and some hydrogen bonds from carbonyl group and N-H group. From shape memory study, an approximately 100% shape fixation ratio and the recovery ratio of above 98% were the evidences for being a novel shape memory polymer, however, shape recovery rate slightly decreased with increasing the deformation cycle.

2.4 Ethylene (Vinyl Acetate) (EVA)

Ethylene vinyl acetate is the copolymer of ethylene and vinyl acetate. The weight percent vinyl acetate usually varies from 10 to 40%, with the remainder being ethylene. It is a polymer that approaches elastomeric materials in softness and flexibility, yet can be processed like other thermoplastics. The material has good clarity and gloss, barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive water proof properties, and resistance to UV radiation.

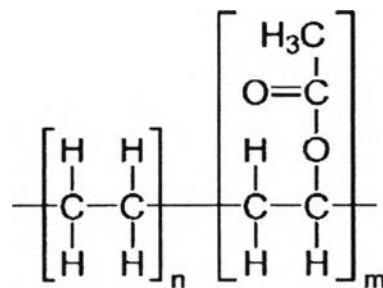


Figure 2.3 Structure of EVA (<http://www.wikipedia.com>).

EVA has little or no odor and is competitive with rubber and vinyl products in many electrical applications. EVA is also used in biomedical engineering applications as a drug delivery device. These devices are used to slowly release a compound over time. While the polymer is not biodegradable within the body, it is quite inert and causes little or no reaction following implantation.

EVA foam is used as padding in equipment for various sports such as ski boots, hockey, boxing, and mixed martial arts. EVA is also used in biomedical engineering applications as a drug delivery device. While the polymer is not biodegradable within the body, it is quite inert and causes little or no reaction following implantation. Hot glue sticks are usually made from EVA, usually with additives like wax and resin. It is also used as a clinginess-enhancing additive in plastic wraps and typically used as a shock absorber in tennis shoes (http://en.wikipedia.org/wiki/ethylene_vinyl_acetate_copolymers).

2.3.1 Literature Survey

In 1995, Helen M. Burt *et al.*, studied a blend of ethylene-vinyl acetate copolymer with poly(DL-lactide) in controlled drug delivery of taxol from microspheres. Due to problems in non-degradable and handling of EVA, PLA was introduced to enhance degradation rate and handling characteristics of the microspheres preparing from the solvent evaporation method. Blends containing 50% or more PLA in the EVA: PLA decreased the extent of coalescence of the microspheres. Size of microspheres depends on emulsifier concentration. The higher the concentration of the emulsifier (PVA), the smaller the microspheres. Drug release rate in small microspheres was higher than that in the large microspheres, as a result of the larger surface area. PLA was hydrolyzed in phosphate-buffered saline (PBS) at 37°C, leading to an inactive sponge-like structure. There was little or no loss of PLA until after 40-50 days even if the induction period and rate of PLA degradation depended on the amount of PLA in the matrix and on process history.

In 1998, Maria L. Cerada *et al.*, studied the influence of the composition and thermal history on the type of lattice developed of vinyl alcohol-ethylene copolymer by using wide-angle X-ray diffraction. The vinyl alcohol-ethylene copolymers were prepared with the compositions of 56, 68 and 71 mol% of

vinyl alcohol, respectively, and were crystallized from the melt at various cooling rate (2.5, 10, 20, 40, 60 and 100 °C/min). They found that the cooling rate was very important. Since the copolymer of 68 and 71 mol% of vinyl alcohol (VAE68 and VAE71, respectively) were found to be in a monoclinic form when the samples were slowly crystallized (2.5 °C/min) from melt, in contrast to the quenched samples (100 °C/min), which the lattices were found to be an orthorhombic form. But for the copolymer VAE56 (56 mol% of vinyl alcohol) resulted in the form of an orthorhombic lattice under all studied conditions. Moreover, the degree of crystallinity of quenched samples were found to be smaller than that in the slowly crystallized samples and the melting temperature of the two crystalline modifications were found to be similar to each other.

In January 2007, F. Becquart *et al.*, studied the microstructure and properties of (PVA-Ac)-g-(PCL). The PVA-Ac used was a block copolymer with an average PVA sequence length of 12.5, confirmed by ¹³C NMR spectrum, in which illustrated that acetate (OAc) and alcohol (OH) units were not randomly distributed along the chain but showed a rather blocky structure. The blocky structure, as well as OH hydrogen bonding leading to crystalline regions of the initial PVA-Ac. When PCL was grafted onto PVA-Ac backbone by alcoholysis and transesterification reactions—which characteristically about 2-5.5% of the total Ac groups—crystallinity of the copolymer presented in thermal analysis was disappeared as a result of destruction of blocky structure during grafting.

In 2008, M. Dolores *et al.*, studied thermal decomposition of copolymers from ethylene with some vinyl derivatives, which were ethylene vinyl acetate (EVA), ethylene-vinyl-3,5-dinitrobenzoate (EVDNB), and ethylene vinyl alcohol (EVAL), using DTA and TGA under isothermal and dynamic conditions in nitrogen. The most stable copolymers was EVAL followed by EVA and EVDNB, respectively. Degradation of copolymers was an additive degradation carried out in two states, the first one was the decomposition of polyvinyl ester or poly vinyl alcohol then followed by the decomposition of polyethylene. The results from TG and DTG showed the thermal decomposition of EVA and EVAL copolymers with no char residue, while the EVDNB copolymers showed the evidence of char residue at 764 K with increasing in amount as VDNB content increased, as a result of crosslink.