EFFECT OF NUCLEATING AGENTS ON PROPERTIES

OF NATURAL RUBBER TOUGHENED

POLYLACTIC ACID

Buncha Suksut

A Thesis Submitted in Partial Fulfillment of the Requirements for

the Degree of Master of Engineering in Polymer Engineering

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ผลของสารก่อผลึกต่อสมบัติของพอลิแลกติกแอซิด
เสริมความเหนียวด้วยยางธรรมชาติ

นายบัญชา สุขสุทธิ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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บัญชา สุขสุทธิ์ : ผลของสารก่อผลึกต่อสมบัติของพอลิแลกติกแอซิดเสริมความเหนียว
ด้วยยางธรรมชาติ (EFFECT OF NUCLEATING AGENTS ON PROPERTIES OF
NATURAL RUBBER TOUGHENED POLYLACTIC ACID)
อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.จันทิมา ดีประเสริฐกุล, 68 หน้า.

พอลิแลกติกแอซิด (polylactic acid, PLA) เป็นพอลิเมอร์ที่มีความแข็งแรงและค่ามอดูลัส
ของยังก์สูงแต่มีความเหนียวและความสามารถในการตกผลึกต่ำ จึงมีการใช้ยางธรรมชาติในการ
เพิ่มความเหนียวและสารก่อผลึกในการปรับปรุงความสามารถการตกผลึก ในการศึกษานี้ได้ใช้สาร
ก่อผลึก 3 ชนิด คือ แคลเซียมคาร์บอเนต (calcium carbonate, $CaCO_3$) ทัลก์ (talc) และ แอลฟา
ไซโคลเดกซ์ตริน (cyclodextrin, α-CD) โดยศึกษาผลของสารก่อผลึกต่อความสามารถการตกผลึก
สมบัติเชิงกลและสัณฐานวิทยาของพอลิเมอร์ผสมระหว่างพอลิแลกติกแอซิดและยางธรรมชาติ
และเปรียบเทียบกับพอลิแลกติกแอซิดล้วน จากผลของดิฟเฟอร์เรนเชียลสแกนนิงคาลอริเมทรีหรือ
ดีเอสซี (differential scanning calorimetry, DSC) พบว่าการเติมทัลก์และแอลฟา ไซโคลเดกซ์ตริน
ลงในพอลแลกติกแอซิดทำให้อุณหภูมิการเกิดผลึกระหว่างการให้ความร้อน (cold crystallization
temperature, T_{cc}) ลดลง เช่นเดียวกับในกรณีของพอลิเมอร์ผสมที่มีทัลก์ สารก่อผลึกทั้งหมดเพิ่ม
ปริมาณผลึก (degree of crystallinity, X_C) ในพอลิแลกติกแอซิด ขณะที่ในพอลิเมอร์ผสมมีเพียง
ทัลก์เท่านั้นที่เพิ่มปริมาณผลึกของพอลิแลกติกแอซิด อิทธิผลของสารก่อผลึกต่อสมบัติเชิงกลซึ่ง
ศึกษาโดยวิธีการทดสอบการดึง การทดสอบค่าความต้านทานต่อแรงกระแทกแบบไอซอดซึ่งทำ
รอยบากตรงกลาง และการวิเคราะห์เชิงกลพลวัตหรือดีเอ็มเอ (dynamic mechanical analysis,
DMA) พบว่าการเติมสารก่อผลึกส่งผลให้ค่าความเหนียวของพอลิแลกติกแอซิดเพิ่มขึ้น
อันเนื่องมาจากการลดลงของขนาดสเฟียรูไลท์ (spherulite) ของพอลิแลกติกแอซิด จากดีเอ็มเอ
พบว่าอุณหภูมิเปลี่ยนสภาพแก้ว (glass transition temperature, T_g) ไม่มีการเปลี่ยนแปลงเมื่อเติมสาร
ก่อผลึกซึ่งตรงกับผลที่ได้จากดีเอสซี การมีอนุภาคของสารก่อผลึกและ โครงสร้างของผลึกในพอลิ
แลกติกแอซิดขัดขวางการเคลื่อนที่ของสายโซ่พอลิเมอร์เป็นผลให้ความสูงของแทนเจนต์สูญเสีย
(tan δ) ลดลง ถึงแม้การเติมสารก่อผลึกจะทำให้ขนาดของอนุภาคยางธรรมชาติเพิ่มขึ้นแต่ก็ไม่ส่งผล
ต่อสมบัติเชิงกล

สาขาวิชาวิศวกรรมพอลิเมอร์   ลายมือชื่อนักศึกษา_____
ปีการศึกษา 2552   ลายมือชื่ออาจารย์ที่ปรึกษา_____

BUNCHA SUKSUT : EFFECT OF NUCLEATING AGENTS ON PROPERTIES OF NATURAL RUBBER TOUGHENED POLYLACTIC ACID. THESIS ADVISOR : ASST. PROF. CHANTIMA DEEPRASERTKUL, Ph.D., 68 PP.

POLYLACTIC ACID/NATURAL RUBBER/NUCLEATING AGENT/CALCIUM CARBONATE/TALC/α-CYCLODEXTRIN

Polylactic acid (PLA) presents high strength and modulus, but very low toughness as well as slow crystallization rate. Natural rubber (NR) is considered to enhance the toughness and nucleating agent is used to improve the crystallization. Three nucleating agents, calcium carbonate ($CaCO_3$), talc and cyclodextrin (CD) were used. Here effects of nucleating agent on crystallization, mechanical properties and morphology of the PLA/NR blend in comparison to the neat PLA were investigated. The differential scanning calorimetry (DSC) results showed that the addition of talc or CD decreases cold crystallization temperature (T_{cc}). Same result was obtained in PLA/NR10 containing talc. All nucleating agents increased the degree of crystallinity (X_C) of PLA, whereas only talc increased X_C of PLA in PLA/NR10 blends. The influence of nucleating agent on mechanical properties was studied by tensile testing, notched Izod impact testing and dynamic mechanical analysis. From mechanical results, the addition of nucleating agent enhanced the toughness of PLA due to the decrement in spherulite size of PLA. Glass transition temperature (T_g) from DMA result did not change with nucleating agent, in good agreement with DSC result. Further, nucleating agent particle and crystalline structure restricted the free chain mobility, leading to the decrease of the height of tan δ peak. Microscopic observation

revealed that the increment in size of NR particle with nucleating agent did not influence mechanical properties of blends.

School of <u>Polymer Engineering</u>　　　　Student's Signature_____

Academic Year 2009　　　　　　　　Advisor's Signature_____

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SYMBOLS AND ABBREVIATIONS

%	=	Percent
°C	=	Degree Celsius
ΔH_c	=	Crystallization enthalpy
ΔH_m	=	Melting enthalpy
ΔH^o_m	=	Melting enthalpy of a 100% crystalline polymer
Φ	=	Weight fraction
μm	=	Micrometer
X_c	=	Degree of crystallinity
Å	=	Angstrom
β	=	Beta
γ	=	Gamma
α	=	Alpha
D_i	=	Diameter of the particle
D_v	=	Volume average diameters
E'	=	Storage modulus
E˝	=	Loss modulus
g	=	Gram
J	=	Joule
kJ	=	Kilojoule
kN	=	Kilonewton

SYMBOLS AND ABBREVIATIONS (Continued)

kV	=	Kilovolt
n_i	=	Total number of diameter particle
nm	=	Nanometer
m^2	=	Square meters
mg	=	Milligram
ml	=	milliliter
min	=	Minute
mm	=	Millimeter
MPa	=	Megapasca
M_w	=	Molecular weights
rpm	=	Revolution per minute
tan δ	=	Tan delta
T_c	=	Crystallization temperature
T_{cc}	=	Cold crystallization temperature
T_g	=	Glass transition temperture
T_m	=	Melting temperature
T^o_m	=	Equilibrium melting temperature
V_i	=	Total volume of diameter particle
wt	=	Weight

CHAPTER I

INTRODUCTION

1.1   General introduction

In recent years, the biodegradable polymers have been attracted increase attention as environmental friendly materials. The most popular biodegradable polymers are aliphatic thermoplastic polyesters, such as poly(butylene succinate) PBS, poly(3-hydroxybutyrate) PHB, poly(ε-carprolactone) PCL and polylactic acid PLA. PLA is a biodegradable polymer produced from renewable biomass such as corn, sugar and beat. In the past decades, PLA is the most widely used and has been applied to many products such as cloths, medical applications, especially in packaging applications. It exhibits the environmentally friendly, good clarity, high strength and moderate barrier properties. However, the problems of PLA are the mechanical brittleness and slow crystallization rate, inducing more difficult to control the processing.

The improvement of mechanical brittleness can be done by adding the rubber material in polymer matrix. Good dispersion of the small rubber particles in the polymer matrix is the basis of the improvement. Based on theories of rubber toughened polymer, the blend morphology and characteristics such as average rubber particles size and the content of rubber influence on the final mechanical properties (Miles and Rostami, 1992). The phase morphology and mechanical properties of rubber toughened polymers depend on type and content of the rubber

(Miles et al., 1992), type and content of the compatibilizer (Tanrattanakul et al., 1997), the viscosity ratio and the mixing condition (Rauwendaal, 1998).

Generally, the improvement of crystallization rate of polymer can be achieved by the addition of nucleating agents. Nucleating agent could help increase nuclei density, reduce spherulite size thus increases overall crystallization rate. When blended with PLA, many biodegradable polymers e.g. poly(butylenes adipate-co-terephtalate) (PBAT) (Jiang, Wolcott and Zhang, 2006), PBS (Yokohara and Yamaguchi, 2008), poly(ethylene oxide) (PEO) (Nijenhuis, Colstee, Grijpma, and Pennings, 1996) and poly(ethylene glycol) (PEG) (Kulinski and Piorkowska, 2005) were found to act as nucleating agents for PLA.

The addition of specific additives or nucleating agents to shorten the induction time of crystallization and accelerate the formation of nuclei is commonly used in industry to shorten the processing times and to govern the polymer properties. One of most popular nucleating agents to improve the crystallization of polymers is talc. Talc is an inorganic filler composed of hydrated magnesium silicate with the chemical formula of $Mg_3Si_4O_{10}(OH)_2$ and is naturally hydrophobic filler (Ibrahim, Mobarak, El-Din, Ebaid, and Youssef, 2009). Although talc is very effective for most polymers, it can induce tumors in the ovaries and lungs of cancer victims (Dong, He, Zhu, Shin, and Inoue, 2005). Calcium carbonate ($CaCO_3$) is commonly used in polymer as inorganic filler. The reinforcement of various polymers (Bartczak, Argon, Cohen, and Weinberg, 1999; Zuiderduin, Westzaan, Huetink, and Gaymans, 2003; Zuiderduin, Huetink and Gaymans, 2006; Jiang, Zhang, and Wolcott, 2007) with micro- and nano-sized $CaCO_3$ particles was studied. It was found that the presence of nano-sized

precipitated calcium carbonate (NPCC) in PLA matrix also act as a nucleating agent to increase the crystallization rate of PLA (Jiang et al., 2007).

Attempts have been made to find an environmental friendly alternative. Cyclodextrin (CD) is a natural and environmental friendly compound which can be used as a nucleating agent for biodegradable polymers (Dong et al., 2005). The cyclodextrins (CDs) are well-known as biodegradable additives. The CDs are produced from renewable natural material, starch. They are environmental friendly additives and have low toxicities in the animals and humans (Dong, Shin, Zhu, and Inoue, 2006). Because of their properties, CDs are considered as green nucleating agent for biodegradable polymers. As shown in Figure 1.1, the CDs are cyclic oligomers of amylose consisting of six, seven or eight glucose units and are named alpha (α), beta (β) and gamma (γ) CDs, respectively (Peet, Rusa, Hunt, Tonelli, and Balik, 2005). Although the depth of cavities for three CDs is the same, about 7.9 angstrom (Å), their internal cavity diameters are about 4.9, 6.2 and 7.9 Å, respectively. Due to the chemical structure of CD molecules, their cavities can form inclusion complexes. The inclusion complex is a complex in which one component forms a cavity so-called the host and the other component is located within so-called the guest. The CDs are the host and the guest polymer chains are included inside the CD cavity. The inclusion complex has been used as nucleating agent in biodegradable polymers (Dong et al., 2005).

There are few publications studying the effect of nucleating agent on rubber toughened PLA. In the present work, the effect of nucleating agent on crystallization and mechanical properties of both neat PLA and rubber toughened PLA were focused. Morphology of rubber toughened PLA was also investigated.
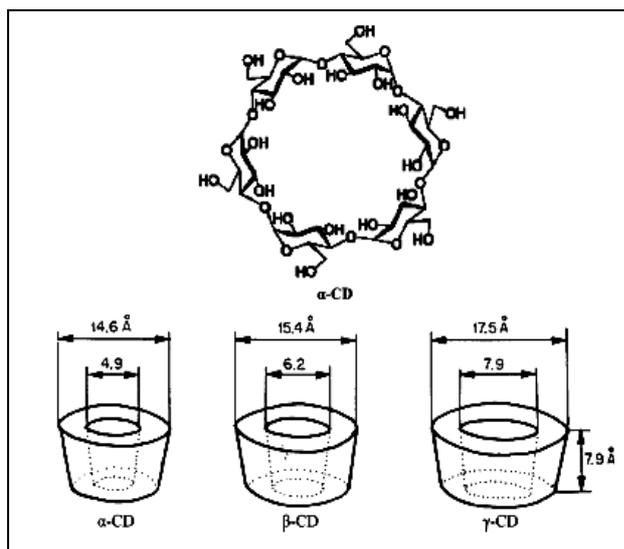
Figure 1.1 Structure and diameter of cyclodextrins (CDs) (Peet et al., 2005).

1.2   Research objectives

The main objectives of this study are:

(i) To understand the effect of nucleating agents on the crystallization behavior of natural rubber toughened PLA.

(ii) To study the effect of nucleating agents on the mechanical properties of natural rubber toughened PLA.

1.3   Scope and limitation of the study

In this study, the effect of nucleating agent on crystallization and mechanical properties of neat PLA and PLA/NR blend were investigated. The blend of PLA/NR at compositions of 90/10 (wt/wt) was prepared. Three types of nucleating agent, calcium carbonate, talc and α-cyclodextrin are used as nucleating agents. Blends with 1wt% nucleating agent were prepared. Properties being investigated include thermal, tensile, impact, dynamic mechanical properties and morphological properties.

CHAPTER II

LITERATURE REVIEW

2.1   Crystallization of polymers

The crystallization process consists of two major steps, nucleation and crystal growth. Nucleation is the step where molecule dispersed in system forms the nuclei. Nucleation is classified as homogeneous or heterogeneous process. For homogeneous nucleation, the nuclei form spontaneously. On the other hand, for heterogeneous nucleation, nuclei are induced by foreign particles such as impurities and nucleating agents (Young and Lovell, 1991). The second step in the crystallization process is the crystal growth where the nuclei grow. Therefore, crystallization is a process which takes place by two distinct steps, nucleation and growth which are separately considered (Tadmor and Gogos, 1979; Young et al., 1991).

2.1.1   Crystallization kinetics

In the nucleation step, the density of nuclei depends on the temperature of crystallization. The nucleation of polymer melt occurs below melting temperature. The random tangled molecules in melt align and form small ordered regions, which are called nuclei (Young et al., 1991). The formation of nuclei depends on degree of supercooling (T^{o}_{m}-T_{c}). T^{o}_{m} and T_{c} are the equilibrium melting temperature and crystallization temperature of crystalline polymer, respectively (Utracki, 2002). At low degree of supercooling, the nuclei densities are low. The small number of large spherulites is obtained. On the other hand, when the degree of supercooling is

increased (low T_c), a high nuclei density and a large number of small spherulite are obtained (Tadmor and Gogos, 1979; Young et al., 1991).

The growth of nuclei can take place in one, two or three dimension with the crystals in the form of rods, discs or spheres, respectively (Young et al., 1991). The growth of polymer crystals takes place by the incorporation of the polymer chain within crystals which are lamellar crystals. The lamellar crystals often aggregate into supermolecular structures known as spherulites. The change of spherulite radius at a given crystallization temperature is usually linear with time and is called growth rate (G). The growth of spherulites stops when the impingement of neighbor spherulites occurs.

Thermal analysis is usually applied to determine the crystallization kinetics either under isothermal or non-isothermal conditions. For isothermal case, the temperature is fixed and crystallization behavior is studied as a function of time. The half-time of crystallization ($t_{1/2}$) can be calculated. In the case of non-isothermal crystallization, crystallization behavior is studied as a function of temperature. The crystallization temperature (T_c) and the crystallization enthalpy (ΔH_c) values are taken as the position of the peak and the area of the crystallization exotherm in the cooling run, respectively (He and Inoue, 2003). The cold crystallization temperature (T_{cc}) value is a maximum of the exotherm in heating run (Li and Huneault, 2007). The melting temperature (T_m) and the melting enthalpy (ΔH_m) values are taken as the position of the peak and the area of the melting endotherm in the heating run, respectively (He et al., 2003). For polymer sample, the T_m is always greater than the T_c and T_{cc}. Usually, a higher T_c, a lower T_{cc} and a narrower crystallization

temperature range indicate a faster crystallization and a higher crystallization rate (Dong et al., 2005)

2.1.2   Nucleating agents

Nucleating agents are small crystalline particles that are dispersed in crystallizing melt and remain solid at the crystallization temperature. When the crystallization temperature is higher than the melting temperature of nucleating agents, the nucleation effect of nucleating agent does not appear in the blend of polymer matrix and additive or nucleating agent (Nam et al., 2006). Nucleating agents are often added to polymer matrix to improve the crystallization behavior. The crystallization temperature, the crystallinity and the crystallization rate increase with the nucleating agent effect (Xu, Lei, and Xie, 2003). Usually, the presence of nucleating agent gives smaller polymer spherulite size (Tadmor et al., 1979; He et al., 2003; Nam et al., 2006; Reignier, Tatiboŭt, and Gendron, 2006). Nucleation occurs at nucleation site on surface of nucleating agents. The larger surface area to volume ratio of nucleating agent gives rise to more nucleating sites (Jiang et al., 2007). Not only small molecule additives, but polymer and stereocomplex can also act as nucleating agent.

2.1.2.1 Small molecule additives

Several important nucleating agents were investigated in the literature. Inorganic additives such as talc and $CaCO_3$ have been widely used to improve the crystallization and mechanical properties of polymers. Many researchers focused on the nucleating effect of talc in polymer matrix. Talc is a good nucleating agent for crystallization of PCL (Reignier et al., 2006) and poly(ethylene terephthalate) (PET) (Agarwal, de Wit and Lemstra, 2002) as shown by the increase

in crystallization temperature upon cooling. The presence of talc gave the smaller spherulite size of PCL crystal (Reignier et al., 2006). In PET, the crystallization rate increased with addition of talc (Agarwal et al., 2002). In the case of PLA, Li and Huneault (2007) reported that both the crystallization rate and crystallinity increased. The addition of 1wt% of talc gave a sharp crystallization peak at 90°C. When the 1wt% of talc and 10wt% of PEG plasticizer were added simultaneously, a very sharp crystallization peak was observed and this peak was shifted to 105°C. This indicates that the talc and PEG have a synergistic effect on crystallization of PLA.

$CaCO_3$ is commonly used filler although it has been reported to be a potential nucleating agent. The addition of micron size of $CaCO_3$ to the polymer matrix was studied. HDPE containing $CaCO_3$ with a particle size of 0.44-3.50 μm was studied (Bartczak et al., 1999). In the case of PP/ethylene-propylene rubber (EPR), $CaCO_3$ with a particle size of 5 μm was used (Zebarjad, Sajjadi, and Tahani, 2006). From differential scanning calorimetry (DSC) results, it showed that the micron particle size filler showed no effect on crystallization behavior and the degree of crystallinity of the polymer composites (Bartczak et al., 1999; Zuiderduin et al., 2006). In contrast to micron size, nanoparticle size filler offers the larger surface area which allows improving the crystallization properties better than microparticle filler. Chan et al. (2002) studied the crystallization of PP and $CaCO_3$ nanocomposites. The average particle size of $CaCO_3$ is about 44 nm. The crystallization temperature of PP was increased about 10°C when the $CaCO_3$ nanoparticles were added to PP matrix. However, the $CaCO_3$ particles aggregated during processing, leading to the decrease of the composite mechanical properties. The filler surface treatment reduces the particle-particle interaction leading to a better dispersion of particles in the polymer

matrix. The presence of $CaCO_3$ nanoparticles coated with polypropylene-maleic anhydride graft copolymer (PPMA) in the isotactic polypropylene (iPP) matrix enhanced the spherulite growth rate (He et al., 2003). Jiang et al. (2007) investigated crystallization behaviors of PLA nanocomposites with nano-sized precipitated calcium carbonate (NPCC) and found that the NPCC shifted the cold crystallization peak to lower temperature and increased the crystallinity when compared with the pure PLA.

The addition of organically modified montmorillonite (OMMT) into PLA matrix has been investigated. Besides the mechanical properties, montmorillonite clay can improve the crystallization of PLA. Jiang et al. (2007) prepared the PLA nanocomposite with MMT. The DSC results showed the cold crystallization temperature decreased with an addition of 5 or 7.5wt% MMT. The MMT gave higher crystallinity when compared with the pure PLA. At the same content, MMT showed more effective than NPCC by giving a lower cold-crystallization temperature and a higher crystallinity. This is due to the larger surface area to volume ratio of the clay particulates.

Nucleating agents are typically either low molecular weight organic or inorganic additives. Nam et al. (2006) studied the crystallization behavior of PLA containing the organic additives having low molecular weight. An aliphatic amide (AA) namely N-N-ethylenebis(12-hydroxystearamide) (WX1) was used as nucleating agent. The addition of WX1 with 1wt% leads to an increase of the overall crystallization rate of PLA. The average spherulite size is decreased by adding WX1 due to the increase in number of nuclei. The average spherulite diameter increased with increasing the crystallization temperature. However, at crystallization

temperature of 150°C, the spherulite size with addition of WX1 does not change. This is because the crystallization temperature is higher than melting temperature of pure WX1. This suggests that the nucleation effect of WX1 does not appear above melt temperature of pure WX1. The melting temperature was used as a key factor to choose the nucleating agent for the polymer.

The use of CDs has been investigated to enhance the crystallization of biodegradable polymers. He et al. (2003) studied the crystallization of PHB with an addition of 1wt% of α-CD. It was found that the α-CD increased the crystallization rate and shifted crystallization to the higher temperature upon cooling. The nuclei density of PHB was increased by adding uncomplexed α-CD, resulting in the small spherulites size. The CDs can form inclusion complexes (ICs) and its ICs acts as nucleating agent. The 2wt% of PCL-IC was used as the nucleating agent for PCL matrix. Both the crystallization temperature upon cooling and the crystallization rate of PCL were increased with addition of PCL-IC. The average spherulite diameter of PCL with addition of PCL-IC is smaller than that of pure PCL. Similar results were observed in the PBS crystallization containing 2wt% of PBS-IC (Dong et al., 2005). Besides the uncomplexed CD and inclusion complexed forms, the coalesced polymer which is obtained by removing the host CD can act as nucleating agent. Wei et al. (2003) studied the crystallization of PLLA coalesced from its α-CD-ICs. The PLLA having low molecular weight (7,000 g/mol) was used in the study. The coalesced PLLA gave the shorter crystallization half time ($t_{1/2}$) than that of pure PLLA. It indicated that the coalesced PLLA can enhance the crystallization rate of PLLA.

Plasticizers are additives having low molecular weights that increase plasticity or flexibility of the polymer matrix. The addition of plasticizer can

also enhance the crystallization behaviors of polymer matrices. Poly(ethylene glycol) (PEG) is the most studied plasticizer for PLA. The effect of molecular weights (M_w) on the plasticization was investigated. Two PEGs with M_w equal to 400 g/mol and 600 g/mol were used as plasticizers for PLA (Kulinski et al., 2005). The lower molecular weight plasticizer enables increased miscibility with more effective reduction of T_g of PLA. The T_g value is decreased with increasing the PEG content. The cold crystallization peak were narrowed and shifted to lower temperature. T_{cc} values depended on the plasticizer content but were independent of the molecular weight. T_{cc} values of PLA were decreased when the PEG content increased. In the case of plasticized PLA with poly(propylene glycol) (PPG), it was found that the PPG enhanced the spherulite growth rate, but that less than the PEG. Both the growth rate of PLA in PLA/PPG and PLA/PEG increased with increasing PPG and PEG content (Piorkowska, Kulinski, Galeski, and Masirek, 2006)

2.1.2.2 Polymer component

Polymer blends can be classified into miscible or immiscible blend. The immiscible polymer blends can crystallize by adding at least one crystalline component. For crystalline/crystalline system, both components are crystallizable, while crystalline/amorphous system, only one component can crystallize either the matrix or the dispersed phase (Utracki, 2002). Crystallization behavior of immiscible polymer blends was widely investigated. It was found that the polymer component can improve the crystallization behaviors of the immiscible polymer blends. Blending PLA with other polymers can also modify the crystallization behavior. These polymers, for example, are PBAT (Jiang et al., 2006), poly(butylene succinate) (PBS) (Yokohara et al., 2008) and poly(ethylene oxide)

(PEO) (Nijenhuis et al., 1996), which are also biodegradable. It was found that the cold-crystallization temperature of PLA shifted to lower temperature (Jiang et al., 2006; Yokohara et al., 2008). The increase in the crystallization rate was observed by adding PBAT. However, in the presence of PBAT, the crystallinity of blends did not significantly change (Jiang et al., 2006). Nijenhuis et al. (1996) investigated the crystallization of the PLLA and PEO blends. The PEO gave the faster crystallization. The cold crystallization peak of PLLA shifted to lower temperature with increasing the PEO content.

Besides the thermoplastic polymer, rubber in the polymer blends also acts as nucleating agent. The presence of polystyrene-poly(ethylene-co-butylene)-polystyrene (SEBS) component led to a small increase in the T_c value of iPP in the iPP/SEBS blends (Fanegas, Go´mez, Marco, Jime´nez, and Ellis, 2007). Same result was observed in the PET/NR blends. By adding the NR, the T_{cc} of PET in the PET/NR blends decreased about 40ºC from the pure PET (Phinyocheep, Saelao, and Buzare, 2007). In the case of PP and ethylene-propylene rubber (EPR) blends, when the molecular weight of EPR decreased, the crystallization rate increased. It was explained by the decrease in viscosity and the increase in polymer chain mobility for the folding process (Choi and Kim, 2004). For the PLA nanocomposite, when the maleic anhydride-grafted ethylene propylene rubber (EPMgMA) was added into the PLA/organo-montmorillonite (OMMT) nanocomposites, the T_cs of PLA, PLA/OMMT and PLA/OMMT/EPMgMA are 113, 100 and 99°C. The T_c of composites did not change with addition of EPMgMA rubber (Chow and Lok, 2009).

Stereocomplexation between PLLA and poly(D-lactic acid) (PDLA) is one of the most effective methods for enhancing the thermal properties of PLA based materials. The stereocomplex forms side by side packing mechanism. Therefore, it has a higher density and melting point than the other crystal form (α-,β- and γ-forms) (Tsuji and Tezuka, 2004). The stereocomplex strongly affects its crystallization behaviors. The crystallization behaviors of PLLA with addition of PDLA were improved by stereocomplex formed as nucleating agent in PLLA/PDLA blends. The solution mixing of PLLA and PDLA in 50/50 blend ratio was prepared. The stereocomplex has a melting temperature of 224°C, which is about 60°C higher than that of pure PLLA or PDLA. The higher spherulite growth rate and density of the stereocomplex spherulite were observed. The crystallization of PLLA blended with 1 to 5wt% of PDLA was studied (Yamane and Sasai, 2003). The blend with PDLA enhanced the crystallization temperature and crystallization peak increased with increasing PDLA content. Low molecular weight of PDLA in PLLA matrix did not form stereocomplex crystallites with a large surface area enough to acts as nucleation site. On the contrary, high molecular weight PDLA chains formed a large stereocomplex crystallite. With increasing the molecular weight of PDLA, the crystallization temperature was increased.

As mentioned earlier, besides the mechanical brittleness of PLA, its slow crystallization limits its application range. Many studies have been done to improve its toughness.

2.2   Toughness of polymers

The application of polymer in automobiles, household appliances, construction and packaging industry requires good chemical and moisture resistance, high stiffness and toughness. The toughness of polymeric material is an important selection criterion for many applications. The toughness can be investigated by the mechanical testing such as impact and tensile testing. Impact toughness of material reflects the degree of energy absorption from the beginning mechanical load to final fracture (Kim and Michler, 1998). In the case of tensile testing, the tensile toughness can be calculated from the area under the stress-strain curve. The elongation at break of tensile testing is also used to represent the toughness. The toughness increased with increasing elongation at break (Kulinski et al., 2005; Jiang et al., 2006; Piorkowska et al., 2006). The improvement of the toughness can be done by adding the filler particles, polymer component such as thermoplastic or rubber material in polymer matrix. When one component was added to polymer matrix to improve the toughness, the decrease in stiffness and strength is usually inevitable.

2.2.1   Fillers

Impact modifiers are additives that enhance toughness when filled to polymers. Commercially available impact modifier is typically blended in PET to improve toughness. Lucalen A3110 MQ 244, which is a commercial ethylene/acrylic acid/acrylate terpolymer and Paraloid EXL, which is a commercial core/shell acrylic was used as impact modifier (Kolarˇıˊk and Pegoretti, 2004). Furthermore, several fillers have been used to improve the stiffness of polymer matrix. It was also found that an increase in the toughness can be obtained with the addition of particulate filler such as silica and $CaCO_3$ particles. With an addition of $CaCO_3$, an increase in notch

Izod impact strength was found in PP (Zuiderduin et al., 2003), HDPE (Bartczak et al., 1999) , ABS (Jiang et al., 2005), and aliphatic polyketone (PK) (Zuiderduin et al., 2006). Furthermore, it was also found that the mechanical properties of polymer filled with nano-sized filler particles are superior to those filled with micron-sized filler particles. This could be due to the larger interfacial area between the particles and polymer matrix (Jiang et al., 2005).

2.2.2 Polymer component

The improvement of the toughness with the blending of polymer/thermoplastics component has been investigated. To improve its toughness, PLA was blended with biodegradable polymers. It was found that the elongation at break of PLA increased while the tensile strength and modulus of PLA decreased with increasing PBAT content (Jiang et al., 2006). At 5wt% PBAT content, the elongation at break of blend greatly increased (>200%) which are higher than that of pure PLA (3.7%) and the elongation continuously increased with the PBAT content. Tensile strength decreased from 63 of pure PLA to 47 MPa of 20wt% PBAT content, while modulus decreased from 3.4 of pure PLA to 2.6 GPa of 20wt% PBAT content. The impact toughness of blend was increased with PBAT content. Impact toughness was increased from 2.6 GPa for pure PLA to 4.4 GPa for 80/20wt/wt% PLA/PBAT. The blend of PLA with PCL increases the elongation at break of blend. At 90/10wt/wt% PLA/PCL, the elongation at break is 55%, which is higher than that of pure PLA (5%) (Sarazin, Li, Orts, and Favis, 2008). Similar result was observed in blending of PLLA with PBS. The blend showed the elongation at break was higher than that of pure PLA, while the tensile strength decreased with increasing PBS content (Shibata, Inoue, and Miyoshi, 2006). The blends with PEO have been investigated. By adding

up to 10wt% PEO, a small increase in the elongation at break and a small decrease in tensile strength were found. Beyond 10wt% PEO content, the elongation at break greatly increased, while the tensile strength greatly decreased. At 80/20wt/wt% PLLA/PEO, elongation at break of the blend increases about six folds and its tensile strength decreases about three folds compared to those of neat PLA (Nijenhuis et al., 1996)

Rubber is widely used material in an improvement of polymer toughness. In PET, the rubber phase showed to be effective in enhancing the notched impact property of the blend. The impact strength of blend was increased with NR content. The tensile testing results showed the Young's modulus of PET/NR blend decreased with NR content. This is due to the elastomeric nature of NR (Phinyocheep et al., 2007). The rubber toughened polymer has been functionalized with reactive functionalities. The addition of SEBS in PET matrix was studied. The functionalization of PET/SEBS elastomer blends with maleic anhydride results in improve in the toughness of the blends. The reacted maleic anhydride acted as an emulsifier, thus decreased interfacial tension and enhanced the adhesion. The particle size of SEBS elastomer depended on the functionality content. The higher functionality gave the smaller the particle size and the narrower the particle size distribution. The toughness was decreased with increasing the functionality content (Tanrattanakul et al., 1997). Similarly, the increase in toughness was observed in rubber toughened PLLA as well as poly(3-hydroxybyrate) (PHB) (Yoon et al., 1997; Jin, Chin, M-N. Kim, S-H. Kim, and Yoon, 2000). The comparison between the use of poly(cis-1,4-isoprene) (PIP) and PIP grafted with poly(vinyl acetate) (PVAc) was investigated. The addition of PIP as well as PIP-g-PVAc caused the decrease in

Young's modulus of PLLA. Note that the Young's modulus of PLLA/PIP-g-PVAc blend is higher than that of PLLA/PIP. The elongation at break and tensile toughness of PLLA decreased with the addition of PIP. Incorporation of PIP-g-PVAc into PLLA increased both the elongation at break and tensile toughness (Jin et al., 2000). Similar observation was reported in the toughening of PHB (Yoon et al., 1997). The elongation at break and tensile toughness of PHB/ PIP-g-PVAc blend increased when compared to that of neat PHB and PHB/PIP blend.

As seen, when one component was added to polymer matrix to improve toughness, it may result in the damage of another property such as stiffness. It is often necessary to add several components in polymer matrix to obtain an optimum balance of the toughness and the stiffness. Several methods have been used to achieve a balance between both properties. The use of nucleating agents as a third component in the polymer blend showed a good balance of the toughness and the stiffness, in addition to the improvement of crystallization process (Fanegas et al., 2007).

2.3   Effect of nucleating agents on properties of toughened polymers

2.3.1   Crystallization behavior

In the rubber toughened polymers, the use of nucleating agents as a third component was investigated. It was shown that both the rubber component and the nucleating agents affect on the crystallization behavior of the blend. By filling the nucleating agent in rubber toughened polymers, the nucleating agent was more effective to improve crystallization than rubber component (Zhang et al., 2002; Fanegas et al., 2007; Bai et al., 2009). When the poly(ethylene-octene) (POE) was

added to PP matrix, the spherulite size of PP is smaller than that of neat PP. The use of the 1,3,2,4-di(p-methylbenzylidene) sorbitol (DM) as nucleating agent for PP/POE blend showed smaller spherulite size compared to that of non-nucleated PP/POE. Thus the DM has a strong influence on PP crystallization. By adding the methylene-bis-(4,6-di-tert-butylphenyl) phosphate sodium salt, ADK STAB NA 11 UH, the effectiveness to enhance the crystallization of iPP in iPP/SEBS or iPP/POE depends on the concentration and nature of rubber component. Similarly, the β-form nucleating agent aryl amides compound (TMB-5) was used as nucleating agent in PP/ethylene alpha-olefin copolymer (TAFMER elastomer) blend. The blend in the presence of nucleating agent gave a faster crystallization and a smaller spherulite size (Bai et al., 2009).

2.3.2 Mechanical properties

The use of nucleating agents not only improves the crystallization behavior of polymer blend but also improve the mechanical properties (Zhang et al., 2002; Trongtorsak, Supaphol, and Tantayanon, 2004; Bai et al., 2009). For example, the toughness of PP in PP/TAFMER blend increased with the addition of nucleating agent. The toughness of blends depends on the content of nucleating agent. The optimum of TMB-5 content is 0.2wt% for PP/TAFMER blends (Bai et al., 2009). The simultaneous use of calcium stearate and pimelic acid (Ca-Pim) as nucleating agents presented synergistic effect to enhance the toughness of iPP/EPR blend (Trongtorsak et al., 2004). When the POE was added to PP matrix, the notched Izod impact stength increased greatly with the elastomer content while the tensile strength decreased (Zhang et al., 2002). The DM was used as nucleating agent in PP/POE blends. It was found that the toughness and the stiffness of PP/POE blends increase because of the

addition of the DM. The toughness and stiffness of PP/POE blends with the addition of nucleating agent are in good balance. Both toughness and stiffness of the blends increased with addition nucleating agent. Zhang et al. (2002) related the improvement of mechanical properties of the PP/POE blends to the decrease of the PP spherulite size by adding nucleating agent. This could attribute to the large number of tie molecules and amorphous regions between the small spherulite structures (Tadmor et al., 1979; Young et al., 1991; Zhang et al., 2002; Xu et al., 2003). On the other hand, the large spherulite containing more perfect crystals results in high modulus and brittleness (Tadmor et al., 1979).

CHAPTER III

EXPERIMENTAL

3.1 Materials

Poly(lactic acid) (PLA 4042D) with a density of 1.24 g/ml was purchased from NatureWorks. PLA was dried at 70ºC for 8 h in an oven before use. High ammonia natural rubber (NR) latex with 60% dry rubber content (DRC) was purchased from Thai Hua Rubber Public Company Ltd. NR latex was cast onto Petri dishes and was dried at 70°C for 3 days in an oven. Calcium carbonate, talc and α-cyclodextrin were used as nucleating agents. Calcium carbonate with an average particle size of 7 to 10 μm, talc with an average particle size of about 10 μm and α-cyclodextrin were purchased from Sigma Aldrich.

3.2 Experimental

3.2.1 Blend preparation

PLA/NR of 95/5, 90/10, 85/15 and 80/20wt/wt% were prepared. As shown with the maximum impact toughness, PLA/NR of 90/10wt/wt% was chosen to study the effect of nucleating agent. Blends with 1wt% nucleating agent content were prepared. PLA/NR blend in the absence and presence of nucleating agent were blended using an internal mixer (Haake Rheomix 600p) at a mixing temperature of 180°C and a rotor speed of 50 rpm for 15 min. The blends were cooled by air for 30

min before grinding with a mechanical grinder (Retsch grinder machine). The samples for tensile and impact testing were prepared by compression molding (Gotech model GT-7014-A30) at 180°C. The blends were preheated for 10 min and then pressed for 10 min. After compression, the samples were cooled at room temperature.

3.2.2 Differential scanning calorimetry

The thermal properties of PLA and PLA/NR at various ratios were determined using differential scanning calorimetry (Perkin Elmer Pyris diamond DSC). The nitrogen gas was purged throughout the measurements. The instrument was calibrated with an indium standard and baseline was subtracted. The sample with a weight between 5 and 10 mg was put in an aluminum pan and sealed with an aluminum cover. The sample was heated from 25°C to 200°C at the rate of 10°C/min (the first heating) and held for 2 min at 200°C to remove the previous thermal history. Subsequently, the sample was cooled to 25°C at the rate of 10°C/min (cooling) and heated again to 200°C at the rate of 10°C/min (the second heating). The glass transition temperature (T_g), melting temperature (T_m), cold crystallization temperature (T_{cc}) and degree of crystallinity (%X_c) were determined.

3.2.3 Tensile testing

The tensile testing samples were prepared by pressing the blends in dog-bone shaped stainless steel mold. Tensile testing was performed according to ASTM 638. The standard type V specimens with the thickness of 4 mm, the width at narrow section of 3.18 mm, the overall width of 9.53 mm, the gage length of 7.62 mm and the overall length of 63.5 mm were prepared. The tensile properties of samples were determined using a universal testing machine (Instron model 5569) with a load cell of 5 kN and a crosshead speed of 1 mm/min at 25°C. A minimum of five

specimens was performed for each composition. Tensile force and elongation were recorded. Elongation at break, elastic modulus and tensile toughness were determined.

3.2.4   Notched Izod impact testing

The impact testing specimens were prepared by pressing the blends in a rectangular stainless steel mold. The specimens have a width of 12.7 mm, a length of 64 mm and a depth of 4 mm. All specimens were stored overnight at room temperature after pressed. The specimen was notched using engine lathe machine with a notch angle of 45° having a radius of 0.25 mm and a depth of 2.54 mm. The depth of specimens after notched was 10.20±0.05 mm. Notched Izod impact test was performed according to ASTM 256 using an Atlas testing machine (model BPI). The pendulum energy of 2.7 J was used at 25°C. The impact toughness (J/m^2) is reported by the failure energy divided by the samples cross section area after being notched. It reflects the amount of energy absorption from the beginning mechanical load to final fracture. A minimum of five specimens was tested for each composition.

3.2.5   Dynamic mechanical analysis

Dynamic mechanical properties were investigated using dynamic mechanical analyzer (Perkin Elmer DMA 7e). Specimens with the thickness of 1 mm, the width of 5 mm and the length of 20 mm were prepared by pressing the blends in rectangular shaped stainless steel mold. All samples were tested using a three-point bending mode at a strain of 0.02% in the temperature range between 20 and 80°C. The heating rate was 5°C/min and the applied frequency was 1 Hz. Oscillating strain (ε) is defined by $\varepsilon = 3ta/L^2$, while elastic component (E´) and damping component (E˝) under rectangular shape are determined by $E' = NL^3\cos\delta/2bt^3a$ and $E'' = NL^3\sin\delta/2bt^3a$.

L, t and b are length between clamp, depth and width of specimen, respectively. N and a are axial force and parallel axes displacement, respectively.

3.2.6 Optical microscopy

The spherulite size of PLA and PLA/NR blends with and without nucleating agent as obtained from isothermal crystallization and as processed crystallization was measured by Nikon polarized optical microscope (POM, model Eclipes E600 POL) equipped with a Linkam THMS 600 hot stage. For the isothermal crystallization, the sample was sandwiched between glass slides. The sample was heated to 200°C at rate of 10°C/min on a hot stage and kept for 2 min at 200°C to erase the previous thermal history. Subsequently, it was cooled to 127°C, and held constant until completion of crystallization. The spherulite structure of sample was observed and recorded by the digital camera.

For the as processed crystallization, the compression molded sample was sliced with an ultramicrotome. The sample was placed between a glass slide and a cover slip. The micrographs of PLA spherulite were captured by the digital camera on the Nikon polarized optical microscope. The magnification of 100X was chosen.

3.2.7 Scanning electron microscopy

Morphology of the impact fracture surface of PLA and PLA/NR blend were observed using scanning electron microscope (SEM, JEOL model JSM 6400) at room temperature. Acceleration voltage of 20 kV was used to collect SEM images for the sample. The fracture surface sample was coated with gold for 3 min before analysis. The average rubber particle size as dispersed in PLA matrix was examined using computerized image analyzer with Axio Vision software.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter focuses on the effect of nucleating agent on properties of PLA and PLA/NR blends. Thermal properties of PLA and PLA/NR blends are discussed in section 4.1. Mechanical properties of PLA and PLA/NR blends are dealt with in section 4.2. Finally, the section 4.3 presents the morphology of fracture surface of PLA and PLA/NR blends.

4.1   Effect of nucleating agent on thermal properties of PLA and PLA/NR

In this section, the effects of nucleating agent on thermal properties in particular cold crystallization temperature (T_{cc}), degree of crystallinity (X_c), glass transition temperature (T_g) and melting temperature (T_m) are discussed. These properties were examined by differential scanning calorimetry (DSC). Optical microscopy (OM) was used to investigate the spherulitic structure of PLA. In the present work, three types of nucleating agent were used. Thermal properties of both PLA and PLA/NR blends with and without nucleating agent were elucidated

Figure 4.1 shows the DSC thermograms of neat PLA as obtained after processed in the internal mixer. In the first heating curve, it presented the glass transition temperature (T_g), the exothermic peak and the endothermic peak at 55, 108 and 145°C, respectively. The onset was used to define T_g. The maxima of the exothermic and endothermic peak correspond to cold crystallization temperature (T_{cc})

and melting temperature (T_m), respectively. In the present work, the PLA crystallization could not be observed under the cooling scan. It means that the PLA chains do not have enough time to form nuclei during the cooling scan at 10°C/min at molten state. During the second heating scan, the T_g, T_{cc} and T_m of neat PLA were observed around 56, 127 and 150°C, respectively. From DSC results confirm that PLA was a semicrystalline polymer.
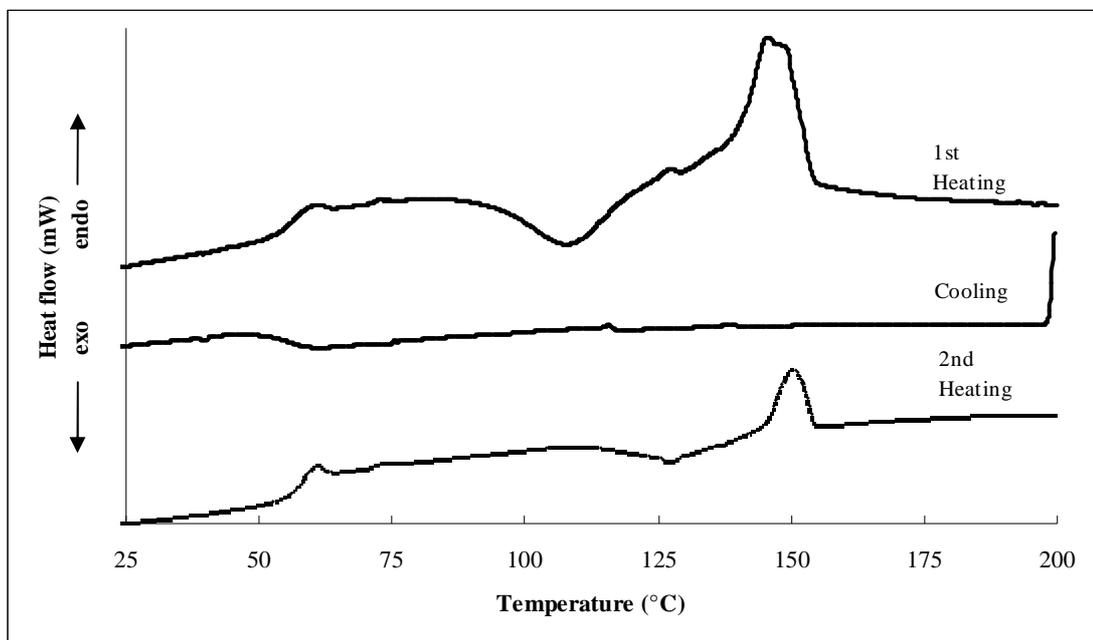
Figure 4.1 DSC thermograms of neat PLA heated and cooled at rate of 10°C/min.

4.1.1 Glass transition temperature (T_g)

In Figure 4.2, for neat PLA, an endothermic peak is observed at 56.44°C, corresponding to the glass transition temperature (T_g). The glass transition in polymer represents the molecular motion of polymer chain. This transition is the temperature where the polymer chain goes from glassy state to rubber like state (Gedde, 1995). Many factors affecting glass transition in polymer included the degree

of crystallinity (Wang, Ribelles, Sánchez, and Mano, 2005). Wang et al. explained that the position and shape of this peak do not change significantly with the X_C of PLLA. Moreover, the reduction of endothermic peak is due to the restriction to the free chain mobility by crystalline structure. In present work, although the addition of nucleating agent, $CaCO_3$, talc or α-CD increased the crystallinity of PLA as seen in Table 4.1, they did not affect the glass transition of PLA. It is noteworthy that the addition of nucleating agent had no influence on glass transition of neat PLA.
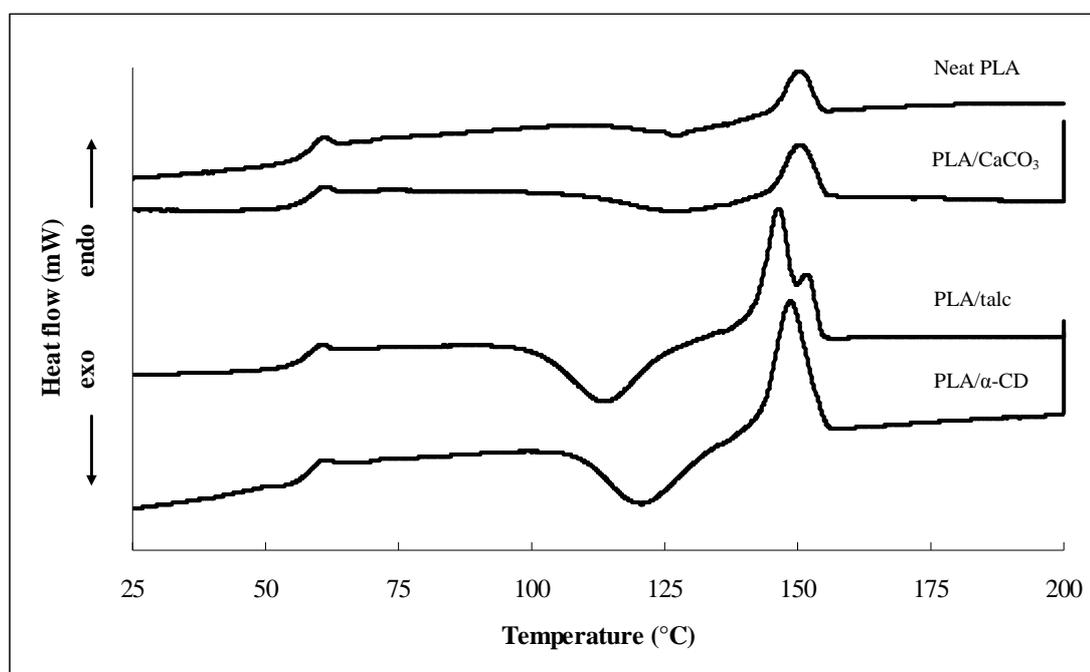
Figure 4.2 DSC second heating thermograms of PLA with different nucleating agents.

The T_g of PLA blended with NR is shown in Figure 4.3 and Table 4.1. When adding NR into PLA matrix, the T_g of this blend was close to that of neat PLA. This result suggests that NR did not affect the glass transition of PLA and PLA/NR blend was immiscible. The same result could be found in PLA/NR blend with

nucleating agent. The glass transition of PLA in PLA/NR blend was independent of nucleating agent as well as NR.

4.1.2 Cold crystallization temperature (T_{cc})

Figure 4.2 illustrates the DSC second heating thermograms at a heating rate of 10°C/min for neat PLA and PLA with different nucleating agents. The T_{cc} are 127.73, 128.05, 113.85 and 120.60°C for neat PLA, PLA/CaCO$_3$, PLA/talc and PLA/α-CD, respectively. DSC results showed that the T_{cc} of PLA/talc and PLA/α-CD are significantly lower than that of neat PLA. It is known that the lower T_{cc} initiates faster crystallization. This result suggested that both talc and α-CD act as good nucleating agents for PLA. As mentioned in section 2.1, heterogeneous nucleation refers to the nucleation under foreign particle such as nucleating agent (Gedde, 1995; Dong et al., 2005). Nucleation is associated with the existence of free energy barrier. Lower free energy barrier favor faster nucleation. Nucleating agent is high energy surface matter, which affects free energy balance. The presence of talc greatly decreased the T_{cc} by approximate 14°C while the addition of α-CD moderately decreased the T_{cc} by approximate 7°C compared with the T_{cc} of neat PLA. This result indicates α-CD was slightly less effective than talc in enhancing crystallization for PLA. On the contrary, incorporation of CaCO$_3$ showed no effect on crystallization temperature.

As shown in Figure 4.3, the incorporation of NR did not affect crystallization temperature of PLA in NR toughened PLA (PLA/NR10 curve). The presence of NR presented a very weak and broad crystallization peak appeared at 127.70°C, which is almost the same as that of neat PLA. This result has been found in many semi-crystalline polymer blends with other rubber, for example, iPP/EO and

SEBS (Fanegas et al., 2007). The crystallization temperature was independent of the addition of rubber particle.
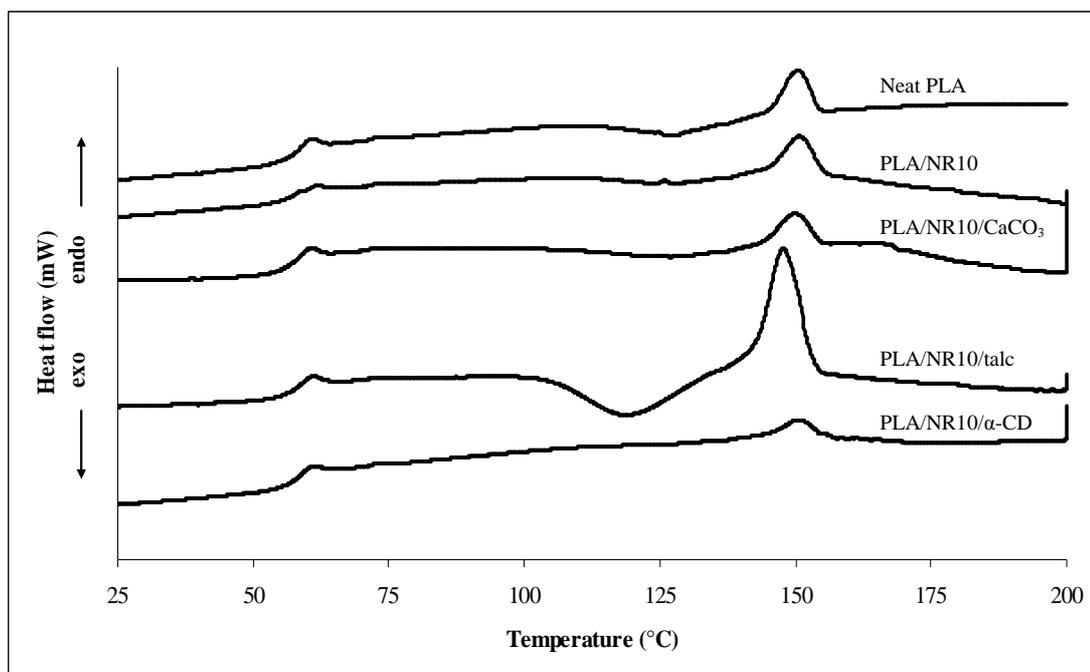
Figure 4.3 DSC second heating thermograms of PLA/NR10 with different nucleating
agents.

The addition of $CaCO_3$, talc and α-CD into PLA/NR blend affects crystallization behavior in different ways as shown in Figure 4.3 and Table 4.1. The T_{cc} of PLA/NR10 with addition of $CaCO_3$ is about 126.86°C, similar to that of non-nucleated PLA/NR10 (127.70°C). When α-CD is added into PLA/NR10, the T_{cc} did not change. The results showed that the value of T_{cc} for the blend with α-CD is 127.08°C. This value is almost the same as that of non-nucleated PLA/NR10 blends (127.70°C). The use of talc as nucleating agent was also investigated. With an addition of talc, the T_{cc} of PLA decreased from 127.70°C (non-nucleated PLA/NR10)

to 118.06°C (PLA/NR10 with talc). These results indicate that only the presence of
talc improved the crystallization of PLA/NR10, while $CaCO_3$ or α-CD did not affect
the crystallization temperature of those blends.

Table 4.1 DSC second heating results of PLA and PLA/NR blend with different
nucleating agents.

Samples	T_g (C°)	T_{cc}(C°)	T_{m1}(C°)	T_{m2}(C°)	X_c(%)
Neat PLA	56.44	127.73	NA	150.04	18.63
PLA/CaCO$_3$	56.82	128.05	NA	150.26	26.30
PLA/talc	56.25	113.85	146.28	152.13	68.55
PLA/α-CD	57.39	120.60	NA	148.49	66.30
PLA/NR10	56.38	127.70	NA	150.55	14.32
PLA/NR10/CaCO$_3$	56.68	126.86	NA	149.63	16.05
PLA/NR10/talc	56.85	118.06	147.59	NA	60.47
PLA/NR10/α-CD	56.71	127.08	NA	150.12	6.37

4.1.3   Melting temperature (T_m)

Melting temperature (T_m) appeared around 150.04°C for neat PLA,
estimated from peak of melting endotherm. This temperature is the characteristic
property of crystalline polymer. The influence of nucleating agent on T_m was
examined. T_m showed insignificant variations in the PLA with added nucleating
agent. The T_ms were listed in Table 4.1. A single sharp melting peak of PLA was
observed in the presence of $CaCO_3$ and α-CD as well as in neat PLA. On the contrary,
incorporation of talc into neat PLA, the double-peak melting temperature (T_m) was
observed. Sarasua et al. explained that the melting peak at higher temperature (T_{m2})
belongs to more perfect crystalline structure than that at lower temperature (T_{m1}). The
less perfect crystals have enough time to melt and reorganize into crystals with higher
structure perfection and remelt at higher temperature (Sarasua, Prud'homme,

Wisniewski, Borgne, and Spassky, 1998). The crystal structure at the lower temperature is called α´ form and that at the higher temperature is called α form (Zhang, Tashiro, Tsuji, and Domb, 2008). Both crystal structures are actually in the same form with different lamellar thickness.

In the recent study (Chow et al., 2009), DSC results showed that the presence of rubber component did not affect the T_m of PLA. There is no significant change of T_m in PLA/OMMT with the addition of EPMgMA. In agreement with present work, the T_m of neat PLA and PLA/NR10 blend is 150.04 and 150.55°C, respectively. The results clearly showed that the T_m of PLA was independent of the addition of NR. When the $CaCO_3$ or α-CD was added into PLA/NR blend, the T_m of PLA was not very sensitive with these particles and the peak of melting was only one melting point (Figure 4.3 and Table 4.1). In contrast to PLA/NR10 containing $CaCO_3$ and α-CD, the melting peak of PLA/NR10 in the presence of talc was lower than that of those blends. Thus the melting temperature was closed to T_{m1}, implying the less perfect crystal generated by the talc.

4.1.4 Degree of Crystallinity ($\%X_C$)

The degree of crystallinity ($\%X_C$) of PLA was calculated using the following equation:

$$\%X_C = \frac{[(\Delta H_m - \Delta H_{cc})/\Delta H^o_m] \times 100}{\Phi_{PLA}} \qquad 4.1$$

where ΔH_{cc} and ΔH_m are the apparent cold crystallization and melting enthalpy of PLA, respectively, Φ_{PLA} is the weight fraction of PLA in the blends and ΔH^o_m is the enthalpy corresponding to the melting of a 100% crystalline PLA which is 93.0 J/g

(Tsuji and Ikada, 1996). The $\%X_C$ of neat PLA and nucleated PLA are listed in Table 4.1. For neat PLA, the X_C is 18.63%. After an addition of $CaCO_3$, talc and α-CD, the $\%X_C$ of PLA are 26.30, 68.55 and 66.30%, respectively. The presence of talc or α-CD greatly increased the $\%X_C$ by approximate 50 and 48%, respectively, while the addition of $CaCO_3$ increased the $\%X_C$ by approximate 8% compared with neat PLA. It can be seen that the incorporation of nucleating agent increased the $\%X_C$ and this effect was pronounced with talc and α-CD. $CaCO_3$ is less effective than talc and α-CD in promoting $\%X_C$. Clearly, talc and α-CD are effective in the rise of $\%X_C$, whereas $CaCO_3$ is less effective to enhance $\%X_C$.

The addition of NR to neat PLA slightly decreased the $\%X_C$. The X_C of 14.32% was found in the presence of NR, which is slightly lower than that of neat PLA, as can be seen in Table 4.1. This could be due to the limitation of chain mobility (Fanegas et al., 2007). Fanegas et al. explained that the addition of rubber component affects chain mobility of polymer matrix, thus affecting crystalline development. In their work, the $\%X_C$ of iPP (57%) was decreased with addition of SEBS as well as EO in iPP. At 10wt% rubber content, the $\%X_C$ of iPP in iPP/SEBS and iPP/EO is 54 and 53%, respectively. An addition of maleic anhydride grafted ethylene propylene rubber (EPMgMA) into PLA/OMMT nanocomposite also decreased $\%X_C$ of PLA (Chow et al., 2009). The $\%X_C$ of PLA/OMMT/EPMgMA is 15.2%, which is lower than that of PLA/OMMT nanocomposite (24.2%) and neat PLA (22%).

The effect of nucleating agent on $\%X_C$ of PLA in NR toughened PLA was summarized in Table 4.1. Incorporation of $CaCO_3$ insignificantly enhanced the $\%X_C$. The $\%X_C$ of this blend is 16.05%, which is close to that of PLA/NR10 blend (14.32%). This result suggests that $CaCO_3$ was less effective to enhance the $\%X_C$ of

PLA. The existence of talc greatly increased the $\%X_C$. The $\%X_C$ of PLA/NR10 containing talc is 60.47%, which is higher than that of PLA/NR10 blend. In the case of α-CD, the huge reduction in X_C of PLA in PLA/NR was found. PLA/NR10 blend in the presence of α-CD displayed the X_C of 6.37%. It was clear that this $\%X_C$ of PLA in PLA/NR10 with α-CD is even lower than that without α-CD. This may associate to two different phenomena. The first one is that the α-CD is preferentially dispersed in NR phase. The second possible explanation is that the α-CD is coated by NR. These lead to poor nucleation ability for PLA. Only the presence of talc still presented an increment of $\%X_C$ of PLA when added to PLA/NR10 blend.

As reported above, the X_C of PLA were obtained by the second heating scan. The previous thermal history of samples as obtained from processing was erased at isothermal temperature of 200°C. Thus, the X_C of PLA samples as shown in Table 4.1 may not represent the X_C as obtained from the processing. The X_C of the as processed sample was also obtained from the DSC first heating thermogram as summarized in Table 4.2. The $\%X_C$ is calculated by equation 4.1. For neat PLA, the X_C is about 9.91%. The X_C of PLA with $CaCO_3$, talc and α-CD is 61.76, 47.34 and 34.66%, respectively. It is clearly seen that the addition of nucleating agent into neat PLA increased the X_C of PLA.

The presence of NR also increased the X_C of PLA, which shows the X_C of PLA of 19.70% (shown in Table 4.2). Similar results were obtained in PLA/NR10 blends with $CaCO_3$ and talc. The blend with $CaCO_3$ and talc showed the X_C of PLA was higher than that of blend without nucleating agent. The $\%X_C$ of PLA with $CaCO_3$ and talc is 29.19 and 27.24, respectively. Unlike in the presence of $CaCO_3$ and talc, the X_C of PLA in the presence of α-CD slightly decreased compared to those of blend

without nucleating agent. The problem of the addition of α-CD to PLA/NR10 is related to the α-CD dispersion and NR encapsulation as mentioned earlier.

Table 4.2 DSC first heating results of PLA and PLA/NR blend with different

nucleating agents.

Samples	ΔH_m (J/g)	ΔH_{cc} (J/g)	$(\Delta H_m - \Delta H_{cc})$ (J/g)	X_c (%)
Neat PLA	37.36	-28.14	9.22	9.91
PLA/CaCO₃	57.44	0.00	57.44	61.76
PLA/talc	44.03	0.00	44.03	47.34
PLA/α-CD	32.96	-0.73	32.23	34.66
PLA/NR10	31.61	-15.12	16.49	19.70
PLA/NR10/CaCO₃	28.65	-4.22	24.43	29.19
PLA/NR10/talc	26.68	-3.88	22.80	27.24
PLA/NR10/α-CD	25.56	-11.21	14.35	17.14

4.1.5 Spherulite structures

Maltese cross pattern is characteristic of the spherulites, which are examined by polarized optical microscope (Young et al., 1991; Rosen, 1993). This pattern reflects the orientation of polymer chain within the spherulites. Spherulites take place by the incorporation of lamellar crystals, which are the polymer chain aligned to from the crystals. Spherical shape is normal form of the many polymer spherulites. Not only crystallization condition affects the diameter of spherulite, but the use of nucleating agent is also factor affecting spherulite size. Lower crystallization temperature as well as the addition of nucleating agent facilitates smaller spherulite size.

As shown in Figure 4.4, the optical micrographs show the spherulite structure for neat PLA and PLA with nucleating agent. The final spherulite morphologies were observed after the isothermal crystallization at 127°C for all samples. The average diameter of neat PLA spherulite after the impingement is about 40 μm (Figure 4.4(a)). The addition of $CaCO_3$, talc or α-CD is presented in Figure 4.4(b-d). The presence of nucleating agent seems to decrease the PLA spherulite size. The reduction in spherulite size may correspond to the increase in the number of nuclei. When the polymer melt is cooled, the dispersive nucleating agents act as the heterogeneous nuclei. These nuclei as the origin of the spherulite then grow as spherical form. When the impingement of another boundary happens, spherulite growth stops. Clearly, these three nucleating agents decreased the spherulite size by which talc gave the smallest size (~10 μm).

Figure 4.5 showed the optical micrograph of PLA/NR10 blend with the addition of nucleating agent. In these micrographs, both the dispersed NR particles and the spherulites of PLA appeared. The spherulite size of PLA in blend without nucleating agent (shown in Figure 4.5(a)) is about the same as that in neat PLA (shown in Figure 4.4(a)). This strengthens that the crystallization behaviors of PLA are not sensitive with the existence of NR particles.

The reductions in spherulite size were found in an addition of $CaCO_3$ and talc in PLA/NR10 blend (Figure 4.5(b-c)). This is in a good agreement with the DSC results. On the other hand, when α-CD is added into PLA/NR10 blend, the spherulite size of PLA increased when compared to non-nucleated PLA/NR10 blend. As mentioned earlier, two phenomena were possibly occurred in PLA/NR10 with α-CD, which are the α-CD dispersion and the NR encapsulation.
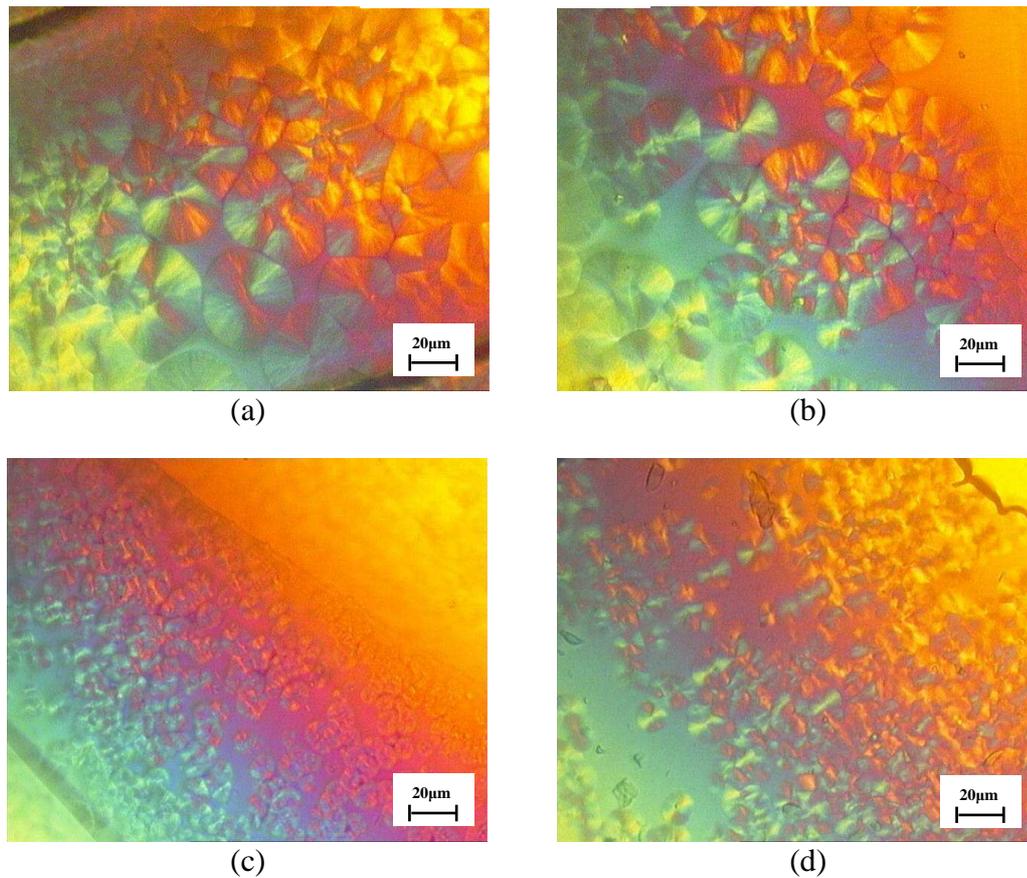
Figure 4.4 Optical micrographs for (a) neat PLA, and neat PLA with nucleating agents
(b) $CaCO_3$, (c) talc, and (d) α-CD at the isothermal crystallization
temperature of 127°C.

In addition, different spherulite morphologies influence mechanical
properties in different way. From the above micrographs presented, the results were
obtained by melting and cooling the samples to the isothermal crystallization
temperature at 127°C. These results may or may not represent the spherulite
morphology of samples as obtained from the processing. Thus, the morphology of the
as processed samples was examined. Figure 4.6 shows the optical micrographs for
thin film notched impact fracture specimens. Compared to those in Figure 4.4-4.5, the

spherulites are not clearly observed in these micrographs. As processed, fine spherulite structures (~5 μm in diameter) were observed for neat PLA (Figure 4.6(a)). The dimension of spherulite slightly decreased with an addition of nucleating agents
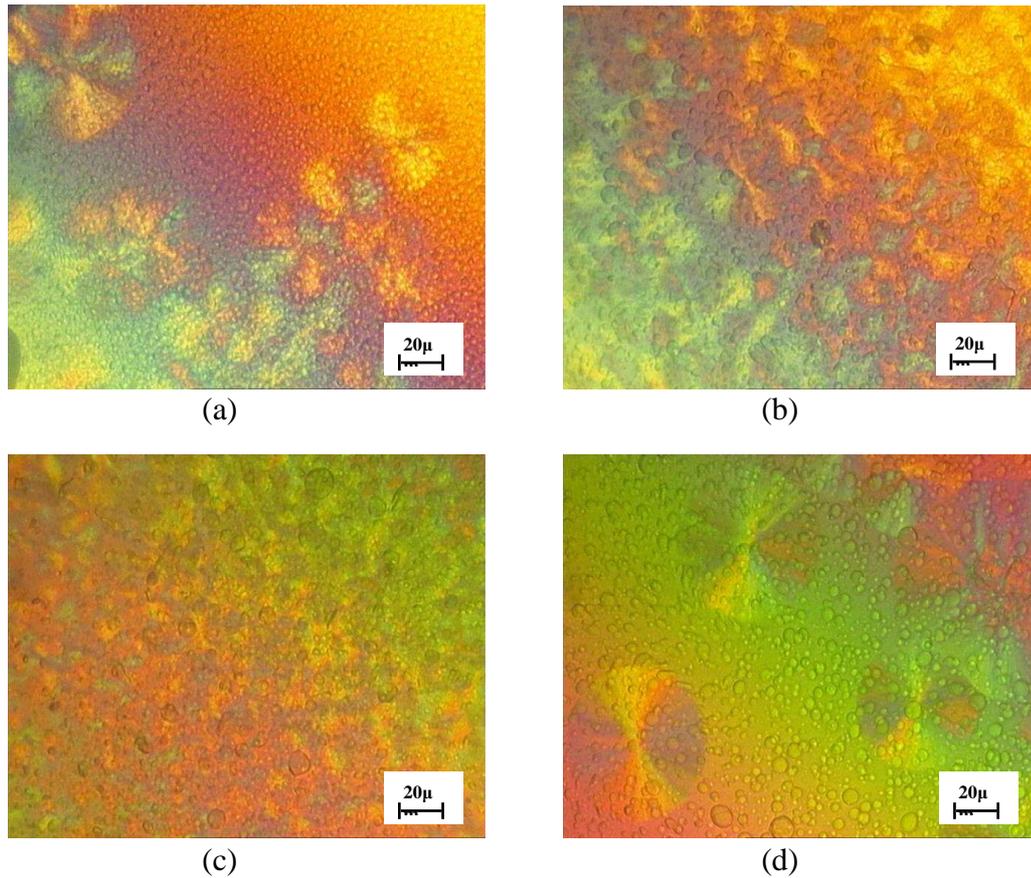
Figure 4.5 Optical micrographs for (a) PLA/NR10, and PLA/NR10 blend with nucleating agents (b) CaCO$_3$, (c) talc, and (d) α-CD at the isothermal crystallization temperature of 127°C.

as observed in Figure 4.6(b-d). Clearly, the spherulite size of PLA containing CaCO$_3$, talc as well as α-CD is smaller than that of neat PLA. In the presence of these nucleating agents, the average diameter of spherulite dropped to 2-3 μm. In the case

of PLA/NR10 blend, the spherulitic structure of PLA in PLA/NR10 with and without nucleating agent could not be detected by optical microscopy (not shown here). Usually, small and large spherulite size present different mechanical properties. The former gives tougher than the latter (Rosen, 1993; McCrum, Buckley, and Bucknall, 1997). The detailed relationship between the spherulite structure and mechanical properties are dealt with in section 4.2.
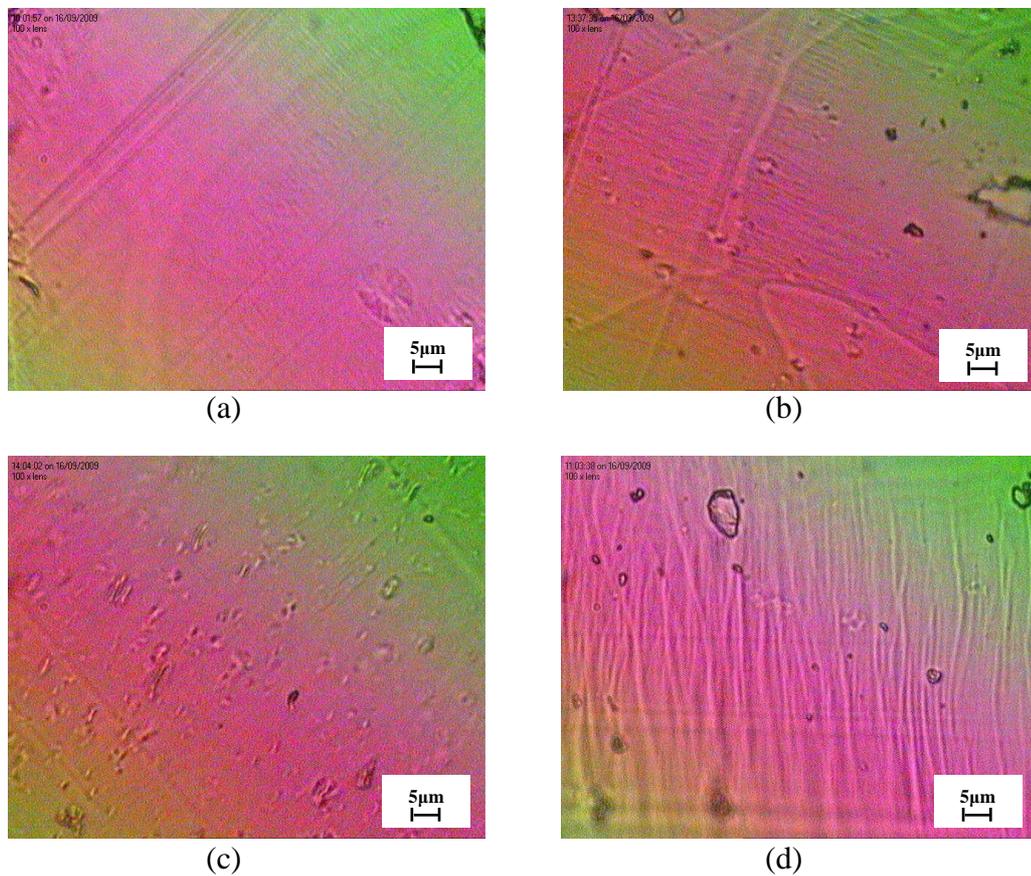
Figure 4.6 Optical micrographs for (a) neat PLA, and neat PLA with nucleating

agents (b) $CaCO_3$, (c) talc, and (d) α-CD.

4.2 Mechanical properties of PLA and PLA/NR10 blends with nucleating agent

4.2.1 Elongation at break and Young's modulus

Elongation at break and Young's modulus are important properties for polymer selection. There were determined from the stress-strain curves. The ductility (strain at bleak) of material is represented by elongation at break, which was calculated from stress-strain curve. It is the extension at the point of rupture. Young's modulus is defined at small deformation (Arends, 1996). It is a fundamental indicator of the stiffness of materials. The tensile stress-strain curves of PLA with and without nucleating agent are presented in Figure 4.7. The tensile stress-strain curve is associated with the elongation at break (strain at bleak) and stiffness (Young's modulus) of PLA. After an addition of nucleating agent, the results showed that it did not significantly affect the feature of the curve. Elongation at break seems to insignificantly change by incorporation of nucleating agent. Similarly, nucleating agent displayed weak influence on the stiffness of PLA. The presence of nucleating agents did not much affect both the elongation at break and the stiffness of PLA.

The elongation at break and stiffness of PLA were strongly dependent on the NR component. When the NR was added, the ductility (strain at break) increased while the stiffness slightly decreased as shown in Figure 4.8. Since the NR is a softer material than the PLA, the stiffness is always lower when the NR is added. The ductility of PLA/NR in the presence of nucleating agent was higher than that of PLA/NR in the absence of nucleating agent. The stiffness of blends with nucleating agent did not change compared to PLA/NR blend.

From tensile stress-strain curves (Figure 4.7), elongation at break and Young's modulus were plotted in Figure 4.9. Plots of elongation at break and Young's modulus of PLA against nucleating agent are shown in Figure 4.9. It was shown that the elongation at break is about 10% and Young's modulus is 758 MPa for neat PLA. When the $CaCO_3$ is added to neat PLA, a small increase in the elongation at break was found, while the Young's modulus changed negligibly. The same effects were observed with talc and α-CD as well. From these results, it can be deduced that the addition of nucleating agents did not significantly improve the elongation at break and Young's modulus of PLA.
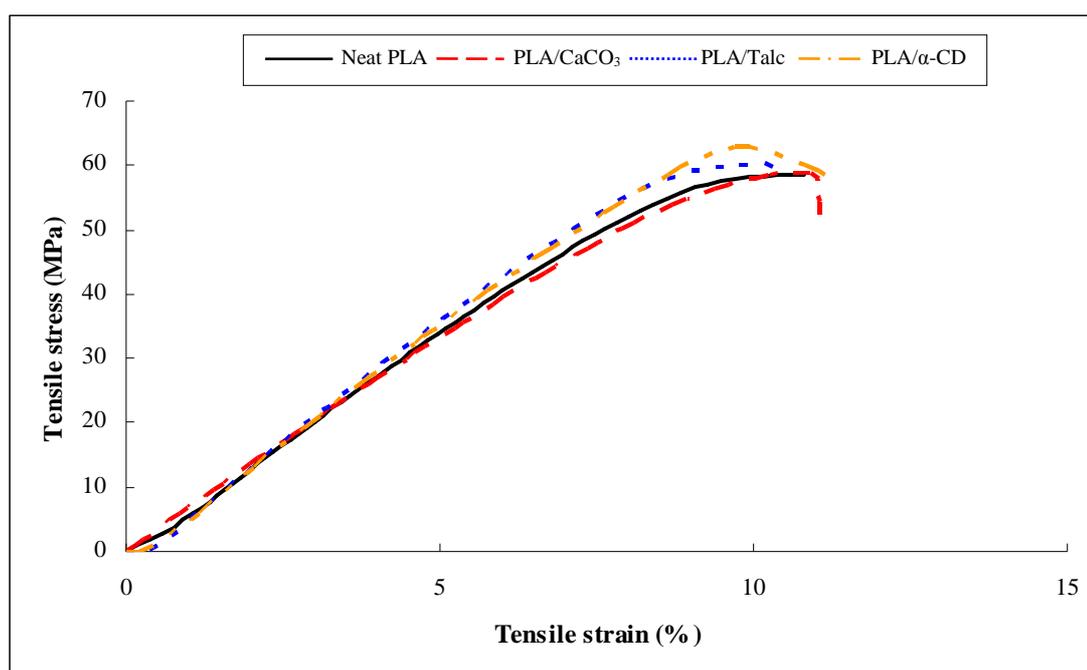
Figure 4.7 Stress-strain curves of PLA with different nucleating agents.
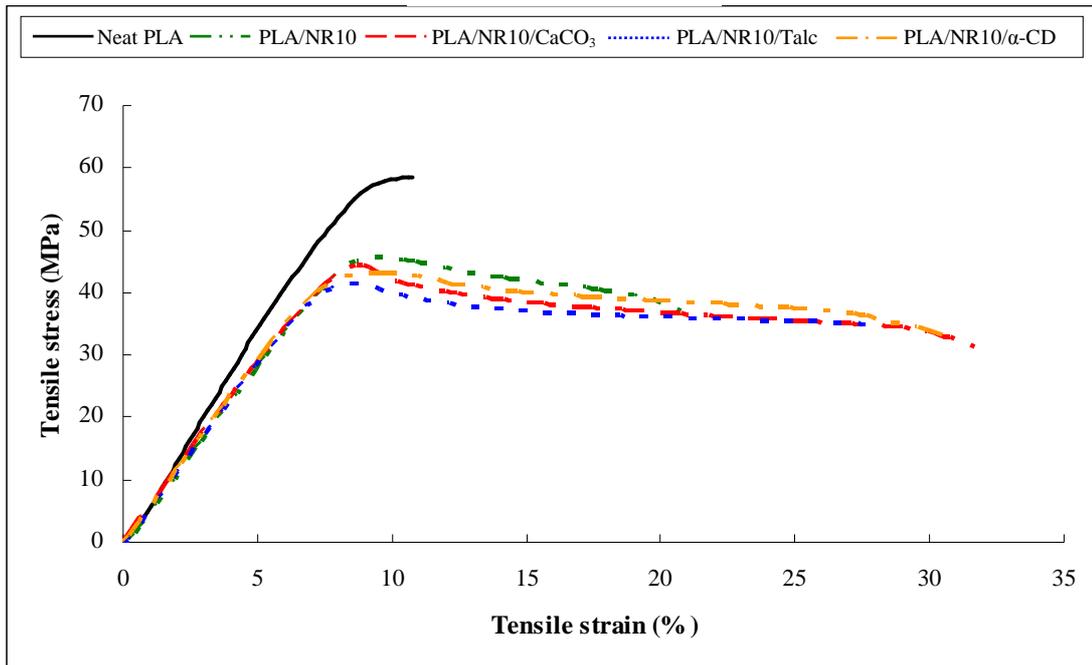
Figure 4.8 Stress-strain curves of PLA/NR10 with different nucleating agents

(Neat PLA curve is presented for comparison.).

Incorporation of nucleating agent affects the crystallization behavior of PLA, changing both the degree of crystallinity and spherulite size of PLA. These may affect both elongation at break and Young's modulus of PLA. The elongation at break and Young's modulus are used to represent the toughness and stiffness. Li and Huneault (2007) reported that the addition of talc as used as nucleating agent to PLA increased the degree of crystallinity, thus influencing the tensile properties of PLA. With increasing the degree of crystallinity, the elongation at break decreased, while the Young's modulus increased. Zhang et al. (2002) concluded that an increment of toughness of PP/EO blends with nucleating agent DM may also associate with the decrement of PP spherulite size. In the present work, the addition of nucleating agent into PLA affected both the degree of crystallinity and spherulite size. However, both

the elongation at break and Young's modulus of PLA with nucleating agents did not significantly change. The degree of crystallinity and spherulite size had distinct influence on the mechanical properties. The detailed relationship between spherulite size and mechanical properties is explained in section 4.2.2.
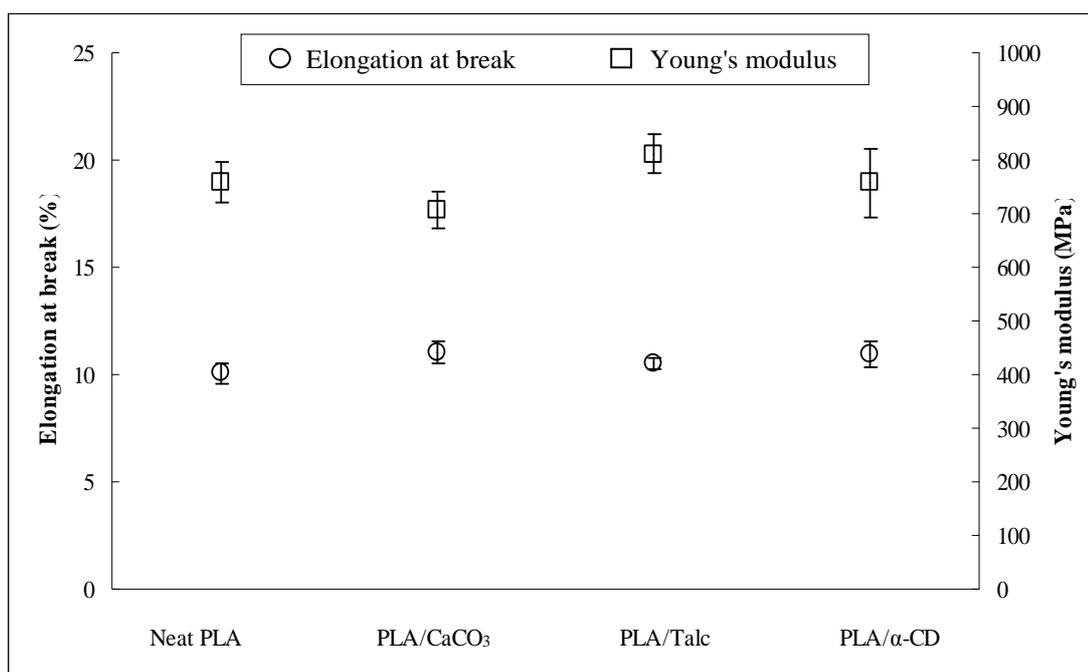
Figure 4.9 Effects of nucleating agent on the elongation at break and the Young's modulus of PLA.

The addition of NR greatly increased the elongation at break of PLA as presented in Figure 4.10. As reported previously (Jin et al., 2000; Jiang et al., 2006), the content of thermoplastic as well as rubber have strong effect on mechanical properties of PLA. In this work, the elongation at break increased progressively with the addition of ungrafted NR up to 10wt% content while the Young's modulus of PLA decreased with increasing NR content (5-20wt%). These observations agree well

with impact testing. The results of various compositions are not shown here. At 90/10wt/wt% PLA/NR, the elongation at break is 21.5%. This value is highest when compared to other composition (95/5, 85/15 and 80/20wt/wt%), suggesting that there is an optimum content of NR for the enhancement of PLA toughness. It is concluded that the use of 10wt% NR content gave maximum elongation at break.
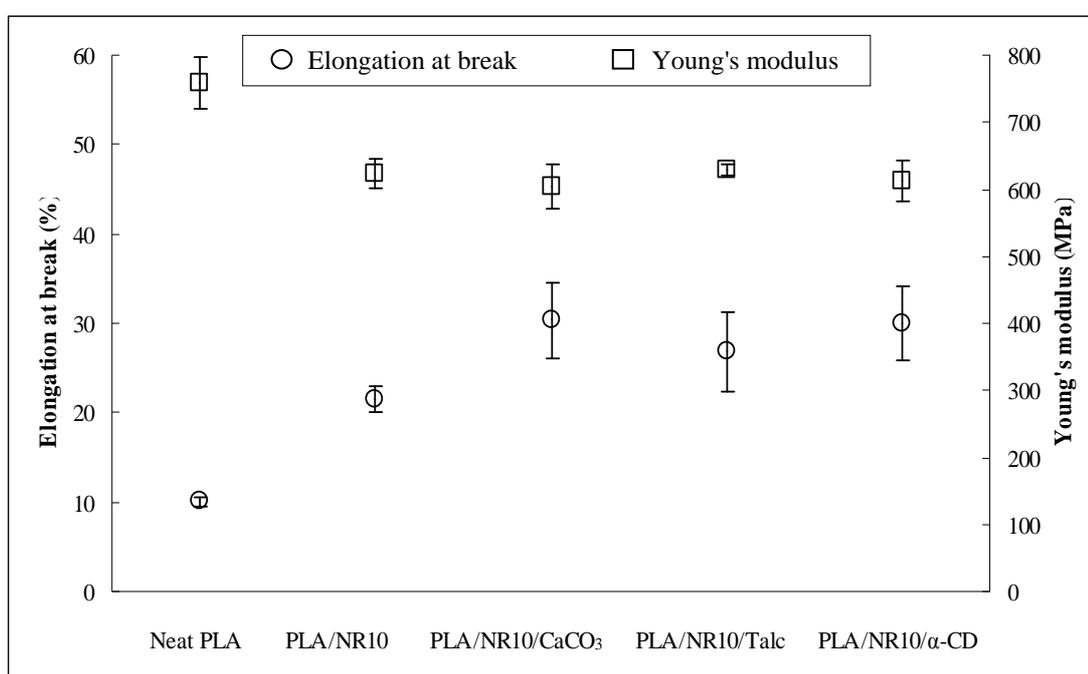
Figure 4.10 Effects of nucleating agent on the elongation at break and the Young's modulus of PLA/NR10.

From above results, it is clear that when the NR component was added to PLA, the elongation at break increased but the Young's modulus decreased. Several methods have been used to achieve a balance between both properties. The use of nucleating agents as a third component in the polymer blend showed a good balance of the toughness and the stiffness, in addition to improvement of

crystallization process (Zhang et al., 2002; Trongtorsak et al., 2004; Bai et al., 2009). When 1wt% of nucleating agent was added into PLA/NR blends, the percent elongation at break is higher than that of PLA/NR blend (21.5%) as shown in Figure 4.10. It suggests that nucleating agent was important in the enhancement of PLA elasticity in PLA/NR10 blends. The percent elongation at break of PLA/NR with adding $CaCO_3$, talc or α-CD is about 30.3%, 26.8% and 30.0% respectively. It is clearly shown that when the $CaCO_3$, talc or α-CD was added, the Young's modulus of PLA/NR10 did not change. Although the addition of nucleating agent increased elasticity of PLA/NR10 blends, it did not affect Young's modulus of the blends.

Although both NR and nucleating agent increased the elongation at break of PLA in blends, NR was more effective in increase this property than the nucleating agent.

4.2.2 Tensile and impact toughness

In this work, toughness is evaluated by tensile toughness and notched Izod impact toughness measurements. The area under stress-strain curve is used to measure the absorption of energy of the material during a tensile test. This ability corresponds to the tensile toughness (MPa) of material. Figure 4.11 presented the tensile toughness and impact toughness of neat PLA in the absence and presence of nucleating agent. For neat PLA, the tensile toughness is 330 MPa. With addition of nucleating agent, tensile toughness is 377, 370 and 399 MPa for PLA with $CaCO_3$, talc and α-CD, respectively. Incorporation of nucleating agent insignificantly increased tensile toughness of PLA.

As presented in Figure 4.11, the notched Izod impact toughness of PLA depended on the presence of nucleating agent. The notched Izod impact testing

results showed that the notched Izod impact toughness of neat PLA is 2.29 kJ/m^2. This property was enhanced when the nucleating agent was added into PLA. The impact toughness of the addition of CaCO$_3$, talc and α-CD are 3.89, 3.92 and 3.63 kJ/m^2, respectively. An increase in the impact toughness of PLA with nucleating agent is due to the decrease of the PLA spherulite.
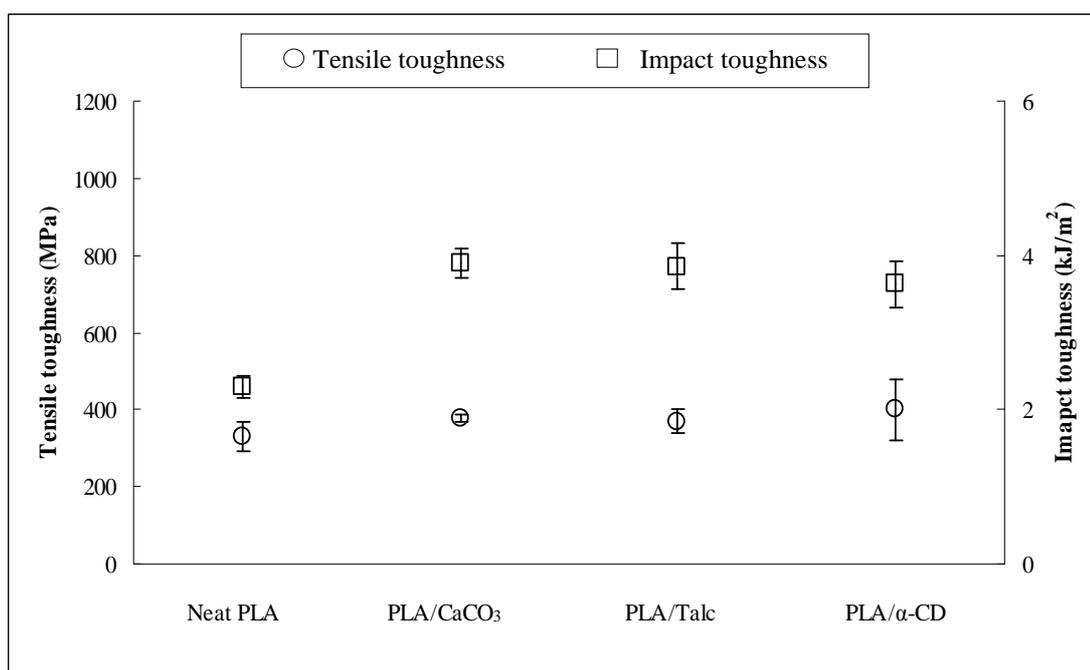
Figure 4.11 Effects of nucleating agent on the tensile toughness and the impact
toughness of PLA.

Although the nucleating agent is not pronounced in the improvement of tensile toughness, it strongly improves the notched Izod impact testing results of PLA (as shown in Figure 4.11). It has been reported that nucleating agent is very important in an increase of PLA impact toughness. These two toughness testings are

different in strain rate, as related to different applications. These results are thus useful for expanding application window for PLA.
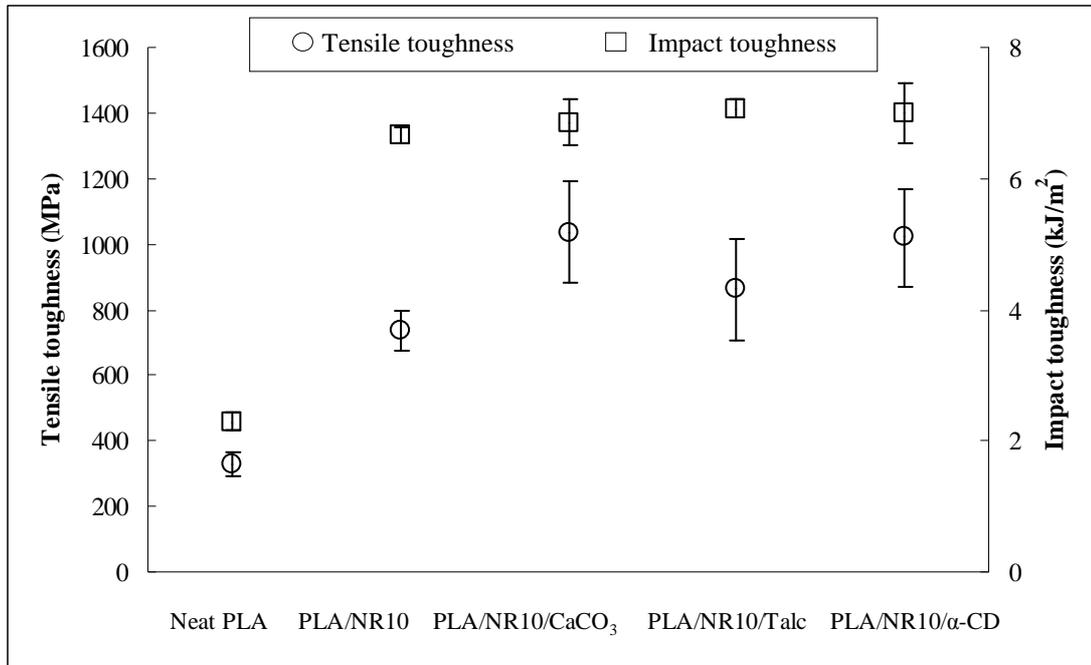
Figure 4.12 Effects of nucleating agent on the tensile toughness and the impact toughness of PLA/NR10.

As expected, the toughness was enhanced with the addition of NR component as shown in Figure 4.12. Tensile toughness of the blend increases from 330 MPa (neat PLA) to 735 MPa (PLA/NR10). Significant increases in this property were observed after an addition of nucleating agent. The tensile toughness of PLA/NR with adding $CaCO_3$, talc or α-CD is about 1036.61, 862.52 and 1020.35 MPa.

In the present study, the natural rubber clearly facilitates the increase of impact toughness for PLA matrix. The impact toughness greatly enhanced with the addition of NR component as shown in Figure 4.12. Notched Izod impact toughness of PLA/NR10 increases three times (to 6.76 kJ/m^2) compared to that of neat PLA. When 1wt% of nucleating agent is added into PLA/NR blends, it slightly increased the impact toughness. Incorporation of $CaCO_3$, talc and CD, the impact toughness is 6.85, 7.07 and 7.01 kJ/m^2, respectively. This impact toughness was very close to that of PLA/NR10 in the absence of nucleating agent (6.76 kJ/m^2). It is noteworthy that the enhancement of impact toughness with addition nucleating agent is less effective, where the enhancement of impact toughness with addition NR is greatly as presented in Figure 4.12.

As discussed above, an increase in toughness of PLA samples can be explained by two ways. The first one is the use of softer materials, which is NR. The second is the addition of nucleating agent. The increase in toughness of PLA samples with nucleating agent corresponds to the changing of PLA spherulite size. As mentioned earlier, the spherulitic structure occurs by the stack of folded chain lamellar crystal. The connections between lamellar crystals are called tie-molecules. The smaller spherulite size leads to higher number of tie-molecule, resulting in an increase of toughness (Arends, 1996; Zhang et al., 2002). It is believed that the reason for an increase in toughness of both neat PLA and PLA/NR10 with addition of nucleating agent is due to the decrease in spherulite size of PLA, which produced higher number of tie-molecule.

4.2.3 Dynamic mechanical properties

Figure 4.13 shows the storage modulus (E') as a function of temperature of neat PLA with addition of 1wt% nucleating agent. For the neat PLA, E' dropped at about 50-60ºC due to the glass transition, in agreement with the result of DSC. Similar behavior was found when adding $CaCO_3$, talc or α-CD. Nucleating agent did not affect the E' below T_g. Beyond T_g, the moduli of all samples increased. A possible explanation given for this phenomenon is that the partial crystallization of PLA in their blends occurs upon heating. An increase in the chain mobility took place at a higher temperature, thus favors the crystallization process (Liu, Dever, Fair, and Benson, 1997).
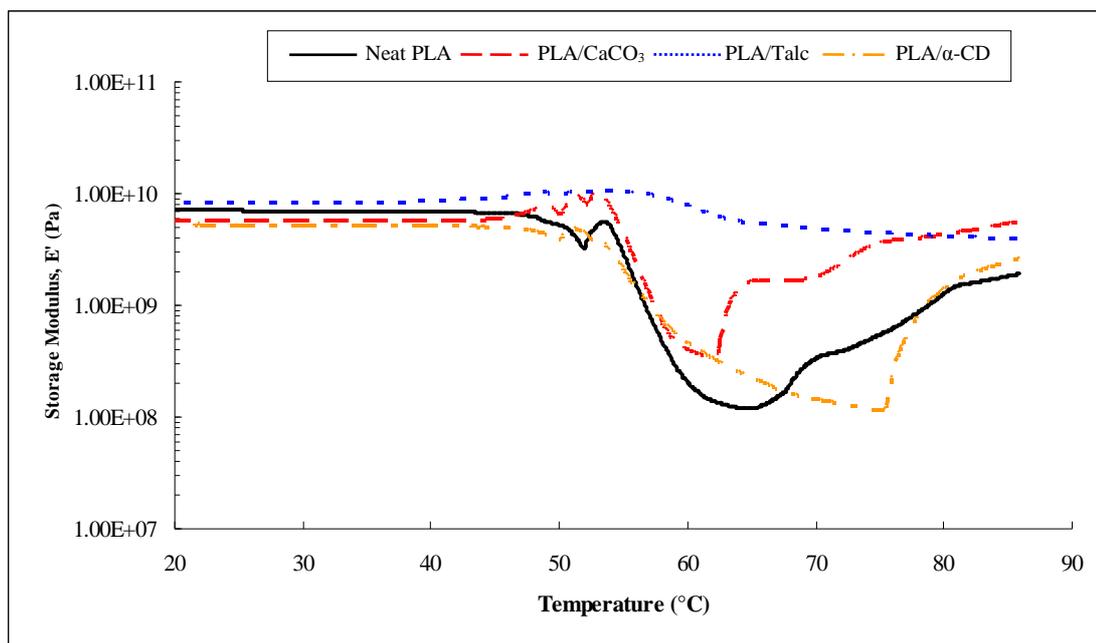
Figure 4.13 Storage moduli, E' of PLA/Nucleating agent as a function of temperature.

The E' of PLA/NR10 blends with addition of 1wt% nucleating agent are shown in Figure 4.14. Below T_g of PLA, the E' showed independent of the NR component. With the addition of NR, the E' at lower temperature (20-50°C) did not significantly change. It suggests that 10wt% NR does not affect the modulus of PLA in the glassy region. In the case of PLA/NR10 blends with the nucleating agent, DMA results are the same as those of neat PLA in the presence of nucleating agent. Nucleating agents including $CaCO_3$, talc and α-CD had no influence on the modulus and glass transition of PLA in PLA/NR10 blend. It is noticed that the drop in E' of both PLA and PLA/NR with addition of talc decreased slightly compared to neat PLA or other blends.
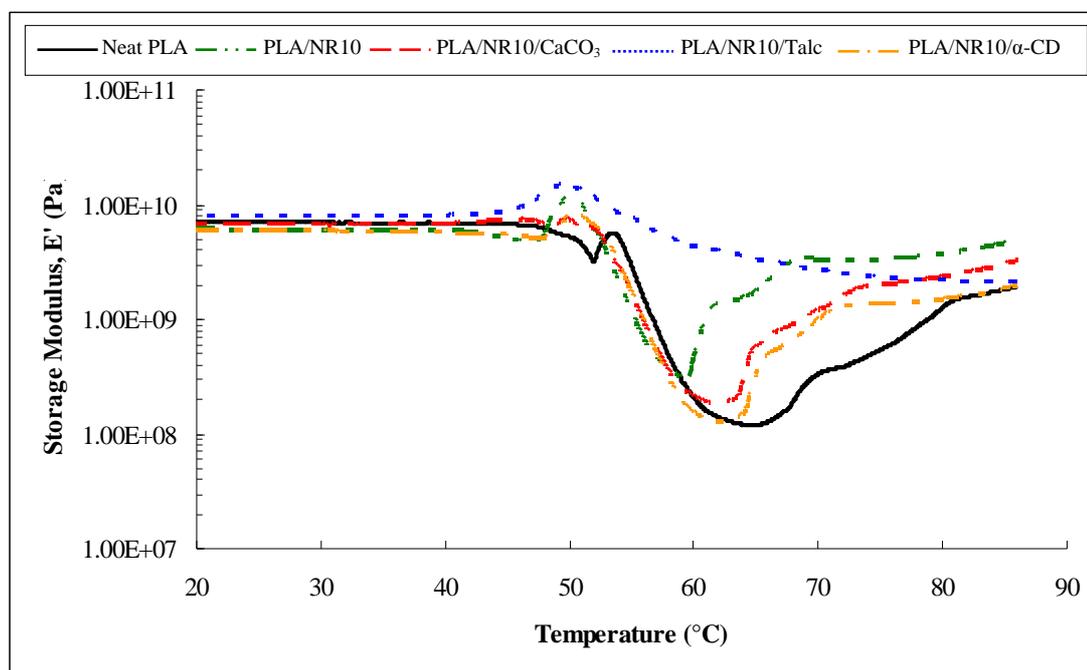
Figure 4.14 Storage moduli, E' of naet PLA and PLA/NR10/Nucleating as a function of temperature.

The tan δ peaks corresponding to T_g are shown in Figure 4.15. The T_g of neat PLA was observed around 60ºC, defined as the temperature at the maximum of the tan δ. With nucleating agent, the T_g of PLA did not change. In addition, the result showed that the height of tan δ peak of neat PLA was higher than that of PLA with nucleating agent, especially in the addition of talc, which is very weak and broad (Figure 4.15). The tan δ is the ratio of the loss modulus (E″) to storage modulus (E′), tan δ=E″/E′. The E′ part is related to stored energy during deformation, whereas the E″ is a measure of dissipated energy. Tan δ is often called damping, which is the measure of the energy dissipation of materials. The dissipated energy is sensitive to molecular chain motions. The decrease in tan δ height represents that the mobility of polymer chains are hindered. Liu et al. explained that the height of tan δ is associated to the motion of free chain segment in the polymer (Liu et al., 1997). The sharp and narrow peak was found in an amorphous polymer, which is due to no restriction to the chain motion. In the case of semicrystalline polymer, the crystalline region restricted molecular mobility, which shows a weak and broad tan δ peak. In our case, the crystallinity of PLA significantly affected the height of tan δ peak. The height of tan δ decreased with degree of crystallinity. The height of tan δ for PLA with or without nucleating agent decreased in the order of PLA/talc < PLA/ α-CD < PLA/CaCO$_3$ < neat PLA, which is associated to the crystallinity of these samples. Another possible explanation is the reduction of polymer chain mobility as hindered by added additive (Huda, Drzal, Mohanty, and Misra, 2007).
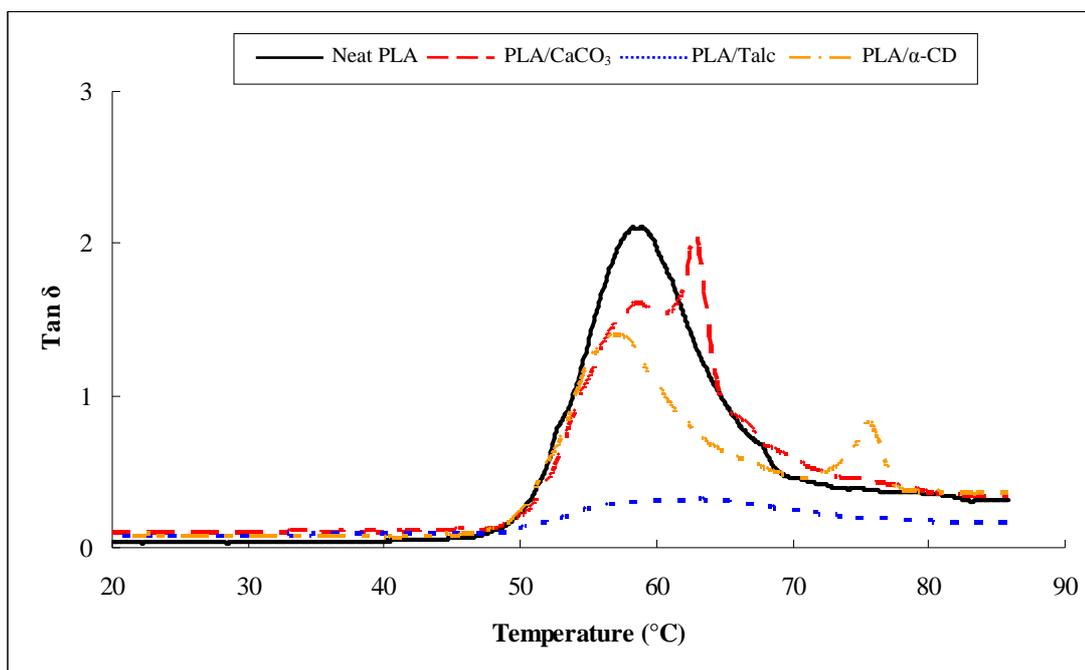
Figure 4.15 Tan δ of (a) PLA/Nucleating agent as a function of temperature.

In the case of PLA/NR blends, the presence of NR as well as nucleating agent did not influence the T_g of PLA in their blends (Figure 4.16). The tan δ peak feature remained unchanged with adding nucleating agent compared to that of neat PLA or nucleated PLA. The addition of NR shows a very sharp tan δ peak, which is no restriction to the motion of the free chain segment. The height of tan δ of PLA/NR blend is much higher than that of nucleated PLA/NR blends. Surprisingly, the height of tan δ of PLA/NR blend with addition of α-CD is lower than that of PLA/NR, although it showed a higher crystallinity. The decrease of this tan δ height seems to be a result of restricted molecular mobility related to the presence of the nucleating agent. However, the presence of talc maintains a very broad of T_g peak.
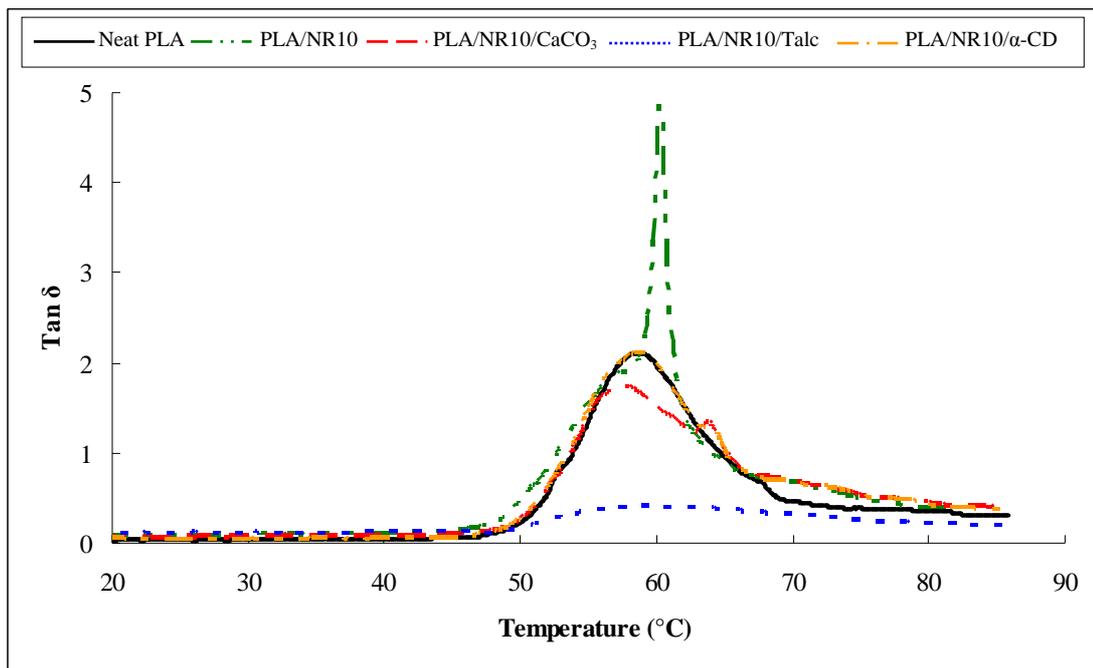
Figure 4.16 Tan δ of naet PLA and PLA/NR10/Nucleating agent as a function

of temperature.

4.3   Morphology

SEM micrographs of impact fractured surfaces are shown in Figure 4.17. In present work, the impact fractured surface of PLA/NR10 without nucleating agent was smoother than that of blends with nucleating agent. In the presence of nucleating agent, an increase in the roughness of impact fracture surface related to increase of impact toughness. In these micrographs, the dark holes represent NR particles, which were coated with gold. PLA/NR10 blend in the absence of nucleating agent showed spherical NR particles evenly dispersed in PLA. The same result can be observed in the addition of nucleating agent. Incorporation of $CaCO_3$, talc as well as α-CD maintained the spherical shape of NR particle, although the average particle size was

(a) (b)

(c) (d)
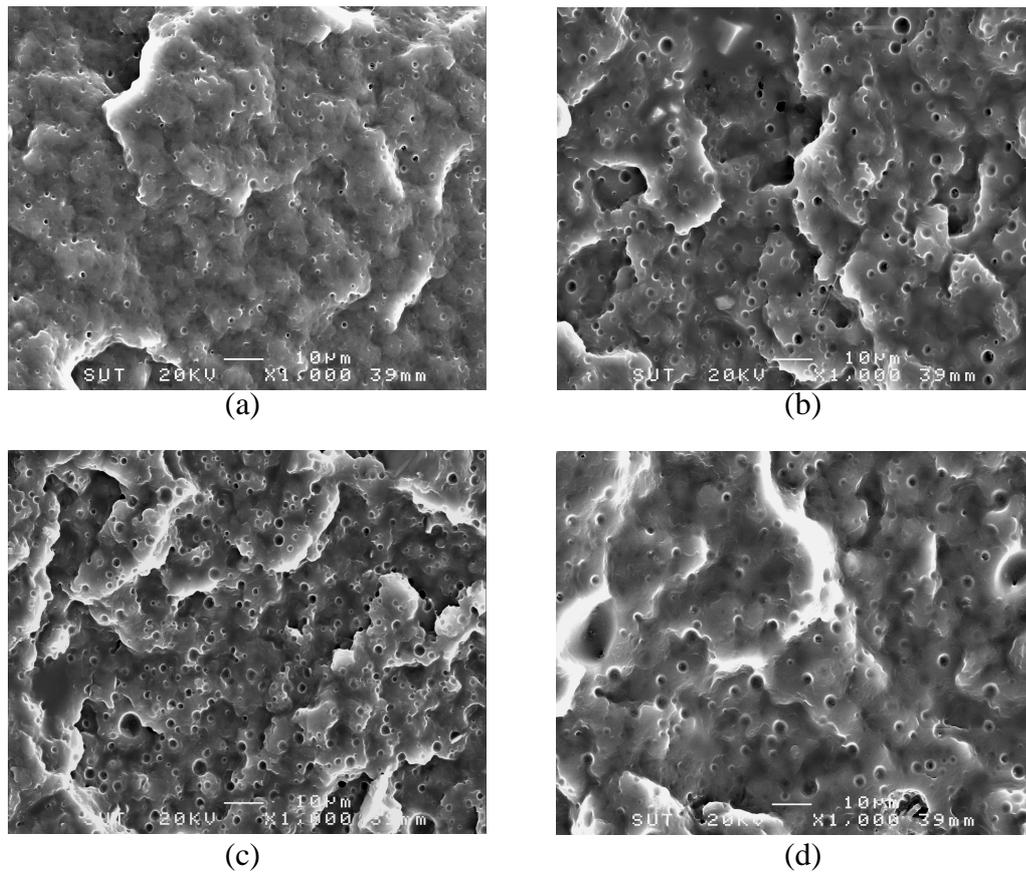
Figure 4.17 SEM micrographs of impact fractured surfaces of (a) PLA/NR10,

and with nucleating agents (b) $CaCO_3$, (c) talc, and (d) α-CD.

quite different with nucleating agent. The volume average diameters, D_v were

calculated according to the following relationship

$$D_v = \frac{\sum_i f(D_i)V_iD_i}{\sum_i f(D_i)V_i} = \frac{\sum_i n_iD_i^4}{\sum_i n_iD_i^3}$$ 4.2

where D_i is the diameter of the particle, n_i and V_i are the total number and total

volume of diameter particle (Grizzuti and Bifulco, 1997), respectively. The average

particles size was also calculated and the results are shown in Figure 4.18.

Incorporation of nucleating agent slightly increased the size of NR particle in the blends. Morphology and characteristics of rubber such as average particle size affect the mechanical properties of polymer blend (Collyer, 1994; Haward and Young, 1997). The optimum rubber particle size gave a highest toughness for several polymer matrices. The large rubber particle size (>20 μm) has no influence on the toughness, whereas the rubber particle size of 0.5-5 μm are the more effective toughening agent. This optimum rubber particle size is in good agreement with our results (1-3 μm). Thus an increase in NR particle size with addition of nucleating agent was less effective to enhance the toughness of PLA. However, the mechanical properties are the same regardless of different NR particle size in these samples. Thus the toughness improvement of PLA is mainly contributed by NR component and PLA spherulite size.
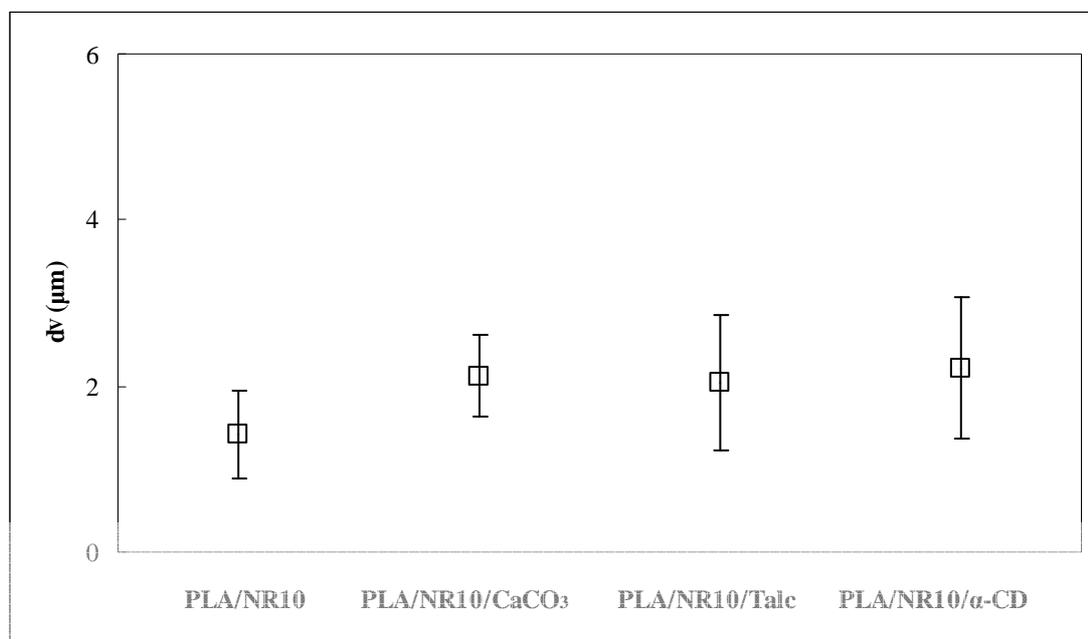
Figure 4.18 The variation of NR particle size with different nucleating agents.

CHAPTER V

CONCLUSIONS

Crystallization of PLA and PLA/NR10 blend added with different nucleating agents was investigated. For neat PLA, it was found the addition of talc had strong effect on crystallization, whereas $CaCO_3$ was ineffective nucleating agent for neat PLA. The α-CD acted as a green nucleating agent to initiate faster crystallization for neat PLA. All nucleating agents increased the degree of crystallinity of PLA. In the case of PLA/NR10 blend, only the blend with addition of talc facilitated faster crystallization of PLA, while both $CaCO_3$ and α-CD had no effect on crystallization temperature of PLA in PLA/NR10. An increase in the degree of crystallinity of PLA in PLA/NR10 was obtained with talc. Although talc was the most effective nucleating agent, which greatly enhanced both the cold crystallization temperature and degree of crystallinity, it gave the less perfect crystal for both neat PLA and PLA/NR blend.

Mechanical properties of both neat PLA and PLA/NR10 blend are affected by nucleating agent. Higher toughness of PLA samples with addition of nucleating agent than without nucleating agent can be explained by smaller spherulite size of PLA. In all samples, the stiffness of PLA did not change with addition of nucleating agent. An independence of glass transition temperature of PLA on nucleating agent was observed in both DSC and DMA tests. However, the nucleating agent particle and high crystallinity of PLA restricted the motion of free chain in amorphous region, resulting in the reduction of the height of tan δ peak. Larger NR particle size in PLA/NR10 blend with nucleating agent than unfilled PLA/NR10 blend has no

influence on mechanical properties of their blends. The toughness improvement of PLA is mainly contributed by NR component and spherulite size of PLA.

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APPENDIX A
PUBLICATION

PHYSICAL STUDY ON TOUHENING OF POLYLACTIC ACID WITH NATURAL RUBBER

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Abstract: This study aims to improve the toughness of polylactic acid (PLA) with natural rubber (NR). Due to their biodegradability, both PLA and NR are of interest. Biodegradable blends of PLA and NR were prepared at various concentrations (5-20 %wt NR content) by melt blending in an internal mixer. Mechanical, thermal properties and phase morphology of the blends were investigated. The percent elongation at break (%) and tensile toughness of PLA/NR blends increased with concentration of NR up to 10 %wt/wt while tensile strength and Young's modulus decreased. At 90/10 %wt/wt PLA/NR, elongation at break is 20.13% and tensile toughness is 499 MPa, which are higher than those of pure PLA, 9.30% and 317 MPa. In agreement with tensile results, impact strength of this blend composition increases three fold (to 6.50 kJ/m^2) compared to pure PLA. Beyond 10%wt NR content, both tensile and impact properties decreased. Morphological examination by scanning electron microscopy (SEM) of impact fracture surface showed spherical rubber particles evenly disperse in PLA matrix up to 10%wt NR content. The average particle size of NR (ranging from <1 μm to ~10 μm) increased with the NR content. From differential scanning calorimetry (DSC) analysis, the glass transition temperature (T_g), crystallization temperature (T_c) and the corrected crystallinity of PLA in PLA/NR blends do not change with addition of rubber. The results indicate that toughness improvement of PLA is mainly contributed by NR content and particle size.

Introduction

Polylactic acid (PLA) is a biodegradable polymer that has been widely used in industrial applications. It is a linear aliphatic polyester which can be synthesized by condensation and ring opening polymerization. Commercially available high molecular weight PLA resin is produced by ring opening polymerization of lactides which are the cyclic dimers of lactic acids [1,2]. PLA has high modulus and strength, but is brittle [3]. Blending with other polymers is commonly used to improve its brittleness.

Many studies on incorporation of both biodegradable and non-biodegradable polymer into PLA for toughness improvement have been reported [4-7]. However, rubbers are always considered as the best candidate for toughening. Various factors such as the molecular weight, the crystallinity of the matrix, type and content of the disperse phase, interfacial

characteristic and particle size play important roles on the level of toughening. For example, impact strength of blends can be improved with increasing rubber content in polymer blends [4,5,8]. Rubber phases dispersed in polymer matrix with most particle size less than 100 nm significantly increased toughness of blends even at very small rubber content (<5%) [9]. In addition to toughness, the incorporation of other polymers also affected crystallization of PLA [5,8]. By adding poly(vinyl butyral) (PVB), degree of crystallinity (X_C) of PLA did not change while crystallization rate increased [10]. The presence of poly(butylene succinate adipate) (PBSA) could decrease X_C of PLA [8].

In this study, natural rubber (NR) was chosen for toughening PLA. Besides its high toughness, NR is a biodegradable polymer that is obtained from renewable resource. Mechanical, thermal properties and morphology of pure PLA and PLA/NR blends were investigated.

Materials and Methods

Material: Commercially available PLA (NatureWorks PLA 4042D) was used. From DSC analysis, its glass transition temperature and melting temperature are 52.14°C and 146.68°C, respectively. High ammonia natural rubber (NR) latex was purchased from Thai Hua Rubber Public Company Ltd., Thailand. NR latex was dried at 70°C in an oven before use.

Sample Preparation: An internal mixer (Haake Rheomix 600p) was employed to mix PLA and NR using a rotor speed of 50 rpm at 180°C. Before mixing, dried rubber and PLA pellets were dried in an oven at 70°C for 8 h. The samples for tensile and impact testing were prepared by compression molding (Gotech model GT-7014-A30).

Thermal properties: Differential scanning calorimetry (DSC, Perkin Elmer model DSC-7) was used for determining thermal properties of the sample. All samples were heated from 25 to 200°C at 10°C/min (first heating) and kept isothermal for 2 min to erase previous thermal history. They were then cooled from 200°C to 25°C at 10°C/min and heated to 200°C again at the rate of 10°C/min (second heating).

Mechanical properties: Tensile testing samples were prepared by compression molding. Tensile testing was performed according to ASTM 638 using universal testing machine (UTM, Instron model 5569). The test was conducted with a crosshead speed of 1 mm/min at 25°C.

Notched Izod impact test was performed according to ASTM 256 using an Atlas testing machine (model BPI). Before testing, all specimens were notched.

Morphological characterization: Morphology of the impact fractured surface of pure PLA and PLA/NR blends was characterized using scanning electron microscope (SEM, JEOL model JSM 6400). The samples were coated with gold for 4 min before analysis.

Results and Discussion

Thermal Analysis: DSC second heating thermograms of pure PLA and PLA/NR blends are shown in Figure 1. For pure PLA, the glass transition temperature was found at 52.14°C. The cold crystallizattion temperature (T_{cc}) appeared at 116.06°C. The double-peak melting temperature (T_m) was observed. Sarasua et al. studied and explained that the melting peak at higher temperature (T_{m2}) belongs to more perfect crystalline structure than that at lower temperature (T_{m1}). The less perfect crystals have enough time to melt and reorganize into crystals with higher structure perfection and remelt at higher temperature [11]. The incorporation of NR did not affect the glass transition of PLA. The T_{cc} was broadened. The T_{m2} peak of the blends was clearly seen and became comparable to the T_{m1} peak as NR content increased.
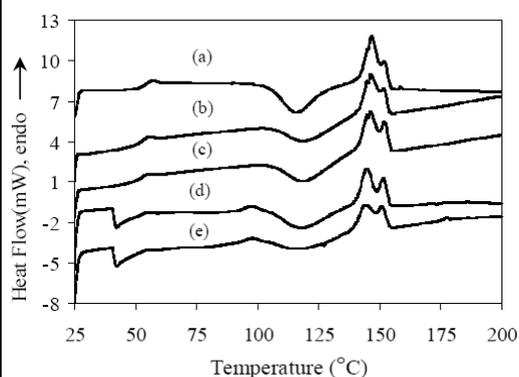
Figure 1. DSC thermograms of PLA/NR blends at heating rate of 10°C/min. Data from the second heat; (a) 0%NR, (b) 5%NR, (c) 10%NR, (d) 15%NR and (e) 20%NR.

The data from the DSC thermograms are summarized in Table 1. The X_C (%) of PLA in the blend was calculated using the following equation:

$$X_C = \frac{100 \times (\Delta H_{m,PLA} - \Delta H_{C,PLA})}{93 \times \Phi_{PLA}}$$

where $\Delta H_{m,PLA}$ is enthalpy of fusion of PLA (J/g), $\Delta H_{C,PLA}$ is enthalpy of crystallization of PLA (J/g), Φ_{PLA} is weight fraction of PLA in blend and enthalpy of fusion of a 100% crystalline PLA is 93 (J/g) [5]. The NR content did not significantly affect the degree of crystallinity. These results suggest that the perfection of PLA crystalline structure can be induced by NR without interfering the crystallinity.

Table 1. Thermal properties of pure PLA and PLA blends.

NR content (wt%)	T_g (°C)	T_{cc} (°C)	T_m(°C)		X_c (%)
			T_{m1}	T_{m2}	
0	52.14	116.06	146.68	151.87	58.76
5	53.31	118.55	146.34	151.69	52.73
10	54.40	118.39	146.17	152.03	57.43
15	54.99	118.14	144.76	151.45	58.68
20	54.58	117.31	144.93	150.96	59.13

Mechanical analysis: Tensile stress-strain curves of pure PLA and blends are shown in Figure 2. Tensile strength is 57 MPa and percent elongation at break is about 9.3% for pure PLA. Tensile strength decreased with increasing NR content. Young's modulus and elongation at break (%) as a function of NR content are shown in Figure 3. Modulus tends to decrease with rubber. Elongation at break increased with NR content up to 10%wt.
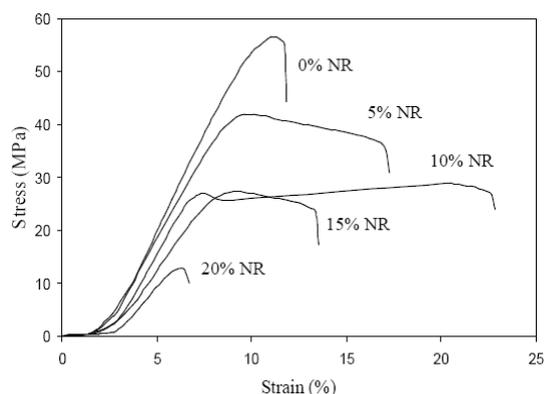
Figure 2. Tensile stress-strain curve of the PLA blends with different NR contents.
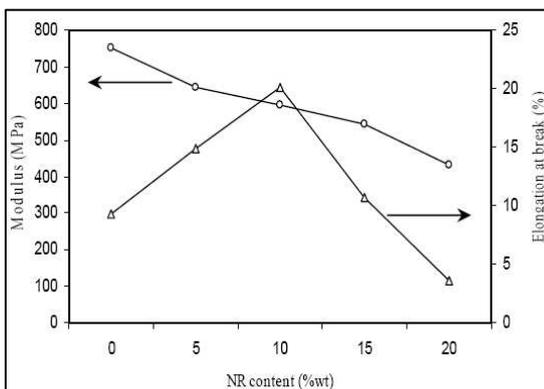
Figure 3. Tensile modulus and elongation at break of PLA blends with different NR contents.

Tensile toughness of PLA blends is also maximum at 10 % wt of NR content as shown in Figure 4. Toughness value of pure PLA is 317 MPa and 10 %wt of NR content is 499 MPa. From tensile results, the optimum NR content for toughening PLA/NR is at 10%wt NR.
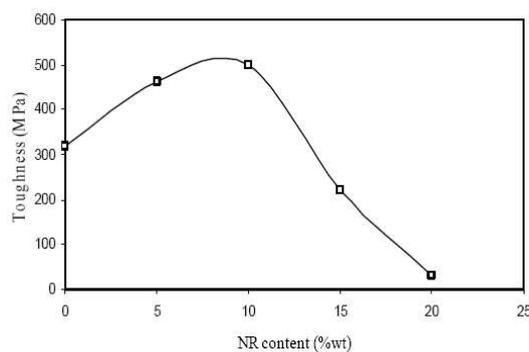
Figure 4. Tensile toughness of PLA blends with different NR contents.
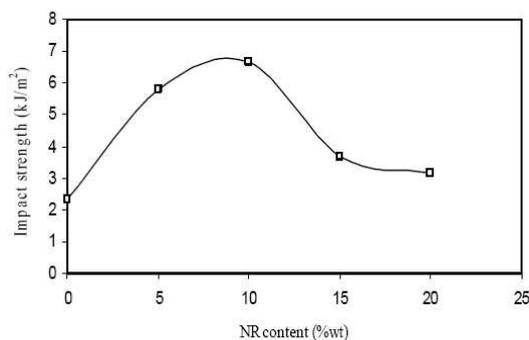
Figure 5. Impact strength of PLA blends with different NR contents.

Impact results are shown in Figure 5. The blend with 10%wt rubber showed maximum impact strength (6.50 kJ/m^2), consistent with the tensile results. Impact strength of this blend composition increases three folds compared to that of pure PLA.

Morphological analysis: SEM micrographs of impact fractured surfaces are shown in Figure 6. It is seen that fractured surface showed spherical rubber particles evenly dispersed in PLA matrix up to 10%wt NR content. When the NR content increased, the average particle size of NR increased (1.19 µm at 5 %wt NR to 2.19 µm at 10 %wt NR). Beyond 10%wt NR, coalescence of NR particles was observed (not shown here). These SEM results indicate that the toughness improvement of PLA when adding NR be due to NR content and size. With evenly dispersed rubber particles, the fracture energy can be effectively dissipated.
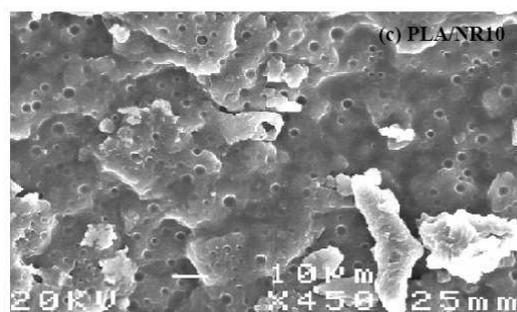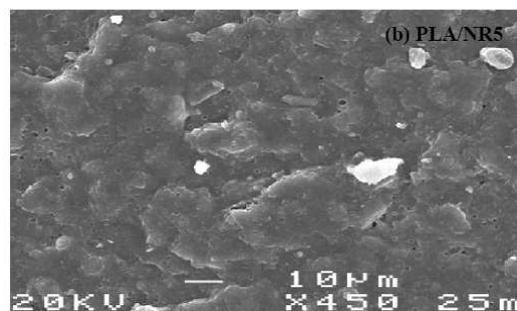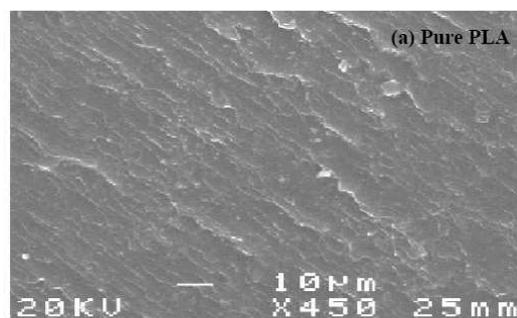
Figure 6. SEM micrographs of PLA/NR blends in the impact testing. (a) Pure PLA (b) PLA-5%NR and (c) PLA-10%NR.

Conclusions

PLA and NR were melt blended. The presence of NR did not affect thermal properties of PLA. Tensile strength and Young's modulus of PLA blends decreased with NR content. Percent elongation at break and impact strength increased with NR content up to 10%wt NR. The SEM results indicated that toughness improvement of PLA is mainly contributed by NR content and particle size.

Acknowledgment

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EFFECT OF NUCLEATING AGENT ON CRYSTALLIZATION AND DYNAMIC MECHANICAL PROPERTIES OF POLYLACTIC ACID AND NATURAL RUBBER BLENDS

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From our previous study, it was found that natural rubber (NR) can improve toughness of polylactic acid (PLA). At 10% wt of NR, the blend gave the highest impact strength and tensile toughness. However, blending with NR decreased the stiffness of PLA. To overcome this, using nucleating agent is considered. Three nucleating agents, calcium carbonate, talc and cyclodextrin are used. Here effects of nucleating agent on crystallization and dynamic mechanical properties of the blend in comparison to the PLA are investigated. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were employed. It was found that the cold crystallization temperature and the degree of crystallinity of both PLA and PLA/NR blends increase the presence of nucleating agent. In the glassy region, nucleating agents did not significantly affect the storage modulus (E') of the samples. For neat PLA, the storage modulus (E') was found to dramatic drop around 50-60 °C and increase at higher temperature before leveling off. In the tan δ plots, two peaks were observed as one at lower temperature corresponding to the glass transition temperature (T_g) and another at higher T. The latter may relate to the cold crystallization, the formation of more perfect crystal forms or temperature rate/frequency dependence of the T_g. Similar results were observed in the PLA with the addition of calcium carbonate or cyclodextrin and PLA/NR blends with cyclodextrin. However, when using talc the drop of E' values is much less and a very weak and broad tan δ peak was observed in both PLA and PLA/NR blends. The addition of nucleating agent to the PLA and PLA/NR samples increase the T_g, of which talc shows the highest increase. These results suggest that nucleating agents not only affect the crystallization of both PLA and PLA/NR blends but also their dynamic mechanical properties in the vicinity of T_g.

BIOGRAPHY

Buncha Suksut was born on May 4, 1984 in Nakhon Ratchasima, Thailand. He graduated his Bachelor's Degree in Polymer Engineering from Suranaree University of Technology (SUT) in 2006. He then continued his Master's degree in Polymer Engineering at School of Polymer Engineering, Institute of Engineering at Suranaree University of Technology. During his Master's degree study, he presented two posters entitled of **"Physical Study on Toughening of Polylactic Acid with Natural Rubber"** in the Pure and Applied Chemistry International Conference 2009 (PACCON 2009), Phitsanulok, Thailand, and **"Effect of Nucleating agent on Viscoelastic and Crystallization Behaviors of Polylactic Acid and Natural Rubber blends"** in the Fourth International Workshop for Far East Asian Young Rheologist (CIAE), Nakhon Ratchasima, Thailand.