



## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

Nowadays, the rapid rise of plastic consumption becomes a serious problem for environment. The development of biodegradable plastics plays an important supporting solution for the waste disposal.

#### 2.1 Biodegradable Polymers

##### 2.1.1 Poly(lactic acid) or PLA

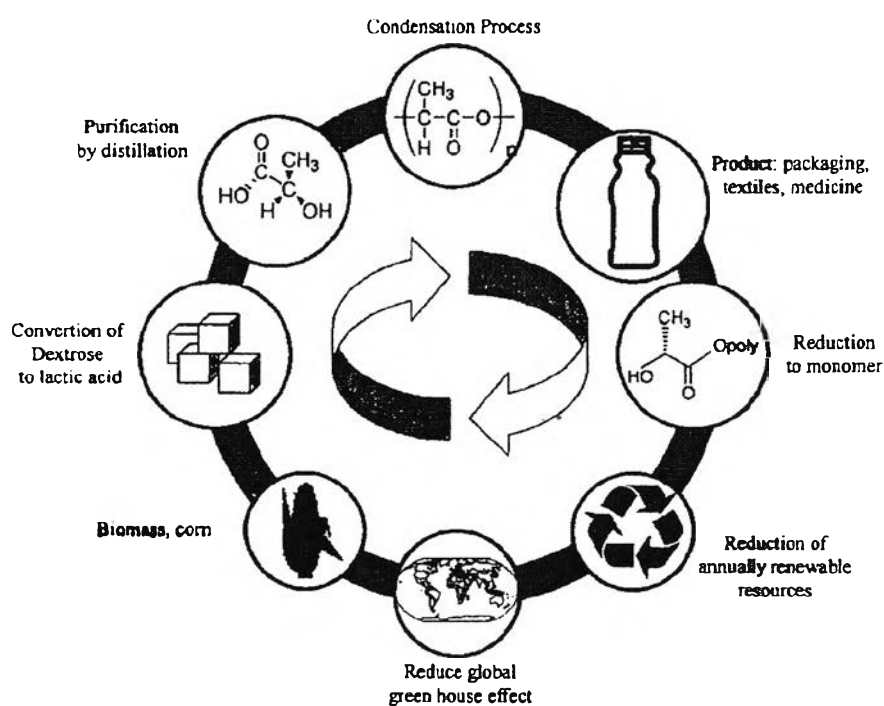
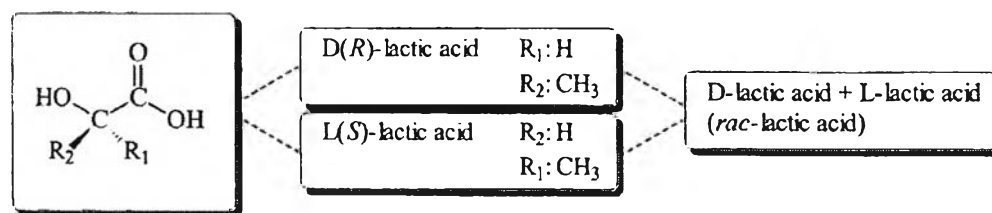


Figure 2.1 Life cycle for poly(lactic acid) polymers (Hartmann, M.H. *et.al.*, 2000).

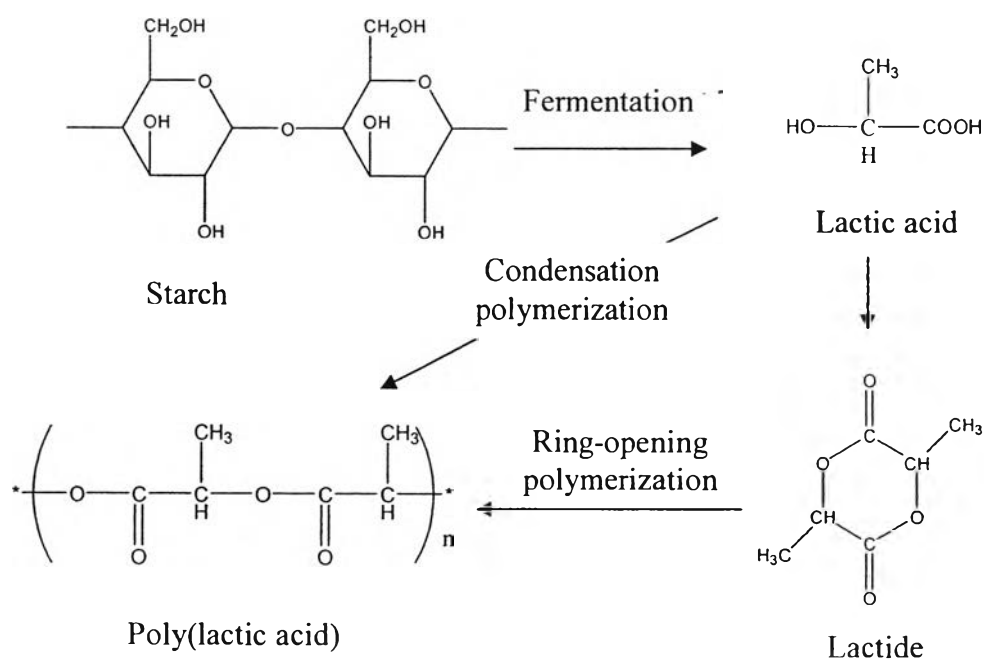
Figure 2.1 shows an ideal PLA based biodegradable plastic life cycle starting from renewable resource to plastic products and the biodegradation to biomass. PLA is a biodegradable thermoplastic polyester derived from lactic acid (2-hydroxypropionic acid). Lactic acid can be obtained from the carbohydrate fermentation or chemical synthesis. It is an optically active molecules, which can be

either of L(+) or D(-) stereoisomer (Figure 2.2). Mammalian systems produce only the L(+) stereoisomer but both stereoisomers are found in bacterial systems. Bacterial fermentation of carbohydrates is the majority of lactic acid production because of the economically viability (Auras, R. *et.al.*, 2004).



**Figure 2.2** Stereoregularity of lactic acid.

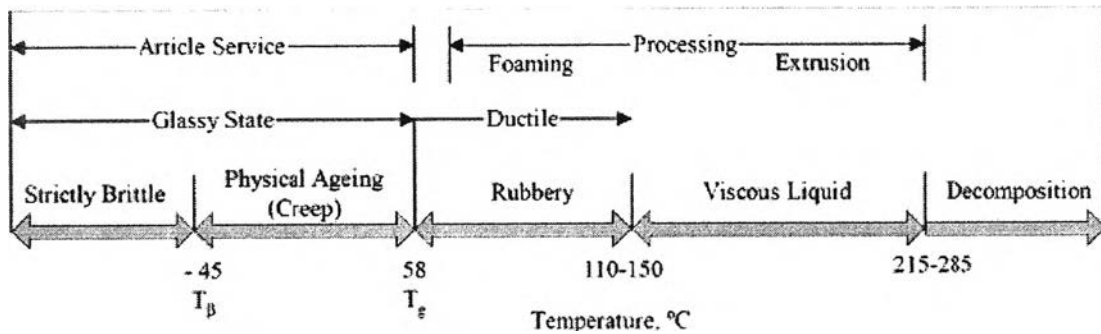
The first report about the isolation of lactic acid from milk was in the early 1780. In later years, the solidification by self-esterification was explored. In 1932, Wallace Carothers reported the dimerization of lactic acid into lactide and its ring-opening polymerization (Södergård, A. and Stolt, M., 2002).



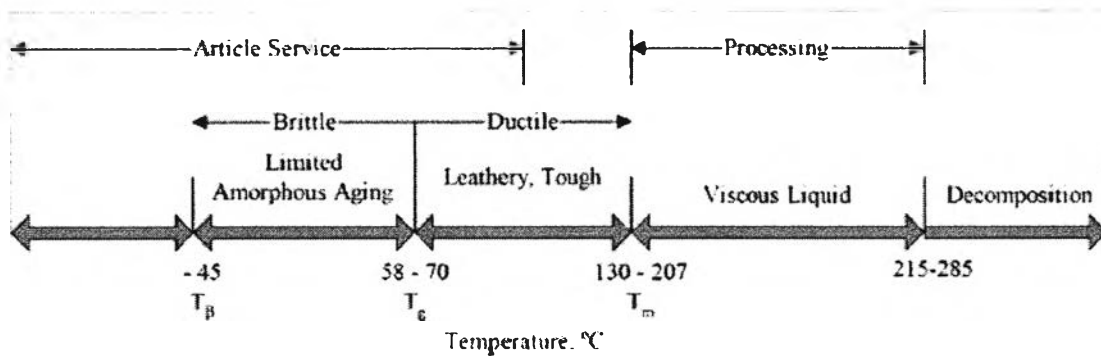
**Figure 2.3** Polymerization of lactic acid to poly(lactic acid).

Lactic acid is turned into PLA by different polymerization routes. For condensation polymerization, the low molar mass with wide distribution polymer is the disadvantage. In order to overcome this problem, many researches have been conducted. For example, the lactic acid is polycondensated directly into high molar mass polymer by manipulating the equilibrium between lactic acid, water, and PLA in an organic solvent. There, a multifunctional branching agent (e.g. dipentaerythritol) is used for a star-shaped polymer, and lactic acid can be polycondensated in the presence of difunctional monomer (e.g. diacids or diols) ending up in telechelic prepolymers. The polymer obtained can be further linked yielding high molar mass polymers in the second reaction step by using a linking molecule, such as diisocyanate. These polymers generally show the same behavior as PLA from the ring-opening polymerization (Södergård, A. and Stolt, M., 2002). The ring-opening polymerization is another approach to obtain PLA via two lactic acid molecules converted into one cyclic molecule called a lactide. The solvent-free melt process causes the ring-shaped lactide polymers to open and join end-to-end to form long chain polymers (Balkcom, M., 2002). Polymers prepared by the ring-opening polymerization are most commonly studied due to the possibility of an accurate control of the degree of polymerization, resulting in a more controlled property, which broadens the application (Södergård, A. and Stolt, M., 2002).

The properties of PLA vary to a large extent depending on the ratio between, and the distribution of, two stereoisomers (Södergård, A. and Stolt, M., 2002). PLA can be produced in either form of totally amorphous or up to 40% crystalline (Auras, R. *et.al.*, 2004). Metastable states, non-equilibrium states that may persist for a very long time, of amorphous and semicrystalline PLA are shown in Figure 2.4 and 2.5, respectively. Enantiomerically pure PLA is a semicrystalline polymer with 55°C glass transition temperature ( $T_g$ ) and 180°C melting point ( $T_m$ ) (Södergård, A. and Stolt, M., 2002). The reduction of  $T_m$  between 20 and 50°C can be obtained by adding D-lactic acid to the poly(L-lactic acid) polymer. The  $T_g$  is also determined by the content of different lactic acid stereoisomers present. These result in PLA with a wide range of hardness and stiffness (Auras, R. *et.al.*, 2004).



**Figure 2.4** Metastable states of high molecular weight amorphous polylactides, adapted from Witzke (Auras, R. *et.al.*, 2004).

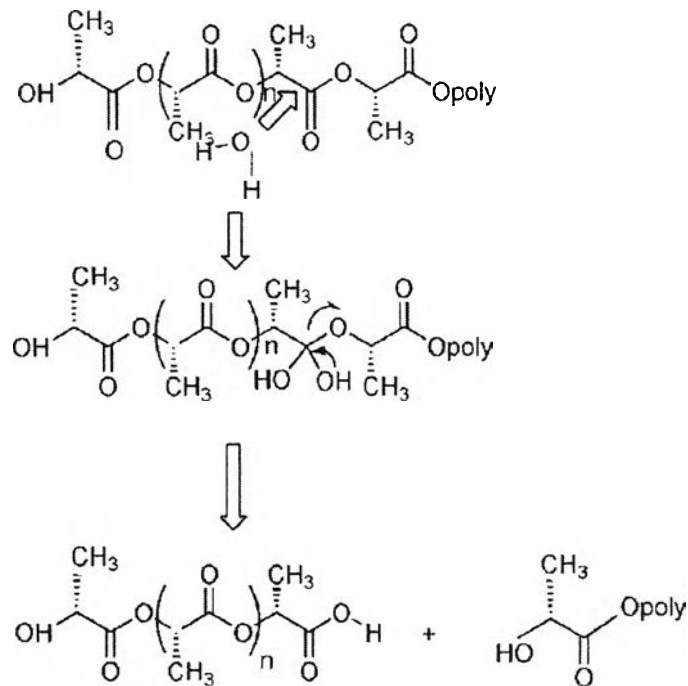


**Figure 2.5** Metastable states of high molecular weight semicrystalline polylactides, adapted from Witzke (Auras, R. *et.al.*, 2004).

The major problem in the melt processing of PLA is the limitation of thermal stability (Södergård, A. and Stolt, M., 2002). When heated above its melting point, PLA quickly loses its thermal stability. Significant molecular weight degradation occurred when PLA is heated up to above 10°C of its melting point for a substantial period of time. PLA degradation is not only a thermal degradation but the amount of residual monomer in the resin also has an important effect in inducing early degradation of the polymer (Auras, R. *et.al.*, 2004).

The solubility of PLA is highly dependent on the molar mass, degree of crystallinity, and other comonomer units present in the polymer (Södergård, A. and Stolt, M., 2002). As summarized in Table 2.1, general PLAs are soluble in



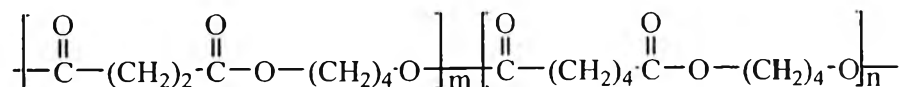


**Figure 2.6** PLA hydrolysis and molecular weight loss.

The advantages of PLA production are,

- obtaining from renewable resources such as corn, tapioca, sugar-cane, wheat, and other starch-rich products;
- recyclable and compostable;
- the physical and mechanical properties manipulating through the petroleum-based polymers;
- degrading to carbon dioxide, water and methane (Wang, H., Sun, X.Z., and Seib, P., 2001); and
- nonvolatile and odorless classified as GRAS (generally recognized as safe) by the Food and Drug Administration in United States (Grengross., 2000).

### 2.1.2 Poly(butylene succinate adipate) or PBSA



**Figure 2.7** Chemical structure of PBSA.

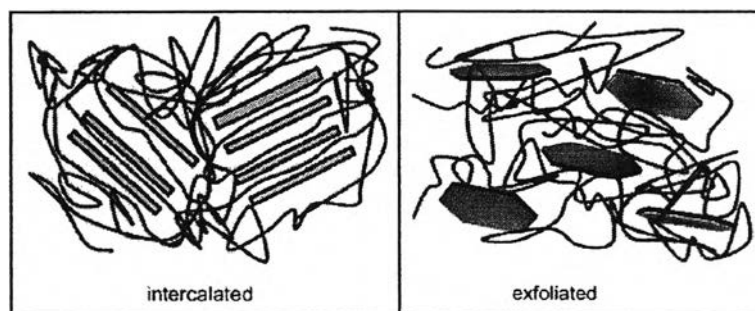
PBSA is a commercially available biodegradable petroleum based aliphatic polyester with high flexibility, excellent impact strength, melt processibility, thermal and chemical resistance (Lee, S. and Lee, J.W., 2005). Showa Highpolymer Co. Ltd. produces PBSA under the trade name of Bionolle<sup>®</sup>. PBSA is produced from condensation polymerization of glycols with aliphatic dicarboxylic (Figure 2.7) to obtain the molecular weight in the range of 10,000 to 100,000 g/mol (Ratto, J.A. *et al.*, 1999). PBSA has glass transition temperature ( $T_g$ ) range of -45 to -10°C and melting point ( $T_m$ ) range of 90 to 120°C. It has an excellent processibility which conventional processes, such as injection, blown film extrusion, and compression, at temperature of 160 to 200°C or about 100 to 230°C under the controlled conditions in to various products are possible (Fujimaki, T., 1998).

PBSA has comparable properties to synthetic polyolefins. For example, its  $T_g$  is closed to polyethylene (PE) and polypropylene (PP). The density 1.25g/cm<sup>3</sup> is similar to that of poly(ethylene terephthalate) (PET), whereas the tensile strength is in between those of PE and PP and the stiffness is about the same as those of LDPE and HDPE. It is a soft and strong material resembling to LDPE, but is fully biodegradable (Fujimaki, T., 1998).

PBSA exhibits significant biodegradation of treatment in soil, water with activated sludge, and sea water within 2 months, which is more readily biodegraded than PLA (Ratto, J.A. *et al.*, 1999).

## 2.2 PLA/PBSA Composites

Schwacch, M.V. and Coudance, G.J. (1995) showed that PBSA was regarded as an efficient plasticizer and crystallinity promoter of PLA. The addition of PBSA favors the crystallization to be around 110°C. The PLA/PBSA blends are incompatible. Thermal stability of the blends was lower than that of pure PLA and PBSA. The improvement of about two and half times of pure PLA in impact strength was realized by using only 10~20 wt% PBSA in PLA (Lee, S. and Lee, J.W., 2005).



**Figure 2.8** Schematic illustration of two different types of thermodynamically achievable polymer/layered silicate nanocomposites

The composition of the PLLA/PBSA blend was fixed at 75/25 on a weight basis because brittleness of PLLA was greatly ameliorated at this blend composition. Epoxy groups on the surface of Cloisite 25A<sup>®</sup> (C25A) were introduced by treating C25A with (glycidoxypropyl)trimethoxy silane (GPS) to produce the twice functionalized clay (TFC) (Figure 2.8). The silicate layers of PLLA/PBSA/TFC were exfoliated to a larger extent than PLLA/PBSA/C25A. Incorporation of the epoxy groups on C25A improved significantly the elongation at break as well as tensile modulus and tensile strength of PLLA/PBSA/C25A. The larger amount of exfoliation of the silicate layers in PLLA/PBSA/TFC as compared with that in PLLA/PBSA/C25A was attributed to an increase of interfacial interaction between polyesters and clay due to chemical reaction. TFC was expected to interact more strongly with the polymer matrix than C25A through the reaction between the epoxy



groups of TFC and the functional groups of the polymer matrix. The PLLA/PBSA/TFC composites showed the higher thermal stability than PLLA/PBSA/C25A. This indicated that the exfoliated clay layers were more efficient for the improvement of thermal stability than the intercalated ones (Chen, G-X. and Yoon, J-S., 2005).

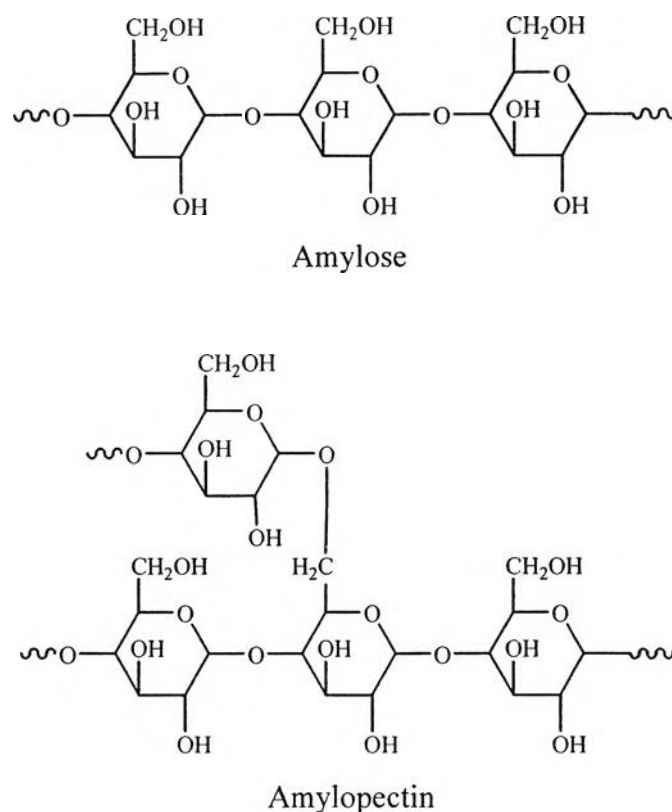
The PLA/PBSA or poly(butylene succinate) (PBS) composites in a weight ratio of from 70:30 to 20:80 are possible to form a film having both flexibility and transparency in a balanced manner. Flexibility can be imparted to the film by adding PBSA to PLA which the tensile modulus is preferably not more than 250 kg/mm<sup>2</sup>. The addition of PLA improves the transparency. When increasing the blow ratio, the flexibility and the transparency are improved. The addition of ethylene-vinyl acetate copolymer improves the shock resistance (Shigenori, T. and Jun, T., 2002).

### **2.3 Compatibility of Biodegradable Polymer/Starch Composites**

Biodegradable polymers are still expensive as compared to the commodity polymers. The price of biodegradable plastics can be controlled by introducing naturally abundant resource fillers such as starch. Starch also functions in the increase of degradation rate and stiffness improvement.

#### **2.3.1 Starch**

Starch is the most naturally occurring polysaccharide consisting of amylose, a linear polymer of  $\alpha$ -1, 4-linked glucose units, and amylopectin, a highly branched polymer of  $\alpha$ -1,4-linked chains connected by 1,6-linkages (Figure 2.9). The amylose content of starch is in the range of as high as 85% or as low as 0%, depending on its source. But in the most starches, the amylose content varies between 20-30%, which leads to the crystallinity of native starches ranging from 20-45% (Soest., 1996). The branching amylopectin molecules dominate the crystallinity and are responsible for the amorphous regions in the starch. The average molecular weight of starch is about 10 million.



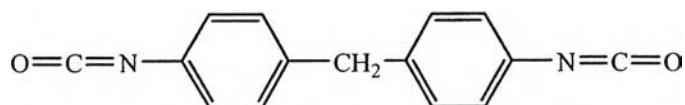
**Figure 2.9** Chemical structure of starch.

Starch is hydrophilic with strong hydrogen bond network, leading to poor adhesion with hydrophobic polymers in starch/polymer blends. An alternative to approach to bring the compatibility in starch and biodegradable polymer is compounding with reactive compatibilizer.

### 2.3.2 Compatibilizers for Biodegradable Polymer/Starch Composites

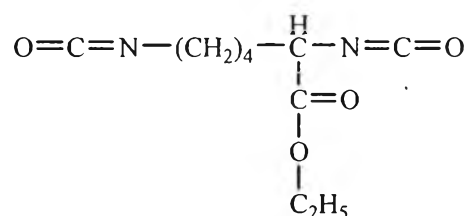
The 20% rice starch loading in PLA was reported about the good balance of tensile properties. This may attribute to a better dispersion or less agglomeration of the rice starch in PLA matrix, as well as better adhesion between rice starch and PLA. Epoxidized natural rubber forms favorable interaction with PLA and rice starch, presumably via hydrogen bonding through the ether groups after epoxy rings were hydrolyzed. The incorporation of epoxidized natural rubber at 5 phr into PLA/rice starch composites was found to increase the tensile strength and elongation at break. The tensile modulus of PLA/starch composites was reported to decrease as the loading of epoxidized natural rubber increased based on the

elastomeric behavior of epoxidized natural rubber. The addition of epoxidized natural rubber enhanced the biodegradability of the PLA/rice starch composites when subjected to water and  $\alpha$ -amylase enzymatic treatments (Yew, G.H. *et al.*, 2005).



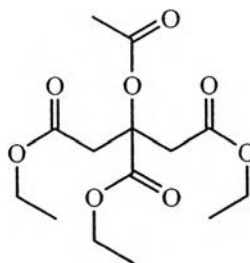
**Figure 2.10** Chemical structure of methylenediphenyl diisocyanate (MDI).

Methylenediphenyl diisocyanate (MDI) (Figure 2.10) was reported as a good coupling agent for PLA/starch composites since it creates a strong chemical urethane linkage between the carboxyl and hydroxyl groups from PLA and starch, respectively. The addition of MDI resulted in an enhancement of mechanical properties (Wang H *et al.*, 2001). However, MDI is considered an environmentally hazardous material.



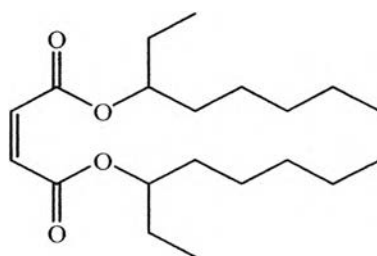
**Figure 2.11** Chemical structure of lysine diisocyanate (LDI).

Lysine diisocyanate (LDI) (Figure 2.11) is a non-toxic bio-based coupling agent. The addition of LDI improved the mechanical properties and interfacial adhesion of the PLA and corn starch components (Ohkita, T. and Lee, S-H., 2006).



**Figure 2.12** Chemical structure of acetyl triethyl citrate (ATC).

The PLA/starch composites with a 55:45 ratio in the presence of maleic anhydride (MA) and the initiator, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (L101), were closed to the mechanical properties of pure PLA (Zhang, J-F and Sun, X., 2004). The addition of a plasticizer namely acetyl triethyl citrate (ATC) (Figure 2.12) was reported for the increase in elongation at break of PLA/starch/MA composites when the ATC loading content was above 8%. However, at that time the tensile strength was found to be decreased. The glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ), was also decreased with the ATC content. Thermally induced ATC migration affected due to ATC is a low molecular weight (Zhang, J-F and Sun, X., 2004).



**Figure 2.13** Chemical structure of dioctyl maleate (DOM).

A derivative of MA, dioctyl maleate (DOM) (Figure 2.13), was explored as a compatibilizer at low concentrations ( $\leq 8\%$ ) and as a plasticizer at high concentrations ( $\geq 10\%$ ). The tensile strength was reduced but elongation was increased remarkably. The fact that DOM gives the blend a fair elongation whereas

MA significantly improves tensile strength, the combination of MA and DOM is variously proposed. The characteristics of DOM as a polymeric plasticizer are useful in producing soft polymeric materials with acceptable mechanical properties without thermal loss in thermal processing or leaching in an aqueous environment application (Zhang, J-F and Sun, X., 2004).

The PLA/starch composite containing acrylic acid grafted PLA starch (PLA-g-AA) was found to be compatible between the two phases, resulting in better mechanical properties, and higher thermal properties than PLA/starch composite. Furthermore, the lower viscosity of PLA-g-AA/starch makes it easier to process than PLA/starch composite (Wu, C-S., 2005).

The blends of biodegradable petroleum based aliphatic polyester and starch were reported to give excellent properties when only small amount of compatibilizers, anhydride functionalized polyesters such as maleic anhydride, were added. Even at a starch level of 70% by weight, the tensile strengths are comparable to that of the synthetic polyester (Mani, R. and Bhattachaya, M., 2001).

Ratto, J.A. *et al.* (1995) showed that a formulation consisting of starch plasticized with 23% ethylene glycol blending with 70% PBSA brought water resistant films and blow molded pots for seedlings. The PBSA/PLA blends containing up to 50% PBSA, were also considered for the trash bag applications with the significant mechanical properties comparable to the starch/PBSA systems (Liu, X *et al.*, 1997). The PBSA/starch films were processed by blown film extrusion and prepared with starch contents of 5–30% by weight. The addition of the starch filler significantly improves the rate of degradation of the PBSA. In conclusion, the addition of starch alters the mechanical properties of the resulting films, increasing the starch content led to an increase in modulus and decreases in tensile strength, elongation at break and toughness (Ratto, J.A. *et al.*, 1999).

Methods to obtain high strength plastic from reactive compounding of PLA and starch comprise forming and heating a blended mixture of PLA, starch, and a linkage group for joining or copolymerizing the PLA and starch. The preferred linkage groups comprise an isocyanate moiety, with diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate, and isophorone diisocyanate. The weight ratio of PLA:starch in the compound was found to be in the range of 1:99 to about 70:30.

The linkage group should be mixed with the PLA and starch at a level of less than about 4% by weight. In compounding the PLA, starch, and linkage group mixture, it is preferred that all of the ingredients simply be mixed together (Wang H. *et al.*, 2001).

The degradation rate of a PLA is almost determined by the hydrolysis rate of PLA, and is relatively slow as compared with that of other microbiologically decomposable polymers. It is expected that the decomposition is accelerated by adding starch or modified starch. A high content of starch is suitable for uses which require high degradation rate. However, the amount of starch is increased, weatherability and tear resistance decreases. Compatibility of PLA and starch can be improved by compatibilizer such as ethyl oleate or calcium stearate (Ajioka, M. *et al.*, 1995).

Starch is incorporated in the hydrophobic biodegradable polymer selected from the group consisting of aliphatic polyesters, or aliphatic-aromatic polyesters, produced by the extrusion of mixtures with ethylene-vinyl alcohol copolymer (EVOH), or selected from the fatty acids and derivatives thereof, acted as coupling agents (Bastioli, C. *et al.*, 2005).

PLA is generally high in hardness and hence has disadvantage of having low flexibility when used in the form of film. The compounding PLA with starch will further reduce its mechanical properties, even though, the compatibilizer is incorporated. A solution to this problem is to add plasticizers.

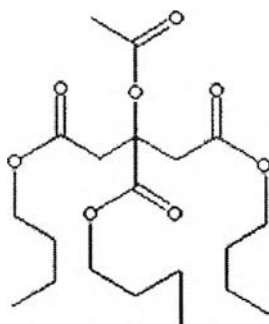
#### **2.4 Plasticizers for PLA**

Glycerol is the least efficient of these plasticizing agents. The lower molecular weight polyethylene glycol (400 g/mol) is the most efficient of these plasticizing agents. A reduction in the glass transition temperature ( $T_g$ ) from 58°C to 12°C was found when the plasticizers were used. Oligomeric lactic acid is also the efficient plasticizer (Martin, O. and Avérouss, L., 2001).

Poly( $\epsilon$ -caprolactone) (PCL) is a biodegradable polymer. The highly crystalline and low glass transition temperature ( $T_g$ ) brings the toughness to PCL.

Poor adhesion was observed at the interface between the PLA/PCL blends, indicating the two components were phase separated (Broz, M.E. *et al.*, 2003). The poly(L-lactic acid) (PLLA)/PCL blend with 2% copolymer of ethylene oxide (PEO) and propylene oxide (PPO) surfactant was reported for the higher elongation and weaker mechanical properties than the PLLA/poly(D,L-lactic acid) (PDLLA) blend with 2% copolymer of PEO and PPO. Elongation of PLLA increased with the addition of PCL, but the strength decreased at the same time (Chen, C-C. *et al.*, 2003). The PLA/PCL blend was seemingly immiscible. The miscibility of poly(D,L-lactide)-co-polyethylene glycol (PELA)/poly( $\epsilon$ -caprolactone)-co-polyethylene glycol (PECL) blend was improved by using PELA and/or PECL block copolymer that contained poly(ethylene glycol) (PEG) as a compatibilizer (Zhang, L. *et al.*, 1995).

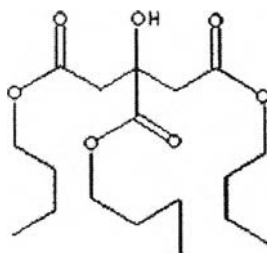
The PLA/PLA-grafted dextran blends films exhibited a lower glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and crystallinity, and higher viscosity properties compared to PLA films. The usefulness of graft-copolymer as a plasticizer was investigated with 1:4 blend films prepared from the graft-copolymers and PLA, although the preparation of graft-copolymer was difficult (Ouchi, T. *et al.*, 2003).



**Figure 2.14** Chemical structure of acetyl tri-*n*-butyl citrate (ATBC).

Acetyl tri-*n*-butyl citrate (ATBC) (Figure 2.14), monomeric plasticizer, is a non-toxic additive. The glass transition temperature ( $T_g$ ) of PLA/ATBC blends decreased with an increase of ATBC content ranging from 0 to 60 wt%. The 50 wt% ATBC saturates its solubility in the polymer. The PLA/ATBC blends melt at the temperatures that decrease with an increase of plasticizer content. The range of

miscibility of the polymer with the polyethylene glycol (PEG), polymeric plasticizer, was found to be decreased with an increase of the PEG molecular weight (30 wt % for PEG 400, 15 wt % for PEG 10 K). The plasticizing efficiency of PEG increases with decreasing molecular weight. A significant increase of the elongation at break of PLA was achieved by plasticizing at the expense of strength and tensile modulus (Baiardo, M. *et al.*, 2003).



**Figure 2.15** Chemical structure of tributyl citrate (TbC).

Tributyl citrate (TbC) (Figure 2.15) drastically decreased the glass transition temperature ( $T_g$ ) of PLA, thus creating a homogeneous and flexible film material. The reduction was largest with the plasticizer having the lowest molecular weight. The higher molecular weight of plasticizer leads to the lower miscibility. Although it was also observed that the plasticizers migrated to the film surface after aging of the materials at ambient temperature for 1–4 months, such a migration was successfully prevented by increasing the molecular weight of the plasticizers. A trimer and a heptamer of tributyl citrate were synthesized by transesterification and by increasing the molecular weight. In this way, the plasticizing agents became less inclined to migrate to the film surfaces (Ljungberg, N. and Wesslén, B., 2003).

When PLA was mixed with 10 wt% acetyltriethyl citrate ester (ATC) (Figure 2.12) plasticizer and 5 wt% of an organically modified montmorillonite (MLS), the nanocomposite films showed 48% improvement in oxygen barrier and 50% improvement in water vapor barrier in comparison to the neat PLA. The Young's modulus for the nano-PLA samples was about 30–40% greater than that of the neat polymer. However, incorporation of the MLS into the PLA matrix produced no significant change in the tensile strength of the resulting films. The elongation



was about 16–40% greater for the nano-PLA films than for the neat films. The onset of the degradation temperature ( $T_d$ ) was approximately 9°C higher than pure PLA. The glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ), and melting temperature ( $T_m$ ) were not significantly influenced by the presence of MLS (Thellen, C. *et al.*, 2005).

The addition of chitosan to PLA was also reported. The decrease in glass transition temperature ( $T_g$ ), from 62 °C to 60.1°C was clarified when adding 50 wt% chitosan, as well as the temperature of the crystallization onset. The tensile strength was found to be decreased with an increase of chitosan content while the modulus was found to be increased. A small amount of chitosan content caused a significant decrease in the elongation. Chitosan displayed intermediate adhesion to the polyester (PLA or PBSA) matrix (Correlo, V.M. *et al.*, 2005).

PLA and 5 to 70 parts by weight of ethylene-vinyl alcohol copolymer (EVOH) were found to achieve an excellent mold releasability upon processing and significantly improved elongation at break and impact strength without affecting the transparency. This compound is potentially applicable to shrink films (Tokushige, Y. *et al.*, 1998).

A porous film which has hydrolyzability consists of 80 to 100% by weight of PLA and 0 to 20% by weight of a plasticizer. Lactic acid, straight chain lactic acid oligomer, cyclic lactic acid oligomer, and lactide are preferably used in the view of their plasticizing effect. When the amount of a plasticizer is 5% by weight or more, flexibility can be clearly observed. However, the amount exceeding 20% by weight gives adverse effect on the melt-extension and stretching of the resin composition and unfavorably decreases mechanical strength of porous film obtained (Morita, K. *et al.*, 1994).

PLA-based products for durable tile or sheet form floor coverings made of one or more layers of polymers suitable for, can be obtained by combination with plasticizer. The plasticizer is an epoxidized vegetable oil, esterified and epoxidized vegetable oil, polyethylene glycol (PEG), polycaprolactone, or poly(lactic acid-co-caprolactone). The plasticizer is typically present in an amount of between about 10 and about 40% by weight based on the polymeric material. Below 10%, the plasticizer does not effectively plasticize the polymeric material, and above 40%, it

tends to leach out of the polymeric material. A compatibilizer is used to keep the polymer and plasticizer miscible and avoid having the plasticizer leach out of the polymer. The suitable compatibilizer is polyolefins modified with maleic anhydride which is advantageously used at a concentration between about 5 to 10% by weight of polymeric material (Mohanty, A.K. *et al.*, 2005).

The film consisting of PLA, specific flexible biodegradable aliphatic polyester and biodegradable plasticizer, is excellent in flexibility. The composition of compound contains 50 to 90% by weight of PLA, 10 to 50% by weight of a biodegradable aliphatic polyester, and 5 to 25 parts by weight of a biodegradable plasticizer. The biodegradable plasticizers include aliphatic polybasic acid ester, aliphatic polyhydric alcohol ester, and oxyacid ester. The addition of an inorganic additive and lubricant such as silica, calcium carbonate, talc, kaolin, kaolinite, and zinc oxide, is recommended in order to improve blocking resistance and sliding property of films and sheets (Yoshida, Y. *et al.*, 2001).

A film, sheet, or bag of PLA is obtained by compounding 100 parts by weight of PLA with 5 to 50 parts by weight of polyglycerol acetic ester or polyglycerol acetic ester and acetic and fatty acid ester of glycerol. The flexible products are produced by molding (Sashida, K. *et al.*, 2004).

## **2.5 Nucleating agents for PLA**

The crystallization rate of PLA is very slow. Moreover, PLA is totally amorphous when the racemic content above about 5% (Baker, G.L. and Smith III, M.R., 2002). Because of the amorphous structure, PLA is not suitable for producing packaging films that is used, stored, or shipped in the high temperature exceeding its glass transition temperature (about 60°C) due to it starts to deform. In order to overcome these limitations, amorphous structure of PLA has to convert to be semicrystalline structure by adding a nucleating agent.

Kolstad found that crystallized PLA can be achieved by mixing of talc that has nucleation effect in PLA matrix (Kolstad, J.J., 1996). Nam, J.Y. *et al.* investigated that montmorillonite particles act as a nucleating agent for PLA because the crystallization rate of pure PLA increases after nanocomposite preparation with

organically modified montmorillonite (C<sub>18</sub>-MMT) (Nam, J.Y. *et al.*, 2003). Moreover, they found that the overall crystallization rate of PLA increased with addition of low-molecular weight aliphatic amide which is *N,N*-ethylenebis(12-hydroxyteramide). This behavior indicated that *N,N*-ethylenebis(12-hydroxyteramide) acts as a nucleating agent for PLA crystallization (Nam, J.Y. *et al.*, 2006).

Cold-crystallization temperature of PLA was about 85°C. When polyethylene glycol (PEG) was incorporated into PLA, the cold-crystallization temperature of PLA decreased slightly as the PEG content increased in parallel with the shift in glass transition temperature ( $T_g$ ). If the cooling rate of 70PLA/30PEG blend was 30°C min<sup>-1</sup> or less, PLA crystallized during cooling, followed by crystallization of PEG at a lower temperature. Crystallization temperature and crystallization enthalpy of PLA and PEG blend increased as the cooling rate decreased. PEG crystals were embedded in the PLA spherulites (Hu, Y.S. *et al.*, 2003).

Because of a lower activation energy barrier of heterogeneous nucleation compared with homogeneous nucleation. The dispersed nano-clay particles acted as nucleating sites for cell formation, observed a lamellar pattern beside the nano-clay particles, and the cell growth occurs on the surfaces of the clay (Ema, Y. *et al.*, 2006).