



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Biodegradable Polymers

Biodegradable polymers are polymer that can be degraded by the vital activity of an organism, and not simply the degradation of a material in a physiological environment. The other broadening definition is the concept of biodegradation to include all the degradation processes of a biomaterial, both in vivo and in vitro. In present, biodegradable polymers can be used in products ranging from wound dressings to arterial and skin grafts, fibers and fabrics have been explored as potential materials for novel applications in medicine and surgery

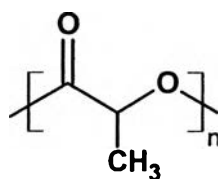
Biodegradable polymers can be either natural (such as catgut, potato starch, and silk) or synthetic polymers. In natural polymers, polymers are formed in nature during the growth cycles of all organisms involved enzyme-catalyzed, chain growth polymerization reactions of activated monomers with formed typically within cells by complex metabolic processes. In case of synthetic polymers, it can be produced under controlled conditions and therefore exhibit in general predictable and reproducible mechanical and physical properties such as tensile strength, elastic modulus and degradation rate. A further advantage is the control of material impurities. Possible risks such as toxicity, immunogenicity and favouring of infections are lower for pure synthetic polymers.

Biodegradable aliphatic polyesters are high molecular weight polymers that have the useful properties of both synthetic polymers and natural polymers. Thus, Biodegradable aliphatic polyesters can represent the most diffuse class of biodegradable polymers to be used in many kind of applications including biomedical application.

### 2.1.1 Polylactic Acid or Polylactide (PLA)

Polylactic acid or polylactide (PLA) is a biodegradable linear aliphatic thermoplastic polyester. PLA is polymerized from lactide, a condensed dimer of lactic acid, which is produced in mammalian muscles during glycogenolysis and correlated with the Krebs cycle through piruvic acid and acetyl CoA. PLA exists two different enantiomeric forms as D and L lactic acids which consequent from the maintenance of the chiral center. The homopolymer of l-lactide (PLLA) is a semicrystalline polymer while the Poly(dl-lactide) (PDLLA) is both mesomeric and racemic D,L-lactide derivatives are fully amorphous as a result of the syndiotacticity and/or atacticity of methyl groups (Fambri *et al.*, 1997).

PLLA exhibit high tensile strength and low elongation, and consequently have a high modulus that makes them more suitable for load-bearing applications such as in orthopedic fixation and sutures. PDLLA has lower tensile strength, higher elongation, and a much more rapid degradation time, making it more attractive as a drug delivery system. Poly(l-lactide) is about 37% crystalline, with a melting point ( $T_m$ ) of 175-178°C and a glass-transition temperature ( $T_g$ ) of 60-65°C. The degradation time of PLLA is much slower than that of DLPLA, requiring more than 2 years to be completely absorbed. Copolymers of l-lactide and dl-lactide have been prepared to disrupt the crystallinity of l-lactide and accelerate the degradation process (J.C. Middleton *et al.*, 2000). The structure of PLA is shown in Figure 2.1.

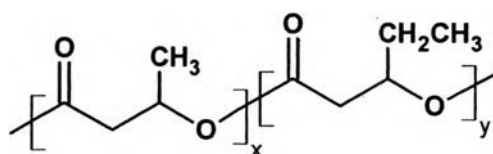


**Figure 2.1** The structure of Polylactic acid (PLA).

### 2.1.2 Poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV)

PHBV is also one type of polyhydroxyalkanoate (PHA). It consists of copolymer between poly-3-hydroxybutyric acid (PHB) and poly-3-hydroxyvaleric acid (PHV). The structure of PHBV is shown in Figure 2.2. It can be made by some organisms. In fermentation, PHB and PHV copolymer are made by supplying mixed glucose and propionic acid substrate. The hydroxyvaleric content of the polymer is controlled by variation of the ratio of glucose to propionate in the food.

PHBV is less crystalline, thus more flexible and more readily processable when comparing with its homopolymer which extends its versatility in end use to applications such as bottle and film manufacture. Its  $T_m$  and  $T_g$  were found to be 143 and  $-4^\circ\text{C}$ , respectively. It is known to be biodegradable and biocompatible and its various properties such as natural origin (Gogolewski *et al.*, 1993, and Avella *et al.*, 2000), biodegradability, biocompatibility, stereospecificity, piezoelectricity (Fukada *et al.*, 1986), optical activity, and thermoplasticity make it suitable for a variety of applications in health industry.

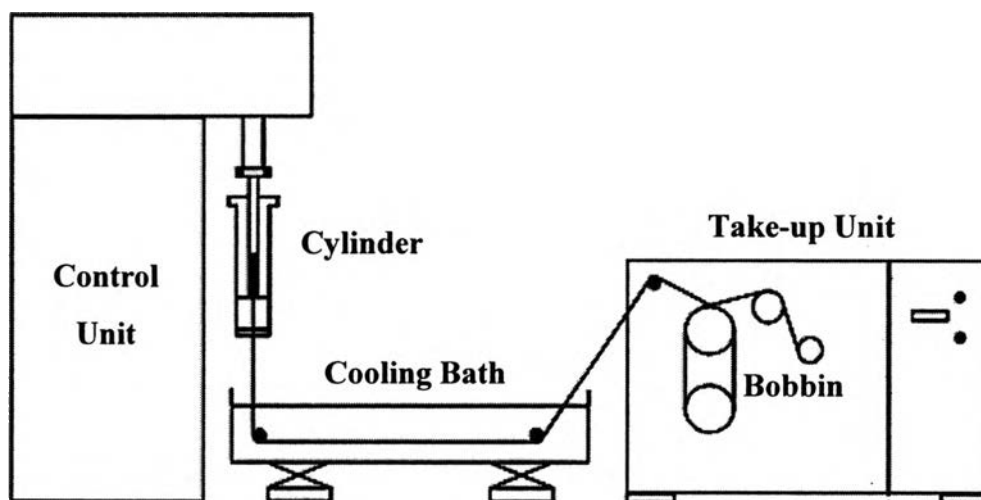


**Figure 2.2** Poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV).

## 2.2. Melt-Spinning

Melt-spinning is a simplest and preferred method of fiber processing because it does not involve problems associated with the use of solvents and it can provides the stable melt fiber. This method involves heating the polymer resins above their melting temperature. They are first dried and then melted in the extruder. The solidification of the fluid fiber occurs at the quenching chamber after they are extruded through narrow channels (spinneret). They are then kept on tube roll and

may be drawn to be finer fiber by either on-line or off-line techniques. The melt-spinning machine is shown in Figure 2.3.



**Figure 2.3** Schematic arrangement of the melt spinning apparatus. (Y. baimark *et al.*, 2005).

A major development in the area of melt-spinning was in the 1970s from conventional spinning at wind-up speeds of around  $1000 \text{ m min}^{-1}$  to high speed spinning at speeds of  $3000 \text{ m min}^{-1}$ . In 1975s, more than half of textured yarn in the world was base on yarn produced using this technology (V.B. Gupta *et al.*, 1997).

Melt-spinning is used in various applications such as clothing, composites, separation membranes and biomedicine. It was well received that contributed to the development for many kinds of polymer for the objective of improvement efficiency to produce higher mechanical properties of fibers by using special device (such as drawing) and special methods (such as annealing).

In present, many people is much concerned about the problems associated with using petroleum-based plastics which is a non-renewable resource and have many effects with environment so they are much interested in studying and developing biodegradable polymers, which can solve this problems.

Fambri *et al.*, (1997) produced PLLA of molecular weight 330,000 by melt-extrusion at various collecting rates and hot-drawing at various drawing rates. The molecular weight of PLLA fell to about 100,000, as a consequence of the production process. The higher the collection rate makes the higher the modulus and strength, and the lower the strain at break. While almost amorphous fibers were obtained at lower collection rates (1.8 and 3.1 m min<sup>-1</sup>), about 30 and 38% crystalline as-spun fibers were produced at rates of 5 and 10 m min<sup>-1</sup>, respectively. Moreover, the capability of fibers to sustain a further hot-drawing process was found to be dependent on the collection speed during extrusion. Tensile modulus of 9.2 GPa and tensile strength of 0.87 GPa were obtained for fibers collected at 5 m min<sup>-1</sup> and drawn 10 times.

In 2001, G. Schmack *et al.* could produce PDLLA in a high speed spinning process with take-up velocities of 1000-5000 m min<sup>-1</sup> and in a spin drawing process at draw ratios of 4-6. The maximum physical break stress and the E-modulus observed in the spin drawn fibres were about 490 MPa and 6.3 GPa, respectively, at an elongation at break of 30%.

And in 2007, Chung Hee Park *et al.* also study the effect of melt-spinning speed and heat treatment on the mechanical properties and biodegradability in PLA fibers at a high spinning speed of 2000-4000 m min<sup>-1</sup>. The results of the experiment reveal that heat treatment of the PLA fibers increased the breaking stress and crystallinity. With increasing spinning speed, breaking stress and crystallinity also increased. And increase in spinning speed was more effective than an increase in heat treatment. For the soil burial test, it was revealed that an increase in spinning speed and heat treatment decreased the biodegradability of the fibers. X-ray analysis of the soil-buried fibers showed that fibers with higher crystallinities began to degrade more slowly.

In case of PHBV is also received interesting to study and develop because it can use in many applications such as packaging, motor oil and personal hygiene items (diapers and sanitary napkins). In medical application, including suture, implants, and can use in a matrix for drug delivery.

T. Tanaka *et al.* (2006) produced PHBV contained HV 8% by melt-spinning in take up speed at  $3\text{-}3.6\text{ m min}^{-1}$ , followed in an amorphous state by quenching near  $T_g$ . High tensile strength fibers of over 1 GPa of low-molecular-weight polyesters were prepared by new drawing technique as one-step drawing with small crystal nuclei grown by isothermal crystallization near the  $T_g$ . And the drawing rate was  $0.27\text{-}0.3\text{ m min}^{-1}$ . All fibers were annealed at  $60^\circ\text{C}$  in a hot oven under constant tension for 30 min. The result shown that fibers consist of a highly oriented helix conformation ( $\alpha$ -form) and planar zigzag conformation ( $\beta$ -form). The  $\beta$ -form after isothermal crystallization is produced by the stretching of molecular chains in the amorphous region between small crystal nuclei which act as cross-linking points followed by the generation of the  $\alpha$ -form during annealing. The mechanical properties were reported in 2 series as fiber with and without isothermal crystallization. In case of fiber without isothermal crystallization, the maximum tensile strength and Young's modulus at draw ratio 10 was 90 MPa and 2 GPa, respectively. While in another case at same draw ratio was 1,065 MPa and 8 GPa, respectively.

### 2.3. Natural Polymer Blends

Polymer blends is a well-used technique that is used for preparing a novel blend of two or more polymers when the properties modification of polymer is required without having to synthesize a totally new material. The advantages for polymer blends are versatility, simplicity, and inexpensiveness. Polymer blending method can be divided into two types as melt processed blends and aqueous blends. In the first method, two or more polymers are mixed in extruder such as co-rotating twin-screw extruder or other kind of extruder and use the mixing temperature over than melting point of all polymers. Then the extrudate is cooled in water and is palletized. In the second method, it is the preferred technique when the polymer cannot be used in melt processing because it can be degraded or it is designed to incorporate with substances that do not stand high temperature such as proteins,

drugs, etc. its method is dissolve two or more polymers in suitable solvent and then remove that solvent until remaining the blending sample.

For biomedical application, aqueous blending is the preferred technology, particularly in biomedical applications because these blends have a range of properties that make them suitable for use in a wide array of biomedical applications, ranging from bone replacement to engineering of tissue scaffolds.

### 2.3.1 PLA Blends

In all of biodegradable polymer, PLA is one of them which have been the focus of much attention because not only it is produced from renewable resources and has very low or no toxicity, but also it has high mechanical performance, comparable to those of commercial polymers. However, PLA is very expensive, very brittle at room temperature and hydrolyzes easily. Moreover, the thermal stability of PLA is generally not sufficiently high enough to be used as an alternative in many commercial polymers application so its applicability has been limited. Blends of PLA with several synthetic and bio-polymers have been prepared in an effort to enhance the properties of PLA and also to obtain novel materials.

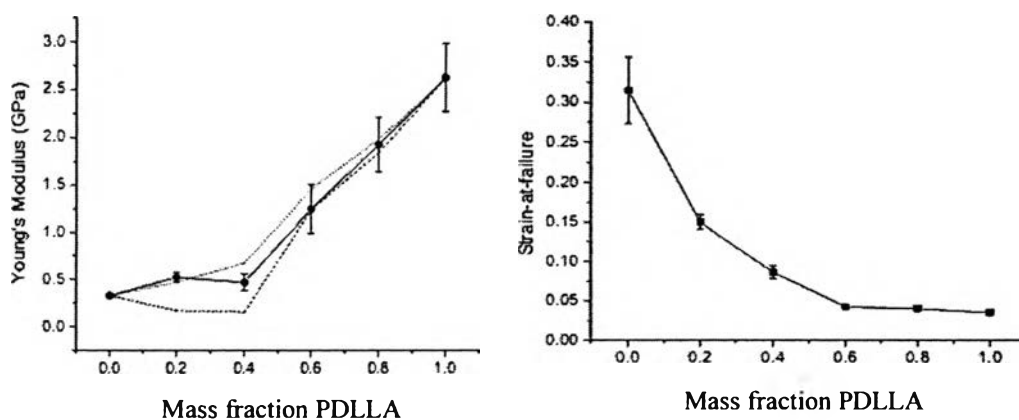
#### - To Blend of PLA for Mechanical Properties

C. C. Chen *et al.* (2002) attempted to increase toughness and degradation time of PLA by blending with Poly(dl-lactide) (PDLLA) which can degrade quickly due to its amorphous structure. In this study, a copolymer of ethylene oxide (PEO) and propylene oxide (PPO) was used as a surfactant to blends. DSC data indicated that PLA/PDLLA blends without the surfactant had two  $T_g$ . while this blends with the addition of the surfactant, there was a linear shift of the single  $T_g$  as a function of composition. DMA data showed that the 40/60 blends without the surfactant had high elastic modulus and elongation, and similar results were observed after adding 2% surfactant into the blends. The 50/50 and 2% surfactant blends had the highest elastic modulus, yield strength, and break strength.

T. Ke *et al.* (2002) attempted to increase the elongation at break and toughness of PLLA by adding triethyl citrate (TC) as a plasticizer to blends of PLLA

and starch in the presence of methylenediphenyl diisocyanate (MDI) by using melt blending. It was previously found that the best mechanical properties would be obtained when the content of starch was 45% in the presence of 0.5% MDI. Therefore, a fixed ratio of starch, PLLA, and MDI at 45/55/0.5 (w/w/w) and varying content of TC were used in this study. The results of SEM showed that MDI improved the adhesion between starch and PLA in the presence of TC and the results of thermal analysis showed that thermal transition temperatures ( $T_g$ ,  $T_c$ , and  $T_m$ ) of this blends with TC decreased as the TC content increased. Moreover, DMA data indicated that the elongation at break and toughness of the blends significantly improved in the TC range of 5-10%. The blends with a TC content of 7.5% resulted in desirable elongation, toughness.

M.E. Broz *et al.* (2003) blended PDLLA with poly( $\epsilon$ -caprolactone) or PCL to improve mechanical properties by casting onto thin film and residual solvent was removed by vacuum. The results showed that the modulus and ultimate tensile strength at PDLLA mass fraction of 0.4 increase almost linearly as a function of composition. The strain-at-failure decreased monotonically with increasing PDLLA content and became flat above PDLLA mass fraction 0.6. These results are shown in Figure 2.4. The DSC, NMR and SEM results suggested that PDLLA and PCL were not miscible and that some adhesion may occur at the PDLLA/ PCL interface when the majority phase was PCL but not when it was PDLLA.

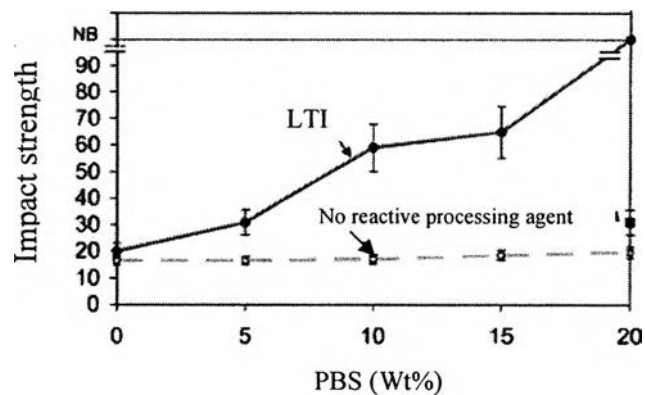


**Figure 2.4** The young's modulus and strain-at-failure of any blend composition



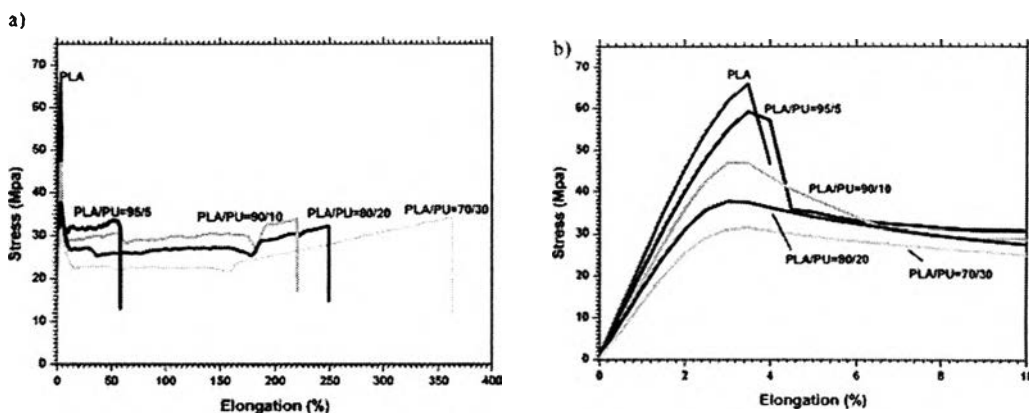
Y. Takagi *et al.* (2004) compared the morphologies, physical properties, and thermal behavior between the blends of poly(3-hydroxyalkanoate) (PHA) with a medium-length side chain in PLA, and the blends of the chemically modified PHA (ePHA) (adding the epoxy group side chain) in PLA. The two kinds of blending is prepared by precipitation in methanol (non-solvent). DSC data showed two distinctive  $T_g$  peak in the curves, supporting the fact that the two kinds of blends are not miscible in the amorphous state over these studied composition ranges. TEM data showed that the finer particle dispersion occurred in the ePHA blend and indicated that the ePHA has a better compatibility for PLA than the nonepoxidized PHA. And for mechanical testing, the ePHA had a more significant effect than PHA in enhancement the impact toughness of the PLA blend. The results of the biodegradation test demonstrated that the PLA blends still maintained their biodegradability and were more accessible to hydrolysis and microbial attack, resulting in a greater weight loss than the pure PLA.

M. Harada *et al.* (2007) blended PLA with poly(butylene succinate) (PBS) by using lysine triisocyanate (LTI) as a reactive processing agent for increasing impact strength of PLA/PBS blends. PLA/PBS blends were produced by a twin-screw extruder and injection molding machine. The results were that the impact strength increased with increasing PBS content and the impact strength of PLA/PBS blends at 90/10 wt% were 18 kJ/m in the absence of LTI, and they increased to 5,070 kJ/m in the presence of LTI at 0.5 wt% shown in Figure 5. The melt mass-flow rate (MFR) value of PLA/PBS at 90/10 wt% decreased from 25 g/10 min at 200°C in the absence of LTI to approximately 3 g/10 min in the presence of LTI. Spherical particles at 1 mm were observed by using laser scanning confocal microscopy (LSCM) in the presence of LTI. These results indicated that the LTI was a useful reactive processing agent to increase the compatibility of PLA/PBS blend to increase the impact strength of PLA.



**Figure 2.5** Impact strength and PBS (wt %) in PLA. Absence of reactive processing agent ( $\square$ ), presence of LTI (0.5wt%,  $\bullet$ ).

Y. Li *et al.* (2007) prepared melt blending of PDLA and a biodegradable poly(ether) urethane (PU) in an effort to toughen the PDLA. DMA data showed that the blends were not thermodynamically miscible and suggested that PU and PDLA were partially miscible and that there were some molecular interactions between the two components. DSC data showed that the addition of PU not only accelerated the crystallization rate of PDLA, but also decreased the PDLA crystallinity. The PDLA/PU blends showed significantly increased elongation at break as well as impact strength, compared with neat PDLA shown in Figure 2.6. The toughening mechanism investigation revealed that shear yielding occurs in the PDLA matrix as induced by the PU domains. The shear yielding may have been initiated by the stress concentrations associated with rubber particles; consequently, debonding at the matrix/particle interface releases the hydrostatic stresses and encouraged shear yielding to proceed.



**Figure 2.6** (a) Stress-strain curves of the blends with different PU contents, and (b) enlarged part of the curves near the yielding region.

#### - To Blend of PLA for Degradability

M. Sheth *et al.* (1997) studied the blend of PDLLA with poly(ethylene glycol) PEG by melt-blended and extruded into films. The results were that PDLLA/PEG blends range from miscible to partially miscible, depending on the concentration. For  $T_g$  result, PEG content increased make  $T_g$  decreased in the 10-30 % PEG content but for higher PEG blend content could not be observed by DSC. The results obtained from enzymatic degradation showed that the weight loss for all of the blends was significantly greater than that for the pure PDLLA. When the PEG content was 30% or lower, weight loss was found to be primarily due to enzymatic degradation of the PDLLA. Above 30% PEG content, the weight loss was found to be mainly due to the dissolution of PEG. During hydrolytic degradation, for PDLLA/PEG blends up to 30% PEG, weight loss occurred as a combination of degradation of PDLLA and dissolution of PEG.

H. Shinoda *et al.* (2002) blended PLLA with poly(aspartic acid-co-lactide) (PAL) and processed into homogeneous press films. Then the degradation behavior of the blends was tested in phosphate buffered solution in compost and in soil. The results suggested that small amount of added PAL enhanced the degradation rate of PLLA effectively in water, soil and compost. The blended PAL resisted hydrolysis unless it came into contact with water, which ensured that the blended

products will have long shelf life and be useful for a wide variety of applications. For miscibility tests, PAL was miscible with PLLA and produced homogeneous blend films without impairing the inherent mechanical properties of PLLA.

### **To Blend of PLA for Medical Application**

Q. Cai *et al.* (2002) developed blending of PLA with natural biodegradable dextran, and a novel sponge-like scaffold by using solvent-casting and particle-leaching techniques. These novel scaffolds were prepared by dissolving PLA and dextran in a mixed solvent of DCM and benzene. The dextran was protected via trimethylsilyl (TMS) groups to obtain a uniform blend of PLA and dextran. This blend solution was cast onto a polytetrafluoroethylene (PTFE) mold and then immersed in distilled water to leach out the salt, and sponge-like foams were obtained. SEM data of PLA and dextran with TMS films showed that this microporous structure was closely related to the phase separation due to the different solubility of PLA and TMSD in benzene, as well as the different evaporation rates of DCM and benzene. SEM data of novel scaffolds showed that micropores had a size of 5–10  $\mu\text{m}$ . This led to the scaffold having higher porosity and an open porous structure. In comparison with PLA, the surface and bulk hydrophilicity of PLA–dextran blend films or foams were significantly improved after the TMS groups were removed in methanol, and the results of cell culture on these polymeric substrates exhibited an enhancement in cell attachment and proliferation.

L. Chen *et al.* (2007) developed a ofloxacin drug-release system consisting of PLA and poly(sebacic anhydride) (PSA) for the treatment of chronic osteomyelitis by dissolving in various ratios in tetrahydrofuran. In vitro drug release results showed that changing the ratio between the two polymers caused the effective ofloxacin-release duration to vary from 6 to 68 days. The in vivo drug release results in rabbits demonstrated that the average ofloxacin concentration in the local bone was  $20.1 \pm 10.3$  mg/g, while that in the plasma was  $35.6 \pm 18.8$  ng/mL, within 8 weeks.

F. L. Mi *et al.* (2007) developed the thermodynamic compatibility of chitin/PLA based microspheres for the delivery of protein prepared by polymer blending and wet phase-inversion methods. The results were found that selected non-

solvents, temperature of water and ratio of polylactide affected the hydration and degradation properties of the blend microspheres. Moreover, formulations of the blends, which are based on the balance among the hydration rate of the chitin phase and degradation of chitin/PLA, can lead to a controllable release of bovine serum albumin (BSA).

#### **2.4. PLA and PHBV with Plasticizers**

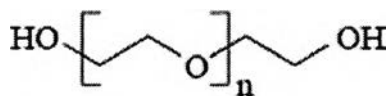
Plasticizer is a high-boiling solvent or low-melting solid, which is used to improve processability, flexibility, ductility of polymer, reduce glass transition temperature ( $T_g$ ) and reduce the melting point and the crystallinity. The effect of plasticizer in any polymer can be explained by gel and lubricity theories. In gel theory, it was devised for amorphous polymers, consider that the van der Waals forces produce gel-like three-dimensional structure by the formation of weak bonds at active centers. And in lubricant theory, the plasticizer reduces the internal resistance to deformation by acting as a lubricant to facilitate movement of the resin macromolecules over each other and provides internal lubricity.

They are a lot of plasticizers used with PLA and PHBV. In PLA, poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG) (Piorkowska *et al.*, 2006), poly(1,3-butanediol), (Kulinski *et al.*, 2005), di-2-ethylhexyladipate (DOA) (Martino *et al.*, 2006), dibutyl sebacate and acethyl glycerol monolaurate (Pillin *et al.*, 2006) are plasticizers. In PHBV, the plasticizers used are soybean oil (SO), dibutyl phthalate (DBP) and triethyl citrate (TEC) and Epoxidized soybean oil (ESO). (Jae Shin Choi *et al.*, 2005)

##### **2.4.1 PLA Blending with PEG**

Polyethylene glycol (PEG) or Polyethylene oxide (PEO) refers to an oligomer or polymer of ethylene oxide. PEG has tended to refer to shorter polymers and PEO refer to longer polymers, which are used in different applications. The physical properties are based on their chain length effects. Poly (ethylene glycol) is a biodegradable plasticizer, non-toxic and soluble in water, methanol, benzene,

dichloromethane but insoluble in diethyl ether and hexane. PEG has proved its efficiency to strongly increase the elongation at break and the impact resistance of polymer. It was reported that PEG is widely used in poly (L-lactide) (S. Jacobsen, HG Fritz., 1999), (Y. Hu *et al.*, 2003). It showed an increase in plasticization with a decrease of PEG molecular weight. The low molecular weight of plasticizer enables an increase in miscibility with PLA in the melt and the crystallization behaviour and is more efficient in reducing the PLA glass transition temperature (E. Piorkowska., 2005). A certain molecular weight of PEG, between PEG and PLA will have a phase separation (Hu Y. *et al.*, 2003). Therefore, the optimization of amount of PEG and molecular weight of PEG is significant for polymer composites in order to obtain desirable properties. The structure of PEG is shown in Figure 2.7. Moreover, PEG can also act as a stabilizer and reducing agent (C. Luo *et al.*, 2005) which is suitable to use in synthesis of metal nanoparticle in a polymer matrix.



**Figure 2.7** The structure of poly(ethylene glycol) (PEG).

O.martin *et al.* (2001) found that PEG 400 g/mol (PEG400) was the efficient plasticizing agent in PLA because it could change  $T_g$  from 58°C to 12°C when adding 20% PEG400. The plasticization of PLA with PEG hydroxyl end group or PEG monomethyl ether end group, showed the similar level of decreasing  $T_g$  and increasing in cold crystallization. The elongation at break increased as the amount of plasticizers was increased.

And in 2005, Z. Kulinski *et al.* studied the effect of different end groups (hydroxyl groups and methyl groups,) on 5% and 10% PEG of both amorphous and semicrystalline PLLA. The results showed that all the type of PEG used decreased  $T_g$  and  $T_{cc}$ . While an amorphous PLLA containing PEG could be deformed to about 550%, a semicrystalline PLLA with the same PEG content showed

nonuniform plasticization of the amorphous phase and less ability to the plastic deformation. Nevertheless, in 10 wt% of PEG, the semicrystalline PLLA can be achieved a 20% elongation at break.

In the study of preparation of silver nanoparticles by using PEG, it was studied by Pim-on *et al.* (2007) who studied the effect of concentration (1-15%) and molecular (2-35 kDa) weight of PEG and concentration (0.5-2.5%) of Ag nanoparticles in electrospinning of poly(ethylene oxide) (PEO)/PEG in various amount of Ag nanoparticles for antibacterial application. The average diameter of the Ag nanoparticles was found to increase with increasing the PEG molar mass and with decreasing PEG concentration. The amount of the element Ag observed was found to increase with the lower molar mass was used as the reducing agent. Lastly, the assessment for the antimicrobial activity of this bending containing 0.5-2.5% AgNO<sub>3</sub> against *S. aureus* and *E. coli* showed that the antibacterial activity of these solutions was found to increase with increasing AgNO<sub>3</sub> content and the as-formed Ag nanoparticles were found to be more effective in the protection against *E. coli*.

#### **2.4. Antimicrobial Fibers**

Antimicrobial fibers are the textile fibers with activity to against microorganisms growth. In recent years, they have been received widely much interest because the problems associated with the microbial contamination in textile is much concerned and people are more and more looking for fresh public living surroundings and a higher level of hygiene in home areas. According to the distinction of antimicrobial fibers, they can be made the possible end-uses: hospital uses, home textiles, carpets furnishing, mattress and pillows fillings, air-liquid filters, non-woven, protective clothing, sportswear etc. Each of these application fields will demand a different bioactivity performance from the fibers.

The application of the antimicrobial treatment can be carried out on the finished woven or non-woven fabric, man-made antibacterial fabric, by using classic textile application process which can be divided to two basic methods: the first is

kneading antibacterial additive during the spinning stage and the second is an after-treatment method in which an antibacterial agent solution is used. The examples of this method are spraying, immersion, padding and coating. Antibacterial agent is linked to the surface through physical bonds or anchored by a cross-linking on the fiber. A highly efficient and durable way of treating man-made fabrics is to add the antimicrobial to the spinning mass or the first method.

In the mixed spinning technology, the antibacterial additive is supplied into the polymer stream before the spinneret or blended into the spinning polymer feeding. The additive characteristics have to be compatible with spinning conditions (e.g. particle diameter, heat and chemical stability, no degradation interactions with polymer, lack of adverse effects on fiber quality).

The most used antibacterial additives are based two kinds as organic compounds and inorganic compound, in case of organic compounds; they are halogenated salicylic acid, anilides, organotin compounds, quaternary ammonium compounds, organosilicon quaternary ammonium salts and quaternary ammonium sulphonamide derivatives. In another case, they are silver, titanium, zinc compound etc. in the first case, they have to be constantly reapplied since most of them are highly water soluble and weakly anchored to the fiber surface.

According to the manufacture technology and the antimicrobial agent nature, the antibacterial fibers can exhibit two kinds of bioactivity mechanism: an elution mechanism and a non-elution mechanism. In the first mechanism, the additive gradually migrates out from the fiber to the solvent external medium, while in the second, it does not dissolve out. Although, sometimes, the two kinds of mechanism coexist in the antimicrobial activity of a bioactive fiber, generally, one of them is the predominant.

The inorganic antibacterial additive which has been received interesting is silver nanoparticles because it is the particles in smaller-size, spherical shape and unagglomerate make it higher efficiency in antibacterial. The research of silver nanoparticles in antibacterial is showed below:

Xiaoyi Xu *et al.* (2006) prepared PLLA ultrafine fibers containing nanosilver particles via electrospinning and then reducing  $\text{AgNO}_3$  in fabric into Ag



nanoparticles by hydrogenation. The SEM, TEM result showed that the fiber diameter increases with increasing amount of AgNO<sub>3</sub> added and the average diameter of the Ag particles is about 30 nm and does not depend on the AgNO<sub>3</sub> content in the fibers. These fibers showed antibacterial activities of 98.5% and 94.2% against *S. aureus* and *E. coli*, respectively and the duration is longer than 20 days.