

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 General Information of Poly(Lactic Acid) (PLA)

Based on environmental concern, PLA is a promising material to replace petroleum-based items, especially in packaging field. Many techniques have been developed to produce high molecular weight PLA in order to broaden its uses which had been limited in medical devices. PLA is aliphatic polyester, derived from 2-hydroxy propionic acid which is a product from carbohydrate fermentation. Its monomer has two optical isomers which are L- and D-lactic acids. The crystallinity (a degree of structural order) of PLA chain can be designed by the content ratio between L- and D-isomers. The cyclic lactide dimer are produced in three potential forms which are D,D-lactide (D-lactide), L,L-lactide (L-lactide), and L,D or D,L lactide (LD-lactide) or so-called *meso*-lactide. All PLAs are practically made up of L-lactide and *meso*-lactide copolymers (Conn *et al.*, 1995; Garlotta, 2002; Auras *et al.*, 2004).

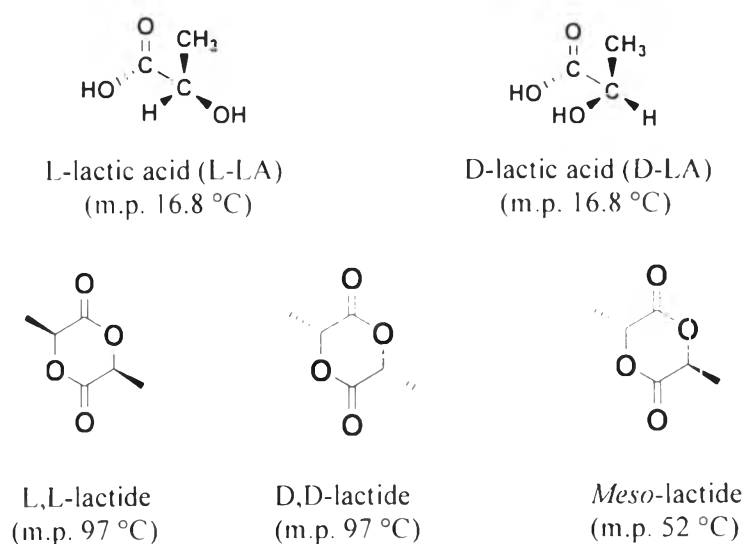
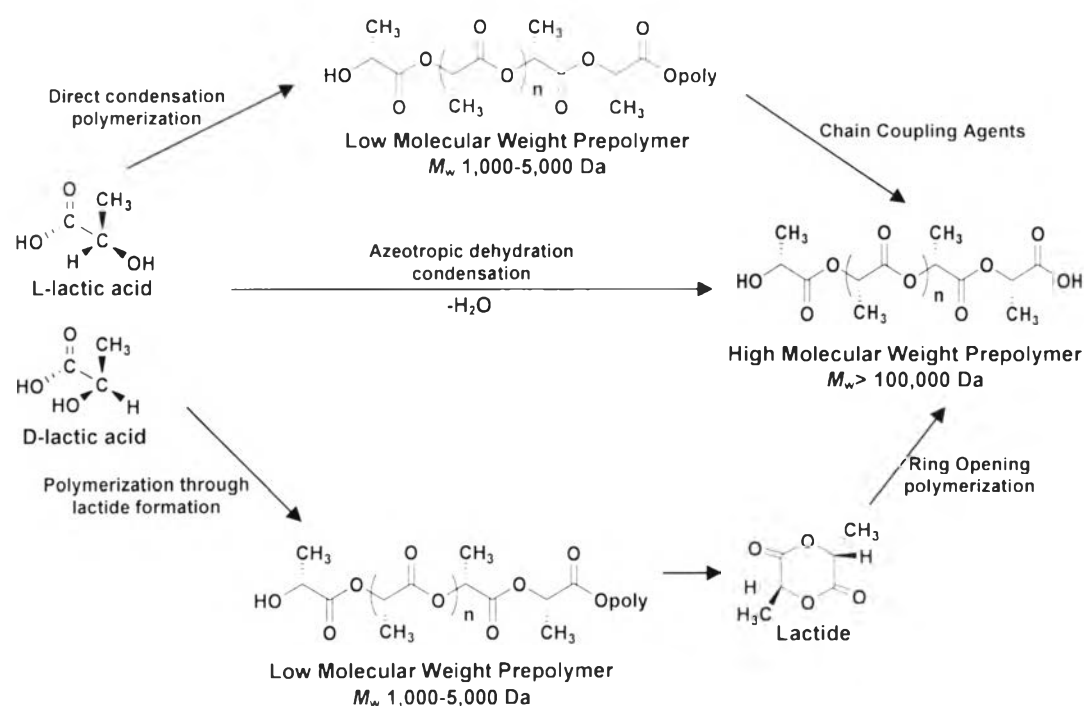


Figure 2.1 Chemical structures of lactic acid and lactide.

PLA with high molecular weight can be prepared by three major ways which are (i) direct condensation polymerization from lactic acid monomers, (ii) azeotropic dehydration condensation and (iii) ring opening polymerization from lactide, as shown in Scheme 2.1 (Auras *et al.*, 2004). The first route is low production cost but it is difficult to obtain a solvent-free high molecular weight PLLA while the chain coupling agents were needed in the system and its consequence is costly. Azeotropic dehydrative condensation is relatively complicated procedure whereas polymerization by means of lactide is the current used for commercial applications.



Scheme 2.1 Schematic draw of synthesis methods for obtaining high molecular weight PLA (Auras *et al.*, 2004).

2.2 Properties of PLA

Properties of PLA, as well as other polymers can be determined from their polymer architectures and molecular mass which control precisely the crystallization

rate, degree of crystallinity, mechanical properties and the processing temperature of materials.

2.2.1 Structure of PLA

Due to the chiral nature of lactic acid, several distinct forms of PLA exist in various studied and applications. Commercial PLA consists mainly of L-lactide with a molecular weight of $\sim 10^5$ g/mol which shows the strong IR bands at 1748 cm^{-1} and 1456 cm^{-1} , assigned to C=O stretching and CH₃ band, respectively. The bands that appear at 1315 cm^{-1} and 1300 cm^{-1} are due to CH bending modes. Additionally, the peaks at 956 cm^{-1} and 921 cm^{-1} can be observed, attributed to the characteristic vibrations of the helical backbone with CH₃ rocking modes. Two peaks relating to the crystalline and amorphous phases also present at 756 cm^{-1} at 871 cm^{-1} , respectively (Kister *et al.*, 1998).

Poly(L-lactide) exists as a polymer helix, crystallizing in three forms (α , β and γ) which depends on the preparation conditions. The stable α -form has a pseudo-orthorhombic unit cell containing 10₃ polymeric helices. The unit cell dimensions are: $a = 10.7\text{ \AA}$, $b = 6.16\text{ \AA}$, and $c = 28.88\text{ \AA}$ (Sasaki and Asakura, 2003). In case of β form, it can be prepared from high draw ratio and high draw temperature. β form presents the orthorhombic unit cell containing 3₁ with lattice parameters: $a = 10.31\text{ \AA}$, $b = 18.21\text{ \AA}$, and $c = 9.0\text{ \AA}$ (Hoogsteen *et al.*, 1990). While γ form is obtained from epitaxial crystallization consisting 2 antiparallel $s(3/2)$ helices in the pseudo-orthorhombic unit cell ($a = 9.95\text{ \AA}$, $b = 6.25\text{ \AA}$, and $c = 8.8\text{ \AA}$) and it assumes the known three-fold helix of polylactides (Puiggali *et al.*, 2000).

The repeat unit of PLA (72 g/mol) contains one stereocenter that is either L(*S*) or D(*R*) in configuration. More than 93% L-lactic acid containing in PLA derivatives can be semi-crystalline whereas 50% to 93% L-lactic acid is strictly amorphous. Both *meso*-lactide and D-lactide induce twists in the otherwise very regular poly(L-lactide) molecular architecture. These molecular imperfections contribute to decrease in both rate and extent of PLA crystallization. However, 1:1 poly(L-lactide):poly(D-lactide) molar ratio enables to form a stereocomplex crystalline structure, having a significantly higher melting point ($230\text{ }^\circ\text{C}$) than the homopolymers (Auras *et al.*, 2004).

2.2.2 Thermal Properties

A representative case of high molecular weight amorphous polylactide is shown in Figure 2.2. Below the β -relaxation temperature (T_β), PLA are completely brittle. Between T_β and T_g , the amorphous polylactide undergoes physical aging and can show brittle or ductile fracture. In the transition between 110 °C to 150 °C, PLA changes from rubbery to viscous and is mainly dependent on the molecular weight and the shear stress. Amorphous PLA properties depend in part on how far below T_g the article is used or stored.

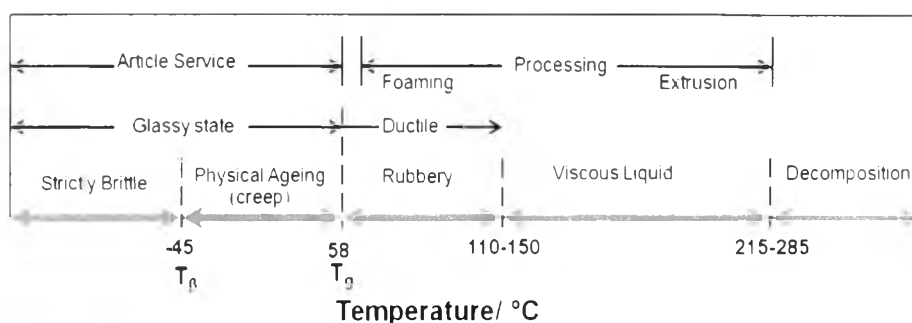


Figure 2.2 Metastable states of high molecular weight amorphous polylactides (Auras *et al.*, 2004).

For semicrystalline PLA (most of commercial PLA) as shown in Figure 2.3, its T_m depends on the presence of *meso*-lactide in the structure which produces a depression of T_m with increasing of *meso*-lactide content. The maximum practically obtainable melting point of stereochemically pure polylactide (either L- or D-) is around 180 °C with an enthalpy of 40-50 J/g. T_g indicates that transition

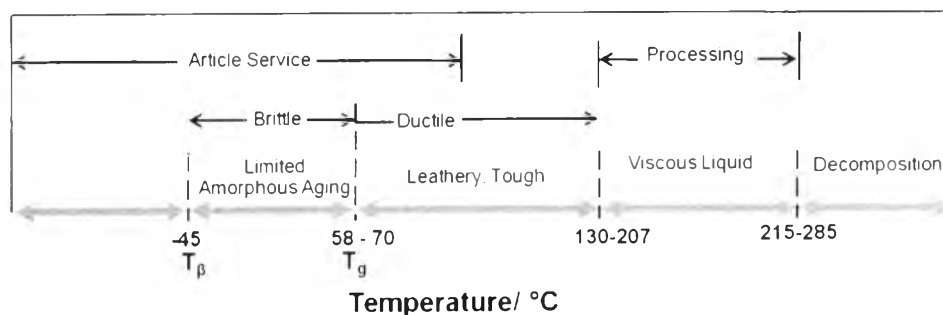


Figure 2.3 Metastable states of high molecular weight semicrystalline polylactides (Auras *et al.*, 2004).

between brittle and ductile fracture, its typical value ranges from 50 °C to 80 °C (Ikada and Tsuji, 2000).

It could be concluded that melting point (T_m) of high molecular weight PLA is around 150 °C to 180 °C and PLA chains can aggregate to be crystallized in the range of 110 °C to 140 °C (T_c) while amorphous PLA region can be moved at above 50 °C to 60 °C (T_g).

2.2.3 Crystallization Behavior

Understanding the crystallization behavior of PLA is particularly crucial in order to control its thermal resistance as well as optical, mechanical and barrier properties. The main molecular structure characteristics of PLA relates firmly to crystallization kinetics (Saeidlou *et al.*, 2012).

Normally, PLLA has the maximized crystallinity of around 37% with T_g between 60°C - 65 °C. Kolstad (1996) studied the crystallization kinetics of poly(L-lactide-*co-meso*-lactide) in the range of 0% to 9% *meso*-lactide which was strongly dependent on the copolymer composition (Kolstad, 1996). The crystallization of PLLA with the presence of D-lactide was investigated, the structure becomes more disordered whereas spherulite size and time for crystallization increases (Tsuji and Muramatsu, 2001). Furthermore, an increase in optical impurity, i.e. increase in minor unit concentration (defined as D-lactate in the case of an L-rich PLA and as L-lactate for a D-rich PLA), decreases the T_g which plays an important role on the PLA crystallization window since it relates directly to polymer chain mobility (Jamshidi *et al.*, 1988; Abe *et al.*, 2001). Due to the kinetic barrier for crystallization when approaching the T_m , polymer crystallization is typically carried out at high undercoolings which limits the crystal thickness. Both molecular weight and D-lactate content can determine the maximum achievable crystallinity which is compared to the melt enthalpy of pure PLA with 100% crystallinity ($\Delta H_m^0 \sim 93$ J/g) (Fischer *et al.*, 1973). The molecular weight effect can be explained by the higher restrictions of chain motion at higher molecular weights, while the reduction in maximum achievable crystallinity by increasing D-lactate content is expected from crystal disruption. (Zhao *et al.*, 2002; Kim *et al.*, 2004; Pitet *et al.*, 2007).

PLA chain architecture also has an influence in T_g value. Hyperbranched PLA copolymerized with glycol (Pitet *et al.*, 2007) and star-shaped PLLA (Zhao *et al.*, 2002) were developed and able to decline T_g of PLA around 5 °C to 10 °C. This is due to the existence of a higher free volume caused by the higher number of chain ends. The T_m of a polymer is expected to increase with the temperature at which it was crystallized (T_c). Moreover, the crystallinity is diminished if branching is imparted to PLA structure as a consequence of more difficult chain segment transportation to crystallization sites.

In general, the overall crystallization kinetics can be studied through either visual observation or calorimetry technique. From visual observation, it is typically examined in terms of two independent phenomena: initial crystal nucleation and of subsequent crystal growth. Optical microscopy is used to determine the nucleation density and spherulite growth rates in isothermal conditions whereas calorimetry enables quantification of transition temperatures and enthalpies in isothermal and non-isothermal modes. The growth phenomenon is evaluated by measuring spherulite radius with time. The crystal growth rate (G) is equal to the slope of the spherulite radius vs. time curve, while extrapolation of this data to zero-

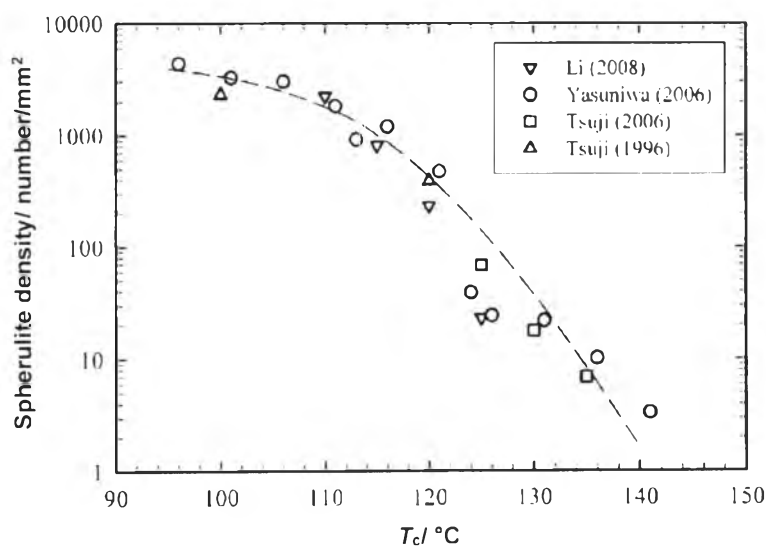


Figure 2.4 Spherulite density as a function of crystallization temperature (Tsuji *et al.*, 2006; Yasuniwa *et al.*, 2006; Li *et al.*, 2008).

radius can be used to determine the induction time. G is usually constant for a specific T_c , implying a constant concentration of impurities like non-crystallizable segments at the growth front because of their rejection to inter-lamellar regions. From Figure 2.4, the spherulite density was shown to decrease with temperature and the decreasing rate gradually accelerates with temperature (Yasuniwa *et al.*, 2006; Li *et al.*, 2008).

D-lactate concentration (0% - 4%) and molecular weight ($\sim 0.5-1 \times 10^5$ g/mol) of PLA effect on spherulite growth rate, increasing the optical impurity and molecular weight decreases dramatically the maximum growth rate. High molecular weight is expected from more restricted chain mobility (Huang *et al.*, 1998; Baratian *et al.*, 2001; Tsuji *et al.*, 2006; Yasuniwa *et al.*, 2006).

In case of isothermal crystallization study observed by calorimetry technique, the Avrami model is applied: $\alpha(t) = [1 - \exp(-kt)^n]$ where $\alpha(t)$ is the fraction of crystallized material at time t , k is a kinetic rate constant, and n is the Avrami exponent. The Avrami exponent is typically between 2 and 4 for polymer crystallization and associated to the nucleation mechanism (homogeneous vs. heterogeneous and simultaneous vs. sporadic) dimensionality of crystal growth and growth mechanism. The Avrami exponents of PLA microspheres containing with carbonated hydroxyapatite were in range of 2.5 - 2.8 for the temperature range of 90 °C - 130 °C, suggesting a change in crystal growth from two to three dimensional with simultaneous nucleation (Zhou *et al.*, 2009).

To rapidly compare the crystallization rates of materials, it is convenient to report the crystallization half-time ($t_{1/2}$) defined as the time required to attain half of final crystallinity. The $t_{1/2}$ of pure PLA is around 14 min which was reduced to 1.8-3.2 min and 0.4 min by starch and talc, accordingly (Ke and Sun, 2003). D-lactate contents and molecular weights of PLA were also varied to determine $t_{1/2}$ under isothermal condition, the maximum crystallization rate or the minimum half-time of PLA was reached in the 105 °C – 110 °C range. Spherulite density sharply decreases above 110 °C. Therefore, at temperatures lower than the optimal growth rate temperature, the crystal growth rate decrease was compensated by a larger number of crystallization sites (higher nuclei density) due to increased

driving force for nucleation (Kolstad, 1996; Tsuji *et al.*, 2006; Li and Huneault, 2007; Pei *et al.*, 2010; De Santis *et al.*, 2011).

Although it has a negative effect on total crystallinity and melting point, higher crystallization rates have been observed for branched PLA compared to linear one (Mihai *et al.*, 2010; Nofar *et al.*, 2011). The cold crystallization temperature was decreased and the crystallization peak was shifted to higher temperatures for branched PLA compared to the linear structure. The magnitude of both the cold crystallization peak and crystallization peak upon cooling was increased due to the faster overall crystallization rate.

2.2.4 Mechanical Properties

The mechanical properties of PLA can be varied to a large extent ranging from soft and elastic plastics to stiff and high strength materials. In general, commercial PLA is preferred to be amorphous polymer when higher mechanical properties are desired. The elongation at break of amorphous PLA is less than 10% whereas the tensile strength is relatively high around 60-70 MPa with flexural modulus of 5 GPa (Törmälä, 1992; Jacobsen and Fritz, 1999; Baiardo *et al.*, 2003). As mentioned previously, the degree of orientation in molecular level and the stereochemical composition of various PLA manipulate the mechanical properties of PLA products. Jamshidi and coworkers found that the modulus and tensile strength were the greatest for PLA polymers with viscosity-average molecular weight above 55,000 g/mol. The impact strength increased with molecular weight and crystallinity (Jamshidi *et al.*, 1988). Grijpma and Pennings varied the crystallinity of PLA by stereo-copolymers with various D-lactide contents and found a maximum in impact strength 37 kJ/m² when the copolymer had crystallinity of 65%. When the crystallinity of PLA was reduced, the density of chain entanglements increased even though the crystallinity was high enough to give physical cross-linking and thus not be as brittle as amorphous or low-crystalline material (Grijpma *et al.*, 1992; Cartier *et al.*, 2000). The crystalline levels achieved in molded or extruded articles can be strongly influenced by the flow and orientation prevailing while the polymer is being cooled and crystallized (Li and Huneault, 2007). It was not possible to prepare fully crystallized neat PLA but formulation comprising as little as 1% talc could be fully

crystallized when using a high mold temperature. Surprisingly, the tensile properties of these crystallized samples are similar to those of the amorphous neat PLA. It has been postulated that this absence of effect is due to the weak linkage between the amorphous and crystalline phases of PLA (Arnoult *et al.*, 2007). 10% PEG as plasticizer for PLA suddenly dropped the modulus and tensile strength by a factor of 2. Conversely, the elongation at break increased drastically 40%. Since the plasticizer cannot penetrate in crystalline phase, a possible cause for this dramatic change can be the explosion of plasticizer from crystalline regions which in turn will increase the local plasticizer concentration in amorphous regions (Martin and Avérous, 2001).

2.3 PLA Heterogeneous Nucleation and Plasticization

It is well known that the overall nucleation and crystallization rate of high molecular weight PLA in homogeneous conditions are relatively low. There were tremendous efforts in improvement of PLA crystallization kinetics by adding nucleating agents to increase nucleation density and by adding plasticizers to increase chain mobility for crystallization acceleration.

2.3.1 Nucleating Agent for PLA

Nucleating agent addition is heterogeneous system, nucleation forms at preferential sites such as phase boundaries or impurities with less required energy than homogeneous system (supercooling or superheating of the medium). Surfaces promote nucleation due to wetting; the contact angles greater than zero between phases encourage particles to nucleate (Mikhail, 2003). In general classification, nucleation can be either physical or chemical. The physical agents can be categorized as inorganic, organic, and inorganic-organic hybrids.

2.3.1.1 Chemical Nucleating Agent

Chemical nucleating agents are those for which nucleation proceeds through a chemical reaction mechanism. Sodium salts such as sodium stearate, sodium benzoate, etc. have been explored for nucleating PLA crystallization but failed to provide significant improvement of the crystallization

rate while severely decreasing the PLA viscosity due to extensive chain scission (Li and Huneault, 2007; Penco *et al.*, 2011).

2.3.1.2 Physical Nucleating Agent

2.3.1.2.1 Inorganic Nucleating Agent

Talc is widely used as nucleating agent for various polymers, it increased nucleation density greatly and reduced crystallization half-time ($t_{1/2}$) (Kolstad, 1996). Only 1% talc can reduce the $t_{1/2}$ of PLA to less than 1 min (Ke and Sun, 2003). Yu and coworkers also found that talc performed the significant nucleation effect and decreased crystallization temperature (T_c) of PLA, it can reinforce and toughen PLA with talc content increment; however, their samples became brittle with 24.3% talc (Kolstad, 1996; Yu *et al.*, 2012).

Clay has been employed to improve thermal, mechanical and barrier properties of polymers. In a qualitative study, narrowing of cold crystallization peaks were observed for PLA in presence of clay (Ogata *et al.*, 1997). The effect of clay exfoliation on crystallization was investigated by four different organo-modified clays. Intercalated and flocculated clay presented the greater crystallinity and nucleation density than exfoliated form whereas the exfoliated clay resulted in a lowering by 10 °C of the cold crystallization temperature compared to intercalated morphology (Sinha Ray *et al.*, 2003). Compared to talc, clay is a less efficient nucleating agent for PLA as the reduction in $t_{1/2}$ is moderate in isothermal mode and it is not effective for high cooling rates in non-isothermal crystallization (Saeidlou *et al.*, 2012).

2.3.1.2.2 Organic Nucleating Agent

This is typically achieved by adding a low molecular weight substance that will crystallize more rapidly and at a higher temperature than the polymer, providing organic nucleation sites. Nam *et al.* (2006) reported that *N,N*-ethylenebis (1.2-hydroxystearamide) (EBHSA) on a PLLA with 0.8% D content can reduce cold crystallization temperature from 100.7 °C to 79.7 °C. Optical micrographs at the interface of PLA and EBHSA showed a well-developed layer of trans-crystallite grown from EBHSA surface, an evidence for epitaxial crystallization of PLA (Nam *et al.*, 2006). Different derivatives of 1,3,5-benzenetricarboxamide (BTA) were solution blended with PLA, 1% of selected derivatives crystallized at

100 °C for 5 min exhibited 44% crystallinity while the neat PLA reference showed a crystallinity of 17% in the same conditions (Nakajima *et al.*, 2010).

Furthermore, hydrazide compounds enabled complete PLA crystallization upon cooling with enthalpy of crystallization (ΔH_c) 46 J/g while talc and EBHSA showed ΔH_c of 26 and 35 J/g in the same condition (Kawamoto *et al.*, 2007).

As mentioned earlier, mixture of PDLA and PLLA can crystallize in the form of a stereocomplex that has a melting point about 50 °C higher than the PLLA or PDLA homopolymers. The small concentrations of PLA stereocomplex may be suitable for nucleating PLA homo-crystallization. Brochu *et al.* disclosed that in presence of the PLA stereocomplex, the spherulite density was higher and homopolymer crystalline fraction was larger than that in the pure polymer (Brochu *et al.*, 1995). PLLA crystals can form epitaxially on stereocomplex lamellae that were previously formed at higher temperatures. For the lower molecular weight PLLA, the $t_{1/2}$ was reduced from 17 min to less than 1 min when 3% of a 14 kg/mol PDLA was melt blended. The same trend is observed for a higher molecular weight of PLLA for which blends are prepared via solution mixing, but the $t_{1/2}$ values are shifted to higher as a consequence of lower chain mobility.

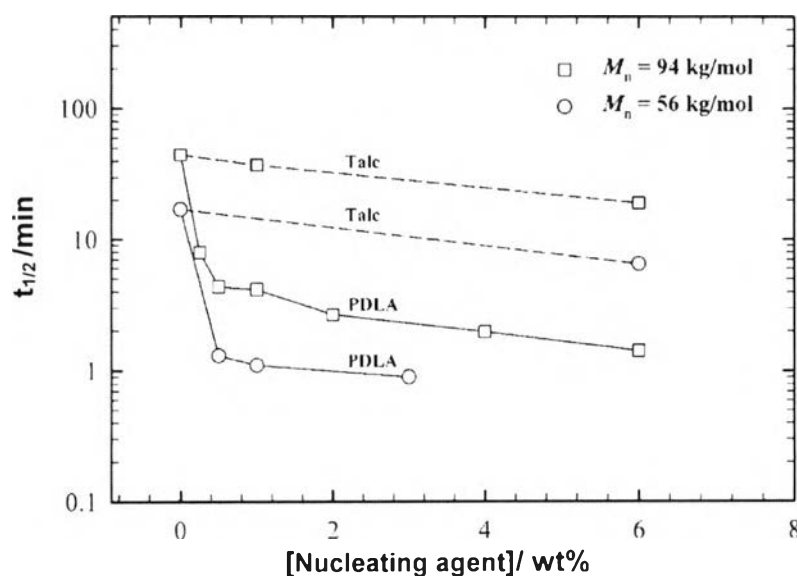


Figure 2.5 $t_{1/2}$ as a function of PDLA ($M_n \approx 14$ kg/mol) and talc concentration for two PLLAs of $M_n = 56$ and 94 kg/mol (Saeidlou *et al.*, 2012).

The crystallinity increased with very low PDLA concentration but trended to level off at higher PDLA concentrations. Rahman *et al.* also confirmed that PDLA with a lower molecular weight resulted in a higher stereocomplex crystallinity than a PDLA with higher molecular weight (Rahman *et al.*, 2009).

2.3.1.2.3 Bio-based Nucleating Agents

Starch is a biopolymer that has raised a lot of interest and its blends with other polymers are under extensive studies. It is relatively modest with the $t_{1/2}$ reduction from 14 min to 1.8 - 3.2 min for samples containing 1% - 40% starch. Starch increased the crystallization rate but the effect was less than that of talc. An additional PLA crystallinity was observed and increased with studied isothermal T_c increase which lowered PLA's T_m (Ke and Sun, 2003). Stronger effects were found by Li and Huneault when using thermoplastic starch (Li and Huneault, 2008). It is an amorphous and highly plasticized polymer and the dispersed phase size of starch reduction, obtained through interfacial modification, had a significant influence on PLA crystallinity. The ΔH_c of PLA was maximized at 50 J/g and the $t_{1/2}$ was reduced to 75 sec. Nevertheless, hydrophobic PLA and hydrophilic starch are thermodynamically immiscible leading to poor and irreproducible performance, including poor mechanical properties (Zhang and Sun, 2004).

Cellulose nanocrystal (CNC) is another attractive material due to its high tensile properties and bio-based origin. It was found that unmodified CNC did not significantly affect PLA crystallinity, excepting partially silylated CNC that had modest positive effect on crystallinity (Pei *et al.*, 2010).

Another organic nucleating agent of PLA that had been widely investigated is starch; it is gained much attention because it is naturally abundant and fully biodegradable. Starch is a polysaccharide with high crystallinity, it can induce polymer chains packing successfully.

2.3.2 Plasticizer for PLA

Thus, PLA exhibits a major trouble from brittleness which limits PLA in range of applications due to high T_g (60 °C, higher than room temperature) and slow crystallization rate (Ikada and Tsuji, 2000). Plasticization depresses T_g , a

measure of plasticization efficiency, it will shift the T_c window to lower temperature. The increased chain mobility will facilitate the movement of chains from the amorphous phase unto the existing crystal surface, especially at lower temperatures. For example in isothermal crystallization mode, spherulite growth rate should increase and the optimum growth temperature should be lowered. In case of cold crystallization, the crystallization peak should be shaper and shifted to lower temperatures. On the other hand, plasticization may also cause melting point and equilibrium melting point depression, adversely influencing the growth rate and overall crystallization rate at a given T_c due to reduced degree of undercooling ($T_m^0 - T_c$) driving the crystallization and primary nucleation processes. Thus, the enhanced chain mobility may be partially compensated for reduced primary and secondary nucleation.

Polyethylene glycol (PEG) is the most investigated plasticizer for PLA. It is available in a wide range of molecular weights and shows the most efficient in decreasing T_g and T_c . Even a PLA with 5% D units which does not readily cold crystallize was found to cold crystallize between 88 °C and 90 °C with 10% PEG and up when heated at a rate of 10 C/min (Jacobsen and Fritz, 1999; Hu *et al.*, 2003). The effect of PEG end-group on plasticization and crystallization was also investigated (Lai *et al.*, 2004; Kulinski and Piorkowska, 2005; Lai *et al.*, 2008). Comparing methyl-methyl, hydroxyl-hydroxyl, methyl-hydroxyl, and amine-amine terminated 2000 g/mol PEG (Lai *et al.*, 2004; Lai *et al.*, 2008), it was found that the miscibility decreased in the following order: $2NH_2 > 2CH_3 > OH-CH_3 > 2OH$. High miscibility of amine-terminated PEG with PLA and highest melting point reduction were associated to the ionic interaction of amine groups with the carboxylic groups at PLA chain ends, it attributes to the lowest fold-surface free energy (Kulinski and Piorkowska, 2005).

With an increase in the PEG component in the PLA/PEG blend, a depression in the melting point is observed. The desired mechanical properties are achieved in quenched PLA/PEG blends at up to 30 wt% PEG. However, these blends are not stable at ambient temperature and the attractive mechanical properties are lost over time. The aging results crystallization and phase separation (Nakane *et al.*, 2004). At certain PEG content, depending on its molecular weight, blends of PLA

with PEG undergo phase separation. Blends of low PLA stereoregularity with 30 wt% of PEG, having molecular weight of 8000 g/mol, are unstable. This is related to the slow crystallization of PEG that depletes the amorphous phase of the plasticizer whereas high stereoregularity PLA blended with PEG at the same concentration also showed immiscibility with no crystallization (Hu *et al.*, 2003).

Polypropylene glycol (PPG) has similar effect on T_g as PEG, however, PPG may be less miscible with PLA. 12.5% PPG blends exhibited a second T_g around -77 °C related to a phase-separated PPG phase (Kulinski *et al.*, 2006).

Additionally, low molecular weight plasticizers for PLA, citrate esters are the most investigated ones. Tributyl citrate and acetyl triethyl citrate were found to be more effective than triethyl citrate and acetyl tributyl citrate (Labrecque *et al.*, 1997). Another study found that tributyl citrate and triacetine led to the strongest T_c decrease, from 100 °C to around 67 °C - 70 °C by incorporation of 20% - 25% plasticizer. 30 wt% triphenylphosphate reduced T_g significantly by 14 °C, and increased the spherulite growth rate. Adipate also decreased T_g with concentration only up to 10% due to limited miscibility with PLA (Martino *et al.*, 2006; Murariu *et al.*, 2008; Martino *et al.*, 2009).

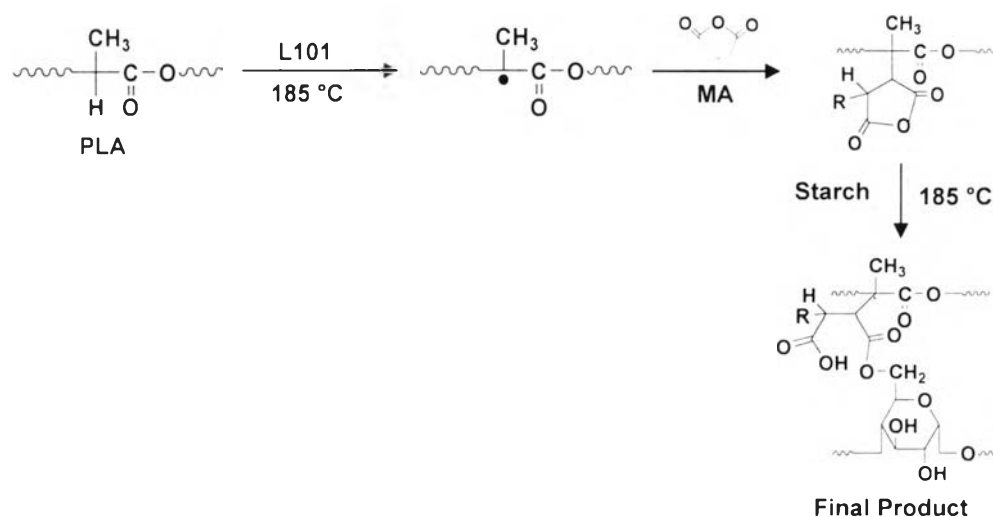
2.4 Miscibility between Binary Polymer Phases Development

Due to highly hydrophobic PLA, as well as other conventional plastics, phase separation always appears when they are blended with other additives or another polymer. There are two main approaches, usually used to improve miscibility. The first one is reactive blending which promotes chemical reactions between two polymers in a molten state, often by introducing either a reactive third component (compatibilizer) with appropriate functional groups or a catalyst. Another way is to introduce a third component into the polymer system which reduces the interfacial energy and improves dispersion simultaneously (Zhang and Sun, 2004).

2.4.1 Reactive Blending

Many efforts have been made to improve the mechanical properties of PLA/starch blends by introducing a reactive compatibilizer or coupling agent to

enhance interfacial interactions. Methylene diphenyl diisocyanate (MDI) is one of the most efficient coupling agents for improving mechanical properties of a PLA/starch blend by creating a strong chemical urethane linkage between the carboxyl and hydroxyl groups from PLA and starch, respectively (Dieteroch *et al.*, 1985; Wang *et al.*, 2001; Wang *et al.*, 2002). However it is highly toxic (Carlson *et al.*, 1999; Dubois and Narayan, 2003), Zhang and Sun used maleic anhydride (MA) instead. By using 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (L101) as initiator in improvement compatibility among PLA, starch and MA; proposed chemical reaction as shown in Scheme 2.2. Mechanical properties increased markedly. the PLA/starch composites at a ratio of 55/45 compatibilized by 1% MA and initiated by 10% L101 (MA basis) resulted in the highest tensile strength and elongation (Zhang and Sun, 2004).



Scheme 2.2 Proposed chemical reactions among PLA, starch, MA and initiator L101 (Zhang and Sun, 2004).

MA derivatives such as dioctyl maleate (DOM) also used as compatibilizer, below 5% DOM tensile strength can improve the tensile strength of the blend. However, DOM is able to function as a plasticizer at concentration over 5% significantly enhancing elongation. Although DOM has the excellent performance, it is still inhibited for leaching in an aqueous environment (Zhang and Sun, 2004).

Organosilane coupling agent, considered as another effective compatibilizer to combine two immiscible phases, comprise of two reactive sites (hydrolysable and organofunctional groups). The hydrolysable group is only intermediate in silanol formation for bonding to mineral surface while the organofunctional group reacts with polymer (Plueddemann, 1982). Starch surface treated by silanes had been investigated to increase the compatibility of polyethylene film containing starch as filler. The silane treated starch addition is restricted to a maximum of 10% by weight (Griffin, 1994). The effect of incorporating an aminopropyltriethoxysilane coupling agent at different contents on physical properties and morphology of the polycaprolactone/starch/pine-leaf composites was studied. This silane coupling agent led to a much better interfacial compatibility between PCL matrix and the fillers, resulting in their improve physical properties (Kim *et al.*, 2007). 1 wt% organo-silane was applied in wood flour/talc-filled PLA composites by melt compounding and injection molding, the crystallinity of composite decreased while tensile modulus was improved (Lee *et al.*, 2008).

2.4.2 Applied Block Copolymer as a Third Component

Chen and coworkers prepared the starch grafted PLLA (St-g-PLLA) by ring-opening graft copolymerization of a L-lactide monomer in the presence of $\text{Sn}(\text{Oct})_2$ as a catalyst. St-g-PLLA showed the amphiphilic character and provided the good adhesion between hydrophobic PLLA and hydrophilic starch, the mechanical properties of the PLLA composite blended with St-g-PLLA were much better than that of the PLLA/starch blending composite(Chen *et al.*, 2005).

Due to the advantages of amphiphilic molecules, most of PLA block copolymers, synthesized in the past, were PLA copolymerized with polyols (polyethylene glycol, polyethylene oxide, polypropylene glycol, etc.) which can also act as plasticizer in blending system. Copolymers of ethylene glycol or ethylene oxide with lactic acid and the possibility to have different chain termination groups are also of great interest to manipulate PLA's properties. Kubies and coworkers (2000) prepared amphiphilic A-B-A block copolymers of polylactide (PLLA) and polyethylene oxide (PEO). $\text{PLLA}_{12000}\text{-PEO}_{6100}\text{-PLA}_{12000}$ copolymer can reduce the phase separation of PEO domains in PDLLA/copolymer blend. When a shorter PEO

block was applied in block copolymer, the melting endotherm could not be observed. This might cause an increase phase compatibility (Kubies *et al.*, 2000). Moreover, di- and triblock copolymers of PLLA and PEG were used as compatibilizers for the immiscible blend of polyhydroxybutyrate (PHB) and high molecular weight PLLA because PEG is compatible to PHB (Yoon *et al.*, 2000).

In 2002, multiblock PLA-PEG copolymers were synthesized by polycondensation of PLA diols and PEG diacids, they could improve miscibility between the two components. The crystallinity of copolymers was largely decreased in comparison with PLA and PEG homopolymers, and could be modulated by adjusting the block lengths of both components. However, these molecules was interesting for biomedical uses (Luo *et al.*, 2002).

A series of diblock copolymers of PLLA-*b*-PEG were investigated, both blocks are crystallizable and biocompatible by PLLA blocks were crystallized first at around 110 °C and PEG blocks were crystallized later, after the samples are further cooled to close to room temperature (Sun *et al.*, 2004).

Recently, PEG-PPG-PEG triblock copolymers were applied to PLA as plasticizers. The crystallization driven phase separation occurred in all the annealed blends but led to different structures depending on the plasticizer used. In addition, PLA crystallization was more enhanced in the blends with copolymers than with PPG while the influence of copolymers on the ductility of amorphous PLA was similar to that of PPG. The copolymers were markedly more ductile after annealing than the annealed neat PLA, with elongation at break up to 12 times larger (Kowalczyk *et al.*, 2012).

2.5 Strain Induced Crystallization of PLA *via* Process

One prevailing in polymer processing operations such as injection molding, extrusion, etc., crystallization is also preceded by rapid polymer flow that can bring to strain-induced crystallization. The strain-induced nucleation of PLA has a positive effect on the overall crystallization of foamed, molded or extruded PLA. In uniaxial processes, high stiffness can be obtained in the drawing direction. However, uniaxially oriented materials exhibit very large differences in the mechanical

properties in the machine (MD) and transverse (TD) directions. The use of a two-stage biaxial drawing process to manufacture the films can provide different values in two directions as a function of the order and extent of drawing, or also can be used to provide equivalent properties in the two directions.

Crystalline structure and orientation of cast amorphous linear and branched PLA films were developed during uniaxial stretching in the temperature range 60-80 °C. The crystal destruction at high deformations observed in the linear films is not observed in the branched films. Upon stretching the material undergoes rapid orientation in the amorphous state and highly oriented β crystalline form chains with -3_1 helix beyond a critical level. At or below T_g , with additional stretching, the films were found to revert to a highly oriented amorphous state through the destruction of the crystalline domains (Kokturk *et al.*, 2002; Stoclet *et al.*, 2012).

Rao *et al* (2008) showed the relationship between microstructure and toughness of biaxially stretched semi-crystalline polyester films. The results indicated that the toughness of a semicrystalline polymeric film is determined by the interconnectivity of the crystalline phase within the amorphous phase and is greatly influenced by the degree of crystallinity and the underlying crystalline morphology (Rao *et al.*, 2008).

Influence of biaxial stretching mode on PLA crystalline texture and structural hierarchy in constrained annealing of PLA films were illustrated by Ou and Cakmak (2008 and 2010). They found that simultaneously biaxial stretching (SB) always leads to films with in-plane isotropy and poor crystalline order. In sequentially biaxial stretching (SEQ), the primary crystals stretched along machine direction (MD) were gradually destroyed during other realignment in the secondary transverse stretching (TD). This destruction was evidenced by decrease of crystallite size in MD. For constrained annealing of as stretched films, it leads to enhancement of structural order by increasing crystal size, perfection and crystalline fraction regardless of deformation mode and extension. The extended helical chain conformation developed during stretching. In-plane isotropy was consistently developed by SB, upon annealing (100) uniplanar texture was found to dominate. Bimodal (cross-hatched) orientation distribution was found that indicated the unbalanced biaxial stretching (SEQ) at intermediate and balanced biaxial

deformation stages. At high deformation levels, in plane isotropy in SEQ could only be attained in unbalanced biaxial deformation conditions (Ou and Cakmak, 2008; Ou and Cakmak, 2010).

PLA blended with thermoplastic starch (TPS) and maleic anhydride grafted PLA/TPS blend were processed by biaxial stretching. Compatibilizing blend reduced the TPS minor phase size and coalescence, and favored deformation in MD during cast extrusion. The tensile modulus and strength of cast sheets decreased with TPS content, while the elongation at break remained similar to that of pure PLA. At 70 °C, the tensile modulus and tensile strength increased as a function of biaxial draw ratio and the elongation at break only increased significantly for the blends having low TPS contents. Whereas the addition of TPS to PLA at 90 °C did not improve its mechanical properties which essentially remained constant (Chapleau, 2007).

2.6 Points of Research

Overcoming PLA brittleness can be achievable by balancing of crystalline and amorphous phases. Blending PLA with nucleating agent and/or plasticizer is an attractive way for toughening PLA film. Starch and thermoplastic starch are promising nucleating agents due to fully biodegradability and cost effectiveness. Also, PEG is a biocompatible and environmental friendly plasticizer. However, the incompatibility issue of PLA-based blends is concerned and limits in utilizations. It is well known that silane coupling agents can improve interfacial adhesion through chemical bonds formation. Additionally, the miscibility is able to be obtained by using block copolymer structure for strengthening physical interaction between block copolymer and polymer matrix. These enhanced interactions lead to the significantly improved PLA performances. Furthermore, the change of PLA physical properties by processing conditions is rarely clarified in details.

On the basis of the above considerations, the present work proposes the simply modified starch by various propyltrimethoxysilane coupling agents with an ultimate goal to enhance compatibility and crystallization with satisfactorily clarified molecular structure (Chapter III). In Chapter IV, the work is focused on PLA

microstructure change under biaxial-stretching process with systematically varied stretching rates and draw ratios. The relationship between various PLA regularization and toughness improvement is established. The first work is extended to develop PLA/TPS modified with silane film in which the physical characteristics are investigated and proposed to further use in agricultural field (Chapter V). Moreover, we also propose PLLA-PEG-PLLA block copolymers with simply preparation as effective plasticizer to promote crystallization and plasticity of PLA films without PEG recrystallization (Chapter VI).