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TOUGHNESS IMPROVEMENT OF POLYLACTIC ACID BLOWN FILMS BY ADDING CARBOXYLATED EPOXIDISED NATURAL RUBBER

Ms. Nattanich Maneechavakajone

A Thesis Submitted in Partial Fulfillment of the Requirements
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By	Ms. Nattanich Maneechavakajone
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Anongnat Somwangthanaroj, Ph.D.
Thesis Co-advisor	Assistant Professor Wanchai Lerdwijitjarud, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………… Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Associate Professor Tharathon Mongkhonsi, Ph.D.)

……………………………………………… Thesis Advisor
(Assistant Professor Anongnat Somwangthanaroj, Ph.D.)

……………………………………………… Thesis Co-advisor
(Assistant Professor Wanchai Lerdwijitjarud, Ph.D.)

……………………………………………….. Examiner
(Associate Professor ML. Supakanok Thongyai, Ph.D.)

……………………………………………….. External Examiner
(Suttinun Phongtamrug, Ph.D.)

ณัฐนิช มณีชวขจร : การพัฒนาความเหนียวของฟิล์มเป่าพอลิแลคติก แอซิดโดยการเติมยางธรรมชาติอิพอกไซด์ที่มีหมู่คาร์บอกซิล. (TOUGHNESS IMPROVEMENT OF POLYLACTIC ACID BLOWN FILMS BY ADDING CARBOXYLATED EPOXIDISED NATURAL RUBBER) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร. อนงค์นาฏ สมหวังธนโรจน์, อ. ที่ปรึกษาร่วม : ผศ.ดร.วันชัย เลิศวิจิตรจรัส 117 หน้า.

พอลิแลคติกแอซิด (PLA) เป็นหนึ่งในพอลิเมอร์ย่อยสลายได้ทางชีวภาพที่ได้รับความสนใจเป็นอย่างมากและเป็นเทอร์โมพลาสติกในเชิงพาณิชย์ที่ได้มาจากแหล่งทรัพยากรทดแทน อย่างไรก็ตามข้อจำกัดของ PLA คือ มีความแข็งและความเปราะสูง ในงานวิจัยนี้ผู้วิจัยได้พยายามปรับปรุงความเหนียวของฟิล์มเป่า PLA จากการเติมยางธรรมชาติอิพอกซิไดซ์คาร์บอกซิล (ENR-COOH) เป็นสารเพิ่มความเหนียว โดยเตรียมยางธรรมชาติอิพอกซิไดซ์ (ENR) ที่ระดับการเกิดอิพอกซิเดชันแตกต่างกันและเปลี่ยนหมู่ฟังก์ชันด้วยกรดไทโอไกลโคลิก (TGA) ทำให้ได้ยาง ENR-COOH ที่มีระดับการเปลี่ยนหมู่ฟังก์ชั่นเท่ากับ 1, 4, 8 และ 37% ตามลำดับเทียบกับยางธรรมชาติ ซึ่งยืนยันผลได้จากเทคนิค Fourier Transforms Infrared Spectroscopy (FTIR) และ Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) จากนั้นทำการศึกษาฟิล์มเป่าของ ENR-COOH/PLA เทียบกับฟิล์ม PLA บริสุทธิ์เพื่อหาระบบและปริมาณการเติมยางที่ดีที่สุด ผลการทดสอบด้วยเทคนิค Differential Scanning Calorimetry (DSC) และ Dynamic Mechanical Analysis (DMA) พบว่า สมบัติทางความร้อนและสมบัติเชิงกลความร้อนมีค่าลดลงเมื่อความเป็นขั้วของ ENR-COOH เพิ่มขึ้น ฟิล์มในระบบที่เติม ENR6-COOH ที่ 3% โดยน้ำหนัก มีค่าความยาว ณ จุดขาดสูงสุดเมื่อเทียบกับฟิล์ม PLA บริสุทธิ์ (มีค่าประมาณ 9.98 เท่าในแนวทิศทางการเป่าฟิล์ม (MD)) จากนั้นจึงนำยาง ENR6-COOH ผสมกับ PLA และแมกนีเซียมสเตียเรท (MgSt) โดยเปลี่ยนแปลงปริมาณยางที่ 1, 3, 4 และ 5% โดยน้ำหนัก จากผลการทดลองพบว่า ฟิล์มในระบบที่เติม ENR6-COOH ที่ 4% โดยน้ำหนักมีค่าความยาว ณ จุดขาดเพิ่มขึ้น 35 เท่าเมื่อเทียบกับฟิล์ม PLA ที่มีการเติมแมกนีเซียมสเตียเรท

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต..........

สาขาวิชา.....วิศวกรรมเคมี..... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..........

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NATTANICH MANEECHAVAKAJONE : TOUGHNESS IMPROVEMENT OF POLYLACTIC ACID BLOWN FILMS BY ADDING CARBOXYLATED EPOXIDISED NATURAL RUBBER. ADVISOR : ASST. PROF. ANONGNAT SOMWANGTHANAROJ, Ph.D., CO-ADVISOR : ASST. PROF. WANCHAI LERDWIJITJARUD, Ph.D., 117 pp.

Polylactic acid (PLA) is one of the most interesting biodegradable polymers and commercially-produced thermoplastic that is derived from renewable resources. However, the limitation of PLA is the stiffness and brittleness. In this research, the authors had tried to improve the toughness of PLA blown film by adding carboxylated epoxidised natural rubber (ENR-COOH) as toughening agent. Epoxidised natural rubber (ENR) samples of various epoxidation level were synthesized and modified with thioglycolic acid (TGA) to yield ENR-COOH with 1, 4, 8 and 37% conversion of its initial NR, respectively, confirmed by Fourier Transforms Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). Then, blown films of ENRs-COOH/PLA compared with neat PLA film were studied to find the optimum type and rubber content. The results from Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) showed that thermal and thermomechanical properties dropped with increasing of polarity of ENRs-COOH. Compared with neat PLA film, 3 wt% ENR6-COOH/PLA films exhibited the highest elongation at break (which was approximately 9.98 times in Machine Direction (MD). Later, ENR6-COOH was selected to blend with PLA and 0.5 wt% magnesium stearate (MgSt) by varying rubber content at 1, 3, 4 and 5 wt%. The results showed that 4 wt% ENR6-COOH/PLA_MgSt film provided the highest elongation at break by increasing 35 times in MD compared with PLA_MgSt film.

Department : Chemical Engineering	Student's Signature
Field of Study : Chemical Engineering	Advisor's Signature
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CONTENTS

Page

Page

Page

LIST OF TABLES

TABLE **Page**

TABLE **Page**

LIST OF FIGURES

FIGURE **Page**

FIGURE **Page**

FIGURE **Page**

CHAPTER I

INTRODUCTION

1.1 General Introduction

Nowadays, most of the packaging plastic is produced from petroleum-based polymer such as polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET). These polymers exhibit not only good properties but also good processability. However, they become the major problem on the environment because of their endurance and low degradation rate. The reason they are not biodegradable or difficult to degrade is their molecules are too large and sticky by chemical bonding to be decomposed by decomposer organisms.

To overcome this problem, many researchers have been searching for biodegradable polymers which can be based on natural or synthetic resins. These polymers have molecules which can be easily degraded into carbon dioxide and water in suitable conditions by microorganisms. The example of these polymers are polylactic acid (PLA), polycaprolactone (PCL), poly (butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB).

One of the most interesting biodegradable polymers and commercially-produced thermoplastic is polylactic acid or polylactide (PLA). PLA is aliphatic polyester produced from renewable resources like plants. It can be easily synthesized by either the simple polycondensation of lactide or the ring-opening polymerization of the cyclic diester of lactide. PLA has many advantages including good thermal stability, processability and low environmental impact. Moreover, it exhibits good mechanical properties such as high modulus and tensile strength. However, the brittleness and stiffness at room temperature of PLA limit its use.

Some researchers found that the toughening of PLA can be enhanced by addition of some elastomeric materials. Although numerous attempts have been made to toughen PLA though blending, the focus has typically been on biomaterials. Therefore, blending PLA by using natural rubber as raw material is in interest.

Carboxylated epoxidised natural rubber (ENR-COOH), a derivative of natural rubber (NR), is an alternative for toughening PLA due to the introduction of the epoxide and carboxyl group lets ENR-COOH have higher polarity than NR which is non-polar. Many researchers found that the polar rubber commonly leads to compatibility with polar polymers such as epoxy resin and nylon 6 (polyamide 6, PA6).

This work aims to synthesize ENR-COOH and use it as toughening agent to improve toughness of polylactic acid blown film.

1.2 Objectives

1. To study the preparation of ENR-COOH/PLA films by using ENR-COOH as toughening agent
2. To study the effect of the epoxide and carboxyl content and loading of ENRs-COOH on the mechanical and thermal properties as well as thermomechanical properties of ENRs-COOH/PLA films

1.3 Scopes of the research

1. Four systems of ENR 6, 19, 24 and 52 mol% epoxide content will be prepared by solvent method and modified with thioglycollic acid (TGA) (1.5 mol TGA/mol of epoxide group) to provide ENR-COOH.
2. 3 wt% ENRs-COOH/PLA blown films will be prepared in which mechanical properties including tensile strength, young's modulus, elongation at break and toughness will be considered.
3. The system which has the optimal mechanical properties will be chosen for blowing film by varying the ENR-COOH loading at 1, 3, 4 and 5 wt%.
4. Thermal and tensile properties of all ENRs-COOH/PLA films will be investigated.

CHAPTER II

THEORY

2.1 Polylactic acid (PLA)

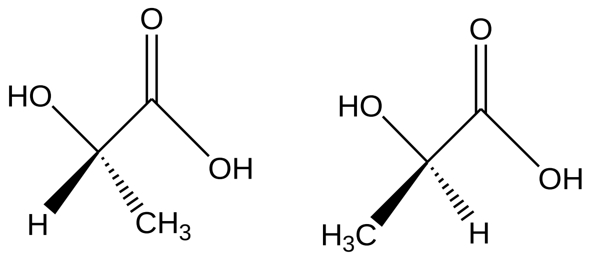
Polylactic acid or polylactide (PLA) is linear aliphatic polyester that is derived from renewable resources such as plants (e.g., corn, wheat, or potato). PLA is a biocompatible and biodegradable material which is decomposed to carbon dioxide and water [1, 2].

2.1.1 Synthesis of PLA

Lactic acid is the monomeric building block of PLA, which is naturally occurring organic acid that can be produced by converting sugar or starch by either bacterial fermentation or chemical synthesis. Lactic acid from chemical synthesis is mainly based on the hydrolysis of lactonitrile by strong acids, which provides two optical isomers that are D-lactic acid (rotates the plane of polarized light clockwise) and L-lactic acid (rotates the plane of polarized light counterclockwise) as shown in figure 2.1 [1, 3].

The examples of other possible chemical synthesis routes for lactic acid are [1]:

- Catalyzed degradation of sugars
- Hydrolysis of chloropropionic acid
- Nitric acid oxidation of propylene
- Oxidation of propylene glycol
- Reaction of acetaldehyde, carbon monoxide, and water at high temperature and pressure



L-Lactic acid D-Lactic acid

Figure 2.1 Lactic acid optical monomers

In the bacterial fermentation, almost L-lactic acid (99.5% of the L-lactic acid and 0.5% of the D-lactic acid) is provided by an optimized strain of Lactobacillus [3]. The fermentation has been used more extensively than chemical synthesis because of its eco-friendly and use of renewable resources instead of petrochemicals. Including, the fermentative production provides several advantages such as low cost of substrates, low production temperature, and low energy consumption [1].

The two main methods to PLA synthesis are (shown in Figure 2.2) [3, 4]:

1) Direct condensation polymerization

The presence of both hydroxyl and carboxyl groups in lactic acid can be directly converted to yield only low molecular weight PLA. The molecular weight is limited due to hydrolysis of the ester bonds and the removal of water is needed. However, the chains length of PLA can be increased and become a high molecular weight PLA by adding chain coupling agents (organic solvents) for azeotropic distillation to give water as byproduct.

2) Ring-opening polymerization (ROP)

This reaction is the most common way to provide high molecular weight PLA. A cyclic dimer intermediate or lactide is formed by catalytic ring opening polymerization of the cyclic lactide. Three stereoforms of lactide are possible obtained: L-lactide, D-lactide, and DL-lactide (meso-lactide), as shown in Figure 2.3.

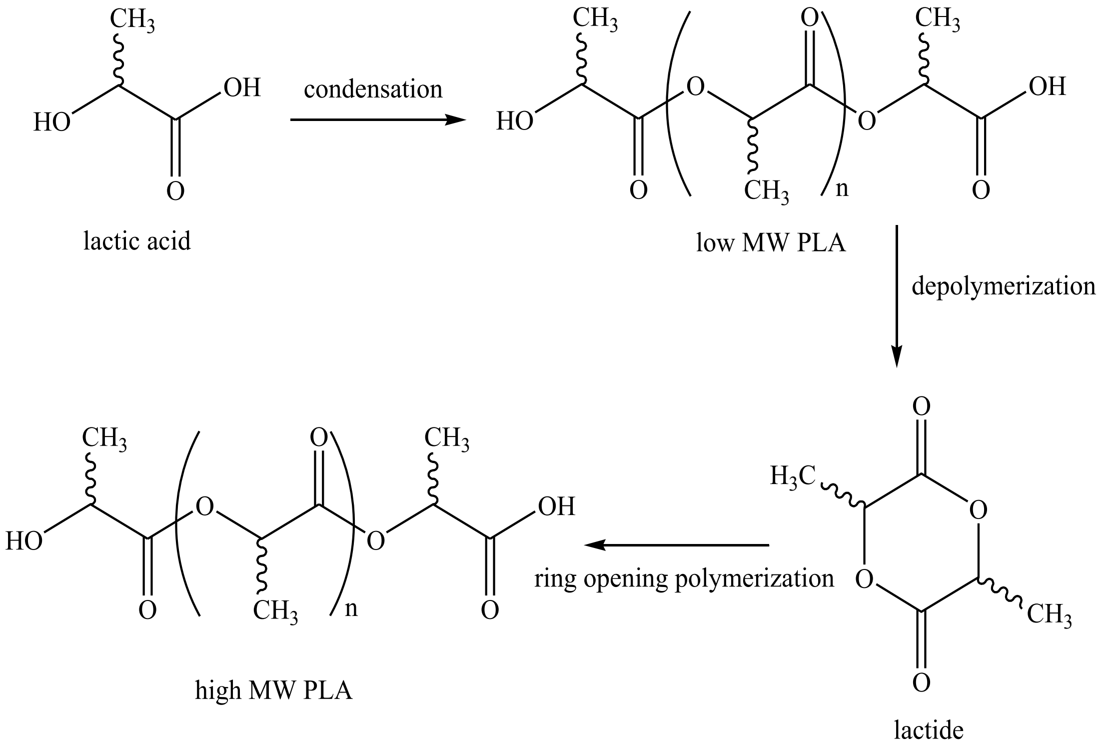
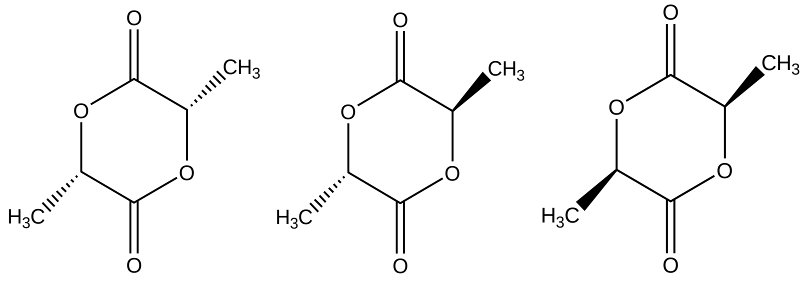


Figure 2.2 Polymerization of lactic acid and ring opening polymerization of lactide



L-lactide Meso lactide D-lactide

Figure 2.3 Stereoforms of lactides [1]

Polymerization of a racemic mixture of L-lactide and D-lactide usually leads to the synthesis of poly-DL-lactide (PDLLA) which is amorphous. Stereospecific catalysts are used to produce heterotactic PLA which is crystalline polymer. The degree of crystallinity and several properties are largely controlled by the ratio of D to L enantiomers used, including the type of catalyst used.

2.1.2 Physical and Chemical Properties [2-4]

PLA has several interesting properties such as good mechanical properties, thermal stability, processability and low environmental impact. In general, PLA are soluble in dioxane, acetonitrile, chloroform, methylene chloride, 1, 1, 2-trichloroethane and dichloroacetic acid, but are insoluble in water, some alcohols and alkanes.

However, the structural unit chain arrangement, processing temperature, annealing time as well as molecular weight have an effect on the properties of PLA, such as Poly(L-lactide), (PLLA), the resulted product from polymerization of L-lactide, has a crystallinity of around 37%, a glass transition temperature (T_g) of 50-80 ^{o}C and a melting temperature (T_m) of 173-178 ^{o}C. The crystallinity of PLA decreases with chain stereoregularity. In the form of stereo complex, the increased crystallinity of PLA also leads to unsatisfactory characteristics such as brittleness, low heat deflection temperature (HDT), and indigent barrier properties.

2.2 Natural rubber and modified natural rubber

2.2.1 Natural rubber (NR)

Natural rubber (NR) is an elastic hydrocarbon polymer that is usually obtained from the latex of the Hevea Brasilliensis tree (para rubber tree), which is native to the tropical Americas [5]. The latex is the white milky liquid, including 30-40% of dry rubber content. Other materials in natural rubber are proteins, fatty acids, resins and inorganic materials (salts) [6]. The latex can be coagulated with methanol, acetic or formic acid. The natural rubber latex is shown in Figure 2.4.

Figure 2.4 Natural rubber latex [7, 8]

Natural rubber is a linear polymer consisting of an unsaturated hydrocarbon called isoprene (2-methylbutadiene). The chemical structure of natural rubber is cis-1,4-polyisoprene (as shown in Figure 2.5) with molecular weights of 100,000 to 1,000,000 g/mol. Commonly, natural rubber is a thermoplastic. However, the rubber can be turned into a thermoset after vulcanization. A process in which the rubber is heated, followed by adding sulfur, peroxide or bisphenol to improve resilience and elasticity as well as to prevent it from perishing is called vulcanization [5].

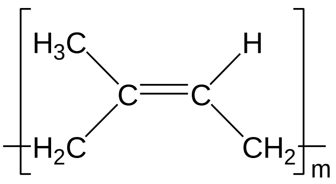


Figure 2.5 Chemical structure of natural rubber

Natural Rubber has properties as follows [6, 9]:

- Transparent and amorphous solid, in which on stretching or prolonged cooling becomes crystalline
- Tough and elastic solid at room temperature (soft and sticky as the increasing temperature)
- Elasticity over a narrow range of temperature from 10 to 60 ^{o}C
- Soluble in ether, carbon disulfide, carbon tetrachloride, petrol and turpentine.
- Insoluble in water, alcohol, acetone, dilute acids and alkalis
- High tear strength with outstanding resistance to fatigue
- High ability to stick to itself and to other materials which makes it is easily fabricated
- High resistance to cutting, chipping and tearing
- High adhesion to brass-plated steel cord
- Moderate resistance to environmental damage by heat, light and ozone
- Low hysteresis which leads to low heat generation
- Low rolling resistance with enhanced fuel economy
- Low tensile strength and abrasion resistance

2.2.2 Epoxidized natural rubber (ENR)

Epoxidized natural rubber (ENR) is an elastomeric polymer derived from the partial epoxidation of the natural rubber molecule [10]. The chemical structure of epoxidized natural rubber is shown in Figure 2.6. Because epoxides are reactive species, epoxidation is one of the most convenient ways to modify natural rubber [11]. Double bonds on backbone molecule are converted to epoxides (oxiranes) by using organic peracid. In the first step, peracid is formed by the reaction between acid and hydrogen peroxide. Then, in the second step, the peracid is reacted with natural rubber latex to give epoxidized liquid natural rubber (ELNR) [12]. The epoxide groups are randomly distributed along the natural rubber molecules [10]. The epoxidation reaction is shown in Figure 2.7.

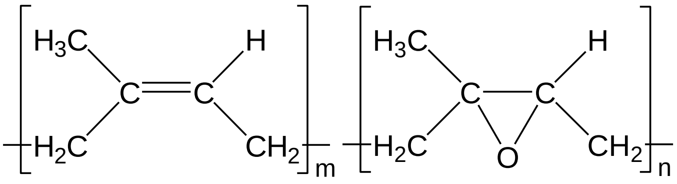


Figure 2.6 Chemical structure of epoxidized natural rubber

Formation of peracid :

$$RCOOH + H_2O_2 \rightleftharpoons RCOOOH + H_2O$$

Epoxidation :

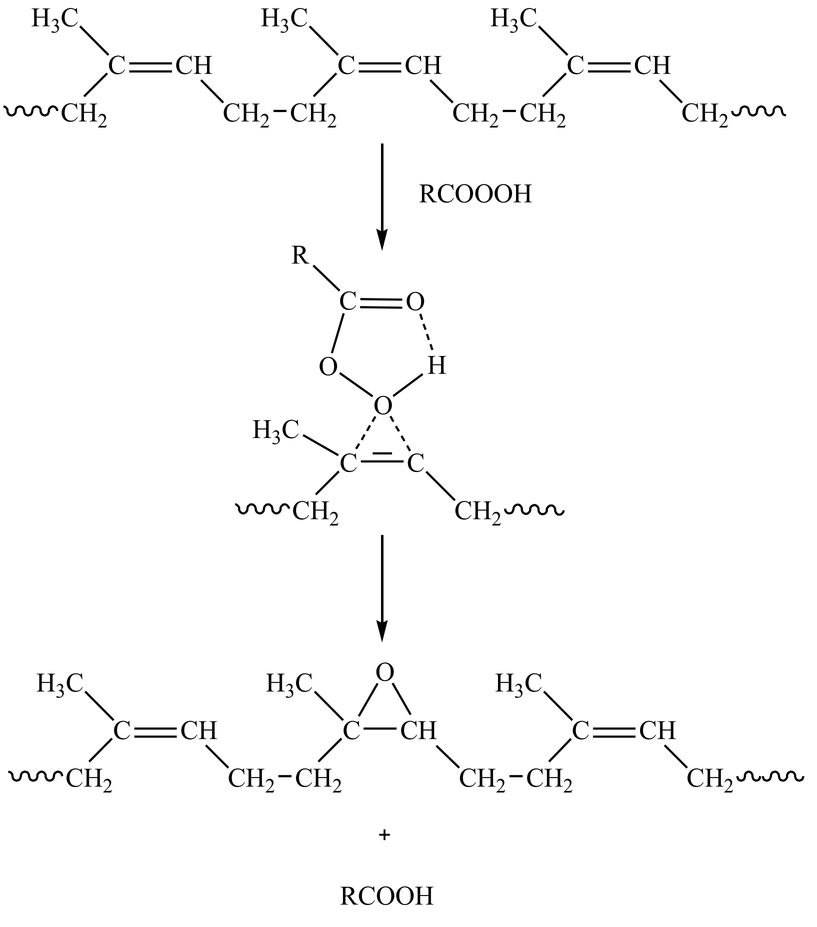


Figure 2.7 Epoxidation reaction of natural rubber [13]

The level of epoxidation of ENR has an effect on polarity and glass transition temperature (T_g) which increases with an increasing of epoxidation level of ENR. The increasing of T_g also improves some mechanical properties such as tensile properties, damping properties and fatigue behavior. Furthermore, increasing polarity of ENR causes high resistance to oil, non-polar solvents, oxygen and ozone while decreases flexibility [14].

2.3 Thioglycollic acid (TGA)

Thioglycollic acid or mercaptoacetic acid (TGA) is an organic compound with the molecular structure as $HSCH_2COOH$. The structure of TGA contains both a thiol (mercaptan) and a carboxylic acid as shown in Figure 2.8. It has unpleasant odor characteristic of the sulfhydryl group and readily oxidized by air and reacts with oxygen to formation of dithiodiglycolic $[SCH_2COOH]_2$ [15]. The principle physical and chemical properties of thioglycolic acid are shown in Table 2.1.

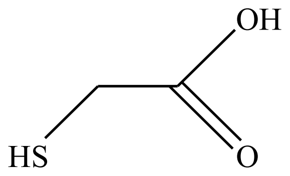


Figure 2.8 Structure of thioglycollic acid

The applications of thioglycollic acid and its derivatives are widely used in the fields of [15]:

- Corrosion inhibition and down-hole acidizing in the oil field industry
- Manufacturing of pharmaceuticals, agrochemicals and fabric dying
- Hair care products (waving hair removal and hair straightening)
- Shrink-resistant treatment of wool
- Leather processing

- Chemical depilatory
- Cold wave permanents
- Making of tin stabilizers for PVC products
- Detection of iron, molybdenum, silver and tin

Table 2.1 Some physical and chemical properties of thioglycolic acid [15]

Properties	
Physical state	Colorless liquid
Molar mass	92.12 g/mol
Density	1.32 g/cm^3
Melting point	- 16.5 °C
Boiling point	120 °C at 20 mmHg
Vapor pressure	10 mmHg at 18 °C
Specific gravity	1.325
Solubility	Miscible with water, ethanol, ethyl ether, and other organic solvents, slightly soluble in chloroform
pH	1.6 (10% solution)
Viscosity	6.35 cps at 20 °C
Auto ignition	350 °C
Refractive index	1.503
NFPA ratings	Health: 3 Flammability: 0 Reactivity: 2
Flash point	112 °C
Stability	Stable under ordinary conditions

2.4 Magnesium stearate (MgSt)

Magnesium stearate (MgSt) is light white powder which has the molecular formula $Mg(C_{18}H_{35}O_2)_2$. It can be produced from both animal and vegetable oils. MgSt consists of the anion of stearic acid and magnesium cation. It has the melting temperature of 88 °C. MgSt is slightly soluble in benzene but is not soluble in ether and water [16]. It is widely used as a lubricant in the manufacture of medical tablets, capsules and powders. It is also used to bind sugar in hard candies and is a common ingredient in baby formulas [17]. The molecular structure of magnesium stearate is shown in Figure 2.9.

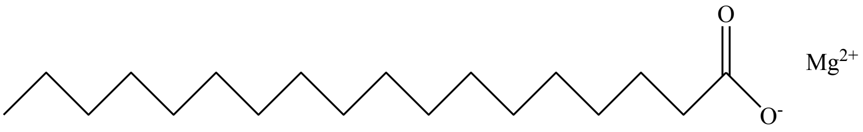


Figure 2.9 The molecular structure of magnesium stearate

CHAPTER III

LITERATURE REVIEW

Polylactic acid or PLA is the interesting biodegradable material which is widely used to produce packaging film because of its excellent thermal stability, process ability and mechanical properties such as high modulus and tensile strength. However, PLA is still limited in some properties, especially, the brittleness and stiffness. The researches on the toughening of PLA usually occur in the blending field. Many researchers have tried to improve its toughness by blending with other rubbery polymers such as natural rubber and its derivative. However, the properties of PLA/ENR-COOH blending film still depend on many factors such as level of functional group in rubber molecules and rubber contents.

3.1 Effect of level of functional group in rubber molecules on thermal and mechanical properties

From thermal properties of modified natural rubber by increasing degree of epoxidation, it was found that glass transition temperature (T_g) increased approximately 0.92 ^{o}C / mol% of epoxide group [18]. The T_g of epoxidised natural rubber (ENR) was higher than that of natural rubber (NR) and increasing with reaction time. Furthermore, the initial thermal degradation temperature and maximum degradation temperature (T_d) of ENR was also higher than those of NR. The T_d of

ENR was 393.1 ^{o}C whereas that of NR was 371.5 ^{o}C [18]. The effect of ENR with 25 and 50 mol% epoxidation level (ENR25 and ENR50) as compatibilizer on the cure characteristics of the melt compounded natural rubber/organoclay nanocomposites indicated that the increasing in degree of epoxidation level of ENR leaded to the increasing in maximum torque, minimum torque and torque difference during blending process by using a Brabender Plasticorder [19]. The dispersion of organoclay in the NR matrix was quite well when ENR50 was used as compatibilizer in which the degree of clay dispersion is followed by the system with ENR25 and uncompatibilizer, respectively. ENR50 nanocomposite had the highest storage modulus (E') above the T_g followed by the ENR25 compatibilized and uncompatibilized nanocomposite. Moreover, the tensile and tear properties of ENR50 nanocomposite were also higher than those of ENR25 nanocomposite. The tensile strength, elongation at break and tear strength of ENR50 nanocomposite were approximately 28 MPa, 1200% and 60 MPa whereas those of ENR25 nanocomposite were 24 MPa, 1150% and 50 MPa, respectively. The Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) micrograghs showed that dispersion of the organoclay in ENR50 nanocomposite was better than that of ENR25 and uncompatibilized nanocomposite [19]. Influence of various levels of epoxide groups (10, 20, 30, 40, and 50%) on mechanical properties, morphology and swelling resistance of the ENR/polypropylene (PP) blends were investigated by Nakason et al.[20]. The results of 75/25 ENR/PP blends with phenolic modified polypropylene (Ph-PP) as compatibilizer showed that the tensile strength increased from 7 to 9 MPa and the hardness increased from 60 to 100 MPa while elongation at break decreased from 320 to 220% with the increasing of epoxide levels in ENR molecules. This was resulted from the increasing of chemical interaction between methylol groups of Ph-PP and polar functional groups of ENR as shown in Figure 3.1. It was also observed that sizes of dispersed vulcanized rubber domains and %swelling of the blends decreased with an increasing of the level of epoxide groups in the ENR molecules.

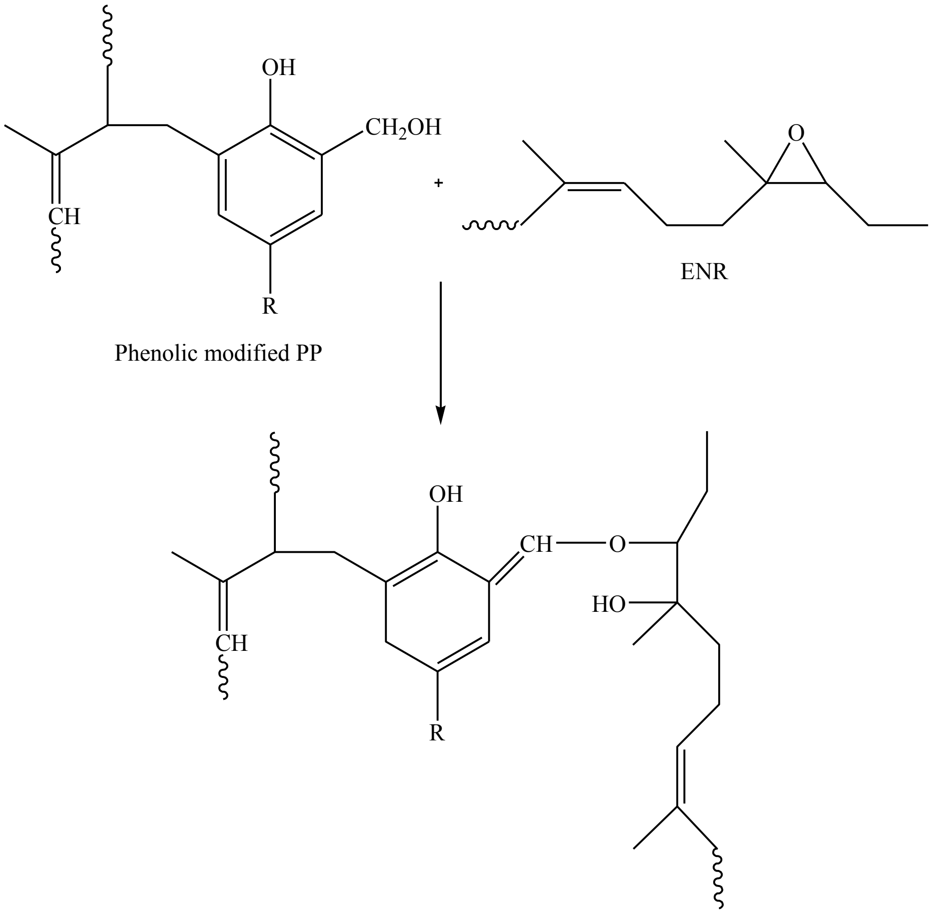


Figure 3.1 Possible mechanism of compatibilization of ENR/PP blends by Ph-PP [20]

3.2 Effect of rubber contents on thermal and mechanical properties

Blends of PLA/ENR/organoclay nanocomposites by compression molding were studied by Thipmanee et al. [21]. To improve the ductility of PLA before blending with organoclay, the optimum ratio of PLA and ENRs (0, 10, 20, 30, 40 and 50%) were investigated. It was found that the blend containing higher amount of ENR reduced modulus and tensile strength whereas impact strength is increased. 90/10 PLA/ENR blends gave the highest tensile strength, modulus and elongation at break as 18.34 MPa, 885.67 MPa and 2.86%, respectively. The probably chemical interactions between PLA and ENR when the ENR content less than or equal to 10% were proposed in Figure 3.2.

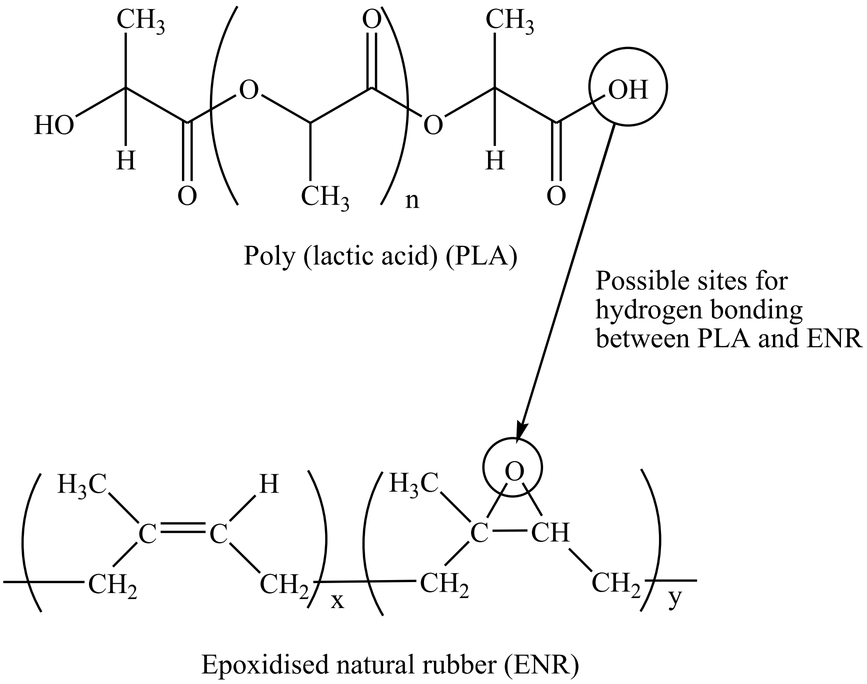


Figure 3.2 Proposed chemical interactions between PLA and ENR [21]

ENR at various weights (0, 20, 30 and 40%) were added to improve the ductility of nylon 6 (polyamide 6, PA6) [22]. It was found that elongation at break of PA6/ENR blends were higher than that of neat PA6 whereas yield stress, yield strain and stress at break were lower than that of neat PA6. Furthermore, the impact strength of PA6/ENR blends was also increased 4 - 6 times compared with that of the neat PA6. The 80/20 PA 6/ENR blend showed the highest elongation at break at 81 ± 15% and the smallest particle sizes of ENR (diameter range ~ 0.11 – 2.20 μm) which was observed by SEM micrograph.

The mechanical properties and swelling resistance of polymer blend between NR and ENR-COOH were studied [11]. Thioglycolic acid (TGA) reacted with oxirane ring in ENR to provide ENR-COOH with 17% conversion. After that, ENR-COOH was blended with NR at 0, 10 and 25 weight%. Vulcanizing agents were then added before preparing the specimens by compression molding technique. It was found that the blending of ENR-COOH and NR could improve modulus (M100 and M300), hardness, resistance to swelling in oil and solvents such as chloroform and toluene whereas elongation at break was decreased because of cross linking between ENR and TGA. Probable reactions of ENR with TGA were shown in Figure 3.3.

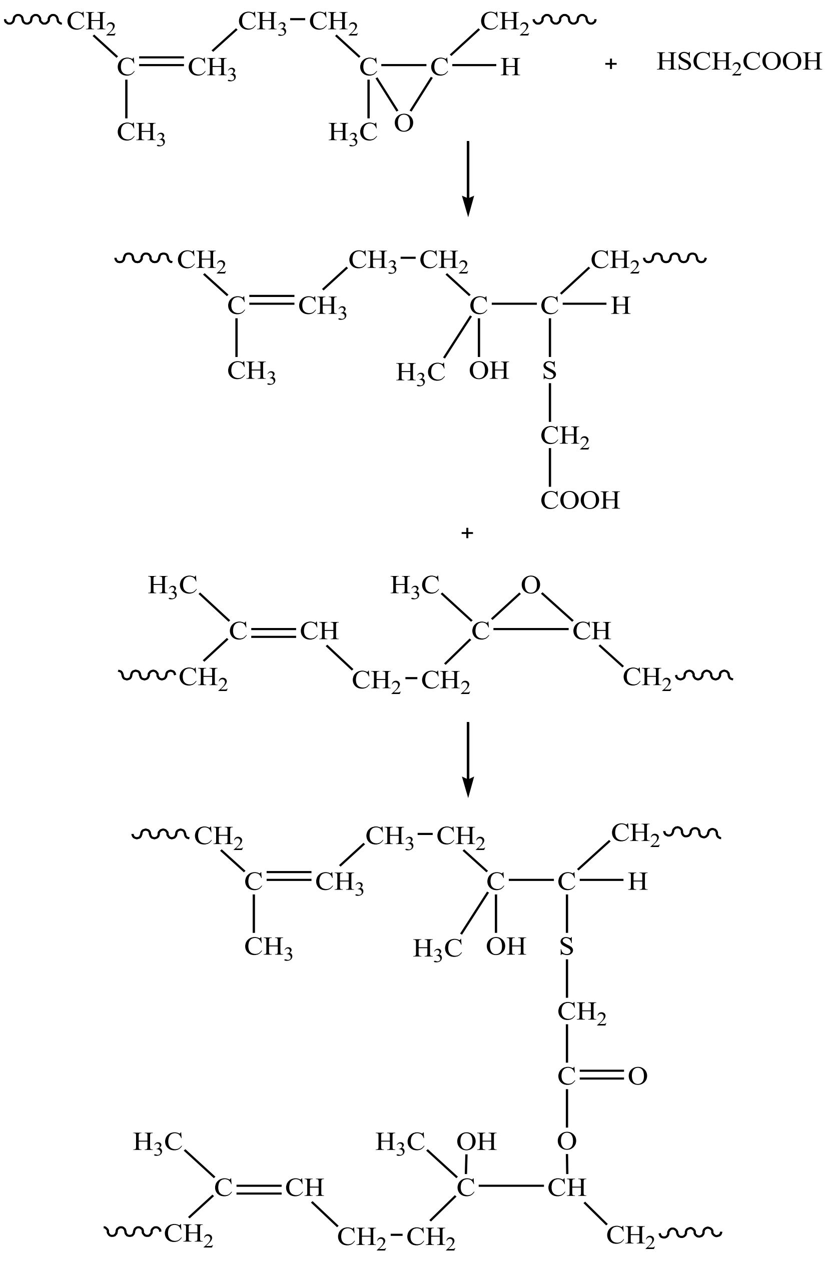


Figure 3.3 Probable reactions of ENR with TGA [11]

Natural rubber and modified natural rubber were added to improve the mechanical properties of thermoplastic starches (TPS) derived from tapioca flour which was plasticized by glycerol at 25 wt% [23]. The influence of adding NR and hydroxylated epoxidized natural rubber (ENR-OH), as impact modifier in various ratios (1, 3, 5, 7, 10% w/w of rubber) on mechanical properties, moisture adsorption and morphology was investigated in term of the amounts and types of rubber loading. As the amount of rubber increased, Young's modulus and tensile strength decreased while percentage of strain at break increased. It was observed that adding 10 wt% of ENR-OH gave the highest elongation at break as 61.52%. In addition, the impact resistance of all TPS/ENR-OH blends was higher than that of TPS/NR blend. The moisture adsorption testing indicated that the moisture adsorption of TPS decreased when the rubber content increased. Furthermore, SEM micrograph of the specimen clearly revealed the poor interaction at the interphase of TPS/NR, whereas the strong interactions at the interphase of TPS/ENR-OH were detected. Chemical structure of ENR-OH is shown in Figure 3.4.

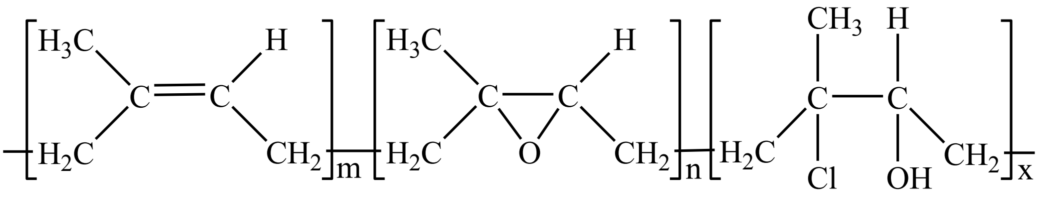


Figure 3.4 Chemical structure of ENR-OH [23]

From the preparation of polycaprolactone/ENR (50% mol of epoxy group) blend as a heat shrinkable material by melt mixing process, it can be seen that tensile strength, 100% tensile modulus, elongation at break and storage modulus decreased approximately 52%, 39%, 47% and 63%, respectively as well as heat shrinkable behavior increased 7% when ENR in the blends increased 40% [24]. Heat shrinkable behavior of ENR/polycaprolactone blend was up to 81% when the blend was crosslinked by dicumyl peroxide (DCP). Interchain crosslinking between PCL and ENR in the interfacial region by DCP is shown in Figure 3.5.

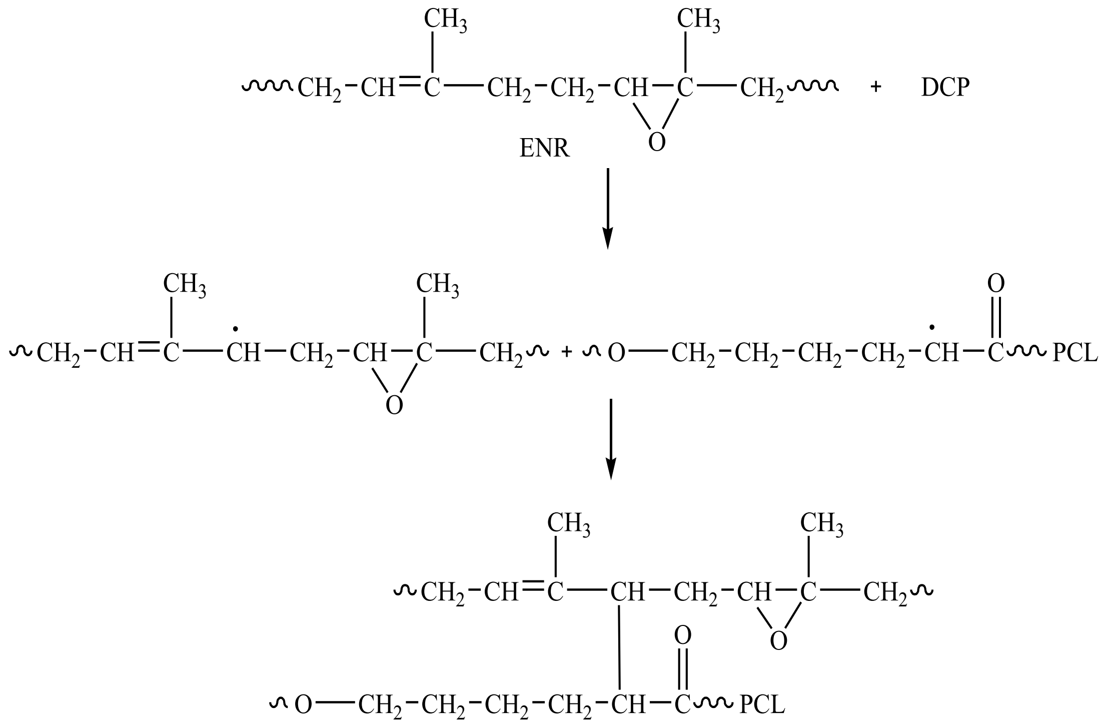


Figure 3.5 Interchain crosslinking between PCL and ENR by DCP [24]

3.3 Effect of rubber types on thermal and mechanical properties

Toughness improvement of nylon 6 (polyamide 6, PA6) by adding NR and ENR50 at 30 wt% were investigated by Tanrattanakul et al.[22]. It was found that adding both NR and ENR decreased yield stress and tensile strength, but slightly increased elongation at break of nylon blended with rubber. NR slightly decreased impact strength of PA6, whereas this property was increased up to six fold by blending with ENR. This phenomenon could be explained in terms of blend morphology. Too large of particle diameters of NR was the main cause of premature failure.

Jorge et al.[13] studied films prepared by casting process from three kinds of rubbers; i.e., NR, ENR25 and ENR25 crosslinked by adding trimethylopropane tris(2-mercaptoacetate) (TMP-SH) at various content (5, 10 and 20 phr). Swelling ratio decreased when TMP-SH increased. Addition of TMP-SH in ENR increased modulus, tensile stress at break, modulus at 100%, elongation and thermal stability. 10 phr TMP-SH added ENR film showed the optimal system in which tensile stress at break, modulus at 100% elongation and degradation temperature were 1.4 MPa, 1.1 MPa and 407.89 ^{o}C, respectively [13].

Akinlabi et al.[25] studied the diffusion and permeability of aldehydes (acetaldehyde and formaldehyde) blends with four kinds of rubber that were NR, low molecular weight natural rubber (LMWNR), NR with 35% epoxidized low molecular weight natural rubber (ELMWNR) and NR with 20% carboxylated low molecular weight natural rubber (ELMWNR-COOH) by using crosslinking agent. NR/ELMWNR-COOH blend could decrease the sorption rate, diffusion and permeability of the solvent better than other systems. It was also observed that the epoxidation was the chemical process which can be used to improve solvent resistance of material.

CHAPTER IV

EXPERIMENTS

4.1 Materials

Polylactic acid (PLA) 2002D was purchased from Nature Works. High ammonia concentrated natural rubber latex with 60% dry rubber content (DRC) was purchased from Rubber research institute of Thailand, Kasetsart University. Igepal CO-890 (poly (oxy-1, 2-ethanediyl)), Sodium carbonate and Magnesium stearate were purchased from Sigma Aldrich, USA. Glycerol was purchased from Scharlau, reagent grade. 90% Formic acid and 30% Hydrogen peroxide were purchased from Ajax Finechem Pty, Australia. Methanol 99% was purchased from Thaioil, Thailand. Chloroform was purchased from RCI Labscan Thailand. Thioglycolic acid was purchased from Sigma Aldrich, Germany.

4.2 Synthesis of carboxylated modified natural rubber (ENR-COOH)

4.2.1 Synthesis of epoxidised natural rubber (ENR)

NR latex was first diluted with distilled water to 30% DRC and stabilized with 7 wt% of Igepal CO-890 (poly (oxy-1, 2-ethanedily)) at room temperature for 24 h. After that, the mixture was acidified by formic acid. Hydrogen peroxide was then slowly dripped at 60 ^{o}C while continuously stirred for 8 h (the reaction time was counted from the first hydrogen peroxide drop). The reaction mixture was neutralized in an aqueous solution of 3 M sodium carbonate. After that, the reaction mixture was precipitated in methanol and washed with distilled water. The rubber was dried in vacuum oven at 60 °C until constant weight was obtained.

The ENRs with various levels of epoxide groups at ~ 6, 19, 24 and 52 mol% epoxide were used in this study. (The calculation of reagents is shown in Appendix A.)

4.2.2 Synthesis of carboxylated modified epoxidised natural rubber (ENR-COOH)

100 g of ENR was dissolved in 2.5 L of chloroform for 48 h. At room temperature, TGA (1.5 mol TGA / mol ENR) was added and continuously stirred for 18 h. Then, the modified ENR was washed several times with distilled water and separated by separatory funnel. The solvent was eliminated by evaporating in air. The rubber was dried in vacuum oven at 60 °C until constant weight was obtained. (The calculation of TGA is shown in Appendix A.)

4.3 Preparation of ENR-COOH/PLA blown films

Part I : Fix content of ENRs-COOH at 3 wt%

Masterbatches of 50 g ENRs-COOH/PLA compound (the weight ratio of PLA : ENR-COOH was 1 : 1) were prepared. The ENRs-COOH/PLA compounds were melt mixed by Brabender mixer at 180 °C for 11 min with screw speed of 50 rpm. Then, each of the masterbatches was diluted with PLA to produce polymer blends with 3 wt% ENRs-COOH by twin screw extruder (ThermoHaake Rhromer) attached to rod capillary die at screw speed of 125 rpm with temperature profile of 170 – 205 ^{o}C before cutting into pellets by pelletizer. Mixed PLA pellets was dried in an oven at 80 ^{o}C for 24 h. The samples were prepared as films by using blown film extrusion process at screw speed of 150 rpm with temperature profile of 160-190 rpm, and roll speed of 380 rpm.

ENR6-COOH, ENR19-COOH, ENR24-COOH and ENR52-COOH were used in this part to find the optimum tensile properties between neat PLA and ENRs-COOH.

Part II : Vary content of ENR6-COOH

In part II, ENR6-COOH was used as toughening agent for PLA film because 3 wt% ENR6-COOH/PLA film was provided the highest elongation at break of ENRs-COOH/PLA films.

Masterbatch of 50 g ENR6-COOH/PLA compound (the weight ratio of PLA : ENR-COOH was 1 : 1) was prepared. The ENR6-COOH/PLA compounds were melt mixed by Brabender mixer at screw speed of 50 rpm, 180 ^{o}C for 11 min. After that, the masterbatch was diluted with PLA including 0.5 wt% magnesium sterate to produce polymer blends with 1, 3, 4 and 5 wt% ENR6-COOH by twin screw extruder (ThermoHaake Rhromer) attached to rod capillary die at screw speed of 125 rpm with the temperature profile of 170–205 ^{o}C before cutting into pellets by Pelletizer. Mixed PLA pellets was dried in an oven at 80 ^{o}C for 24 h. The samples were prepared as films by using blown film extrusion process at screw speed of 150 rpm with temperature profile of 160-190 rpm and roll speed of 380 rpm.

4.4 Equipments

4.4.1 Internal mixer

Internal mixer (Brabender 30/50 EHT) is a machine for melt blending that is used to prepare master batch of PLA and ENRs-COOH. The ENRs-COOH/PLA compounds were blended at screw speed of 50 rpm, at 180 ^{o}C for 11 min.

4.4.2 Twin Screw Extruder

A Thermo Haake twin screw extruder (Rheomex PTW 16/25, Germany) was used for blending PLA with ENRs-COOH by melt mixing process. This extruder is a counter rotating type with three heating zones. Screw diameter is 16 mm with L/D of 25. Die type is multistrand die for pelletizer and blown film die for blown film process.

4.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of ENR and ENR-COOH were confirmed by Fourier transform infrared spectroscopy (FTIR) (Bruker Optik GmbH: Vertex 70, Germany), using the ZnSe/diamond crystal in the attenuated total reflectance (ATR) mode. The spectra were recorded in the range 4000-650 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans.

4.4.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy (NMR) (Varian: Unity Inova, USA) was used to consider the chemical structure and% functional group of ENR and ENR-COOH. The samples were performed in deuterated chloroform ($CDCl_3$) at 500 MHz with a 8384.9 Hz spectral width, a relaxation delay of 6.0 s and a pulse width of 90°.

4.4.5 Differential Scanning Calorimetry (DSC)

Thermal properties of raw materials and ENR-COOH/PLA blown films including ENRs/PLA films were measured by Differential scanning calorimeter (DSC) (Mettler Toledo: DSC1, Switzerland). The samples (3–10 mg) were heated from -80 to 250 ^{o}C at heating rate of 10 ^{o}C/min. After the first heating scan, the samples were cooled down to -80 ^{o}C and then heated again to 250 ^{o}C at the same heating rate.

4.4.6 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical behavior of ENRs-COOH/PLA blown films was studied by DMA in the tension mode. The sample size was 6.5 x 30 x 0.035 mm. The thermomechanical properties were measured under nitrogen gas in the temperature range of 30 to 120 °C with a heating rate of 2 °C /min at a constant frequency (ω) of 1 Hz and strain amplitude of 0.05%.

4.4.7 Universal Testing Machine

Universal testing machine (Instron: model 5567, UK) was used to characterize mechanical properties of ENRs-COOH/PLA films according to ASTM D882. The obtained results are the stress-strain behaviors of PLA films. In this study, the gauge length was 100 mm and the width was 10 mm. Load cell and crosshead speed were set at 1 kN and 12.5 mm/min, respectively.

CHAPTER V

RESULTS AND DISCUSSION

Epoxidised natural rubber (ENR) of various epoxidation degrees were synthesized and modified with thioglycolic acid (TGA) to yield carboxylated epoxidised natural rubber (ENR-COOH) in order to use as toughening agent in polylactic acid (PLA) blown film. The functional group and chemical structures of ENR and ENR-COOH were characterized. The effect of epoxide levels and ENR-COOH loading on the mechanical and thermal properties as well as thermomechanical properties of ENR-COOH/PLA blown films were also investigated.

5.1 Characterization of epoxidised natural rubber (ENR)

5.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

In this research, epoxidised natural rubber (ENR) samples of various epoxidation degrees at ~6, 19, 24 and 52 mol% epoxide, corresponding to ENR6, ENR19, ENR24 and ENR52, respectively, were synthesized by using formic acid and hydrogen peroxide as reactants. The chemical structure of ENRs is shown in Figure 5.1. The functional groups of ENR molecules were confirmed by Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra of ENR6, ENR19, ENR24 and ENR52 compared with NR is shown in Figure 5.2. The IR spectrum of ENR showed the new absorption bands at 1249 and 870 cm^{-1} corresponding to C-O stretching and oxirane ring stretching, respectively. While the absorption bands at 1662 and 835 cm^{-1} related to C=C stretching and C=C-H bending of cis-1, 4 polyisoprene were observed. It can be clearly seen that an increasing trend of new absorption bands at 1249 and 870 cm^{-1} and a decreasing trend of absorptions bands at 1662 and 835 cm^{-1} were observed as increasing levels of epoxide groups in the ENR molecules.

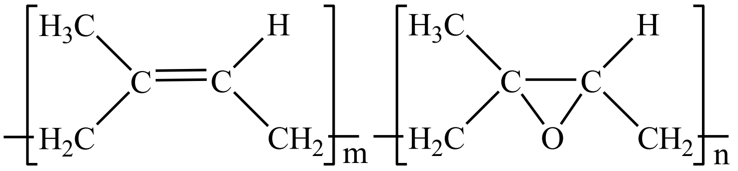


Figure 5.1 Chemical structure of epoxidised natural rubber (ENR)

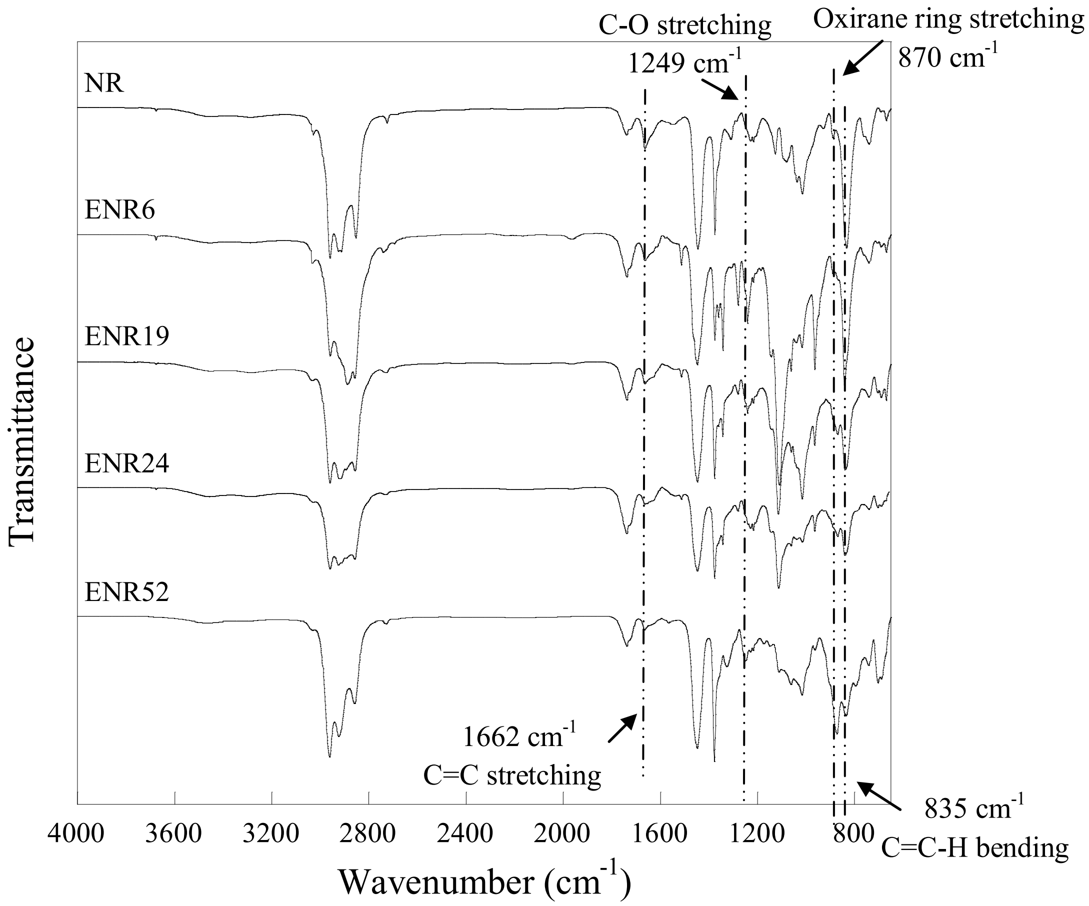


Figure 5.2 FTIR spectra of NR and ENRs

5.1.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The level of epoxy ring in the ENR molecules was determined from intensity ratio by ^{1}H-NMR technique. Figure 5.3 shows ^{1}H-NMR spectrum of ENR6. The signals of methine proton of epoxy group and unsaturated methine proton of isoprene unit of ENR appeared at 2.7 and 5.1 ppm, respectively, while hydroxyl group which occurred from side reaction during epoxidation and end chain of ENR appeared at 3.6 ppm [26]. The possible structure of ENR is shown in Figure 5.4.

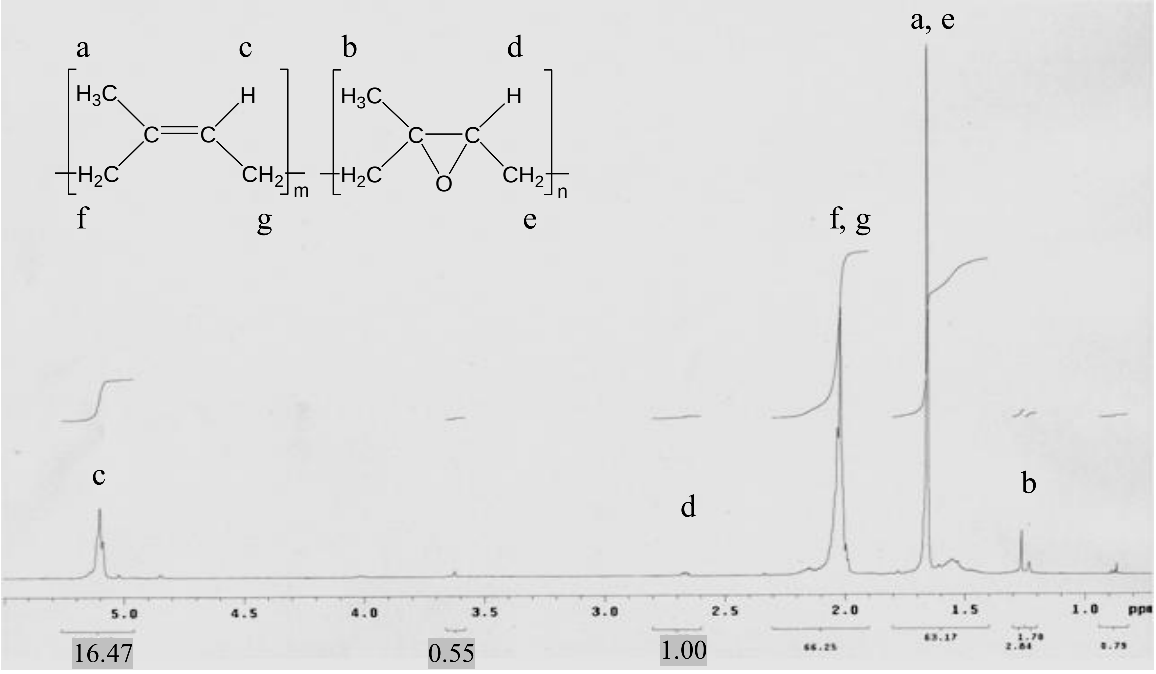


Figure 5.3 ^{1}H NMR spectra of ENR6

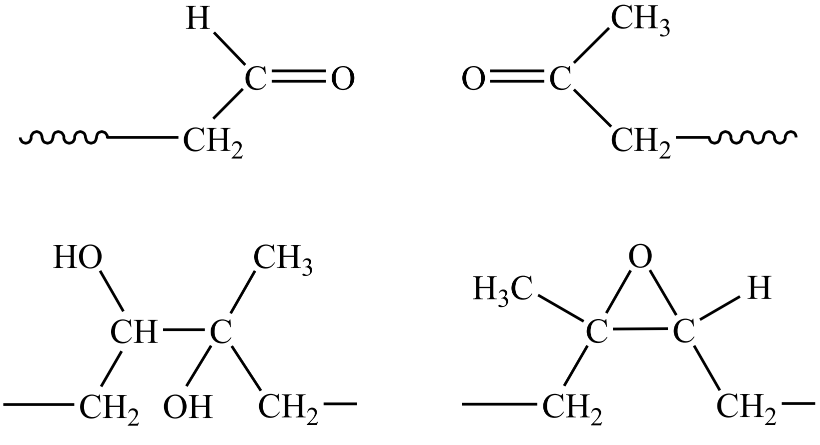


Figure 5.4 Possible structure of ENR [27, 28]

% epoxidation (% oxirane ring) and% ring-opening (% hydroxyl group) were calculated by equation as;

$$\% \text{ oxirane ring} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100 \qquad \text{(eq. 5.1)}$$

$$\% \text{ hydroxyl group} = \frac{(I_{3.6}/2)}{I_{2.7} + (I_{3.6}/2) + I_{5.1}} \times 100 \qquad \text{(eq. 5.2)}$$

where $I_{2.7}$, $I_{3.6}$ and $I_{5.1}$ are the peak integrated areas at chemical shifts 2.7, 3.6 and 5.1 ppm, respectively. The estimated epoxy and hydroxyl group content of ENRs used in this study are shown in Table 5.1

Table 5.1 The estimated epoxy and hydroxyl group content of ENRs

Samples	$I_{2.7}$	$I_{3.6}$	$I_{5.1}$	% epoxide ring	% hydroxyl group
ENR6	1	0.55	16.47	5.72	2.00
ENR19	1	0.58	4.27	18.98	5.00
ENR24	1	0.16	3.14	24.15	1.90
ENR52	1	0.08	0.92	52.08	2.04

5.1.3 Differential Scanning Calorimetry (DSC)

Figure 5.5 demonstrates the glass transition temperature (T_g) of epoxidised natural rubber at various epoxidation levels. The samples were heated at the rate of 10°C/min from -80 to 25 °C and then cooled down at the same rate. The second heating was performed in order to avoid the effect of thermal history. From the DSC thermograms, only a single dominant exothermic peak which is demonstrated the glass transition temperature (T_g) of ENRs was observed. The T_g of ENR6, ENR19, ENR24 and ENR52 were found to be -57.88, -49.34, -39.13 and -24.06 °C, respectively. The maximum T_g peak was shifted to higher temperature when epoxide group in ENR molecules increased. That is, the rotation and vibration of ENR chain decreased with an increase in epoxidation levels. Furthermore, higher polarity of ENR exhibited higher chemical interaction between their molecules [29].

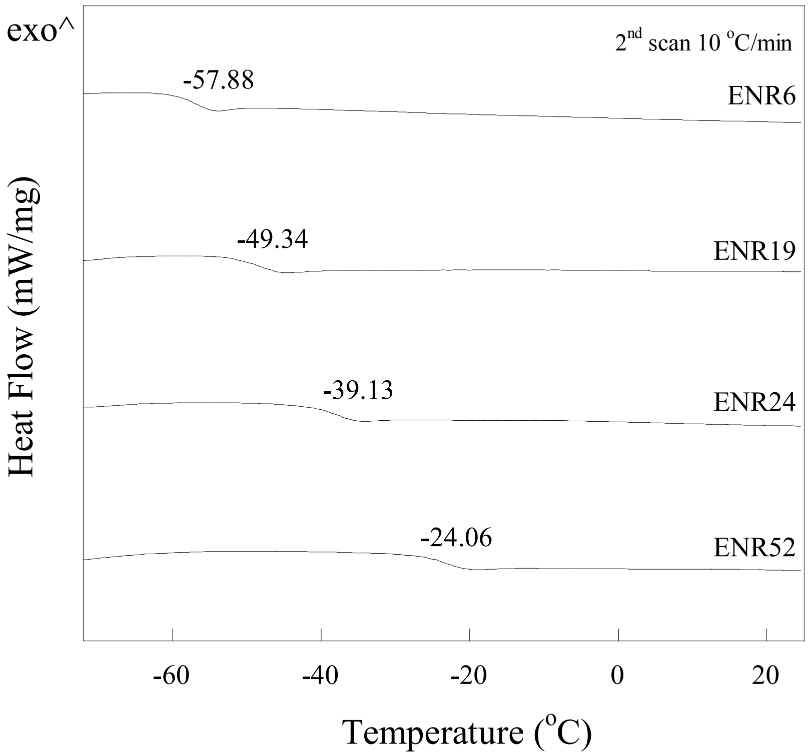


Figure 5.5 DSC thermograms from the second heating scan of ENRs

5.2 Characterization of carboxylated epoxidised natural rubber (ENR-COOH)

5.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Four systems of epoxidised natural rubber (ENR) were then modified with thioglycollic acid (TGA) (1.5 mol TGA / mol epoxide unit) to provide carboxylated epoxidised natural rubber (ENR-COOH). The chemical structure of ENR-COOH is shown in Figure 5.6. Thiol group (-SH) in TGA reacted with oxirane ring in the ENR molecules which was confirmed by FTIR technique. The FTIR spectra of ENR6-COOH, ENR19-COOH, ENR24-COOH and ENR52-COOH are shown in Figure 5.7. The broad absorption bands at 3200-3600 cm^{-1} can be assigned to –OH stretching of hydroxyl group while C=O stretching peak of carboxyl group and C-O stretching peak of alcohol group appeared at 1722 and 1010 cm^{-1}, respectively. Figure 5.7 also showed the peak at 1722 cm^{-1} of carboxyl group from ring opening by side reaction. In addition, the absorption peak of carboxyl group cannot be detected because of the strong and broad peaks of hydroxyl group at 3200-3600 cm^{-1}. However, it can be observed that the intensity of –OH stretching and C-O stretching of alcohol group increased with increasing of epoxide and carboxyl contents.

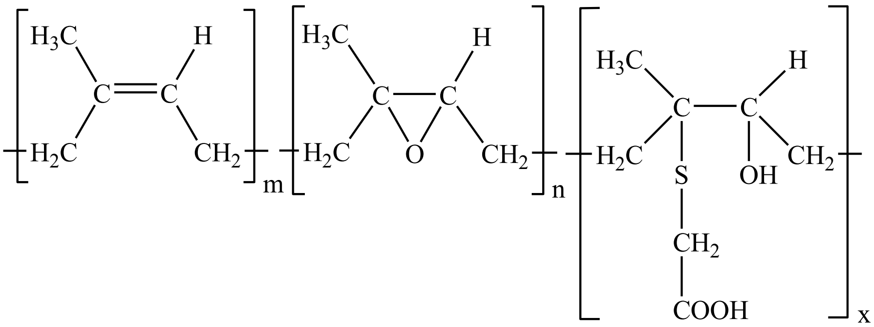


Figure 5.6 Chemical structure of carboxylated epoxidised natural rubber

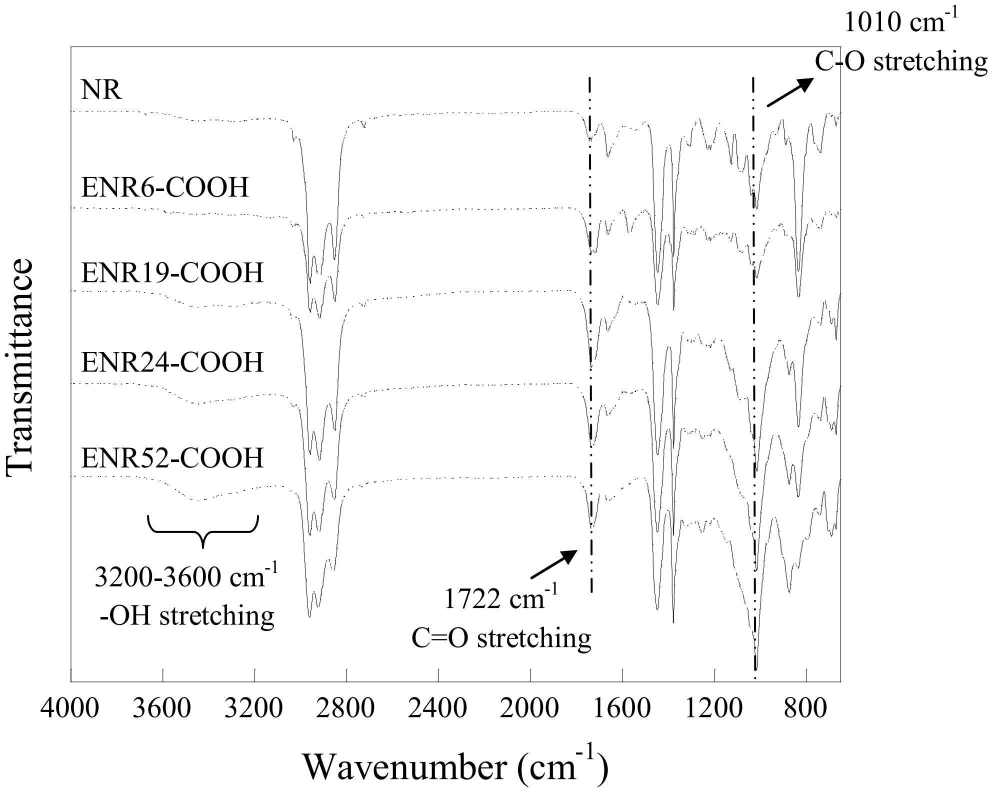


Figure 5.7 FTIR spectra of NR and ENRs-COOH

5.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The content of epoxide and carboxyl group of the ENRs-COOH was estimated from intensity ratio by using ^{1}H-NMR technique. Figure 5.8 shows ^{1}H-NMR spectrum of ENR6-COOH. The signals of methine proton of epoxy group and unsaturated methine proton of isoprene unit of ENR appeared at 2.7 and 5.1 ppm, respectively, while the carboxyl group was estimated by the intensity ratio of thiol group at 3.6 ppm. However, the intensity ratio at 3.6 ppm also assigned to hydroxyl group which occurred from side reaction of previous ENR synthesis.

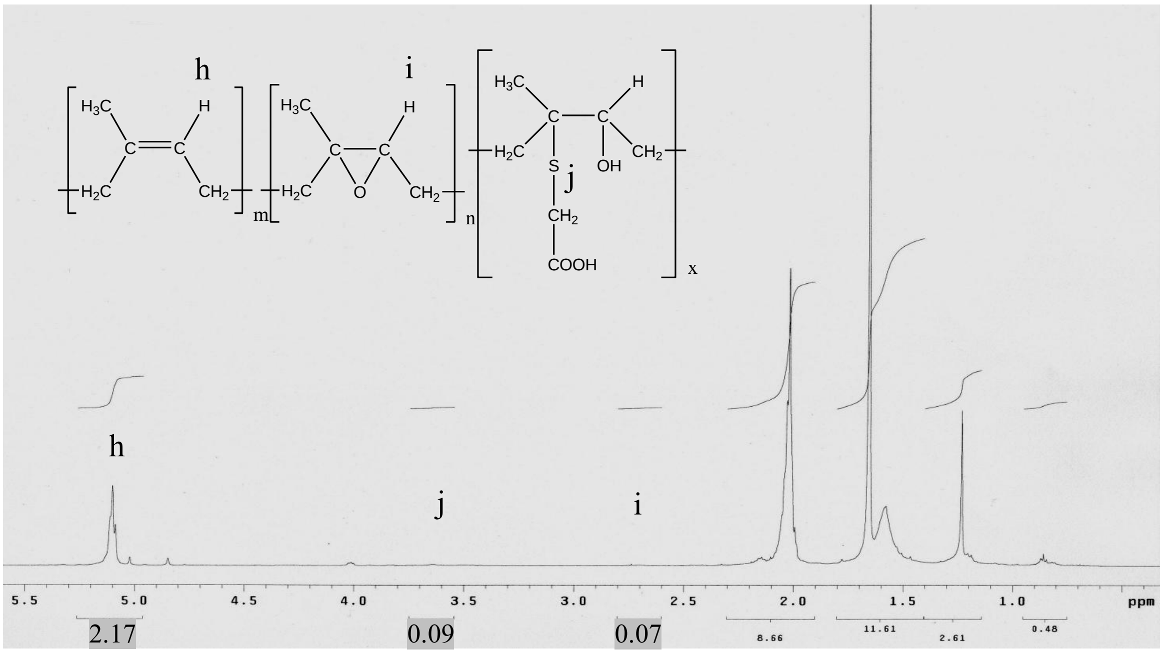


Figure 5.8 ^{1}H NMR spectra of ENR6-COOH

Epoxidised natural rubber (ENR) samples of various epoxidation degrees were modified with thioglycolic acid (TGA) to yield ENR-COOH with 1, 4, 8 and 37% conversion of its natural rubber (i.e ENR6-COOH, ENR19-COOH, ENR24-COOH and ENR52-COOH, respectively).% epoxidation (% oxirane ring) and % ring-opening (% carboxyl group) were calculated by eq.5.1 and eq.5.2, respectively. Since hydroxyl group in ENR-COOHs also occurred from side reaction during epoxidation of ENR synthesis, so calculated % carboxyl group was subtracted by % hydroxyl group from side reaction. The estimated epoxide and carboxyl group content of ENRs-COOH were shown in Table 5.2

Table 5.2 The estimated content of epoxide and carboxyl group of ENRs-COOH

Samples	$I_{2.7}$	$I_{3.6}$	$I_{5.1}$	% epoxide group	% carboxyl group
ENR6-COOH	0.07	0.09	2.17	3	1.98
ENR19-COOH	0.25	0.28	1.45	12.63	3.00
ENR24-COOH	0.15	0.14	0.91	12.5	4.10
ENR52-COOH	0.03	0.13	0.16	9.36	24.96

5.2.3 Differential Scanning Calorimetry (DSC)

Figure 5.9 shows second heating scan for ENR-COOHs. The samples were heated at the rate of 10°C/min from -80 to 25 °C and then cooled down at the same rate. The second heating scan was used in order to avoid the effect of thermal history. It was found that ENR52-COOH showed the highest glass transition temperature (T_g)

followed by ENR24-COOH, ENR19-COOH and ENR6-COOH at T_g values of -17.90, -38.26, -45.21 and -57.80 °C, respectively. The T_g of ENRs-COOH was shifted to higher temperature when the content of epoxide group and carboxyl group in ENR molecules increased. High secondary attractive forces (due to high polarity or hydrogen bonding) decrease the mobility of amorphous polymer chains, leading to high T_g [30].

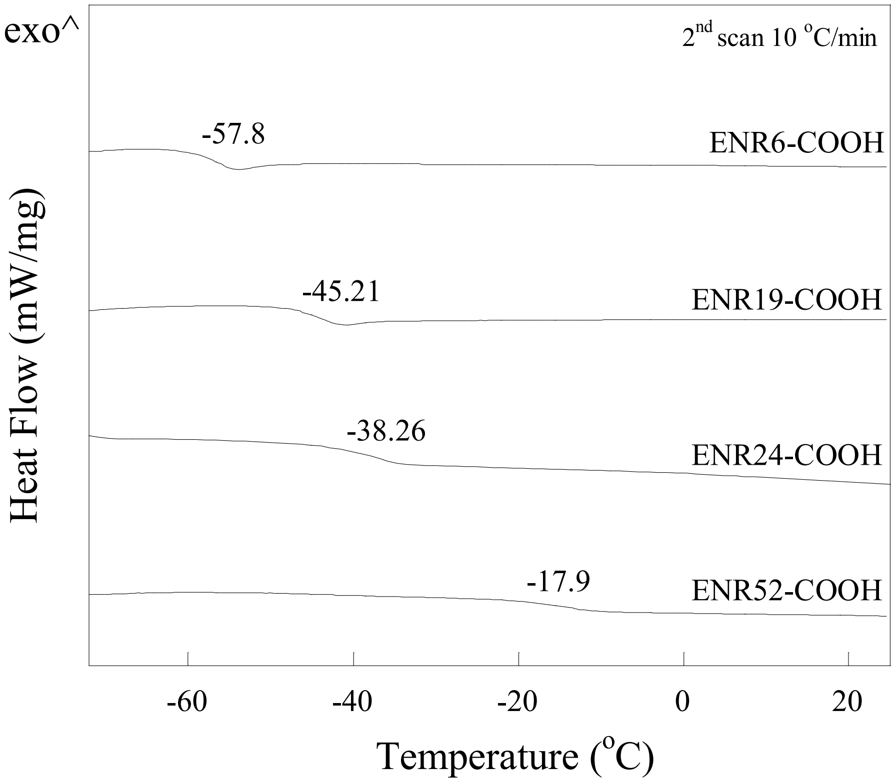


Figure 5.9 The DSC thermogram from the second heating scan for ENRs-COOH

5.3 The effect of carboxylated epoxidised natural rubber (ENR-COOH) types on properties of PLA blown films

Physical characteristics of neat PLA, 3 wt% NR/PLA and 3 wt% ENRs-COOH/PLA films are shown in Table 5.3. In the case of 3 wt% NR/PLA film, the film was smooth, translucence and no gel although it was not compatible. Because NR can be well dispersed in PLA matrix, this film shows homogeneous appearance. The addition of 3 wt% ENR6-COOH also showed film characteristics similar to that of NR. For adding 3 wt% ENR19-COOH, ENR24-COOH and ENR52-COOH, it was found that those films were rough and transparence. Furthermore, gel content increased with an increasing level of epoxide and carboxyl group since PLA could be crosslinked with ENRs-COOH as shown in Appendix F. At higher level of epoxide and carboxyl groups, masterbatch between PLA and ENRs-COOH was difficult to melt during melt blending or blown film process [31]. Therefore, homogeneous film could not be formed when ENR19-COOH, ENR24-COOH and ENR52-COOH were added in neat PLA.

Table 5.3 Characteristics of neat PLA, 3 wt% NR/PLA and 3 wt% ENRs-COOH/PLA films

Type	Characteristics	
	Smooth/Rough	Transparence/Translucence
PLA	Smooth	Transparence
NR/PLA	Smooth	Translucence
ENR6-COOH/PLA	Smooth	Translucence
ENR19-COOH/PLA	Rough	Transparence
ENR24-COOH/PLA	Rough	Transparence
ENR52-COOH/PLA	Rough	Transparence

5.3.1 Thermal properties

The DSC technique is used to measure the glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m) as well as enthalpy of cold crystallization (ΔH_c) and melting (ΔH_m). Figure 5.10 shows the DSC thermograms from the second heating scan for the neat PLA, NR/PLA and ENR-COOH/PLA blown films and the relevant data is listed in Table 5.3. Estimated degree of crystallinity of these samples (X_c) was calculated by using eq.5.3 [31] and was shown in Table 5.3.

$$X_c\ (\%) = (\Delta H_m / \Delta H^*_m) \times 100 \qquad \text{eq.5.3}$$

where ΔH_m is the melting enthalpy and ΔH^*_m (135 J/g) is the melting enthalpy of 100% crystalline PLA [31].

From Table 5.4, it was found that ENRs-COOH slightly decreased T_g from 52.85 °C of neat PLA to about 50 °C whereas NR did not affect T_g of neat PLA. This could be due to partial miscibility between PLA and ENRs-COOH which was confirmed by Fox equation [32]. It can be seen that the calculated T_g from Fox equation is nearby the T_g from DSC technique.

$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{1-x_1}{T_{g,2}} \qquad \text{eq.5.4}$$

where T_g belong to the blend, $T_{g,i}$ to neat component i, and x_i is the weight fraction of component i.

It was also noticed that T_{cc} and ΔH_c disappeared in the case of ENR24-COOH and ENR52-COOH. This was probably caused by large molecular chain network with high crosslink density that inhibited mobility of PLA chain segment. Furthermore, the crystallinity of PLA can be increased by blending with both NR and ENR-COOH. The crystalline phase formed during cold crystallization is confined in the range of 7-20%. When adding 3 wt% ENRs-COOH, T_m also shifted to lower temperature when compared with ENR19-COOH/PLA film with the increasing of polarity. This may be attributed to the increasing of epoxide and carboxyl groups in ENR-COOH molecules affected to the increasing of crosslink density which interrupted the crystallization of PLA. Probable crosslinking reaction of ENR-COOH with PLA is shown in Figure 5.11.

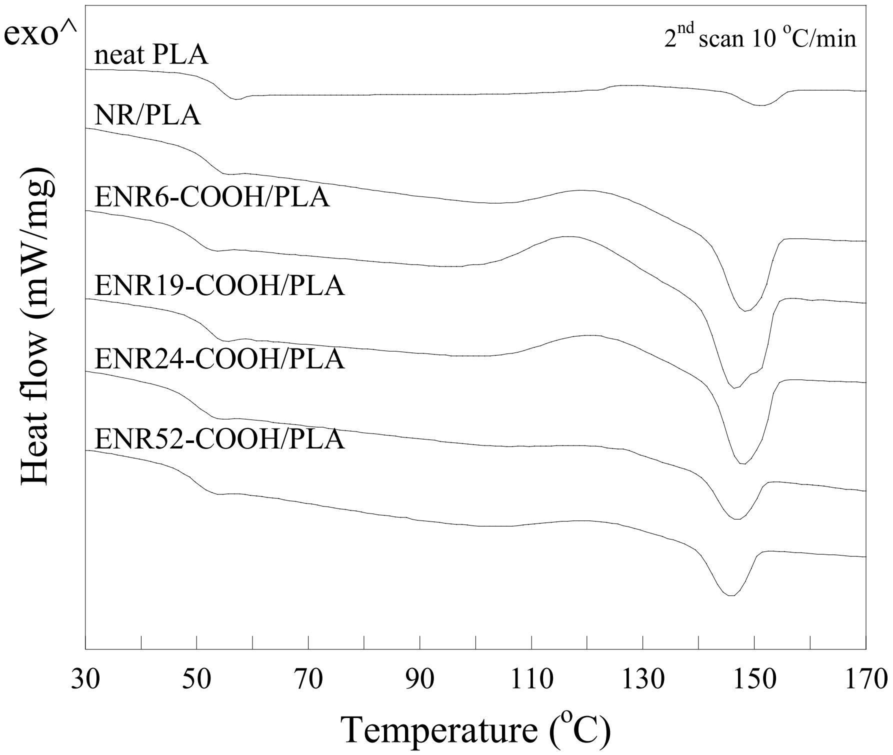


Figure 5.10 DSC thermograms from the second heating scan for neat PLA, 3 wt% NR/PLA and 3 wt% ENRs-COOH/PLA blown films

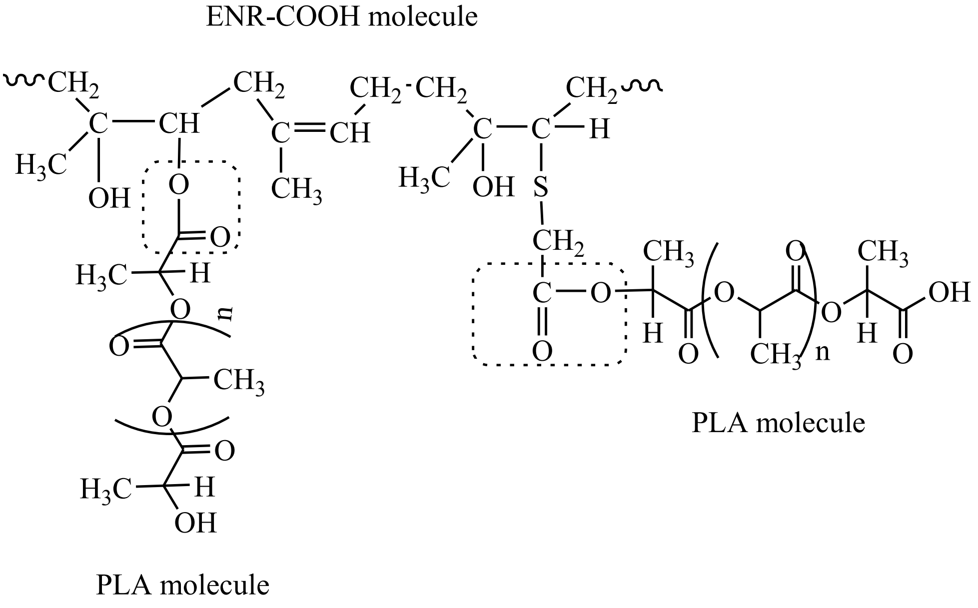


Figure 5.11 Probable crosslinking reaction of ENR-COOH with PLA

Table 5.4 Thermal properties and the degree of crystallinity of neat PLA, 3 wt% NR/PLA blown films and 3 wt% ENR-COOH/PLA blown films from the second heating scan of DSC technique including the calculated T_g of the ENR-COOH/PLA films by Fox equation

Samples	T_g (°C)	T_{cc} (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_g (°C) (Fox eq.)
neat PLA	52.85	126.42	2.93	151.23	2.70	2.00	-
NR/PLA	52.33	121.61	11.33	148.25	18.94	14.03	-
ENR6-COOH/PLA	49.51	117.03	17.55	146.50	27.22	20.16	47.9
ENR19-COOH/PLA	49.22	121.18	12.98	147.85	20.53	15.21	48.7
ENR24-COOH/PLA	50.18	-	-	146.75	8.84	6.55	49.1
ENR52-COOH/PLA	50.62	-	-	145.67	9.96	7.38	50.16

5.3.2 Thermomechanical properties

Figure 5.12 represents temperature dependence of (a) storage modulus and (b) tan δ for neat PLA and 3wt% ENRs-COOH/PLA blown films. The values of storage modulus and Tan δ are shown in Table D.1 (Appendix D). The storage moduli of all films was not changed at low temperature, and then decreased with heating due to several thermal transitions. Within the glassy plateau, neat PLA showed the highest storage modulus at 2800 MPa whereas the storage modulus above T_g dramatically decreased, corresponding to the lowest degree of crystallinity as can be confirmed by

DSC technique. The addition of ENRs-COOH in the PLA films resulting in decreasing of storage modulus. It was also found that the storage modulus of ENRs-COOH/PLA films decreased with an increasing level of epoxide and carboxyl groups in ENRs-COOH molecules because a lot of defects (gel) existed when the polarity of ENRs-COOH increased. This directly deteriorated the thermomechanical properties of these films.

From Figure 5.12 (b), the glass transition temperature can be observed from tan δ peak that was slightly different by few degrees compared with the T_g from DSC technique. That is, 1 Hz DMA data may correspond to 20-40 K/min heating rate via DSC technique [33]. It was found that T_g of PLA showed the highest value of 80.70 ^oC. However, the T_g trend of films when increasing polarity of ENRs-COOH cannot be clearly observed. The introduction of ENR-COOH into PLA resulted in the decrease of T_g and the height of tan δ peak. In contrast, the height of tan δ peak decreased with an increasing level of epoxide and carboxyl groups in the ENR-COOH molecules. This may be resulted from the crosslinking networks which hampered the mobility of the chain segments.

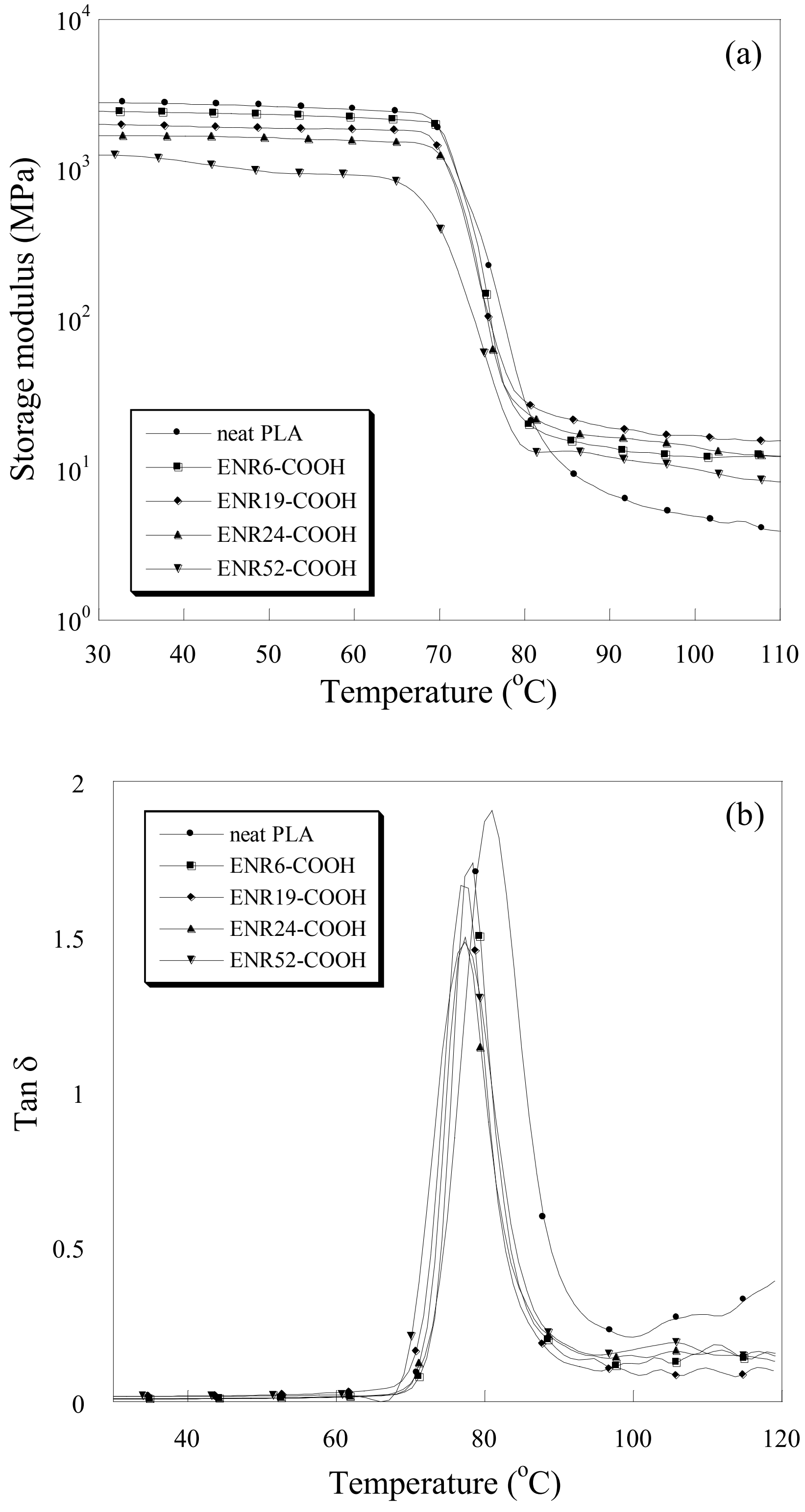


Figure 5.12 Temperature dependence of (a) Storage modulus and (b) Tan δ for neat PLA and 3 wt% ENRs-COOH/PLA blown films

5.3.3 Mechanical properties

The tensile properties of the samples, such as tensile strength, Young's modulus, elongation at break and toughness are measured in accordance with ASTM D882. The tensile strength is the maximum stress that a material can withstand before failure. Young's modulus is a material property that described its stiffness which was determined from the initial linear slope of stress-strain curve. The elongation at break is the strain on a sample when it breaks which was usually expressed as a percent. Toughness, the ability of a material to absorb energy and plastically deform without fracturing, is determined by measuring the area underneath the stress-strain curve.[30]

The examples of stress-strain curves for neat PLA and 3 wt% ENR6-COOH/PLA blown films in machinery direction (MD) are presented in Figure 5.13. It can be seen that the neat PLA film which was very stiff and brittle showed pretty high tensile strength, but fractured shortly after yielding. The addition of 3 wt% ENR6-COOH as toughening agent showed 26% elongation at break compared with 3.5% for the neat PLA. The tensile strength of film also decreased by about 50% when 3 wt% ENR6-COOH was added. This result indicated that ENR6-COOH can improve the toughness of PLA films.

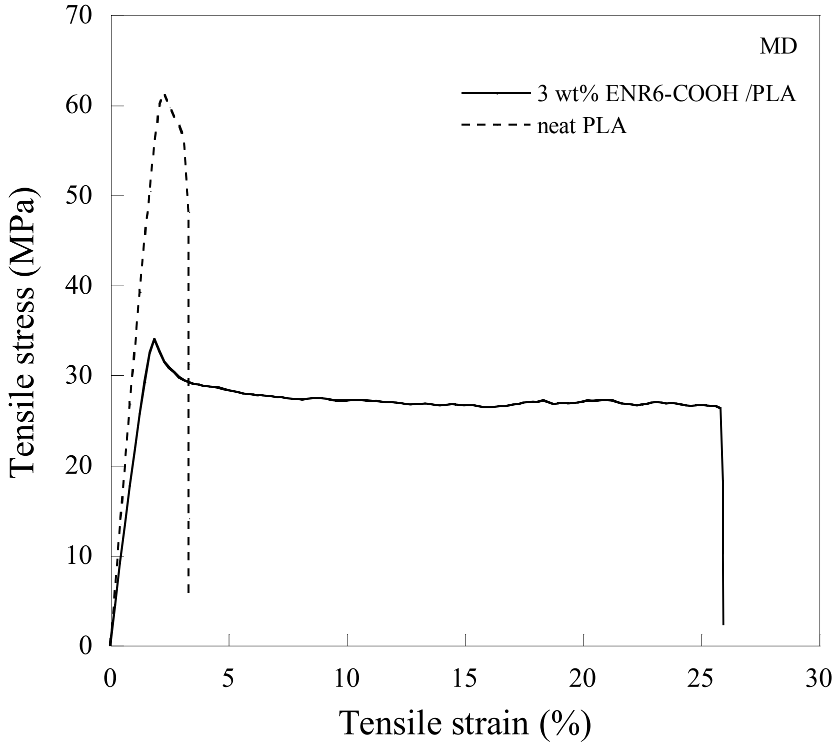


Figure 5.13 Stress-strain curves of neat PLA and 3 wt% ENR6-COOH/PLA blown films

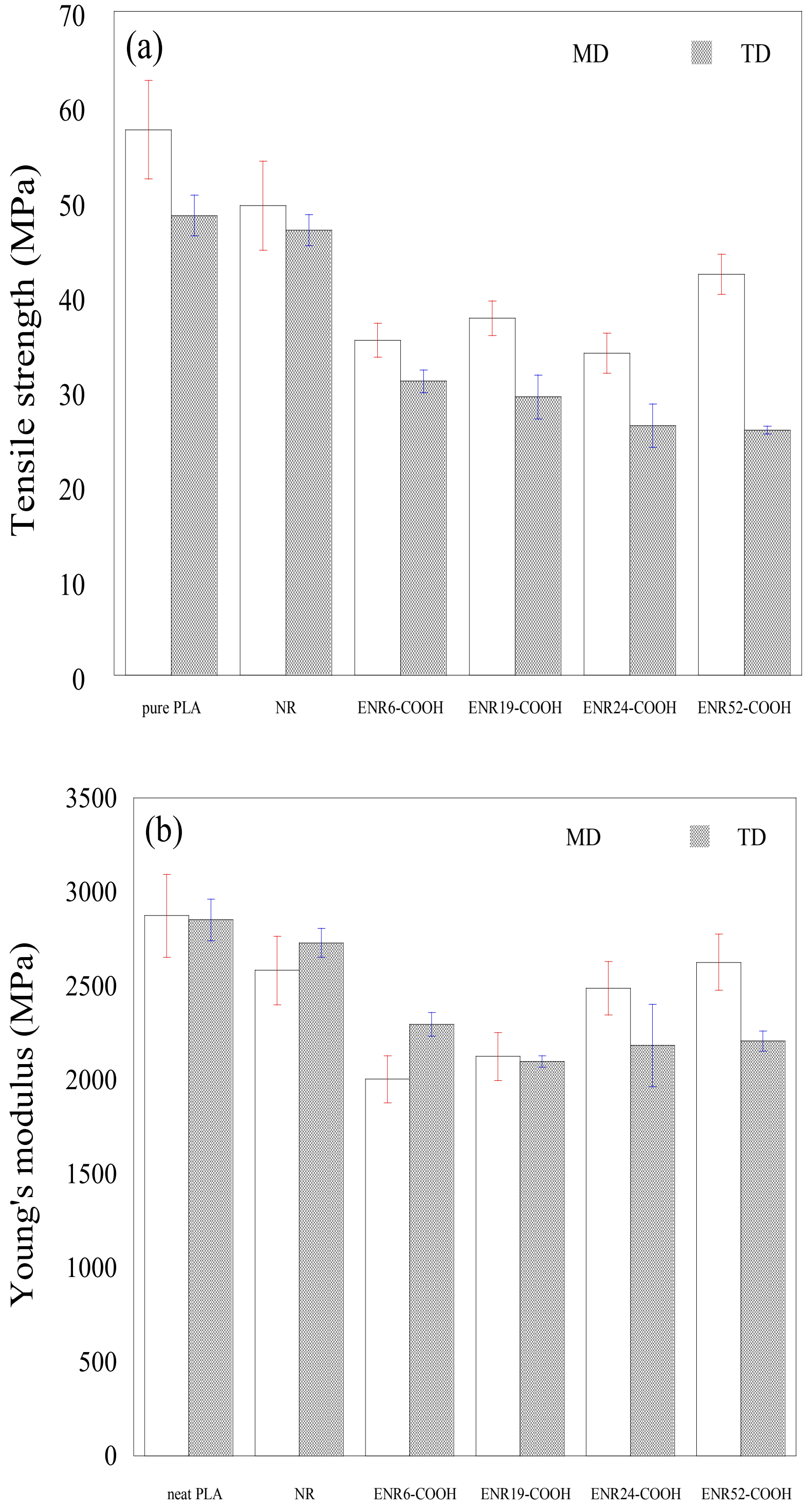
Tensile properties including (a) tensile strength (b) Young's modulus (c) elongation at break and (d) toughness of the neat PLA film compared with those of 3 wt% ENRs-COOH/PLA films and 3 wt% NR/PLA films as reference are shown in Figure 5.14. It can be seen that tensile strength of all rubber films is lower than that of the neat PLA. This is related to the fact that the tensile strength of NR or modified NR is generally lower than that of PLA. It was found that tensile strength of NR/PLA was higher than that of ENRs-COOH/PLA because NR was well dispersed in PLA although NR was not compatible with PLA resulting in smooth film surface which can be observed from film characteristics (Table 5.3). It was also found that tensile strength in MD was unclearly changed when increasing level of ENRs-COOH up to

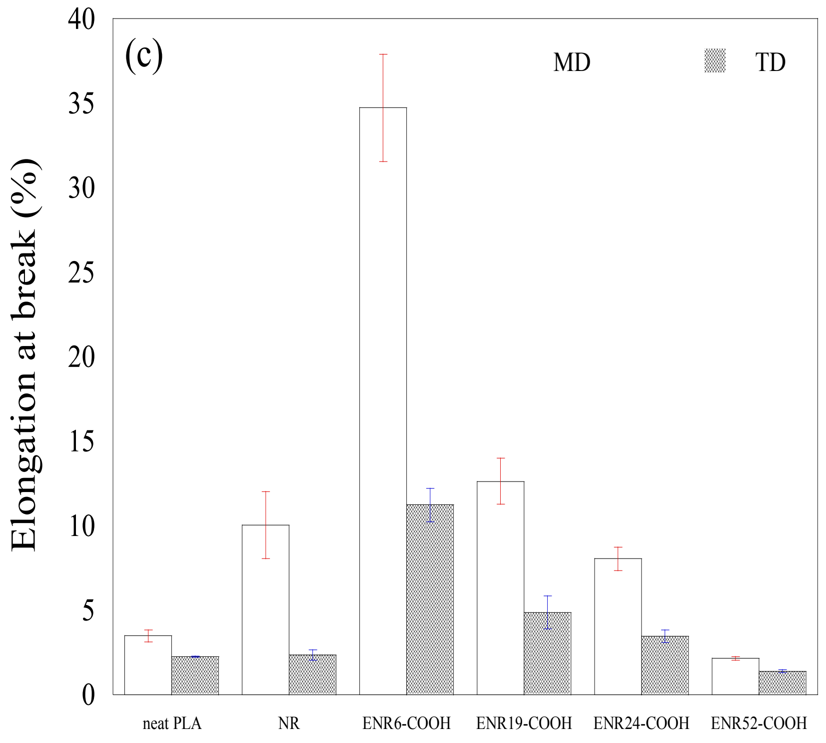
ENR24-COOH whereas tensile strengths in TD gradually decreased. In the presence of ENRs-COOH in system, the highest tensile strength of 42.3 MPa (MD) was obtained for ENR52-COOH/PLA films. It could be ascribed to the increased stiffness of that film due to its high crosslinked nature between the epoxide groups and the carboxyl groups on rubber molecules or hydroxyl end groups in PLA molecules and carboxyl groups on the chains of ENR52-COOH [11]. However, tensile strength in TD of 3 wt% ENR52-COOH/PLA film showed the lowest tensile strength of 25.86 MPa. This may because the chain orientation of ENR52-COOH/PLA enormously resisted to the tension direction.

The addition of ENR-COOH in PLA blown films resulted in the decrease of Young's modulus from 2873.66 to 2004.89 MPa in MD and from 2852.52 to 2098.65 MPa in TD. Young's modulus in MD of the 3 wt% ENR-COOH/PLA films increased with an increasing epoxide and carboxyl groups of ENR-COOH. Meanwhile, the addition of ENR6-COOH showed the highest Young's modulus in TD at 2296.63 MPa compared with other ENRs-COOH.

It was also observed that elongation at break and toughness of the ENRs-COOH/PLA films decreased with an increasing epoxide and carboxyl groups of ENR-COOH. Compared with neat PLA film, ENR6-COOH/PLA film exhibited the highest elongation at break (which was approximately 10 times in MD and 3 times in TD) and toughness (which was approximately 7 times in MD and 4 times in TD). This is attributed to ENR6-COOH had lowest polarity resulting in the lowest crosslink with PLA. Hence, when the samples are in tension, the arrangement of molecules in ENR6-COOH/PLA along the tensile force can easily occur [11]. Therefore, ENR6-

COOH was selected to be blended with PLA in order to study the effect of rubber contents on thermal and mechanical properties.





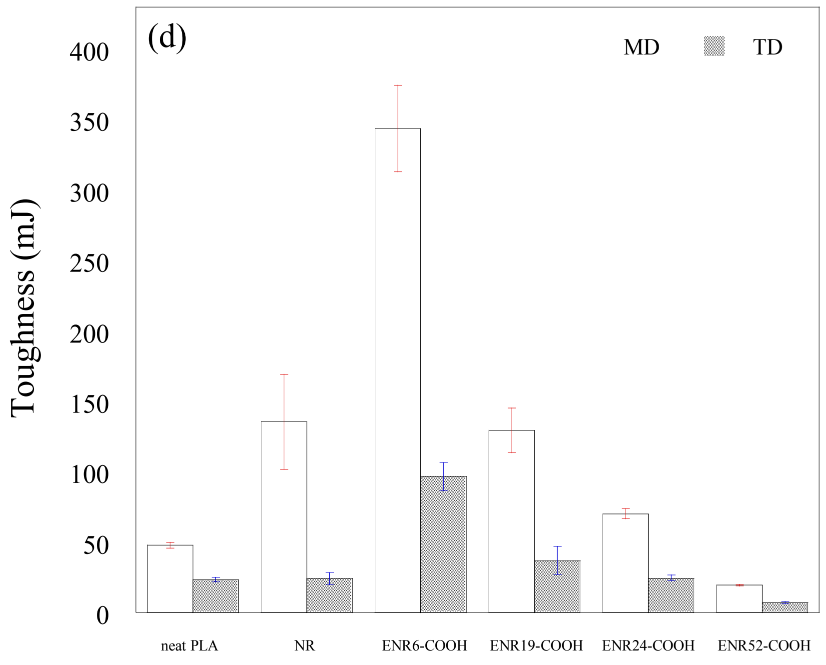


Figure 5.14 Tensile properties of the neat PLA, 3 wt% NR/PLA and 3 wt% ENRs-COOH blown films (a) Tensile strength (b) Young's modulus (c) Elongation at break and (d) Toughness

5.4 The effect of amount carboxylated epoxidised natural rubber (ENR-COOH) on properties of PLA blown films

In this section, 0.5 wt% of magnesium stearate (MgSt) was added into polymer blends between PLA and ENR6-COOH in order to protect rubber agglomeration from blow film processing. ENR6/PLA_MgSt films with various content of ENR6 were prepared to compare with ENR6-COOH/PLA_MgSt films.

5.4.1 Thermal properties

Figure 5.15 shows the DSC thermograms from the second heating scan for neat PLA, PLA_MgSt and PLA_MgSt with 1, 3, 4 and 5 wt% ENR6/PLA blown films. From the DSC results in the range of -80 to 30 ^{o}C, it was found that the T_g of ENRs cannot be observed. This was probably caused by the ENR contents in PLA films was too low. It can also be observed double peaks from melting temperature when MgSt and/or rubbers were added in neat PLA due to the nucleation effect promoted by the presence of small particles [34]. Including, the reorganization of crystalline phases consists of α' (low thermodynamic stability) and α (high thermodynamic stability) forms corresponding with $T_{m,1}$ and $T_{m,2}$, respectively [35]. In general, there are four types of PLA crystalline phase, i.e., α, α', β and γ forms, depending on the preparation conditions. The α form of PLA originates from the arrangement and packing of molecular chains in the crystalline phase because of high interchain interactions of hydrogen bonding. The α' phase is formed at lower temperature than the α phase. The molecular packing within the unit cell of α' form PLA is looser and disordered, corresponding to weaker interchain interaction.

Annealing of PLA at low temperatures can also produce α' form and transforms into the ordered α form. The β phase is mostly prepared by hot-drawing the melt PLA or stretching the α form at high temperature and high draw ratio (DR). Therefore, the β form crystals of PLA have higher tensile strength and Young's modulus than their α form. The γ form has been obtained via epitaxial crystallization on hexamethylbenzene (HMB) substrate [36]. From the DSC results, the lower melting peak probably is α' form because it is not occurred from the stretching of sample at high temperature. In this research, thermal properties of films were characterized by the second heating scan of DSC thermograms in order to eliminate thermal history of PLA blown film. Furthermore, the presence of rubber or MgSt reduced hydrogen bonding between PLA chains by penetrating, corresponding to α' crystal formation. The addition of ENRs in PLA film resulted in the decrease of T_g, T_{cc} and T_m, and in the increase of ΔH_c, ΔH_m and degree of crystallinity (See in Appendix C). Furthermore, the T_g, T_{cc} and $T_{m,2}$ of ENR6/PLA_MgSt film were slightly increased from 48.41 ^oC, 94.67 ^oC and 151.43 ^oC to 49.72 ^oC, 97.11 ^oC and 151.76 ^oC with the increasing of ENR contents from 1 wt% to 5 wt%. Meanwhile, the degree of crystallinity was dramatically increased because ENR6 acted as nucleating agent for crystallization of PLA. However, degree of crystallinity slightly decreased when adding more than 3 wt% of ENR6. This was probably caused by the increasing of ENR content restricted crystallization of PLA.

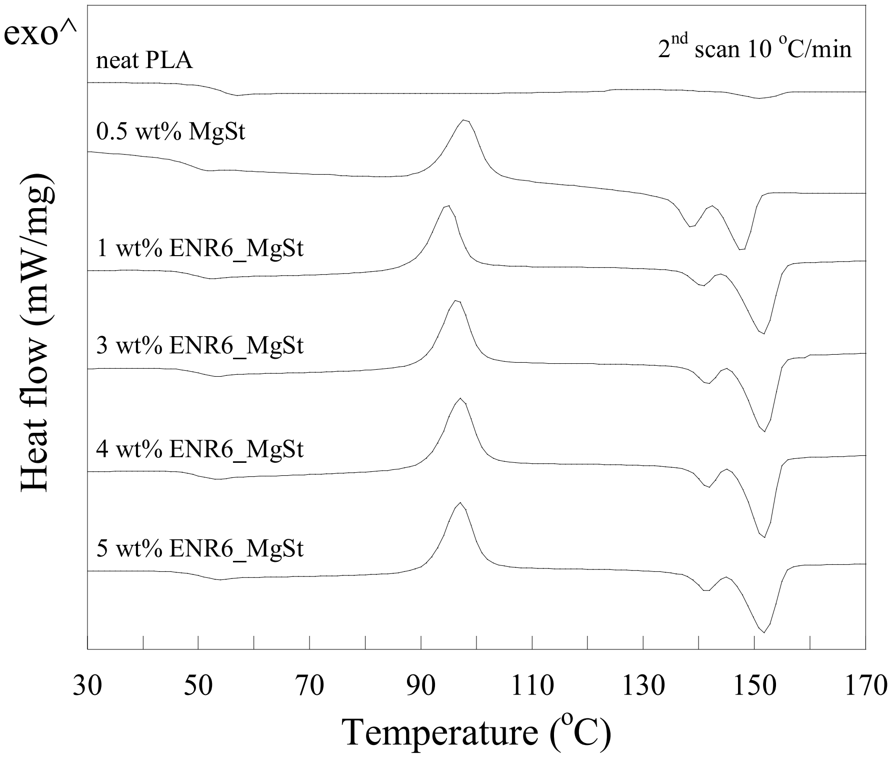


Figure 5.15 The DSC thermogram of neat PLA, PLA_MgSt and PLA_MgSt with 1, 3, 4 and 5 wt% ENR6 blown films

Figure 5.16 displays the DSC thermogram from the second heating scan for neat PLA, PLA_MgSt and PLA_MgSt with 1, 3, 4 and 5 wt% ENR6-COOH films. It can be noticed that T_{cc} and T_m tended to increase with the increasing of ENR6-COOH content from 1 wt% to 5 wt%, but T_g was slightly decreased (See in Appendix C). On the other hand, the increasing of ENR6-COOH contents leaded to decrease of ΔH_c and ΔH_m. This was probably caused by the increasing of stearic hindrance of carboxyl group in ENR6-COOH molecules restricted the crystallization of PLA. Compared with neat PLA, the degree of crystallinity was clearly increased when (1, 3, 4 and 5 wt%) ENR6-COOH were added because ENRs-COOH also acted as nucleating agent to crystallization of PLA as can be seen as two melting peaks from DSC thermogram.

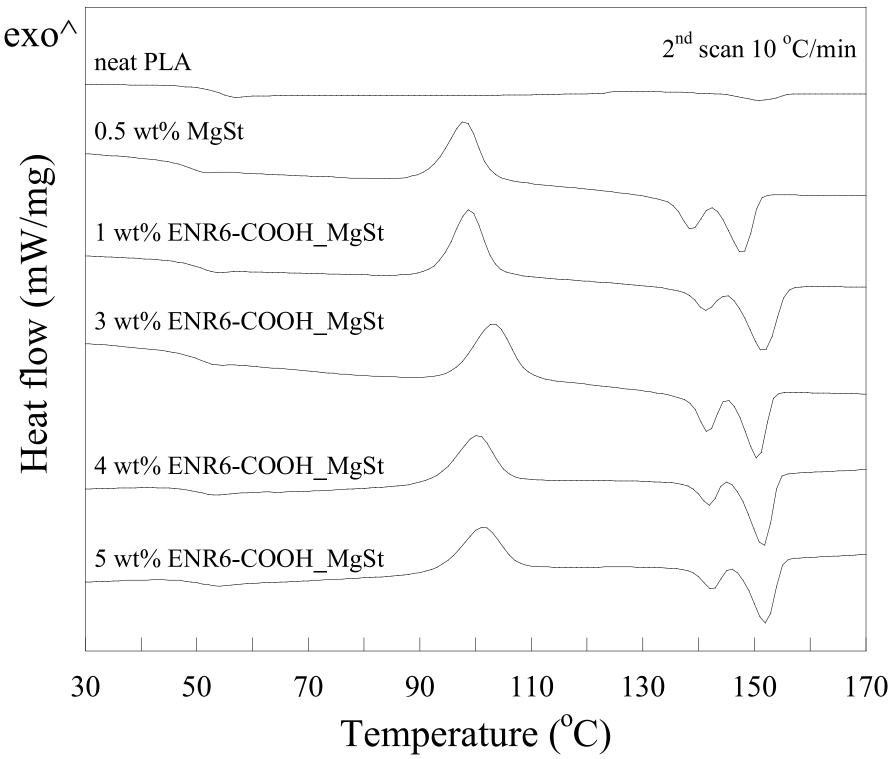


Figure 5.16 The DSC thermogram of neat PLA, PLA_MgSt and PLA_MgSt with 1, 3, 4 and 5 wt% ENR6-COOH blown films

Figure 5.17 shows the DSC thermogram of ENR6/PLA_MgSt films compared with ENR6-COOH/PLA_MgSt films at 3, 4 and 5 wt%. At the amount of rubber equal or more than 3 wt%, T_g and T_{cc} of ENR6-COOH/PLA film were higher than those of ENR6/PLA film. This is probably caused by the higher polarity of ENR6-COOH, the higher hydrogen bonding. Meanwhile, ΔH_c and ΔH_m as well as the degree of crystallinity of ENR6-COOH/PLA film were lower than those of ENR6/PLA film. This may cause by the carboxyl groups (-COOH) in ENR-COOH molecules inhibited the crystallization process of PLA. Including, the presences of crosslinking structure dramatically increased with increasing of ENR-COOH contents.

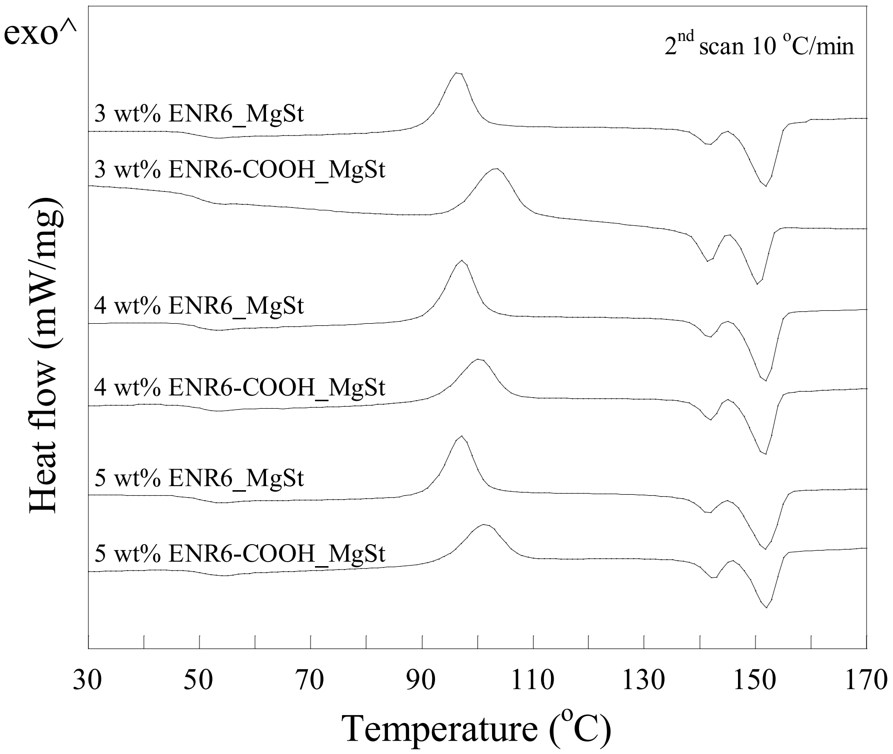
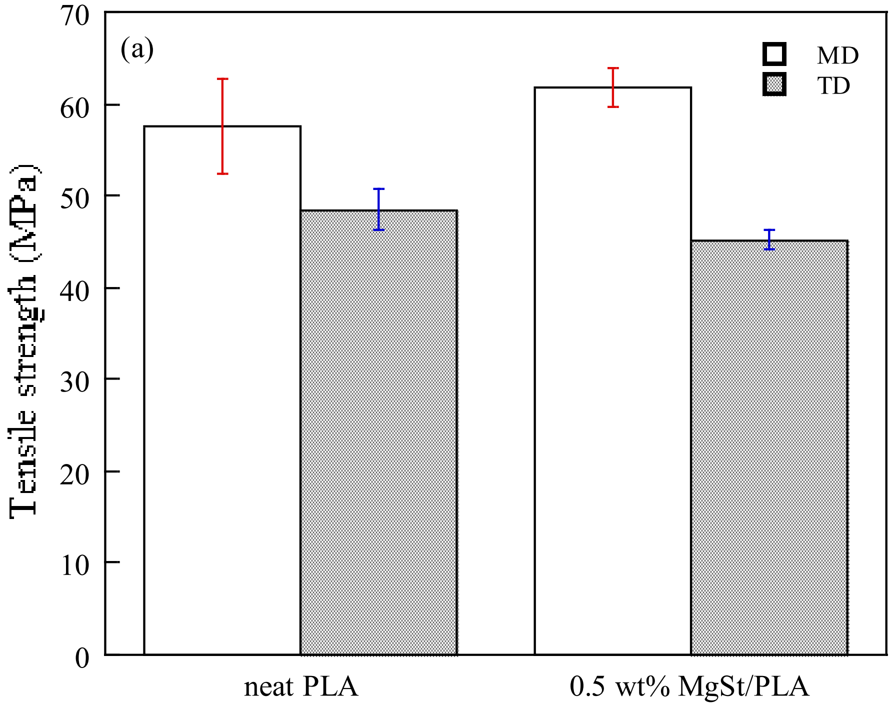


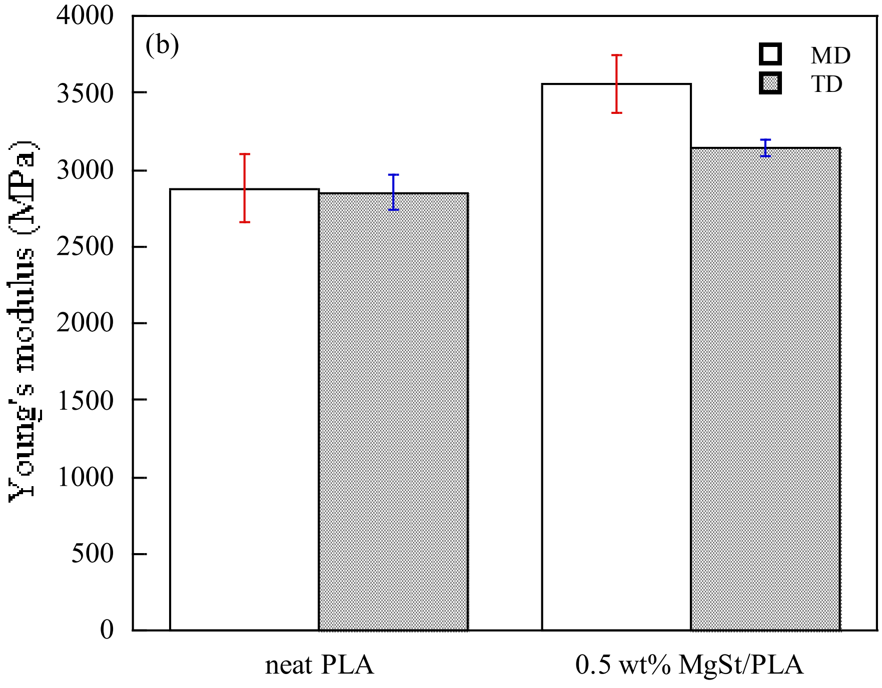
Figure 5.17 The DSC thermogram of ENR6/PLA_MgSt films compared with ENR6-COOH/PLA_MgSt films at 3, 4 and 5 wt% ENR6-COOH

5.4.2 Mechanical properties

5.4.2.1 Effect of 0.5 wt% magnesium stearate (MgSt) on tensile properties of neat PLA film

Figure 5.18 represents tensile properties of the neat PLA compared with PLA_MgSt blown films. The introduction of magnesium stearate into PLA resulted in the increase of tensile strength and Young's modulus when compared with neat PLA film in which the average tensile strength and Young's modulus in MD are increased by 7.36 and 23.77%, respectively. While the elongation at break and toughness in MD of PLA_MgSt film decreased from 3.48 to 2.03% and from 47.98 to 25.21 mJ, respectively, because magnesium state acted as nucleating agent in PLA which leaded to the increasing of degree of crystallinity from 2% to 27.27% in PLA_MgSt film by DSC technique (See in Appendix C) so the stiffness of PLA_MgSt film was increased. In addition, the compatibility between PLA and magnesium stearate was not completely miscible which magnesium stearate particles on film surface could be observed. The tensile properties in TD also give similar trend with those in MD.


(a)
Tensile strength (MPa)
0
10
20
30
40
50
60
70
MD
TD
neat PLA
0.5 wt% MgSt/PLA


(b)
Young's modulus (MPa)
0
500
1000
1500
2000
2500
3000
3500
4000
MD
TD
neat PLA
0.5 wt% MgSt/PLA

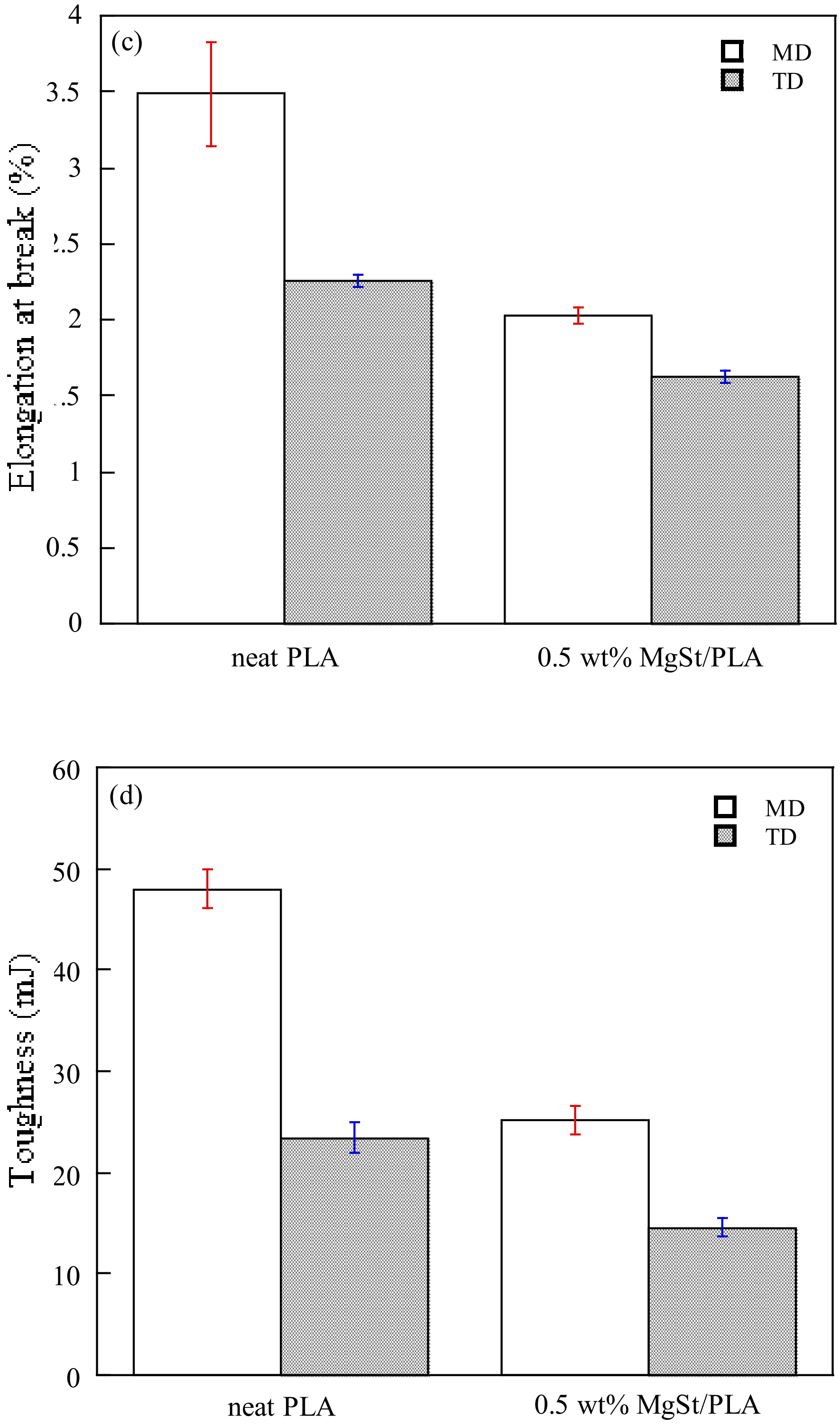
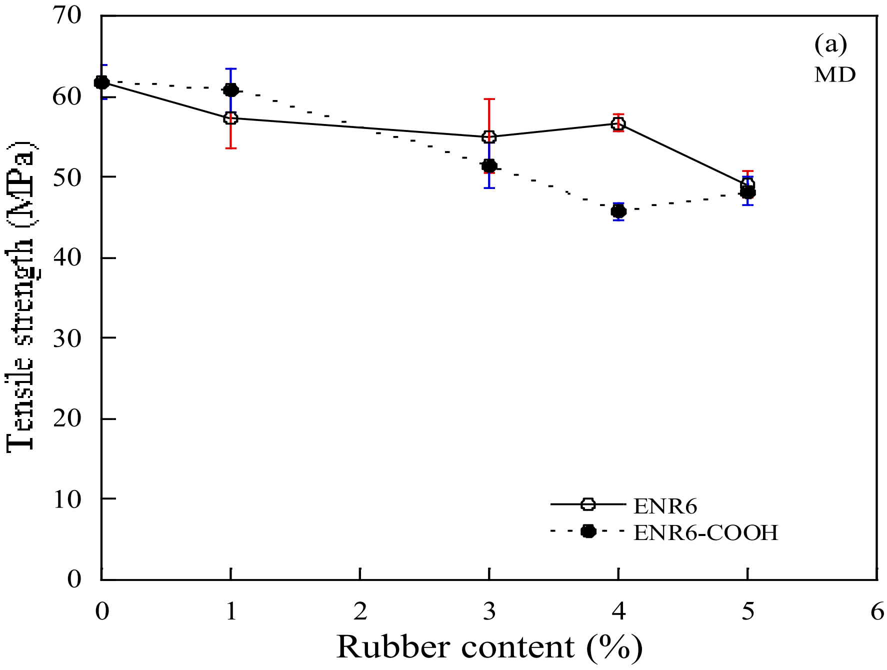
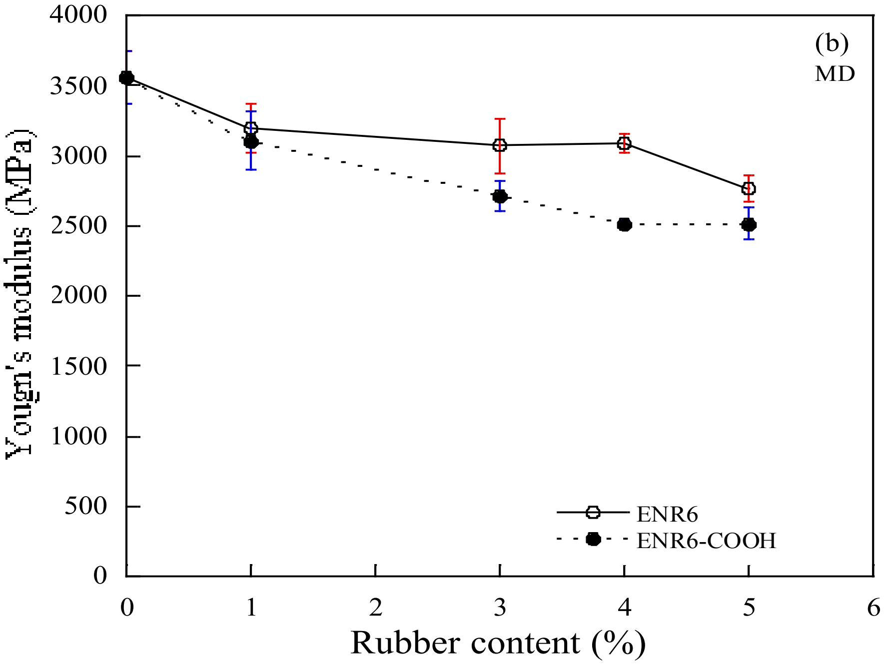


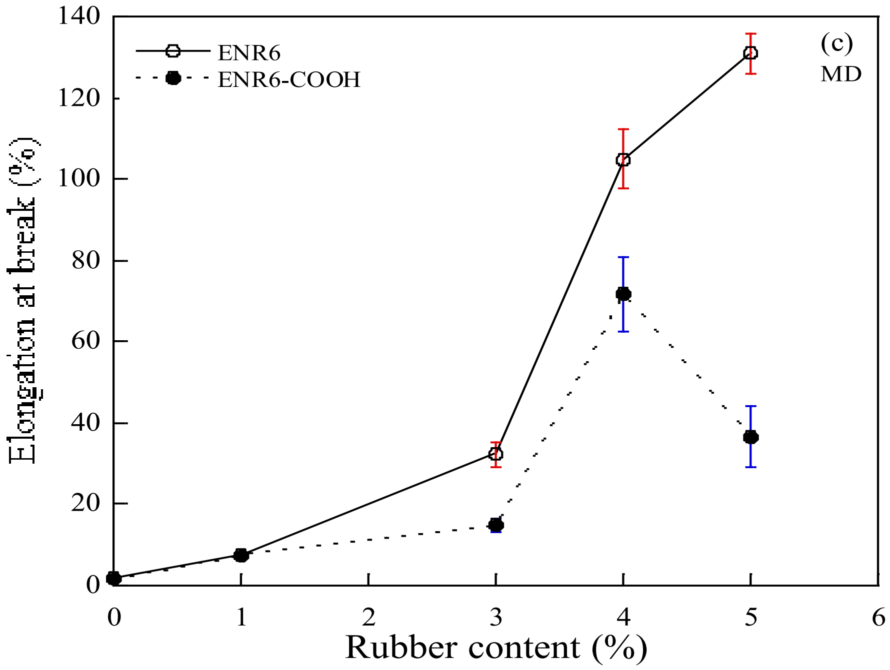
Figure 5.18 Tensile properties of the neat PLA and PLA_MgSt blown films (a) Tensile strength (b) Young's modulus (c) Elongation at break and (d) Toughness

5.4.2.2 Effect of the ENR6-COOH contents on tensile properties of neat PLA film

Figure 5.19 illustrates tensile properties in MD of ENR6/PLA_MgSt films and ENR6-COOH/PLA_MgSt film by various contents at 1, 3, 4 and 5 wt% of ENR6 and ENR6-COOH. It can be seen that ENR and ENR-COOH substantially improved tensile properties of neat PLA film. Tensile strength and Young's modulus tended to decrease while elongation at break and toughness tended to increase with increasing of rubber content. Compared with neat PLA, elongation at break remarkably increased up to 64 times and 35 times, tensile strength decreased from 61.74 MPa to 49.06 MPa and 45.72 MPa, and Young's modulus decreased from 3556.80 MPa to 2767.1 MPa and 2516.7 MPa by adding 5 wt% ENR6 and 4 wt% ENR6-COOH, respectively. Furthermore, it can be noticed that tensile properties of ENR6/PLA films are higher than those of ENR6-COOH/PLA films because the arrangement of PLA molecules were not hampered by ENR6 domain in tension. In contrast, the crystallization arrangement of PLA molecules was hindered by carboxyl group in ENR6-COOH molecules including of the crosslinking structure, although, hydrogen bonding between PLA molecules and ENR6-COOH molecules can be occurred higher than that of ENR6, corresponding with the results of ΔH_m and degree of crystallinity from DSC technique. The possibility of hydrogen bonding between PLA molecules and ENR-COOH molecules is shown in Figure 5.20. Furthermore, the excess crosslink structure in 5 wt% ENR6-COOH/PLA film resulted in the roughly film surface consistence with the decrease of elongation at break. So, the optimum of ENR6-COOH contents for this study is supposed to be 4 wt%.


(a)
MD
Tensile strength (MPa)
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
Rubber content (%)
ENR6
ENR6-COOH


(b)
MD
Yougn's modulus (MPa)
4000
3500
3000
2500
2000
1500
1000
500
0
0
1
2
3
4
5
6
Rubber content (%)
ENR6
ENR6-COOH



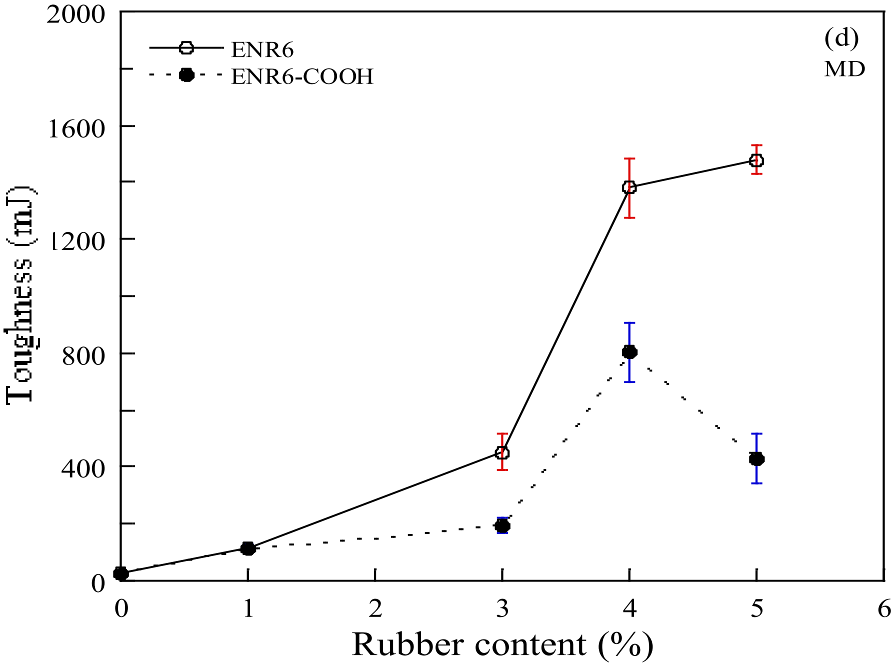


Figure 5.19 Tensile properties in MD of ENR6/PLA_MgSt films and ENR6-COOH/PLA_MgSt film by various content of rubbers a) Tensile strength, b) Young's modulus, c) Elongation at break, d) Toughness

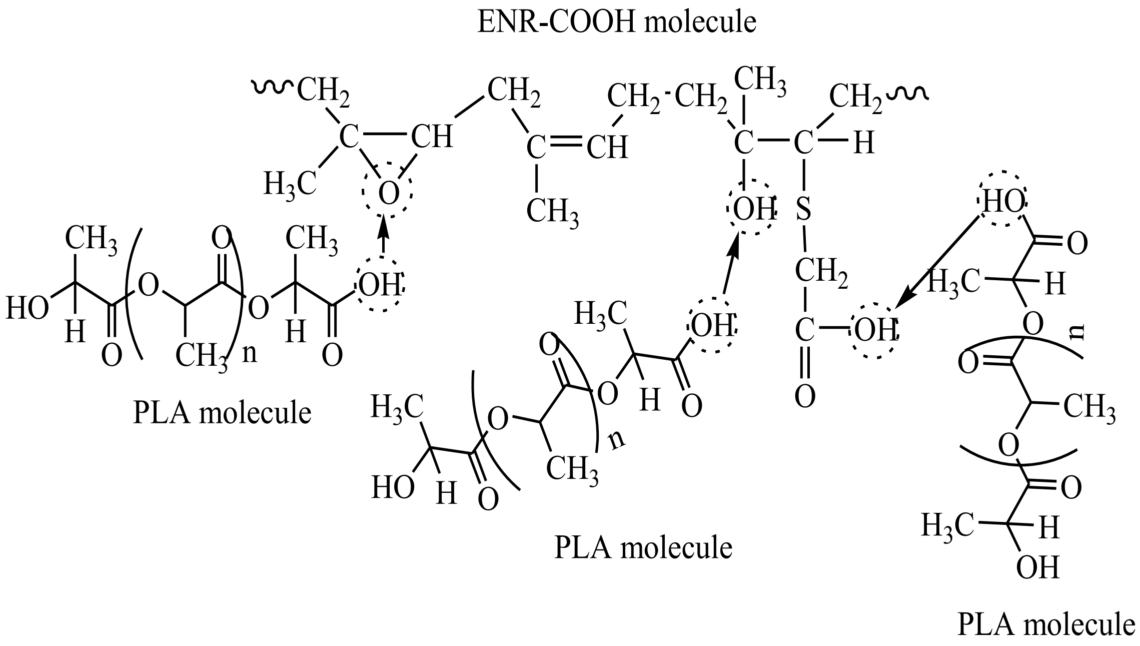
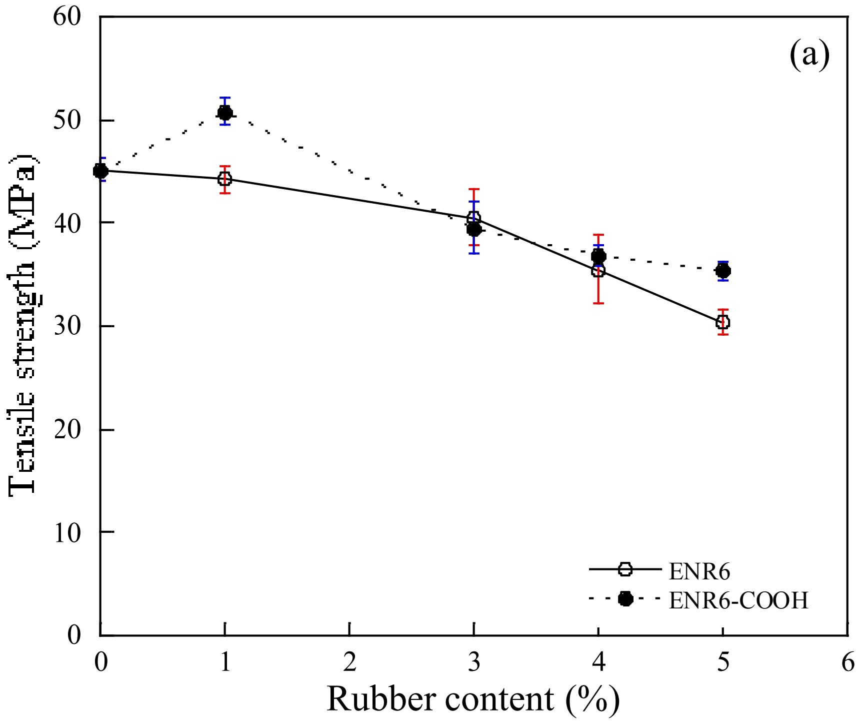
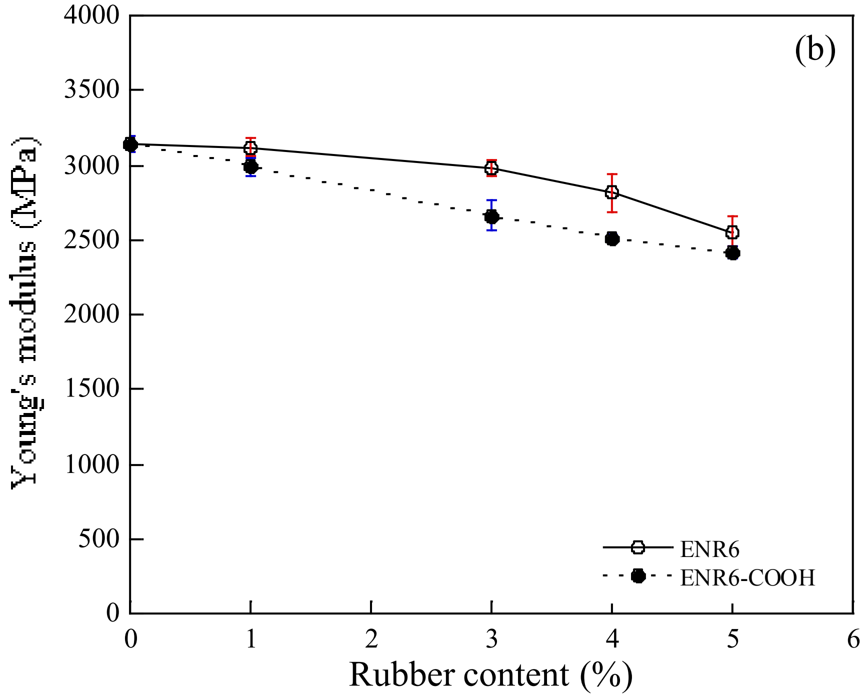
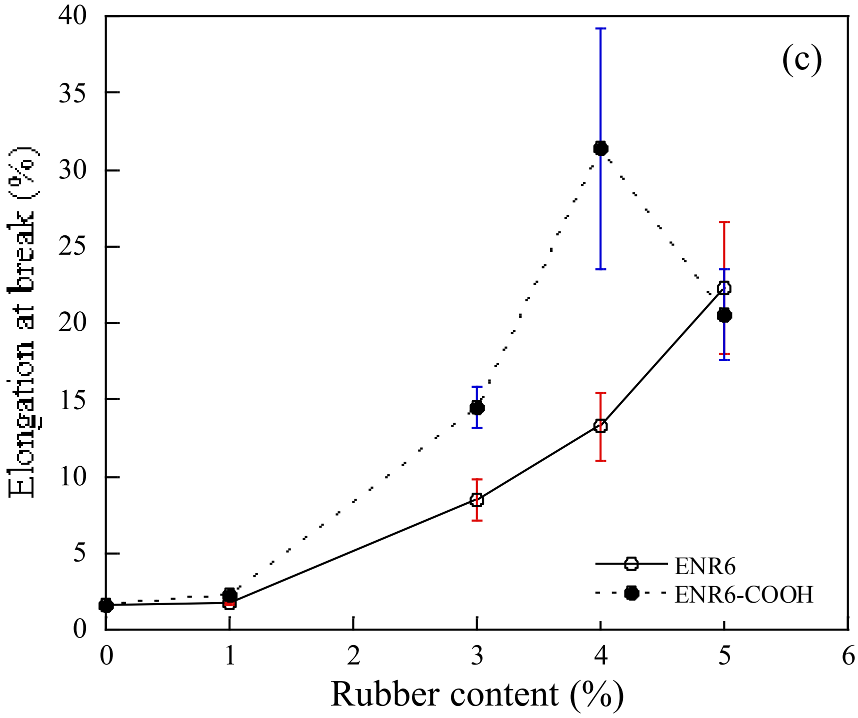


Figure 5.20 Possibility of hydrogen bonding between PLA molecules and ENR-COOH molecules

Figure 5.21 displays tensile properties in TD of ENR6/PLA_MgSt films and ENR6-COOH/PLA_MgSt film various content of rubbers. It was found that tensile strength and Young's modulus in TD and MD of ENR6 and ENR6-COOH were in the same trend. At the rubber contents more than 3 wt% elongation at break and toughness in TD of ENR6-COOH were higher than those of ENR6. It probably dues to the different in the orientation between PLA and ENR6 or ENR6-COOH during blow film process. That was, the molecular orientation between PLA and ENR6 was easy in MD. So, PLA and ENR6 molecules can absorb high energy of tension in MD before failure, while those molecules cannot absorb energy of tension in TD. In contrast, the crosslink between PLA and ENR6-COOH provided molecular orientation in MD was restricted. Therefore, the crosslinking structure between PLA and ENR6-COOH can absorb some energy of tension in TD before failure.


(a)
Tensile strength (MPa)
0
10
20
30
40
50
60
Rubber content (%)
0
1
2
3
4
5
6
ENR6
ENR6-COOH


(b)
Young's modulus (MPa)
0
500
1000
1500
2000
2500
3000
3500
4000
Rubber content (%)
0
1
2
3
4
5
6
ENR6
ENR6-COOH



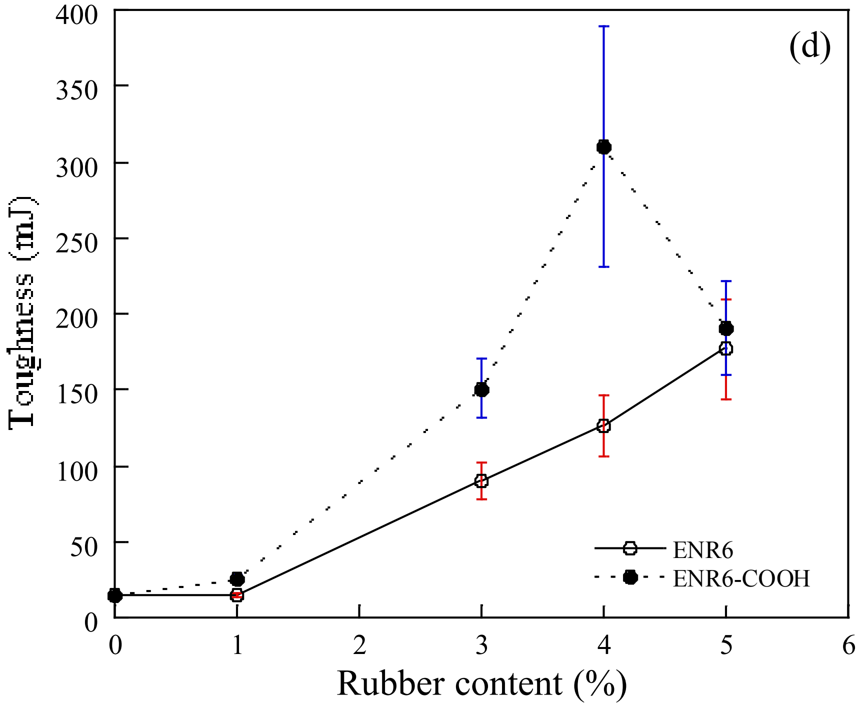


Figure 5.21 Tensile properties in TD of ENR6/PLA_MgSt films and ENR6-COOH/PLA_MgSt film various content of rubbers a) Tensile strength, b) Young's modulus, c) Elongation at break, d) Toughness

CHAPTER VI

CONCLUSIONS

6.1 Conclusions

In this research, ENRs-COOH at various epoxide and carboxyl contents was prepared to use as toughening agent. Then, 3 wt% ENRs-COOH was blended and blown film with PLA in order to find the type of ENRs-COOH which provided the optimum tensile properties. After that, the selected ENRs-COOH was blended and blown film with PLA and 0.5 wt% magnesium stearate by various contents at 1, 3, 4 and 5 wt% to find the optimum content. It can be concluded that ENRs-COOH including ENR6-COOH, ENR19-COOH, ENR24-COOH and ENR52-COOH can be synthesized by solvent method which were confirmed from the functional group and chemical structure as well as the level of epoxide and carboxyl groups by FTIR and ^{1}H NMR techniques. The thermal properties of ENRs-COOH/PLA blown films decreased with increasing the level of epoxide and carboxyl groups. 3 wt% ENR6-COOH/PLA films provided the highest elongation at break and toughness; therefore, ENR6-COOH was selected to blend with PLA and 0.5 wt% magnesium stearate to obtain the highest tensile properties of the PLA film by varying contents of ENR6-COOH. The addition of 4 wt% ENR6-COOH provided the highest tensile properties in the ENR6-COOH/PLA_MgSt film.

6.2 Recommendations for further study

From the study, the recommendations for the further research are as follows

1) Some additives that prevent crosslinking reaction should be added in the melt mixing process before blow film process.

2) Some plasticizers should be used in rubber/PLA film in order to improve elongation at break.

3) There should be more investigation in the properties of the PLA blown films such as impact properties, tear resistance, gas transmission properties.

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APPENDICES

APPENDIX A

Calculation of ENR and ENR-COOH preparation

5 phr of surfactant for 380 g natural rubber latex concentrate with 60% dry rubber content (DRC) :

$$380\,\mathrm{g\,NRL}\left(\frac{60\,\mathrm{g\,NR}}{100\,\mathrm{g\,NRL}}\right)\left(\frac{5\,\mathrm{g\,surfactant}}{100\,\mathrm{g\,NR}}\right) \quad = \quad 11.40\,\mathrm{g} \quad \mathrm{surfactant}$$

Formic acid :

- Molar ratio of formic acid : NR = 0.3 : 1
- Molecular weight of repeating unit of NR = 68 g/mol
- Molecular weight of formic acid = 46.03 g/mol
- Density of formic acid = 1.22 g/mol

$$380\,\mathrm{g\,NRL}\left(\frac{60\,\mathrm{g\,NR}}{100\,\mathrm{g\,NRL}}\right)\left(\frac{1\,\mathrm{mol\,NR}}{68\,\mathrm{g\,NR}}\right)\left(\frac{0.3\,\mathrm{mol\,formic\,acid}}{1\,\mathrm{mol\,NR}}\right)\left(\frac{46.03\,\mathrm{g\,formic\,acid}}{1\,\mathrm{mol\,formic\,acid}}\right)$$
$$\left(\frac{1\,\mathrm{ml\,formic\,acid}}{1.22\,\mathrm{g\,formic\,acid}}\right)\left(\frac{100\,\mathrm{ml\,Soln\,formic\,acid}}{90\,\mathrm{mol\,formic\,acid}}\right) \quad = \quad 42.17\,\mathrm{ml} \quad \mathrm{Sol}^{\mathrm{n}}\ \mathrm{formic\,acid}$$

Hydrogen peroxide (H_2O_2) :

- Molar ratio of hydrogen peroxide : NR = 3 : 1
- Molecular weight of repeating unit of NR = 68 g/mol
- Molecular weight of hydrogen peroxide = 34 g/mol
- Density of hydrogen peroxide = 1.1961 g/mol

$$380\,\mathrm{g\,NRL}\left(\frac{60\,\mathrm{g\,NR}}{100\,\mathrm{g\,NRL}}\right)\left(\frac{1\,\mathrm{mol\,NR}}{68\,\mathrm{g\,NR}}\right)\left(\frac{3\,\mathrm{mol\,H_2O_2}}{1\,\mathrm{mol\,NR}}\right)\left(\frac{34\,\mathrm{g\,H_2O_2}}{1\,\mathrm{mol\,H_2O_2}}\right)$$

$$\left(\frac{1\,\mathrm{ml\,H_2O_2}}{1.1961\,\mathrm{g\,H_2O_2}}\right)\left(\frac{100\,\mathrm{ml\,Soln\,H_2O_2}}{30\,\mathrm{mol\,H_2O_2}}\right) = 953.10\,\mathrm{ml}\quad \mathrm{Sol^n\,H_2O_2}$$

In this work, 4 levels (25%, 40%, 50%, and 75%) of reagents (formic acid and hydrogen peroxide) are used to synthesis ENR6, ENR19, ENR24 and ENR52, respectively.

Example of used reagents for ENR6 :

Assume that 100% formic acid = 42.17 ml
So 25% formic acid = 42.17 x (25/100) = 10.54 ml
And assume that 100% hydrogen peroxide = 953.10 ml
So 25% hydrogen peroxide = 953.10 x (25/100) = 238.28 ml

Table A.1: Amount of reactants for ENRs preparation

ENR	Formic acid (ml)	Hydrogen peroxide (ml)
ENR6	10.54	238.28
ENR19	16.87	381.24
ENR24	21.09	476.55
ENR52	31.63	714.83

Thioglycollic acid (TGA) :

- Molar ratio of thioglycollic acid : ENR = 1.5 : 1
- Molecular weight of repeating unit of NR = 68 g/mol
- Molecular weight of thioglycollic acid = 92.12 g/mol
- Density of thioglycollic acid = 1.326 g/mol

Example of used TGA for ENR6-COOH :

$$100\,\mathrm{g\,rubber}\left(\frac{5.72\,\mathrm{g\,ENR}}{100\,\mathrm{g\,rubber}}\right)\left(\frac{1\,\mathrm{mol\,ENR}}{84\,\mathrm{g\,ENR}}\right)\left(\frac{1.5\,\mathrm{mol\,TGA}}{1\,\mathrm{mol\,TGA}}\right)\left(\frac{92.12\,\mathrm{g\,TGA}}{1\,\mathrm{mol\,TGA}}\right)$$

$$\left(\frac{1\,\mathrm{ml\,TGA}}{1.326\,\mathrm{g\,TGA}}\right)\left(\frac{100\,\mathrm{ml\,Soln\ TGA}}{99\,\mathrm{ml\,TGA}}\right) \quad = \quad 7.17.\mathrm{ml} \quad \mathrm{Sol}^{n}\ \mathrm{TGA}$$

Table A.2: Amount of TGA for ENRs-COOH preparation

ENRs-COOHs	TGA (ml)
ENR6-COOH	7.17
ENR19-COOH	23.78
ENR24-COOH	30.26
ENR52-COOH	65.26

Appendix B

^{1}H NMR spectra of ENRs and ENRs-COOH

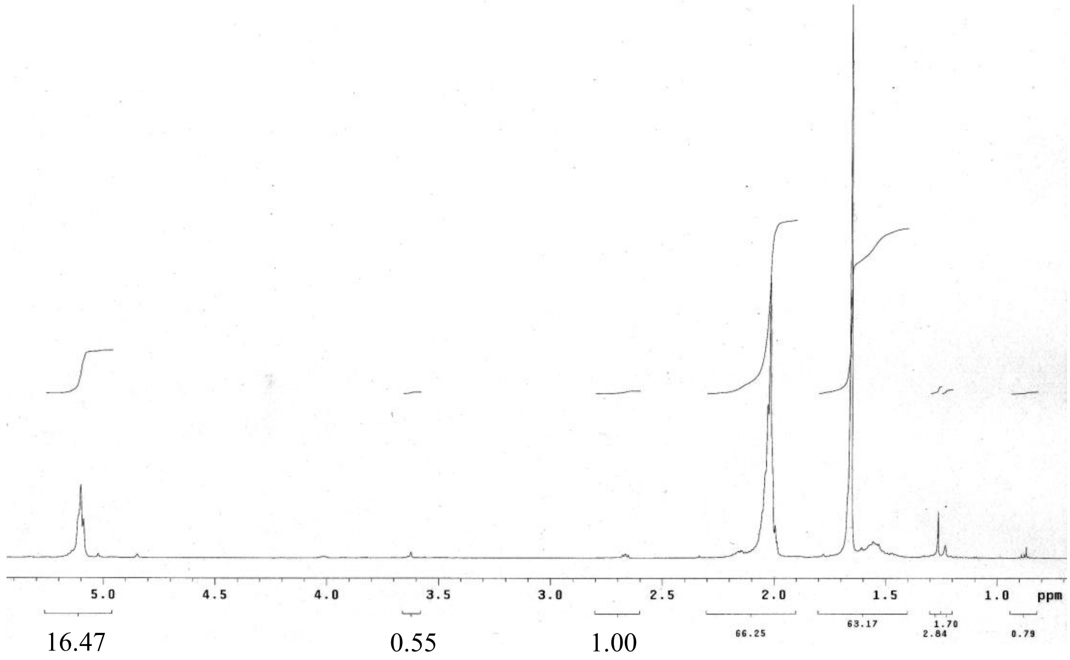

Figure B.1 ^{1}H NMR spectrum of ENR6

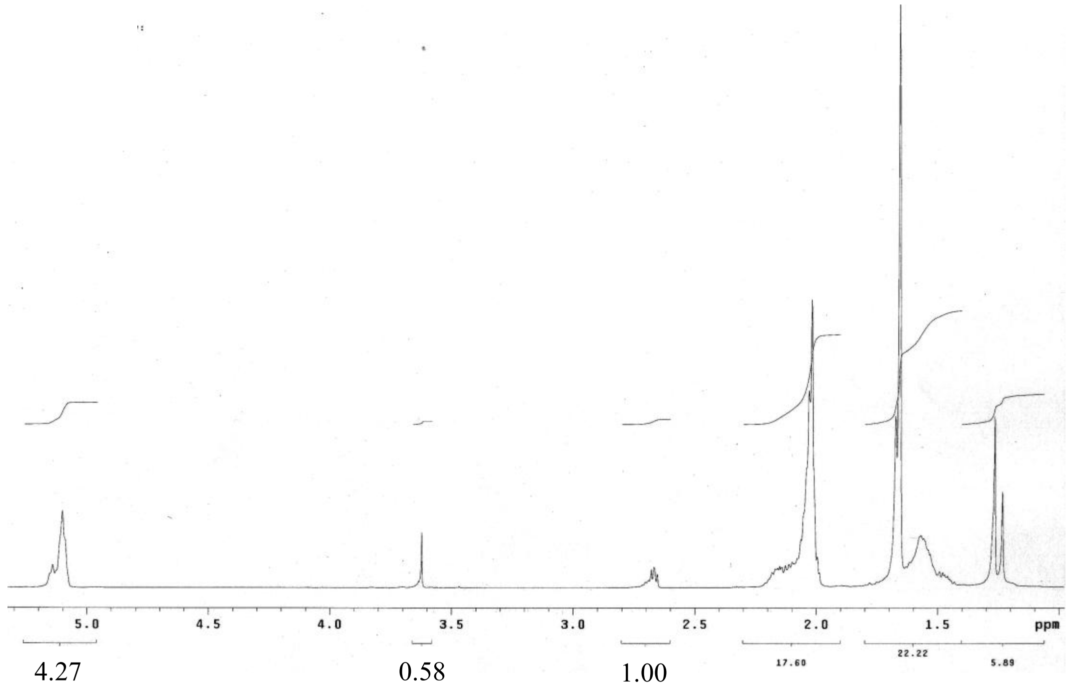

Figure B.2 ^{1}H NMR spectrum of ENR19

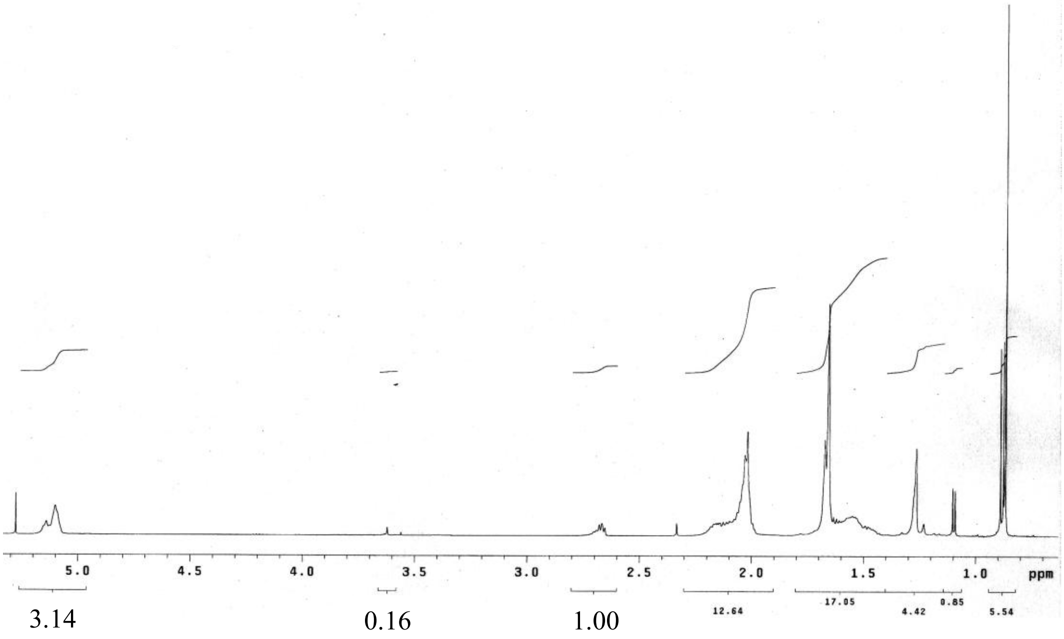

Figure B.3 ^{1}H NMR spectrum of ENR24

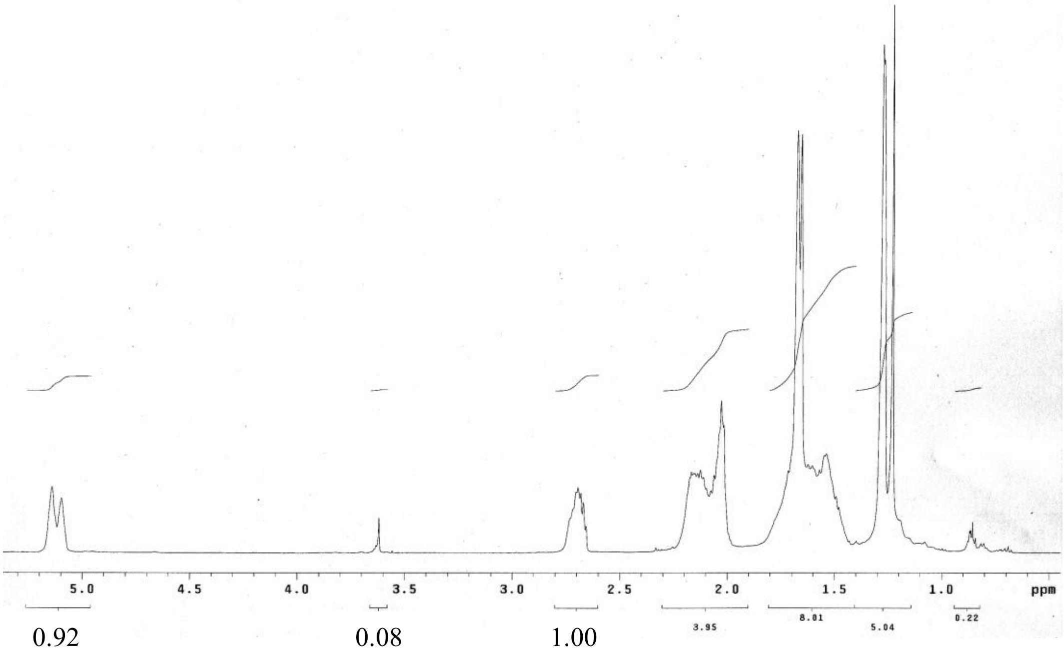

Figure B.4 ^{1}H NMR spectrum of ENR52

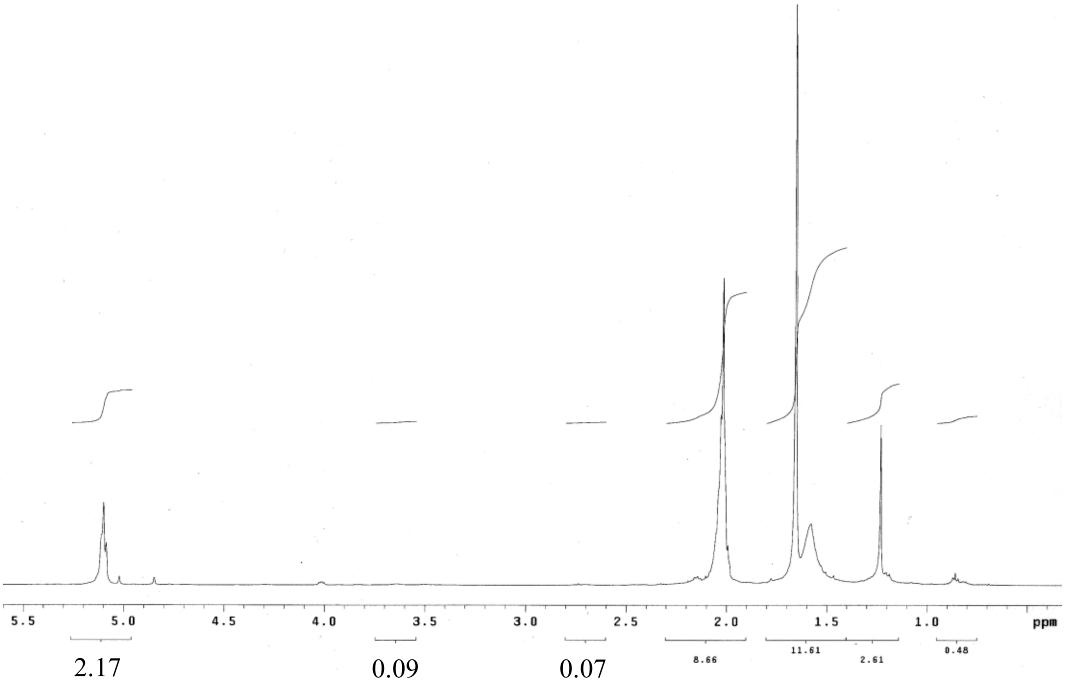

Figure B.5 ^{1}H NMR spectrum of ENR6-COOH

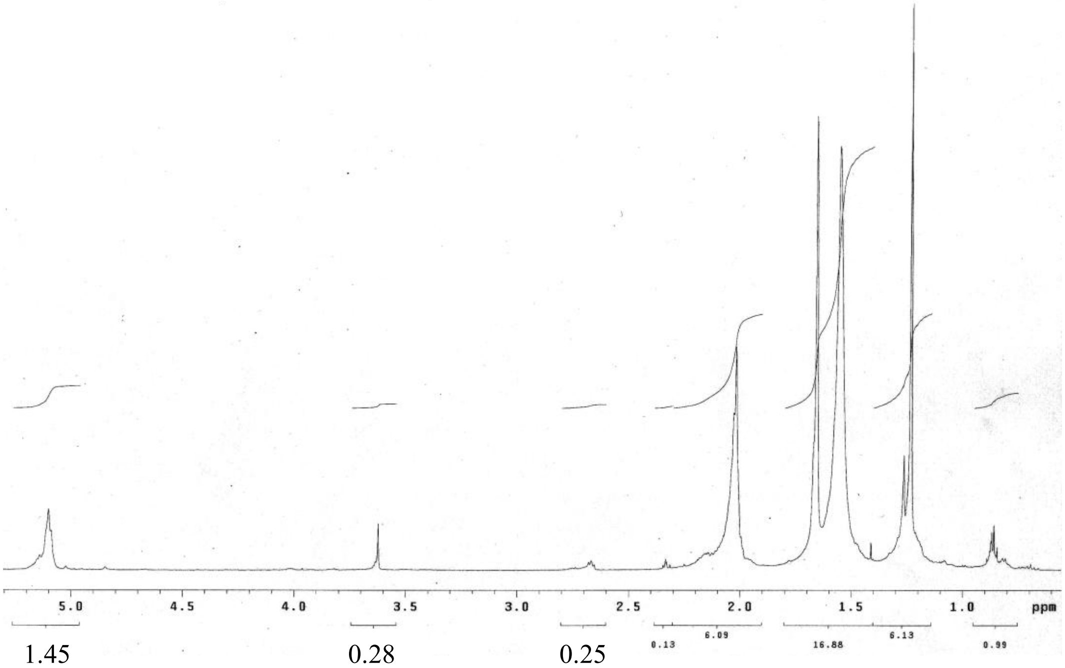

Figure B.6 ^{1}H NMR spectrum of ENR19-COOH

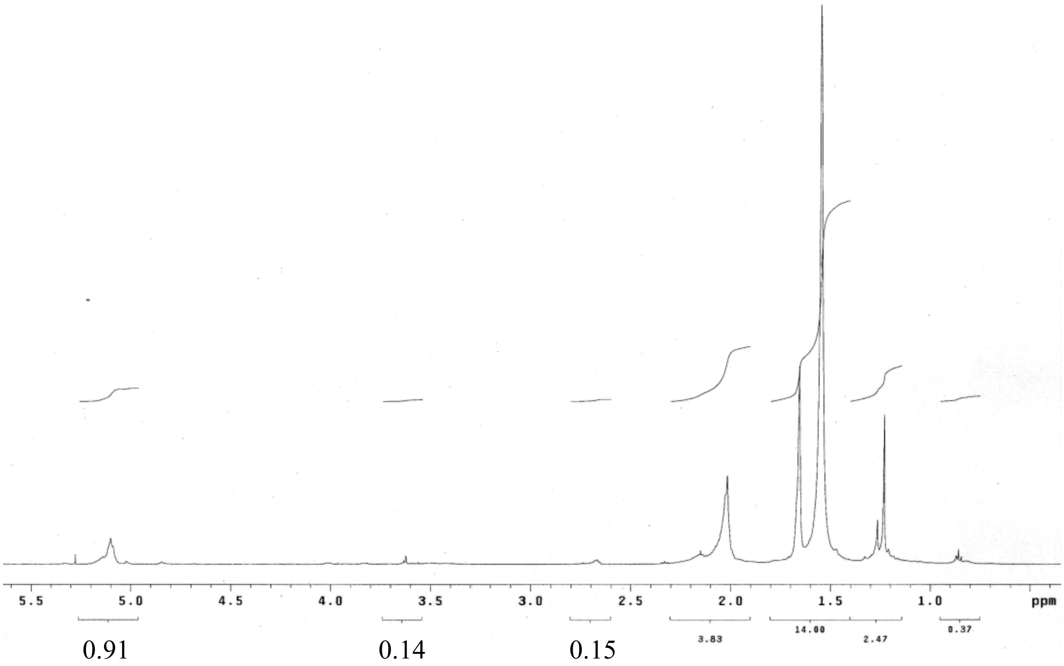

Figure B.7 ^{1}H NMR spectrum of ENR24-COOH

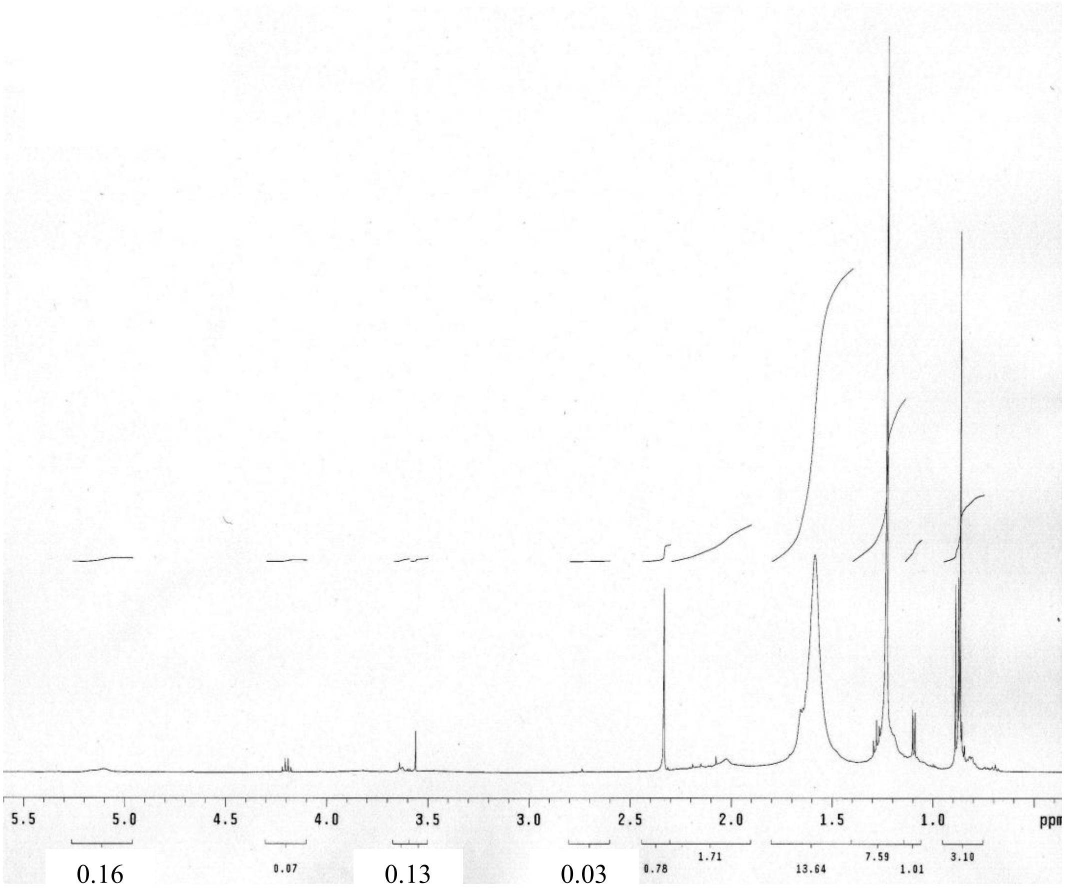

Figure B.8 ^{1}H NMR spectrum of ENR52-COOH

Appendix C

Differential scanning calorimetric results

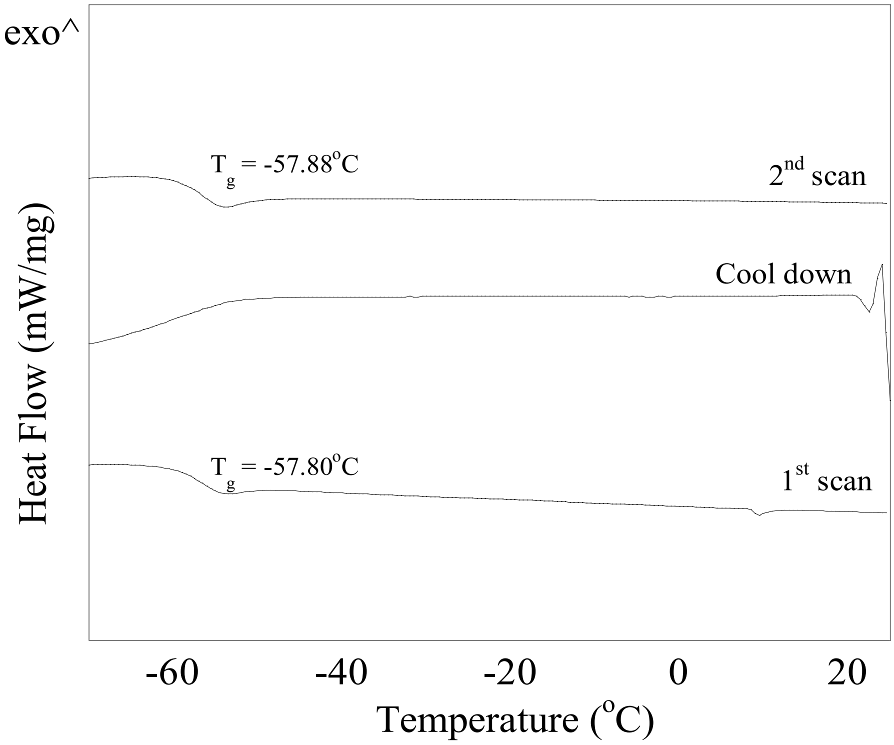

Figure C.1 DSC spectrum of ENR6

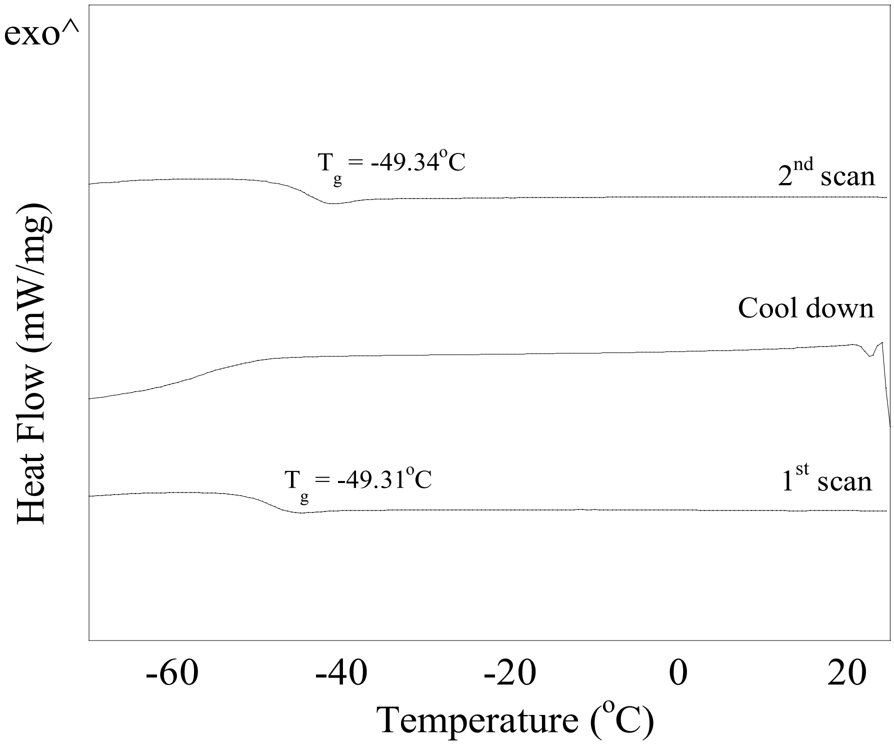

Figure C.2 DSC spectrum of ENR19

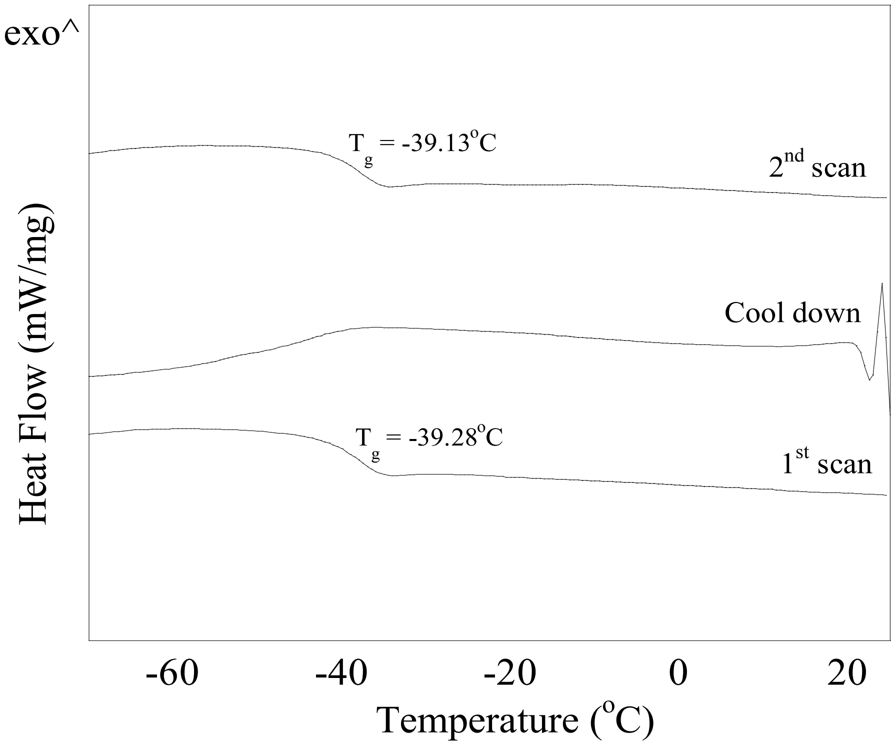

Figure C.3 DSC spectrum of ENR24

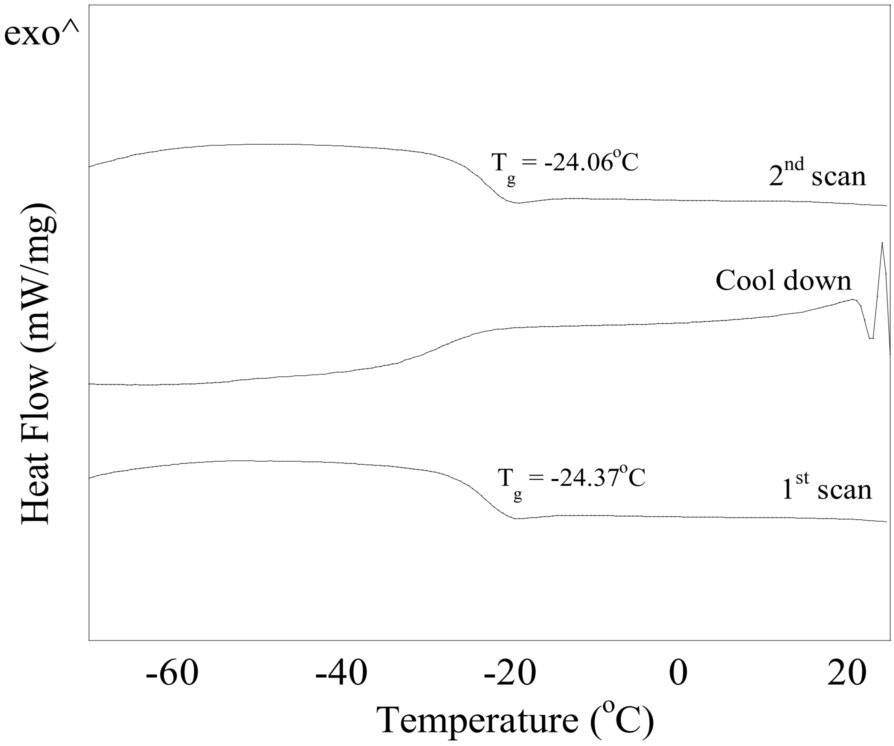

Figure C.4 DSC spectrum of ENR52

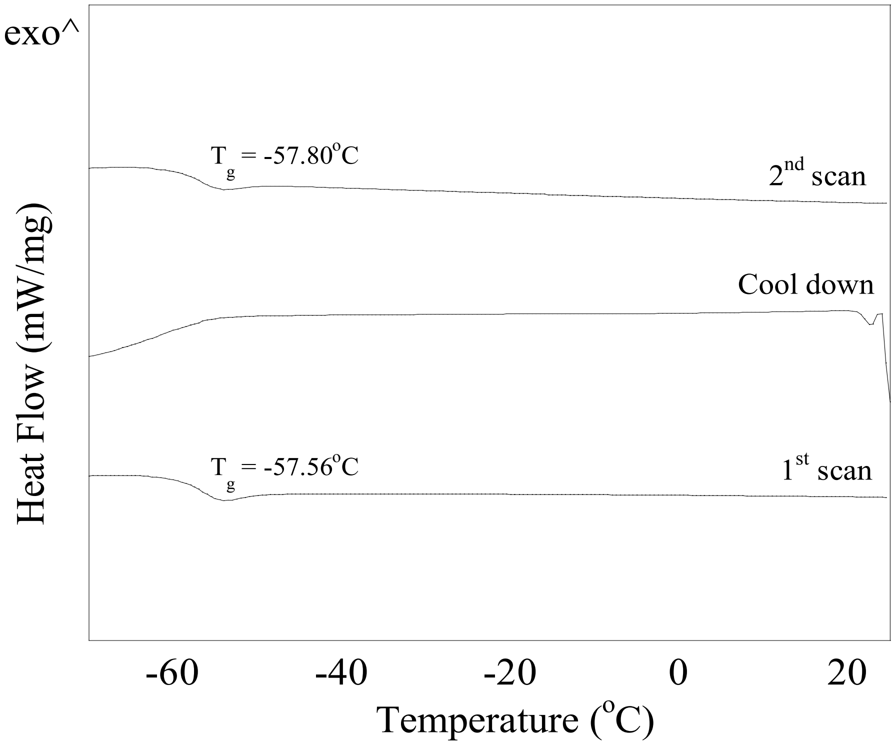

Figure C.5 DSC spectrum of ENR6-COOH

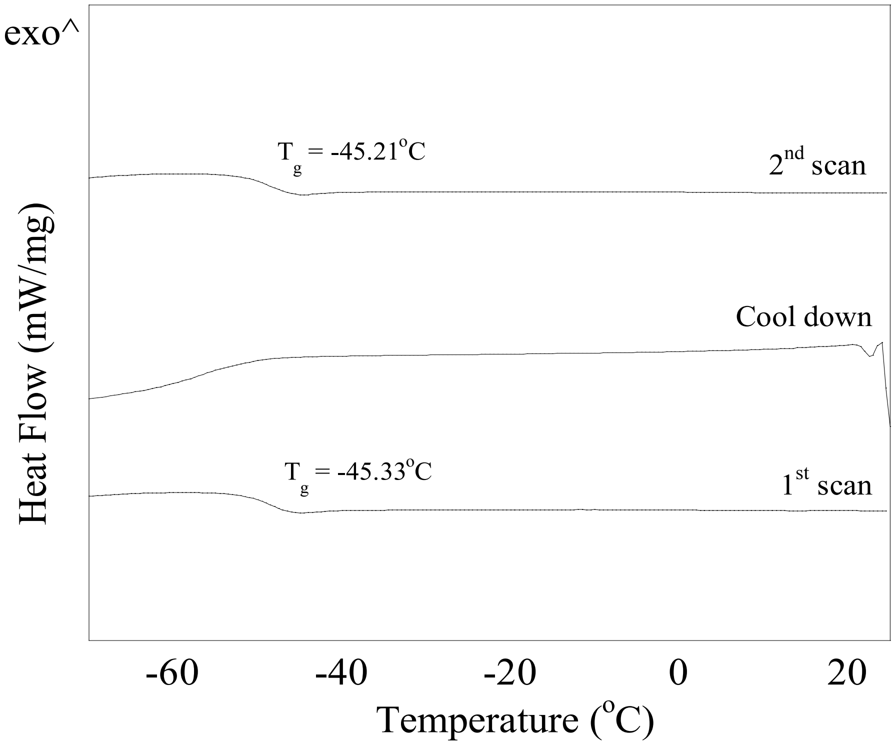

Figure C.6 DSC spectrum of ENR19-COOH

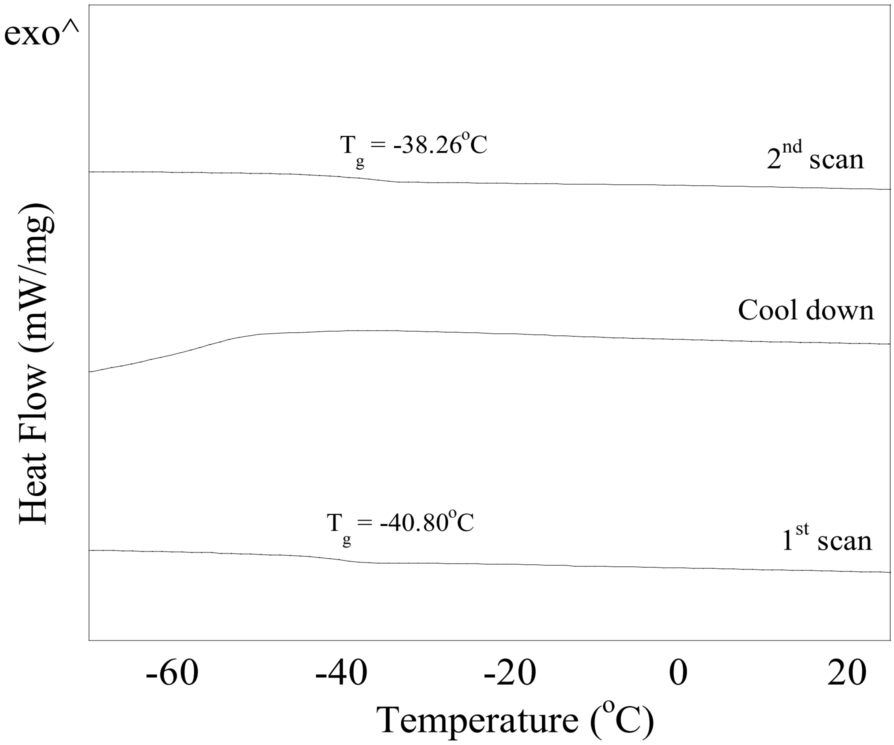

Figure C.7 DSC spectrum of ENR24-COOH

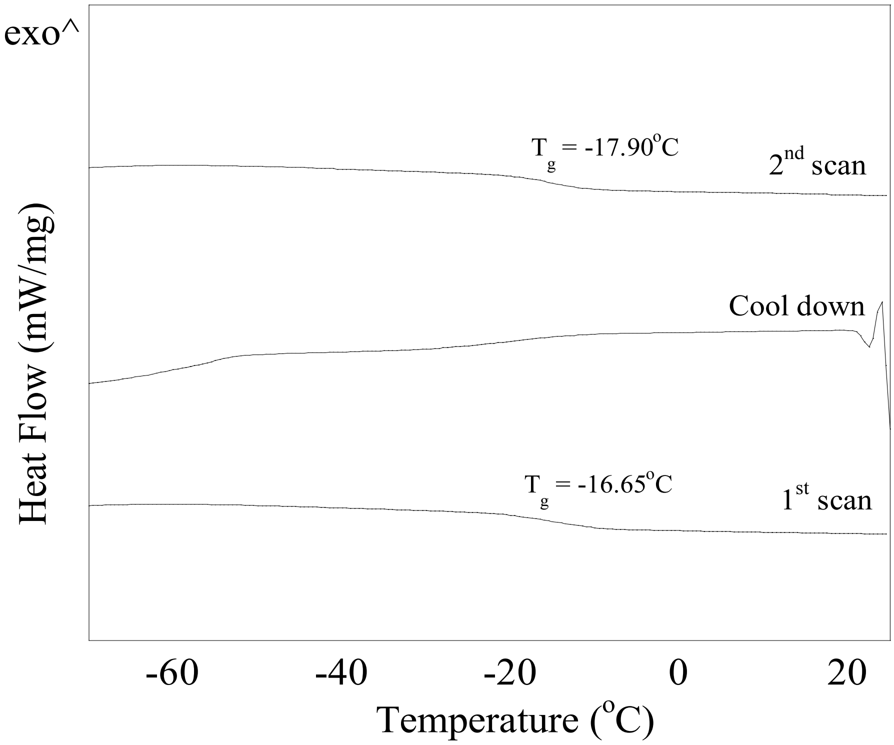

Figure C.8 DSC spectrum of ENR52-COOH

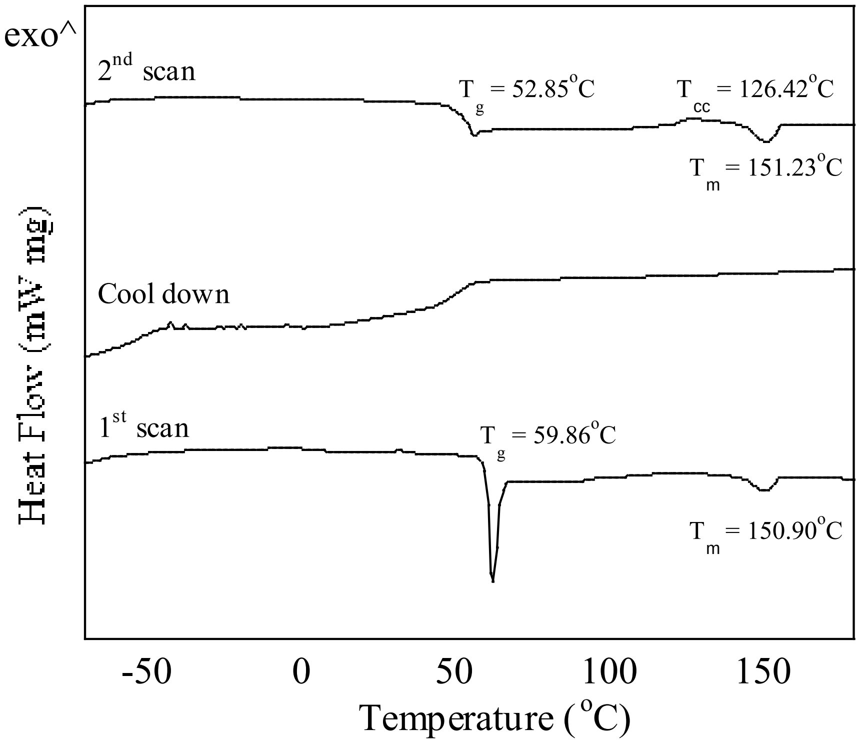

Figure C.9 DSC spectrum of neat PLA film

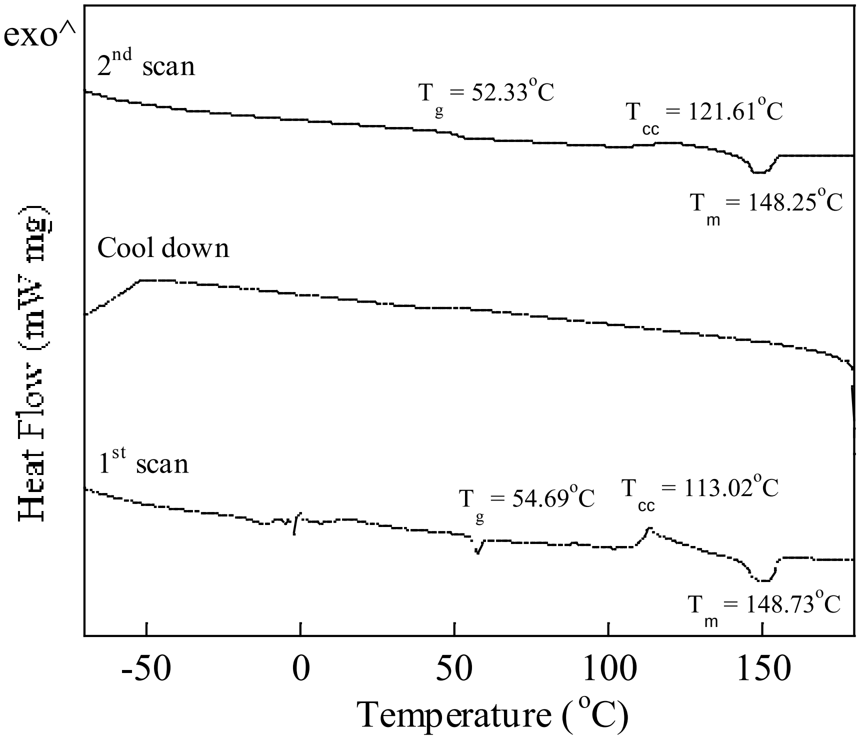

Figure C.10 DSC spectrum of 3 wt% NR/PLA film

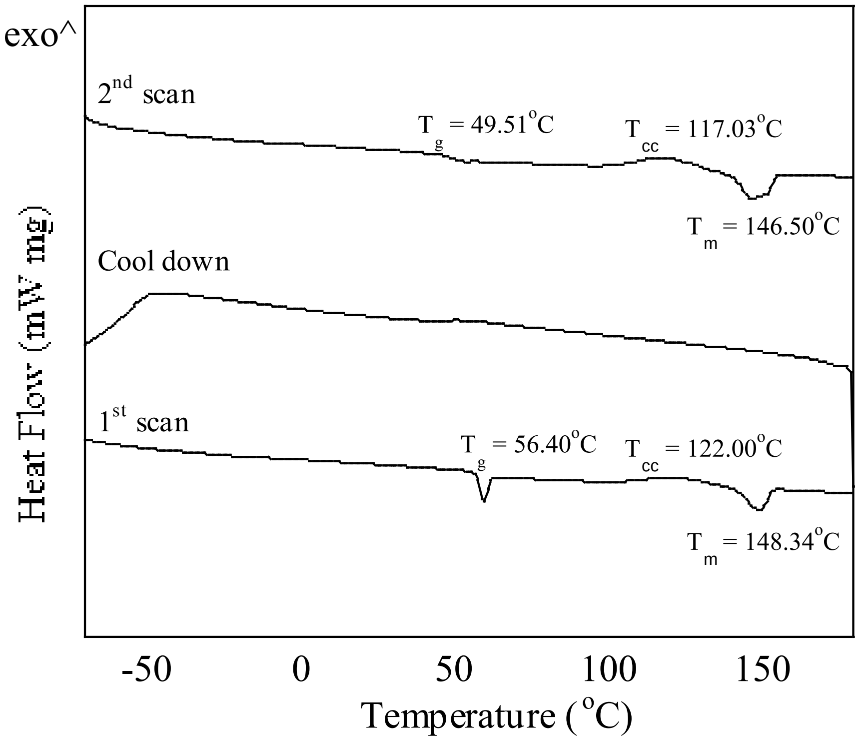

Figure C.11 DSC spectrum of 3 wt% ENR6-COOH/PLA film

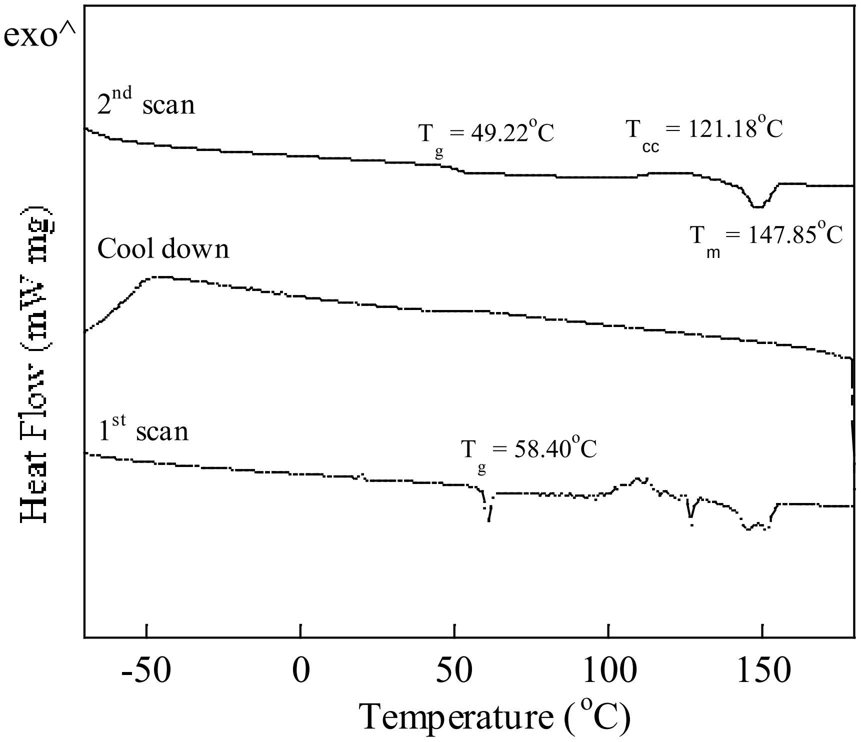

Figure C.12 DSC spectrum of 3 wt% ENR19-COOH/PLA film

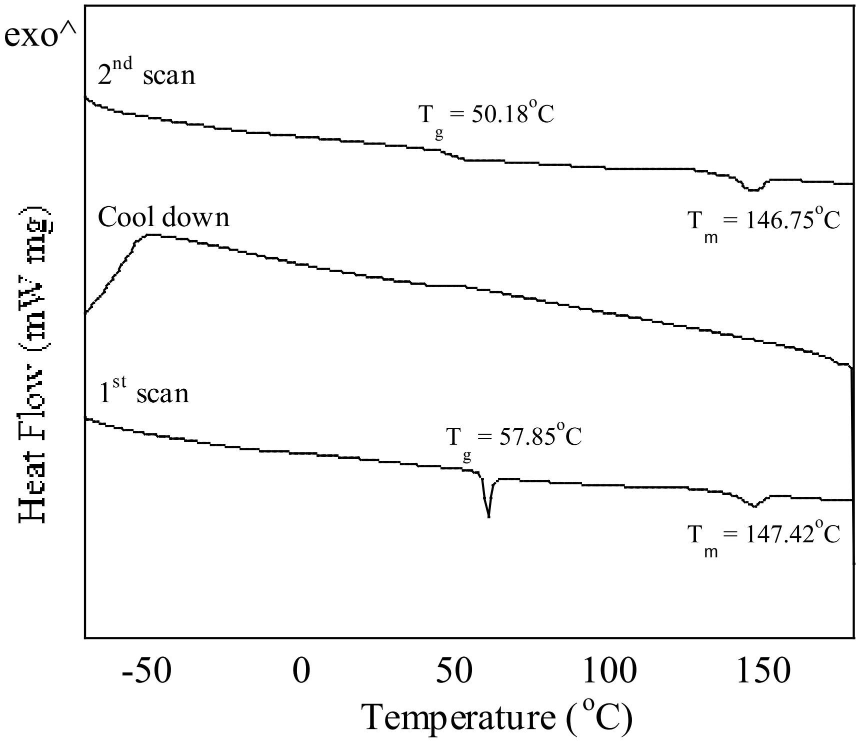

Figure C.13 DSC spectrum of 3 wt% ENR24-COOH/PLA film

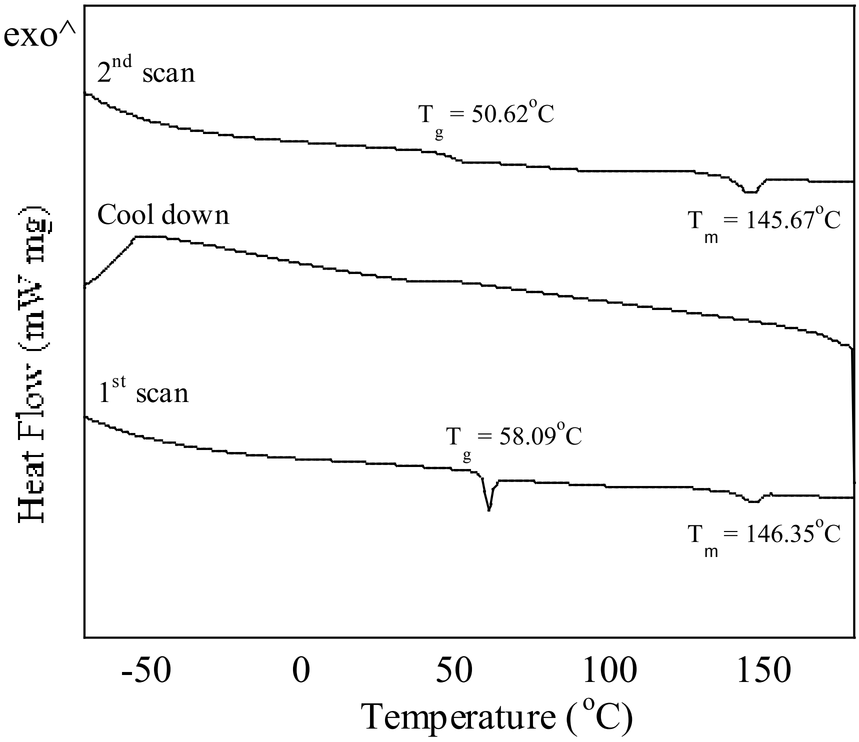

Figure C.14 DSC spectrum of 3 wt% ENR52-COOH/PLA film

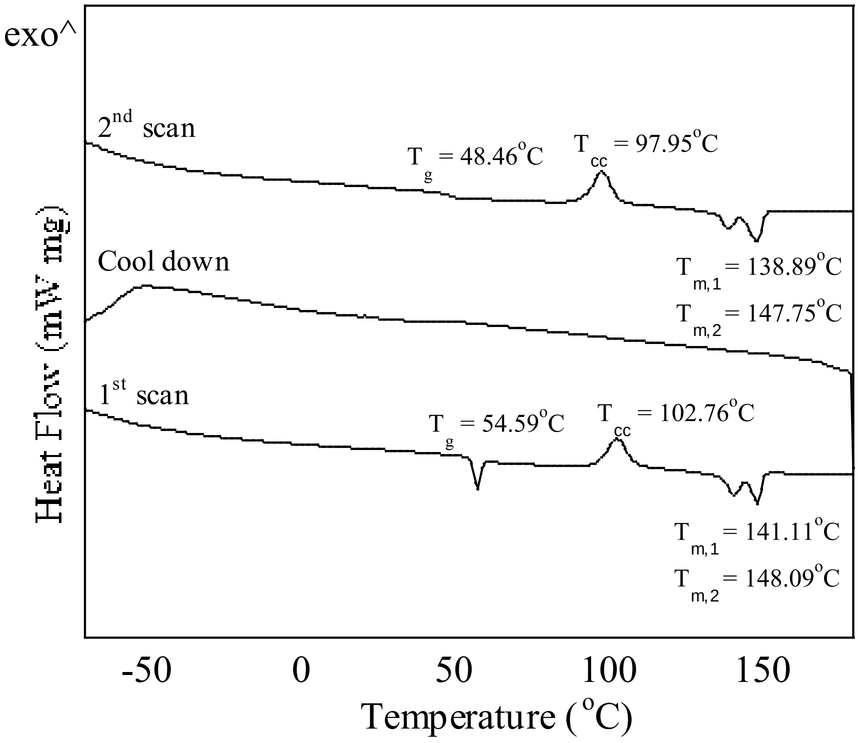

Figure C.15 DSC spectrum of PLA_MgSt film

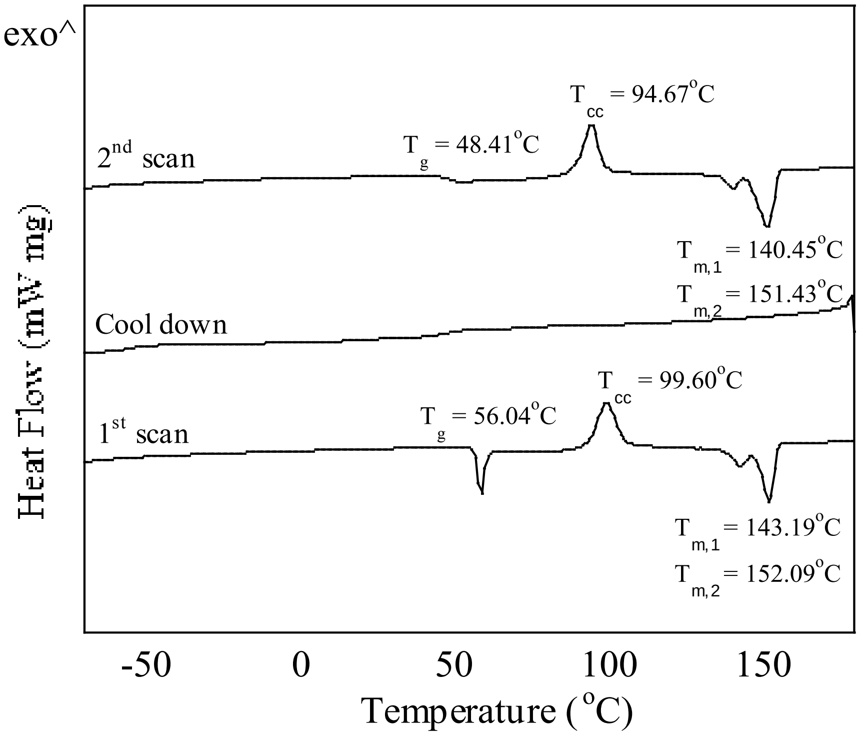

Figure C.16 DSC spectrum of 1 wt% ENR6/PLA_MgSt film

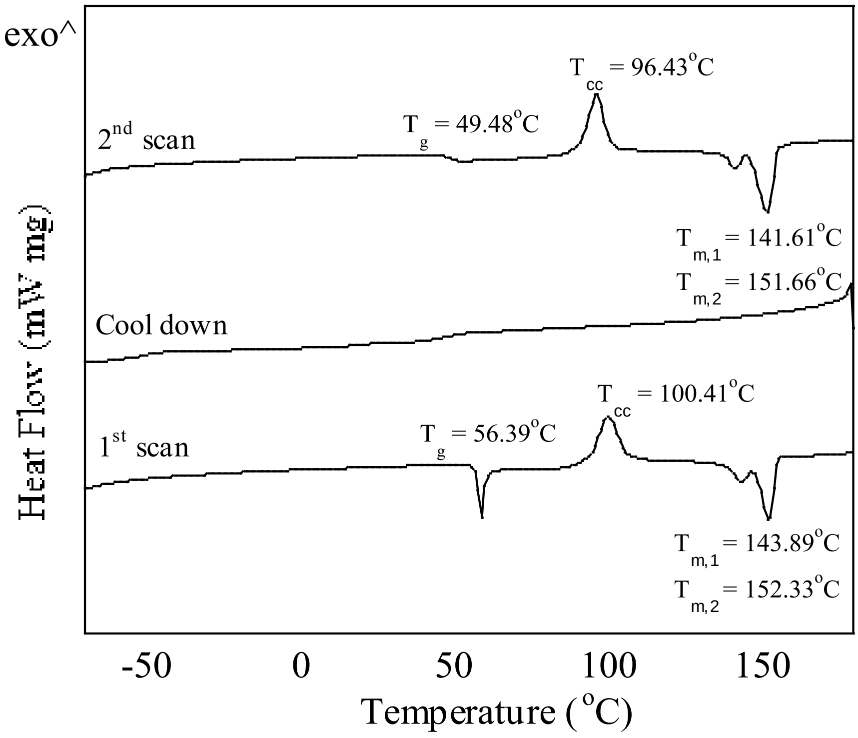

Figure C.17 DSC spectrum of 3 wt% ENR6/PLA_MgSt film

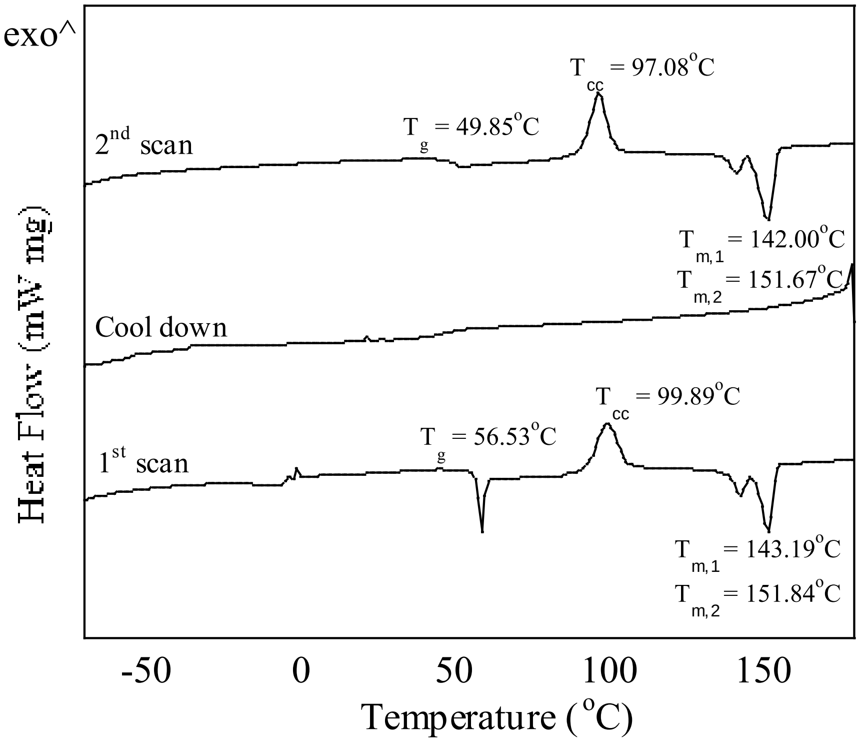

Figure C.18 DSC spectrum of 4 wt% ENR6/PLA_MgSt film

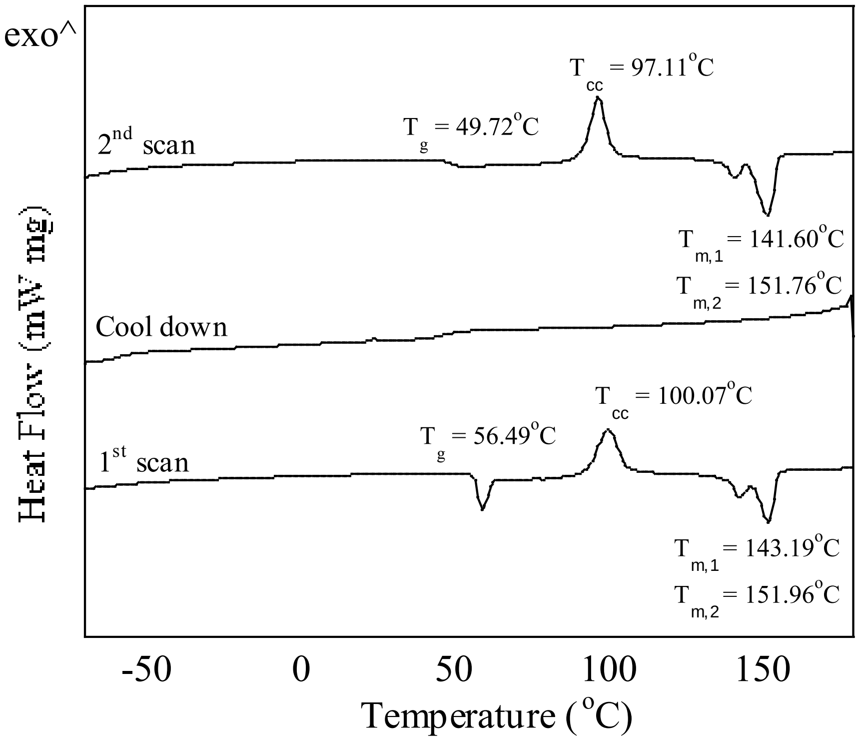

Figure C.19 DSC spectrum of 5 wt% ENR6/PLA_MgSt film

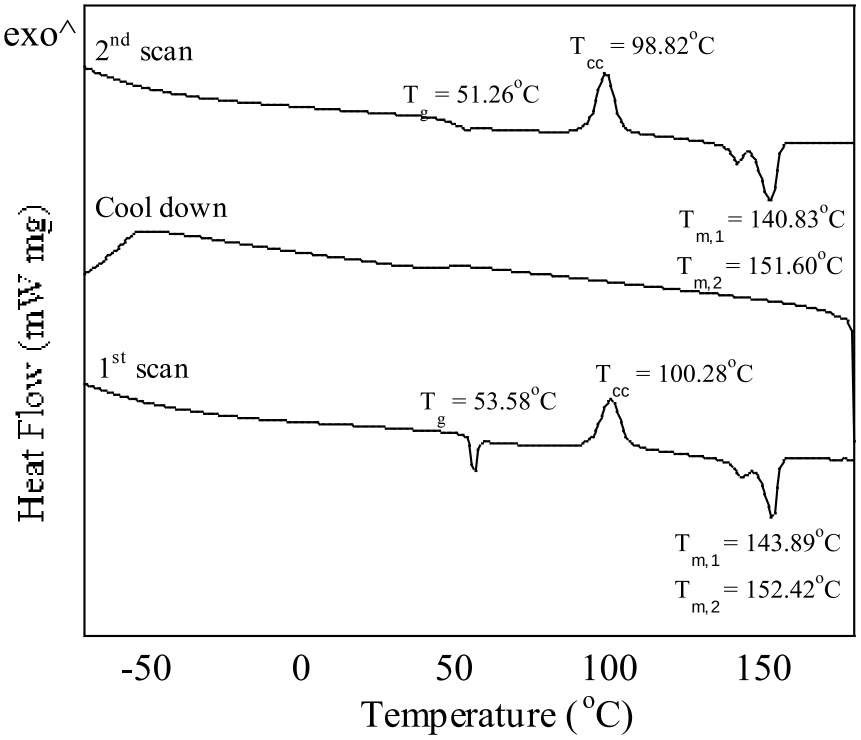

Figure C.20 DSC spectrum of 1 wt% ENR6-COOH/PLA_MgSt film

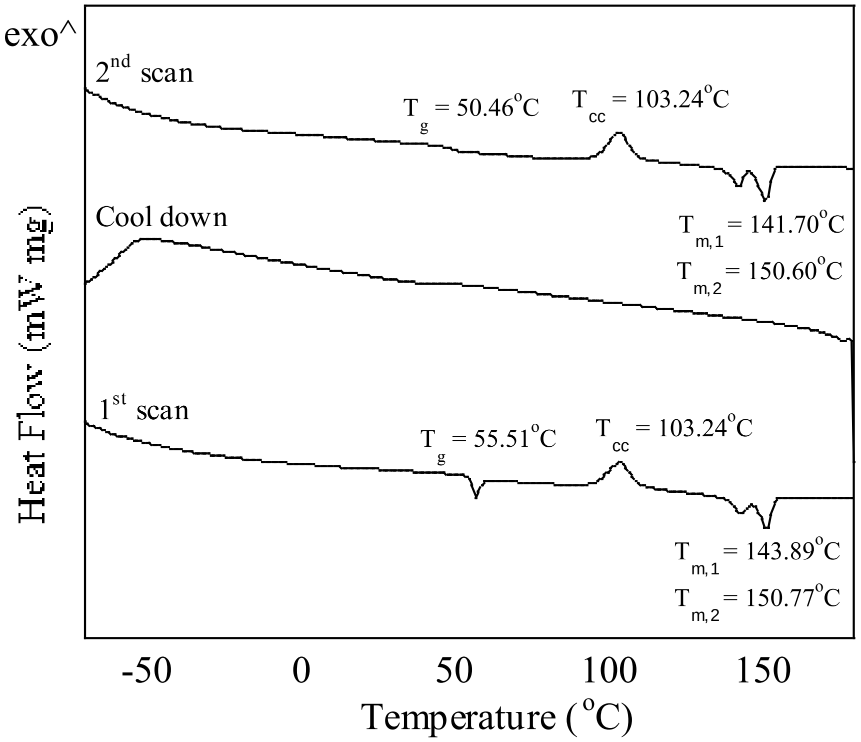

Figure C.21 DSC spectrum of 3 wt% ENR6-COOH/PLA_MgSt film

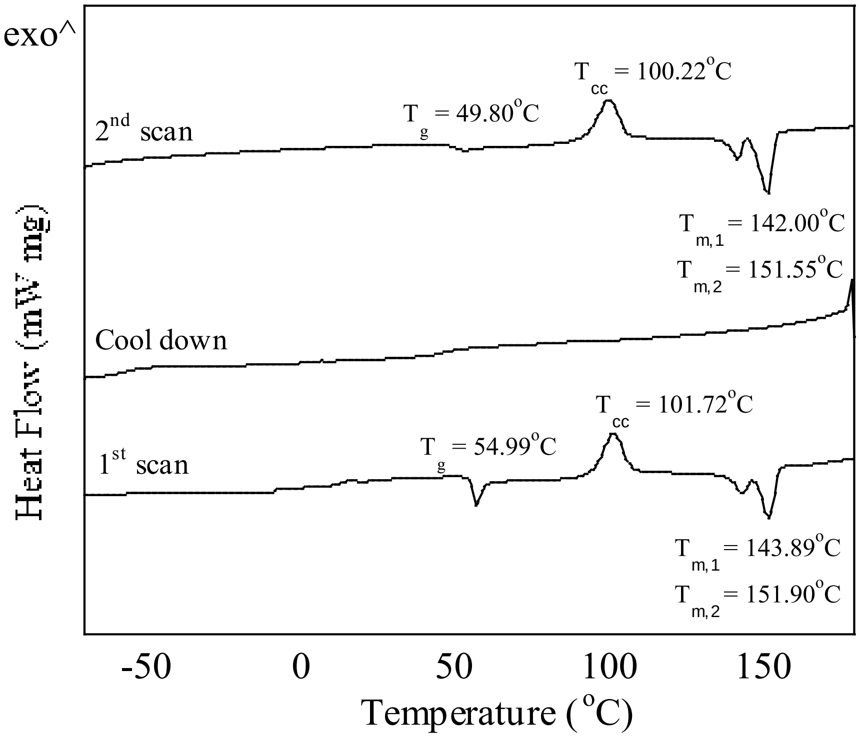

Figure C.22 DSC spectrum of 4 wt% ENR6-COOH/PLA_MgSt film

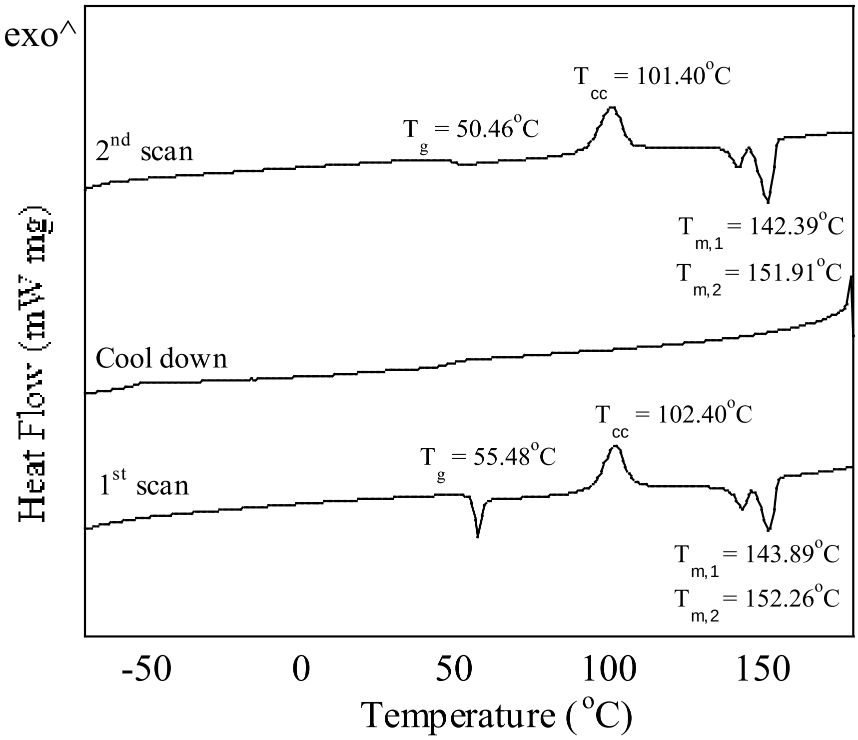

Figure C.23 DSC spectrum of 5 wt% ENR6-COOH/PLA_MgSt film

Table C.1 Thermal properties for neat PLA, PLA_MgSt and PLA_MgSt with 1, 3, 4 and 5 wt% ENR6 films

Samples	T_g (°C)	T_{cc} (°C)	ΔH_c (J/g)	$T_{m,1}$ (°C)	$T_{m,2}$ (°C)	ΔH_m (J/g)	X_c%
neat PLA	52.85	126.42	2.93	-	151.23	2.70	2.00
PLA_MgSt	48.46	97.95	28.87	138.89	147.75	36.82	27.27
1ENR6/PLA_MgSt	48.41	94.67	30.30	140.45	151.43	36.01	26.67
3ENR6/PLA_MgSt	49.48	96.43	30.45	141.61	151.66	37.50	27.78
4ENR6/PLA_MgSt	49.85	97.08	31.04	142.00	151.67	37.38	27.69
5ENR6/PLA_MgSt	49.72	97.11	30.36	141.60	151.76	35.12	26.01

Table C.2 Thermal properties for neat PLA, PLA_MgSt and PLA_MgSt with 1, 3, 4 and 5 wt% ENR6-COOH films

Samples	T_g (°C)	T_{cc} (°C)	ΔH_c (J/g)	$T_{m,1}$ (°C)	$T_{m,2}$ (°C)	ΔH_m (J/g)	X_c%
neat PLA	52.85	126.42	2.93	-	151.23	2.70	2.00
PLA_MgSt	48.46	97.95	28.87	138.89	147.75	36.82	27.27
1 wt% ENR6-COOH/PLA_MgSt	51.26	98.82	30.93	140.83	151.60	36.30	26.89
3 wt% ENR6-COOH/PLA_MgSt	50.46	103.24	32.81	141.70	150.60	33.64	24.91
4 wt% ENR6-COOH/PLA_MgSt	49.80	100.22	28.21	142.00	151.55	33.31	24.67
5 wt% ENR6-COOH/PLA_MgSt	50.46	101.40	27.62	142.39	151.91	29.14	21.58

Appendix D

Dynamic mechanical analysis results

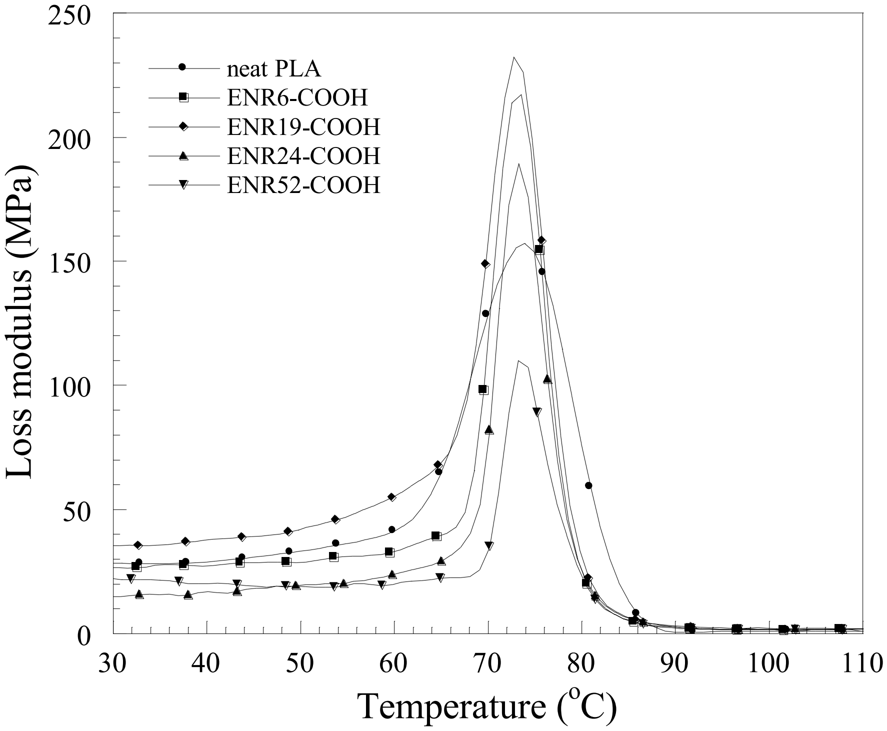

Figure D.1 Loss modulus of 3% ENRs-COOH/PLA blown films

Table D.1 Thermomechanical properties of 3% ENRs-COOHs-PLA blown films

System	E' (MPa)	$T_{g, E''}$ (°C)	$T_{g, \tan\delta}$ (°C)
neat PLA	2800.00	73.80	80.70
ENR6-COOH/PLA	2456.98	73.40	77.80
ENR19-COOH/PLA	2020.14	73.30	77.20
ENR24-COOH/PLA	1687.64	73.40	77.20
ENR52-COOH/PLA	1253.78	73.80	77.30

Appendix E

Tensile properties of each types of PLA blown films

Part I : Tensile properties of PLA blown films at 3 wt% of difference rubber types

Table E.1 Tensile properties of neat PLA blown films in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	61.29	3023.93	3.31	48.37
2	53.34	2695.63	3.83	50.61
3	61.10	3047.55	3.25	47.33
4	61.30	3026.10	3.15	45.32
5	50.51	2575.11	3.88	48.29
mean	57.51	2873.66	3.48	47.98
STDEV	5.19	221.86	0.34	1.91

Table E.2 Tensile properties of neat PLA blown films in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	47.71	2803.19	2.26	23.30
2	49.51	2839.95	2.23	22.81
3	45.10	2698.69	2.22	21.71
4	49.70	2966.03	2.32	25.69
5	50.44	2954.75	2.21	23.76
mean	48.49	2852.52	2.25	23.45
STDEV	2.15	111.34	0.04	1.46

Table E.3 Tensile properties of 3 wt% NR/PLA blown films in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	50.05	2450.00	10.07	125.96
2	46.30	2522.53	9.13	116.80
3	44.33	2457.09	12.24	148.38
4	50.28	2593.80	7.23	99.72
5	56.59	2893.91	11.51	186.93
mean	49.51	2583.47	10.04	135.56
STDEV	4.69	183.02	1.98	33.66

Table E.4 Tensile properties of 3 wt% NR/PLA blown films in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	47.86	2764.00	2.02	19.39
2	46.71	2633.82	2.35	24.00
3	44.17	2815.35	2.33	23.48
4	47.59	2662.64	2.82	31.27
5	48.28	2767.26	2.24	22.69
mean	46.92	2728.61	2.35	24.17
STDEV	1.64	76.82	0.29	4.36

Table E.5 Tensile properties of 3 wt% ENR6-COOH/PLA blown films in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	37.01	2061.28	29.82	299.25
2	37.50	2073.76	36.12	384.09
3	34.42	1904.08	36.64	353.73
4	32.62	1844.70	37.68	335.52
5	37.45	2140.62	33.40	346.54
mean	35.80	2004.89	34.73	343.83
STDEV	2.18	124.67	3.17	30.75

Table E.6 Tensile properties of 3 wt% ENR6-COOH/PLA blown films in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	30.68	2194.19	10.44	86.08
2	32.20	2334.46	11.28	98.44
3	29.17	2315.60	11.54	100.22
4	31.92	2354.27	12.68	110.25
5	31.03	2284.63	10.21	88.08
mean	31.00	2296.63	11.23	96.61
STDEV	1.20	62.75	0.98	9.82

Table E.7 Tensile properties of 3 wt% ENR19-COOH/PLA blown films in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	35.41	1961.26	11.14	112.78
2	37.67	2075.85	12.39	126.38
3	38.06	2166.61	14.86	155.36
4	36.79	2106.66	12.57	129.12
5	40.33	2309.93	12.21	123.11
mean	37.65	2124.06	12.63	129.35
STDEV	1.81	127.95	1.36	15.80

Table E.8 Tensile properties of 3 wt% ENR19-COOH/PLA blown films in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	30.73	2127.90	5.97	48.70
2	30.86	2111.98	5.86	46.67
3	30.53	2121.42	4.23	27.98
4	25.35	2073.77	4.36	29.90
5	29.27	2058.18	3.96	30.99
mean	29.35	2098.65	4.88	36.85
STDEV	2.32	30.86	0.96	9.98

Table E.9 Tensile properties of 3 wt% ENR24-COOH/PLA blown films in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	33.49	2560.20	8.32	73.38
2	31.19	2346.60	9.04	69.10
3	35.11	2501.74	7.15	73.64
4	33.17	2349.61	7.86	64.96
5	36.82	2680.95	7.85	70.60
mean	33.96	2487.82	8.04	70.34
STDEV	2.12	142.98	0.70	3.56

Table E.10 Tensile properties of 3 wt% ENR24-COOH/PLA blown films in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	28.25	2440.40	3.10	23.91
2	23.70	2064.61	3.51	23.12
3	24.96	2000.30	4.05	25.71
4	25.52	2006.70	3.36	22.33
5	29.18	2404.90	3.33	27.42
mean	26.32	2183.38	3.47	24.50
STDEV	2.31	220.21	0.36	2.06

Table E.11 Tensile properties of 3 wt% ENR52-COOH/PLA blown films in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	42.69	2582.06	2.14	19.37
2	42.41	2784.87	2.08	19.23
3	42.99	2762.38	2.06	18.90
4	41.78	2582.75	2.17	19.74
5	41.69	2421.56	2.29	20.22
mean	42.31	2626.72	2.15	19.49
STDEV	0.57	149.53	0.09	0.51

Table E.12 Tensile properties of 3 wt% ENR52-COOH/PLA blown films in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	25.74	2169.12	1.49	7.98
2	26.11	2200.63	1.38	6.96
3	26.12	2262.94	1.36	6.87
4	26.12	2261.15	1.28	6.32
5	25.20	2143.59	1.43	7.08
mean	25.86	2207.49	1.39	7.04
STDEV	0.40	53.75	0.08	0.60

Part II : Tensile properties of ENR5-COOH/PLA blown films compared with ENR5/PLA blown films by various content of rubbers

Table E.13 Tensile properties of neat PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	62.00	3553.01	1.96	23.83
2	58.16	3238.93	2.07	24.32
3	63.96	3672.29	2.08	27.43
4	62.05	3593.58	2.00	24.67
5	62.52	3725.99	2.02	25.82
mean	61.74	3556.76	2.03	25.21
STDEV	2.15	189.98	0.05	1.44

Table E.14 Tensile properties of neat PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	44.99	3097.90	1.58	13.97
2	46.07	3161.90	1.63	14.84
3	46.16	3195.60	1.65	14.95
4	45.24	3195.70	1.67	15.81
5	43.53	3078.10	1.58	13.35
mean	45.20	3145.84	1.62	14.58
STDEV	1.06	55.02	0.04	0.95

Table E.15 Tensile properties of 1 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	62.11	3308.02	6.21	98.15
2	59.82	2979.62	6.94	107.61
3	59.47	2989.57	7.84	124.01
4	57.68	2896.20	8.37	126.62
5	64.72	3342.73	7.24	124.29
mean	60.76	3103.23	7.32	116.14
STDEV	2.72	206.37	0.83	12.60

Table E.16 Tensile properties of 1 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	51.60	3013.05	2.16	23.93
2	49.61	2889.57	2.16	22.90
3	51.72	2994.34	2.15	23.20
4	51.83	3027.04	2.54	30.34
5	49.12	3027.97	2.45	27.13
mean	50.78	2990.39	2.29	25.50
STDEV	1.30	57.99	0.19	3.19

Table E.17 Tensile properties of 3 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	54.65	2854.59	17.63	243.13
2	49.22	2579.52	15.13	191.40
3	51.90	2685.13	13.49	177.44
4	53.66	2799.37	13.77	193.69
5	48.07	2654.28	14.75	177.13
mean	51.50	2714.58	14.95	196.56
STDEV	2.82	111.28	1.64	27.14

Table E.18 Tensile properties of 3 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	42.91	2801.21	14.66	166.90
2	37.51	2604.33	12.55	124.28
3	38.84	2569.28	14.38	147.19
4	36.98	2604.07	14.40	142.00
5	41.30	2737.92	16.29	173.24
mean	39.51	2663.36	14.46	150.72
STDEV	2.53	100.51	1.33	19.73

Table E.19 Tensile properties of 4 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	45.42	2525.31	75.63	828.95
2	47.26	2490.14	83.95	960.67
3	45.32	2504.17	73.78	797.96
4	44.46	2522.38	61.27	676.32
5	46.12	2541.44	64.50	750.37
mean	45.72	2516.69	71.83	802.85
STDEV	1.05	19.88	9.09	105.33

Table E.20 Tensile properties of 4 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	36.79	2529.33	31.29	317.03
2	35.52	2468.96	23.73	225.34
3	37.97	2501.58	23.86	237.48
4	36.33	2493.67	41.80	407.73
5	37.48	2543.87	36.15	362.50
mean	36.82	2507.48	31.37	310.02
STDEV	0.96	29.63	7.85	78.71

Table E.21 Tensile properties of 5 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	48.52	2557.30	25.92	313.48
2	45.29	2322.89	41.13	462.19
3	49.29	2524.49	38.19	443.09
4	49.68	2540.67	32.97	390.29
5	48.50	2639.77	45.16	543.74
mean	48.26	2517.02	36.67	430.56
STDEV	1.73	117.25	7.48	85.58

Table E.22 Tensile properties of 5 wt% ENR6-COOH/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	34.44	2417.98	21.34	197.00
2	36.36	2359.69	15.97	145.93
3	35.92	2393.89	21.16	196.38
4	35.63	2477.96	24.12	232.26
5	34.41	2438.17	20.02	184.13
mean	35.35	2417.54	20.52	191.14
STDEV	0.89	44.67	2.96	31.01

Table E.23 Tensile properties of 1 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	56.13	3182.53	7.97	118.19
2	58.94	3288.33	7.94	122.84
3	52.16	2945.69	7.50	102.54
4	57.25	3145.55	7.82	116.69
5	62.05	3406.63	7.03	114.22
mean	57.31	3193.75	7.65	114.90
STDEV	3.64	171.93	0.39	7.59

Table E.24 Tensile properties of 1 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	44.66	3159.29	1.67	15.04
2	45.36	3183.30	1.71	15.74
3	45.18	3116.12	1.78	16.74
4	42.61	3028.57	1.63	13.65
5	43.22	3096.03	1.69	14.74
mean	44.21	3116.66	1.70	15.18
STDEV	1.23	60.09	0.06	1.15

Table E.25 Tensile properties of 3 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	56.00	3135.77	33.52	481.77
2	49.01	2769.07	33.27	414.21
3	52.17	3022.78	26.75	356.52
4	60.78	3285.67	32.91	497.44
5	57.44	3154.27	34.99	503.20
mean	55.08	3073.51	32.29	450.63
STDEV	4.59	194.08	3.20	63.46

Table E.26 Tensile properties of 3 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	42.76	2966.03	7.44	81.19
2	42.64	3070.46	8.04	86.98
3	36.58	2926.17	8.52	86.96
4	38.96	2937.86	10.84	110.70
5	41.83	3003.00	7.68	82.74
mean	40.55	2980.70	8.50	89.71
STDEV	2.70	58.26	1.37	12.01

Table E.27 Tensile properties of 4 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	57.50	3022.58	112.76	1460.72
2	56.58	3066.58	103.30	1325.18
3	57.17	3158.39	105.26	1440.49
4	57.35	3042.17	93.44	1221.14
5	55.00	3147.33	110.33	1458.43
mean	56.72	3087.41	105.02	1381.19
STDEV	1.02	61.87	7.50	105.55

Table E.28 Tensile properties of 4 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	36.42	2657.54	11.56	115.39
2	30.85	2711.11	15.99	136.01
3	33.60	2871.12	11.93	103.21
4	39.09	2890.90	15.20	156.14
5	37.59	2947.82	11.51	122.42
mean	35.51	2815.70	13.24	126.63
STDEV	3.29	124.64	2.18	20.32

Table E.29 Tensile properties of 5 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in MD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	46.49	2599.57	136.52	1432.75
2	51.24	2837.88	129.37	1530.40
3	49.59	2837.22	125.76	1430.83
4	48.77	2764.43	135.86	1541.51
5	49.21	2796.56	127.49	1465.08
mean	49.06	2767.13	131.00	1480.11
STDEV	1.71	98.57	4.91	52.91

Table E.30 Tensile properties of 5 wt% ENR6/PLA blown films added with 0.5 wt% magnesium stearate in TD

No.	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Toughness (mJ)
1	30.59	2714.90	15.38	120.95
2	31.26	2577.32	20.55	172.45
3	28.21	2503.63	25.36	201.02
4	30.93	2482.96	25.04	198.75
5	30.62	2506.71	25.01	189.80
mean	30.32	2557.10	22.27	176.59
STDEV	1.21	95.14	4.33	33.07

Notice : This test is assumed that all tested samples have 100 mm of width and 35 µm of thickness.

Appendix F

Characteristics of neat PLA, 3 wt% NR/PLA and 3 wt% ENRs-COOH/PLA blown films

Figure F.1 Characteristic of neat PLA film

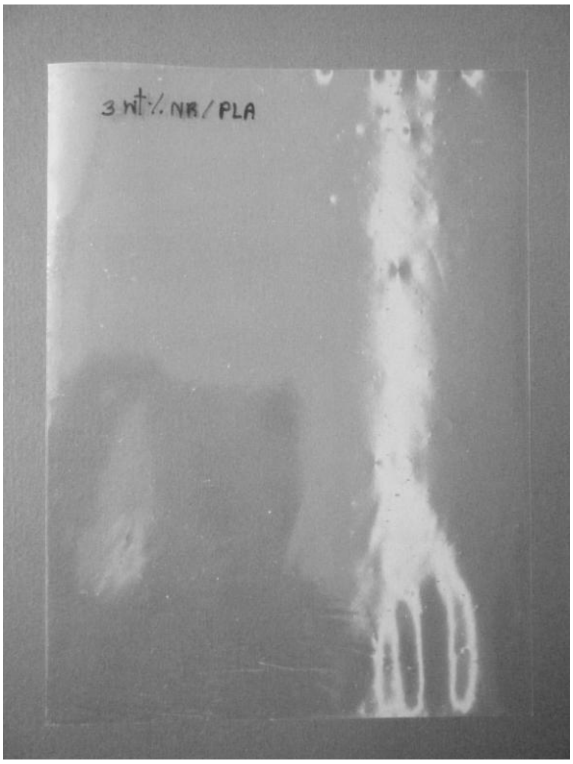

Figure F.2 Characteristic of NR/PLA film

Figure F.3 Characteristic of 3 wt% ENR6-COOH/PLA film

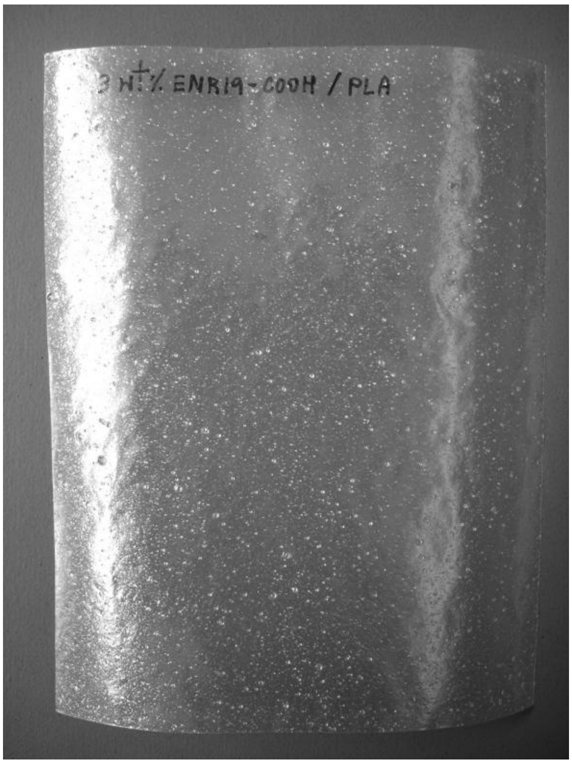

Figure F.4 Characteristic of 3 wt% ENR19-COOH/PLA film

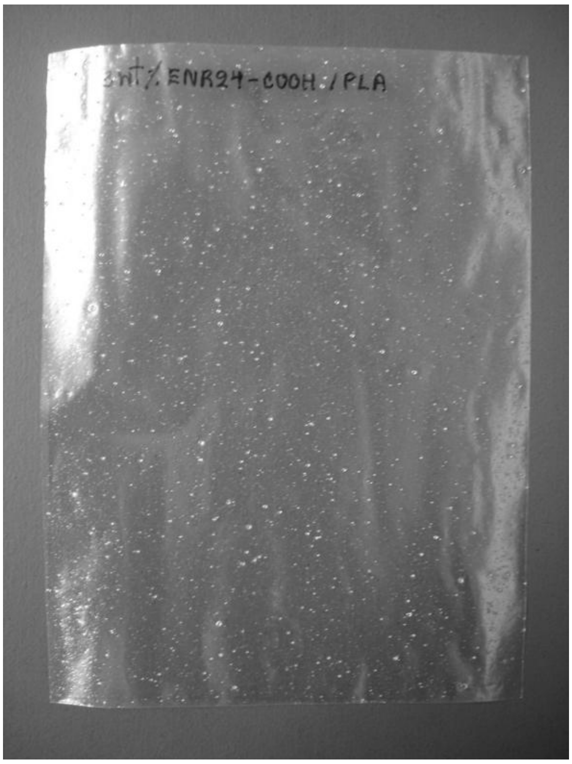

Figure F.5 Characteristic of 3 wt% ENR24-COOH/PLA film

Figure F.6 Characteristic of 3 wt% ENR52-COOH/PLA film

VITA

Ms. Nattanich Maneechavakajone was born on March 1st, 1987, in Bangkok, Thailand. She studied high school from Satreemahaprutaram. She received her Bachelor degree of Chemical Engineering from King Mongkut's University of Technology Thonburi, Thailand in March 2009. She entered the Master degree of Engineering from the department of Chemical Engineering, Chulalongkorn University in 2009.

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