การทำให้เข้ากันได้ของพอลิเมอร์ผสมพอลิแล็กติกแอซิด/ยางธรรมชาติโดยใช้ยางธรรมชาติกราฟต์พอลิแล็กติกแอซิด

นางสาวพิจิตรา สุขประเสริฐ

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ปีการศึกษา 2557

COMPATIBILIZATION OF POLY(LACTIC ACID)/NATURAL RUBBER BLENDS USING NATURAL RUBBER-*GRAFT*-POLY(LACTIC ACID)

Miss Phijittra Sookprasert

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
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Thesis Title	COMPATIBILIZATION OF POLY(LACTIC ACID)/NATURAL RUBBER BLENDS USING NATURAL RUBBER-*GRAFT*-POLY(LACTIC ACID)
By	Miss Phijittra Sookprasert
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Assistant Professor Napida Hinchiranan, Ph.D.

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พอลิแล็กติกแอซิดหรือพอลิแล็กไทด์เป็นพลาสติกชีวภาพซึ่งได้จากผลผลิตทางการเกษตรที่สามารถสร้างทดแทนใหม่ ที่สามารถสลายตัวได้ทางชีวภาพโดยใช้เอนไซม์ พอลิแล็กติดแอซิดมีความแข็งแรงสูง แต่มีความเปราะและมีความทนทานต่อแรงกระแทกต่ำซึ่งทำให้เกิดข้อจำกัดในการนำไปใช้งาน ดังนั้นวิจัยนี้ศึกษาการปรับปรุงสมบัติของพอลิแล็กติกแอซิดโดยการนำมาผสมกับอิลาสโตเมอร์ เช่น ยางธรรมชาติที่มีความยืดหยุ่นเพื่อลดความเปราะและเพิ่มความสามารถในการรับแรงกระแทก อย่างไรก็ตามการผสมพอลิแล็กติกแอซิดที่เป็นพอลิเอสเตอร์มาผสมโดยตรงกับยางธรรมชาติที่มีสภาพขั้วต่ำก่อให้เกิดความไม่เข้ากันนำมาสู่สมบัติเชิงกลที่ด้อยลง ดังนั้นงานวิจัยนี้จึงมีวัตถุประสงค์ในการใช้ยางธรรมชาติกราฟต์ด้วยพอลิแล็กติกแอซิดเป็นสารเสริมความเข้ากันได้ในพอลิเมอร์ผสมระหว่างพอลิแล็กติกแอซิดยางธรรมชาติ การสังเคราะห์ธรรมชาติกราฟต์ด้วยพอลิแลคติกแอซิดประกอบด้วย 2 ขั้นตอน เริ่มจากการกราฟต์มาเลอิกแอนไฮไดรด์เพื่อเพิ่มสภาพขั้วของยางธรรมชาติให้สูงขึ้นก่อนนำไปกราฟต์กับพอลิแล็กติกแอซิดผ่านปฏิกิริยาเอสเตอริฟิเคชัน ศึกษาปัจจัยที่มีผลต่อปริมาณการกราฟต์พอลิแลคติกแอซิดบนยางธรรมชาติ ผลการทดลองพบว่าปริมาณพอลิแล็กติกแอซิดที่กราฟต์บนยางธรรมชาติมีปริมาณเพิ่มขึ้น (27.5 – 46.4 เปอร์เซ็นต์) เมื่อเพิ่มมาเลอิกแอนไฮไดรด์ในการทำปฏิกิริยา (5 - 20 ส่วนจากยางธรรมชาติ 100 ส่วน) สภาวะที่เหมาะสมในการสังเคราะห์ยางธรรมชาติกราฟต์ด้วยพอลิแล็กติกแอซิด คือ อัตราส่วนโดยน้ำหนักระหว่างยางธรรมชาติต่อพอลิแล็กติกแอซิดที่ 1/1 โดยน้ำหนัก ความเข้มข้นของตัวเร่งปฏิกิริยา 4-ไดเมทิลอะมิโนไพริดีนที่ 0.05 โมลาร์ และอุณหภูมิในการทำปฏิกิริยาที่ 140 องศาเซลเซียส นาน 16 ชั่วโมง นอกจากนี้การเติมสารเชื่อมผสานยางธรรมชาติกราฟต์ด้วยพอลิแล็กติกแอซิดท (ระดับการกราฟต์ 2.66% โดยน้ำหนัก) ปริมาณ 5% ในพอลิเมอร์ผสมพอลิแล็กติกแอซิด/ยางธรรมชาติที่อัตราส่วน 80/20 โดยน้ำหนัก สามารถเพิ่มความต้านทานต่อแรงกระแทกที่ 62.7 จูล/เมตร มากกว่าพอลิแล็กติกบริสุทธิ์ที่มีค่า 22.8 จูล/เมตร การใช้สารเชื่อมผสานช่วยเพิ่มความเข้ากันได้ระหว่างวัฏภาคของพอลิแล็กติกแอซิดและยางธรรมชาติทั้งด้านสัณฐานวิทยาและสมบัติเชิงความร้อน สำหรับการสลายตัวทางชีวภาพของพอลิเมอร์ผสมด้วยปฏิกิริยาไฮโดรไลซิส และเอนไซม์โปรติเอส เค แสดงให้เห็นว่าพอลิเมอร์ผสมพอลิแล็กติกแอซิดกับยางธรรมชาติที่ใส่และไม่ใส่สารเสริมความเข้ากันได้พอลิแล็กติกแอซิดกราฟต์ยางธรรมชาติจะมีอัตราการสลายตัวทางชีวภาพน้อยกว่าพอลิแล็กติกแอซิดบริสุทธิ์เพียงเล็กน้อย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5472241523 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: POLY(LACTIC ACID) / NATURAL RUBBER / BIODEGRADABLE / GRAFT COPOLYMER

PHIJITTRA SOOKPRASERT: COMPATIBILIZATION OF POLY(LACTIC ACID)/NATURAL RUBBER BLENDS USING NATURAL RUBBER-*GRAFT*-POLY(LACTIC ACID). ADVISOR: ASST. PROF. NAPIDA HINCHIRANAN, Ph.D.{, 74 pp.

Poly(lactic acid) (PLA) or polylactide is bioplastics produced from agricultural products, which are renewed and also bio-degraded by enzyme. PLA has high strength, but it has the brittleness and low impact strength, which limit its applications. Thus, several previous research works studied the properties improvement of PLA by blending with elastomers such as natural rubber (NR) with excellent elastic property to reduce PLA's brittleness and to increase its impact strength. However, the direct blending of PLA, which is the polyester and NR with low polarity leads the incompatible blend resulting in its poor mechanical properties. Thus, the aim of this research was to use the NR grafted with PLA (NR-*g*-PLA, NR-PLA) as the compatibilizer for PLA/NR blends. There were 2 steps to prepare NR-PLA compatibilizer. Firstly, NR was functionalized by maleic anhydride (MAH) (NR-MAH) to increase the polarity of NR. Then, NR-MAH was grafted with PLA via esterification. The effects of grafting parameters in the esterification step on the %grafting PLA were investigated. The result showed that the increase in the MAH contents (5-20 phr) led the higher %grafted PLA content in NR-MAH from 27.5 to 46.4 wt%. The suitable condition to increase the %grafted PLA was 1/1 (w/w) NR-MAH/PLA and 0.05 M 4-dimethylaminopyridine (DMAP) at 140 $^{\circ}$C for 16 h. Moreover, the addition of 5 wt% NR-PLA (%grafted PLA = 2.66) on the PLA/NR blends (80/20 (w/w)) increased the Izod impact strength to 62.7 J/m higher than neat PLA (22.8 J/m). The compatibility of PLA/NR blends with NR-PLA compatibilizer was also improved by morphology and thermal properties. For the bio-degradation of the blends via hydrolysis and enzyme proteinase K, it was shown that the degradation rate of PLA/NR blends with/without addition of NR-PLA compatibilizer was slightly decreased from the neat PLA.

Field of Study: Petrochemistry and Polymer Science
Academic Year: 2014

Student's Signature ....
Advisor's Signature ....

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CONTENTS

Page

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 The Statement of problem

The limited supply of petroleum-based plastic and the problem of plastics pollution have been concerned in recent years. Hence, the commercial scale of bio-plastics have been developed to replace petroleum-based plastics (Gramlich, Robertson et al., 2010). Both bio-based and biodegradable plastics are in a family of bioplastics. Poly(lactic acid) (PLA) is a long chain polyester, which is produced from renewable sources like sugar cane, corn, and stretch (Bitinis, Verdejoa et al., 2011). PLA has an excellent properties in terms of flexural modulus and high tensile modulus (Dorgan, Lehermeier et al., 2000). However, the inherent brittleness and low impact strength limit its application due to the low entanglement density and chain stiffness (Ho, Wang et al., 2008, Hassouna, Raquez et al., 2011).

Some previous works suggested that the brittleness of PLA could be improved by blending with some elastomers such as polyisoprene-*co*-polylactide (PI-PLA) in PI/PLA blends (Schmidt and Hillmyer, 1999), ethylene-*co*-vinyl acetate (EVA) in PLA/EVA blends (Ma, Hristova-Bogaerds et al., 2012) and thermoplastic polyolefin elastomer-*graft*-polylactide (TPO-PLA) in PLA/TPO blends (Ho, Wang et al., 2008). This was expected that the elastomer particles dispersed in the PLA phase act as a stress energy absorber for PLA. Nevertheless, the immiscibility of polymeric constituents in the blends resulting from the polarlity difference could lead the finishing product having poor mechanical properties (Bitinis, Verdejo et al., 2012). Since the graft copolymerization is one of the techniques to adjust the polarity of the constituents in the blends, the graft products are normally used as the compatibilizer for improving the compatibility in the blends containing dissimilar polarity.

Therefore, the aim of this research was to synthesize the natural rubber (NR) grafted with PLA (NR-PLA) for applying as a compatibilizer in PLA/NR blends. The first step was to functionalize NR by various maleic anhydride (MAH) contents to produce

NR grafted with MAH (NR-MAH) having higher polarity than NR. Then, NR-MAH was grafted with PLA via esterification using 4-dimethyaminopyridine (DMAP) as a catalyst (Ho, Wang et al., 2008). The chemical structures of the NR-MAH and NR-PLA were examined by using Fourier Transform Infrared (FT-IR) and Proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy. The quantities of the grafted MAH in the NR-MAH structure was determined by titration of the acidic group derived from the anhydride functions (Nakason, Kaesaman et al., 2004). The parameters influencing the grafting efficiency of PLA onto NR-MAH such as DMAP content, PLA/NR-MAH wt ratio, reaction time and temperature were investigated. The morphology, mechanical and thermal properties of PLA/NR blends with and without the addition of NR-PLA compatibilizer were studied. Moreover, the degradation of PLA/NR blends with and without the addition of NR-PLA was compared to the neat PLA.

1.2 Objectives of the reach work

The objectives of this research were stated as followed:

1. To synthesize the NR-PLA via graft copolymerization for using as the compatibilizer in the PLA/NR blends.
2. To evaluate the effect of the MAH content, DMAP content, PLA/NR-MAH wt ratio, reaction time and reaction temperature on the degree of grafted MAH and grafted PLA.
3. To investigate the effect of the NR-PLA used as the compatibilizer in PLA/NR blends on their morphology and properties in terms of mechanical, thermal and biodegradable aspects.

1.3 Scope of the research work

The detail of the experimental procedure was presented as followed:

1. Review related previous literatures.
2. Prepare the NR-PLA compatibilizer via graft copolymerization of PLA onto NR modified by MAH graft copolymerization.

3. Characterize the structure of NR-MAH and NR-PLA by using FT-IR and ^{1}H NMR spectroscopy.
4. Prepare the PLA/NR/NR-PLA blends by using an internal mixer and a hot compression mold.
5. Study the mechanical properties of PLA/NR blends with and without the addition of NR-PLA or NR-MAH as the compatibilizer.
6. Study the thermal properties of PLA/NR blends with and without the addition of the NR-PLA compatibilizer using Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC).
7. Study the effect of the NR-PLA on the morphology of NR/PLA blends using Scanning Electron Microscope (SEM).
9. Investigate the degradation of PLA/NR/NR-PLA blends using enzymatic degradation and hydrolysis processes.
10. Analyze data, summarize and conclude the results.

CHAPTER 2

THEORY AND LITERATURES REVIEWS

2.1 Poly(lactic acid)

Poly(lactic acid) or poly(lactide) (PLA) is producible from renewable sources such as starch and it can be degraded in both human body and environment. Thus, PLA has been studied for more than 40 years in scientific and industrial aspects (Tsuji and Ikada, 2009). PLA was firstly discovered by Swedish chemist Sheele in 1780. The lactic acid monomer can be produced by fermentation or chemical synthesis (Datta and Henry, 2006). The life cycle of PLA (Figure 2.1) starts with trapped solar energy by photosynthesis process to produce carbohydrates and starch. The carbohydrate crops such as rice, sugar beets, sugarcane, wheat and sweet potato can be used as a feedstrock to produce lactic acid and lactide. The lactide monomers were polymerized to produce PLA by controlling processed (Vink, Rabago et al., 2003). The obtained PLA is naturally degraded as non-toxic carbon dioxide and water within a few weeks under a typical compost condition (Henton, Gruber et al., 2005). Since PLA is classified as a biodegradable and non-hazardous materials, PLA is a great choice for the production of short-term packaging that is typically end up in landfill.

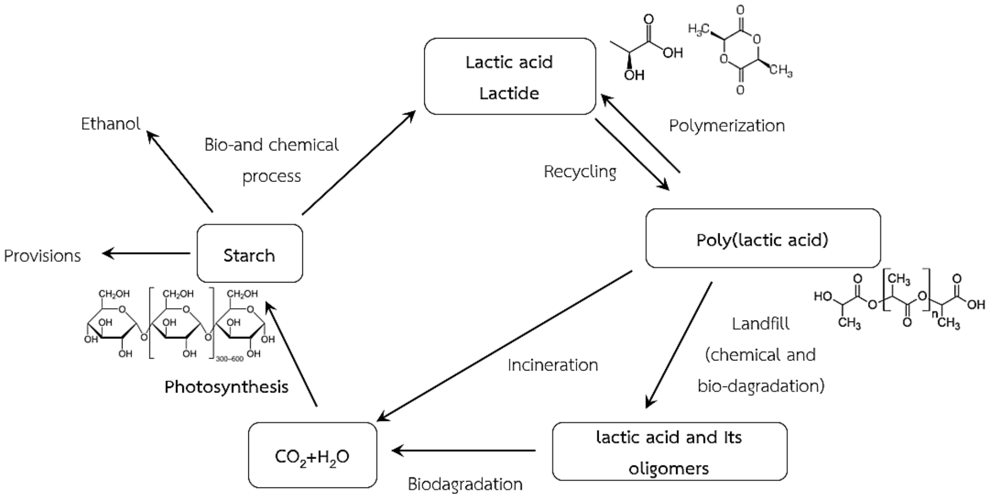


Figure 2.1 Life cycle of PL0041 (Tsuji and Ikada, 2009).

The synthesis of PLA is initiated from the production of lactic acid. Figure 2.2 shows that the PLA can be synthesized from three main routes. For the first route, it is the direct condensation polymerization and water is eliminated by using a solvent under high vacuum and temperature. PLA obtained from this route has low- to intermediate-molecular weight and it is also brittle. The most part of the obtained PLA is unstable unless reacts with chain coupling agents to increase its chain length. The disadvantage of the direct condensation is water release during polymerization and impurities. Moreover, the large reactor equipped with evaporation unit and solvent recovery is required. Secondly, the azeotropic dehydrative condensation of lactic acid provides high yield and high molecular weight PLA without the use of chain extenders. Thirdly, the main process to produce PLA is ring-opening polymerization of lactide (ROP). In the beginning of operation, water is removed under mild condition without the use of solvent to produce low molecular weight pre-polymer. The pre-polymers are then catalytically depolymerized to form a cyclic intermediate dimer, which is further purified by distillation to achieve the polymer grade lactide. The purified lactides are polymerized by ring-opening polymerization without solvent and shaped as PLA pellets. This method generates high molecular weight PLA (Vink, Rabago et al., 2003, Averous, 2008).

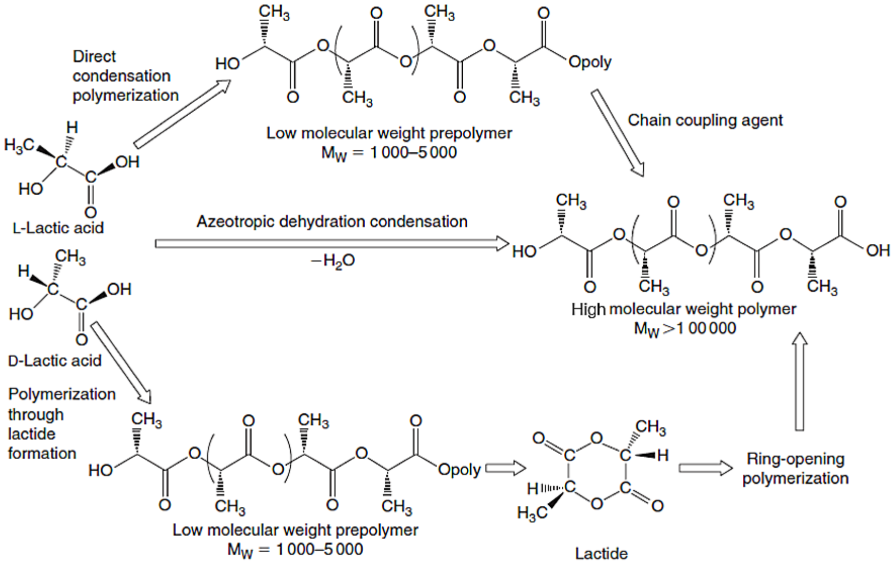
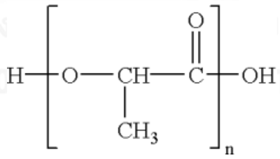


Figure 2.2 Synthesis routes of PLA (Averous, 2008).

2.1.1 Properties of PLA

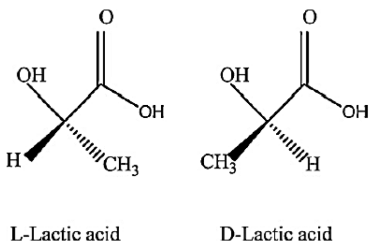
PLA (Figure 2.3) is one of thermoplastics, which its colorless, glossy, rigid, white powder in room temperature. Its physical properties are similar to polystyrene (Xiao, Wang et al., 2012). The PLA structure is semi-crystalline or amorphous depended on the steriopurity of the polymer backbone (Tsuji and Ikada, 2009). The synthetic routes for lactic acid has two optical isomers such as L-lactic acid and D-lactic acid (Figure 2.4), while the optical purity of the lactide has three isomers such as *D*-lactide (PDLA), which is crystalline material with a regular chain structure; *L*-lactide (PLLA) which is hemicrystalline, likewise with a regular chain structure; *D,L*-lactide (PDLLA) which is amorphous and *meso*-lactide (Henton, Gruber et al., 2005, Tsuji and Ikada, 2009, Xiao, Wang et al., 2012). Some of the physical and chemical properties of each PLA type are summarized in Table 2.1 (Xiao, Wang et al., 2012).

The variety of physical properties of the commercial grades PLA is optimized for both processing and performance for extending its applications. For example, the properties of extrusion grade PLA (2000D) obtained from NatureWorks PLA, Cargill Dow LLC are shown in Table 2.2.



$\mathrm{H{-}\left[O{-}CH(CH_3){-}C({=}O)\right]_n{-}OH}$

Figure 2.3 Chemical structure of PLA.



L-Lactic acid D-Lactic acid

Figure 2.4 Lactic acid optical monomers (Rasal, Janorkar et al., 2010).

Table 2.1 Properties of PLA (Xiao, Wang et al., 2012)

Properties	PDLA[1]	PLLA[2]	PDLLA[3]
- Crystalline structure	Crystalline	Hemicrystalline	Amorphous
- Melting temperature (T_m, °C)	~180	~180	Variable
- Glass transition temperature (T_g, °C)	50-60	50-60	Variable
- Decomposition temperature (°C)	~200	~200	185-200
- Elongation at break (%)	20-30	20-30	Variable
- Breaking strength (g/d)	4.0-5.0	5.0-6.0	Variable
- Half-lift in 37°C normal saline (months)	4-6	4-6	2-3
- Solubility	All are soluble in benzene, chloroform, acetonitrile, tetrahydrofuran (THF), dioxane etc. but they are insoluble in ethanol, methanol and aliphatic hydrocarbons		

PDLA[1] = Poly(*D*-lactic acid); PLLA[2] = Poly(*L*-lactic acid); PDLLA[3]= Poly(*D,L*-lactic acid)

To compare with other commodity polymers: high density polyethylene (HDPE), polypropylene and polystyrene (Figure 2.5) (Dorgan, Lehermeier et al., 2000), PLA has many attractive features, such as high strength, high modulus, transparency, biocompatibility, biodegradable and processability. However, PLA still has brittleness and poor toughness (Ho, Wang et al., 2008) to limit in some applicatons.

Table 2.2 Properties of PLA grade 2000D (Henton, Gruber et al., 2005)

Properties		ASTM
Physical properties		
- Specific gravity (g/cc)	1.25	D792
- Malt index (g/10 min)	4-8	D1238
- Clarity	Transparent	-
Mechanical properties		
- Tensile strength at break (kpsi)	7.7	D882
- Tensile yield strength (kpsi)	8.7	D882
- Tensile modulus (kpsi)	500	D882
- Elongation (%)	6.0	D882
- Notched izod impact (ft-lb/in)	0.24	D256
Thermal properties		
- Glass transition temperature (T_g, °C)	55-65	-
- Melt temperature (T_m, °C)	160-180	-

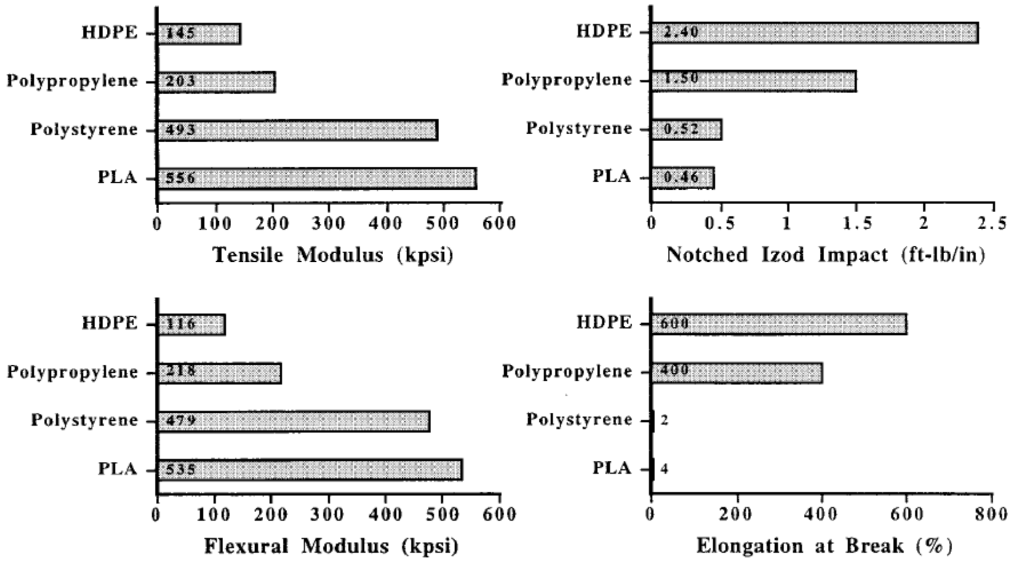


Figure 2.5 Comparison of the mechanical properties of PLA with common plastics for packaging (Dorgan, Lehermeier et al., 2000).

2.1.2 Processing of PLA

The main important parameters for PLA processing via melting method are temperature, contact time, moisture content, atmosphere and specific condition in thermo-mechanics. PLA can be processed by using the general method for processing thermoplastics such as compression molding, injection molding, extrusion, film casting and spinning. However, the problem in processing of PLA is the thermal instability during processing. To solve a such problem, the blending with other materials can provide a homogenous phases of PLA blends, or to give the specific properties (Averous, 2008). For example,

♦ *Plasticization*

Plasticizer is an additive that is applied to disrupt the crystallinity of polymers to provide more flexible, but it does not change the chemical structure of the polymers. However, the isomer ratio can disturb the compatibility and distribution of plasticizer resulting in the low efficiency and heterogeneous phase in blends.

♦ *Blends and compatibilization*

Compatibilizer is used to improve the miscibility of the constituent phases. The compatibilizer may be the modified polymers to be applied in the blends. For the PLA blends, the compatibilizer can be classified as: (a) the functionalized PLA or other components in the blends, (b) a coupling agents and (c) the copolymers.

♦ *Multilayers*

The multilayers are low cost materials used for the packaging. For example, the moisture barrier properties and identical thickness of PLA and starch are interesting (Martin, Schwach et al., 2001). The multilayers were prepared by co-extrusion and compression molding techniques. However, the disadvantage of co-extrusion is the interfacial instability.

♦ *Biocomposites and nano-biocomposites*

There are several research works that reported the use of biocomposites. The results showed that cellulose fibers (Mathew, Oksman et al., 2005) and organoclays (Bitinis, Verdejo et al., 2012) could enhance the mechanical properties of the obtained composites.

2.1.3 Applications of PLA

PLA has a wide variety of physical properties and it can be used in many applications such as packaging, textiles, and biomedical field. PLA can be used like other petroleum-based polymers and the demand of PLA tends to be increased due to the concern of environmental aspect resulting in the use of non-toxic and environmental friendly materials, which do not promote the emissions of greenhouse gases. PLA differs from the petroleum-based plastics because it is produced from renewable and biodegradable resources. The production cost of PLA has been falling which becomes more competitive to other polymers in the market (Henton, Gruber et al., 2005, Tsuji and Ikada, 2009, Rasal, Janorkar et al., 2010). Figure 2.6 shows the examples of PLA products.

Fiber is the largest PLA application. PLA fiber can be used for producing pillows and comforters because of its natural soft feel, ease of processing and also low smoke release during burning. Films are the second largest PLA application. PLA films after modification have several structures such as optical isomer, branching and various molecular weights resulting in the applications of PLA in many purposes (Henton, Gruber et al., 2005). PLA is also used in the biomedical products such as fractural fixation devices like screw or plate because of its non-hazardous and compatibility with in human body (Averous, 2008).

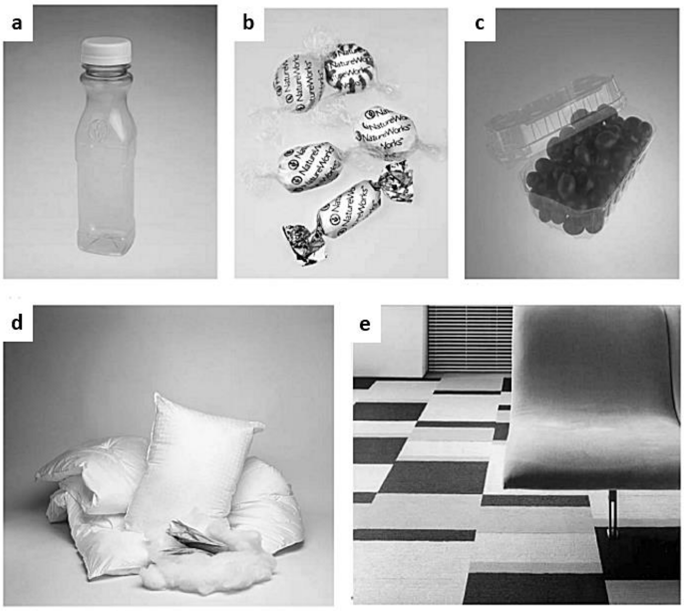


Figure 2.6 Examples of PLA products: (a) injection stretch blow molding bottles, (b) films, (c) extrusion-thermoformed containers, (d) carpet and coverings (Henton, Gruber et al., 2005).

2.1.3 Degradation of PLA

The degradation rate of PLA is dependent on temperature and humidity. The higher temperature and higher humidity increase the degradation rate of PLA. Figure 2.7 shows the hydrolysis degradation of PLA occurring at the ester linkages (Henton, Gruber et al., 2005). The hydrolysis of PLA is initiated by water uptake to randomly break the ester bonds. The water molecules hydrolyze crystalline part of PLA resulting in the mass loss of PLA (Henton, Gruber et al., 2005, Averous, 2008).

The hydrolysis rate is dependent on various factors such as molecular weight of PLA and its distribution, shape of specimen samples, the degree of crystalline and hydrolysis conditions (Huang, Zhang et al., 2013).

Another route of degradation is biotic process. Proteinase K is an enzyme to normally digest protein by breaking the peptide bonds; especially, alanine and lactic acid, which has similar structure (Tsuji and Ikada, 2009). Proteinase K also acts as a catalyst for the hydrolysis. The enzymatic hydrolysis rate using Proteinase K

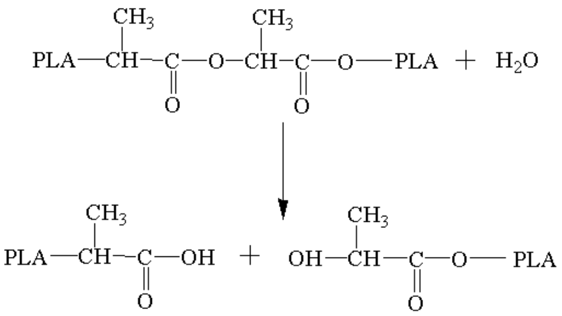


Figure 2.7 Hydrolysis reaction of PLA (Henton, Gruber et al., 2005).

depends on the stereochemical composition of PLA. The increase in the crystallinity of PLA decreases the hydrolysis rate (Yamashita, Kikkawa et al., 2005).

The degradation of PLA has been reported in many research works such as:

Li, Tenon et al. (2000) investigated the enzymatic degradation of three PLA sterocopolymers (PLA_{50}-rac, PLA_{50}-mes and $PLA_{62.5}$) by using Proteinase K at 37°C in the presence of Tris-HCL buffer solution (pH = 8.6). PLA_{50}-rac and PLA_{50}-mes were compared in order to elucidate the effect of the distribution of lactyl repeating unit and to verify the inhibiting effect of *L-D-L* triads (%(*L/D*) of PLA_{50}-rac and PLA_{50}-mes = 50/50, $\overline{M_w}$ of PLA_{50}-rac = 40,000 and $\overline{M_w}$ of PLA_{50}-mes = 57,000). $PLA_{62.5}$ (%(*L/D*) = 62.5/37.5, $\overline{M_w}$ = 55,000) was also used to investigate the influence of stereochemistry. It was found that %weight loss of samples were detected after 77 h degradation using enzyme Proteinase K. The weight of PLA_{50}-rac was lost ca.25%, which was lower than that of $PLA_{62.5}$ (34.1%) and PLA_{50}-mes (64.5%). However, the weight loss of these samples was not observed when Proteinase K was not applied. To consider the %water absorption, PLA_{50}-mes absorbed water about 45%, while PLA_{50}-rac and $PLA_{62.5}$ absorbed water nearly 20% and 5% after 77 h immersion period. It could be explained by the inhibiting effect of L-D-L triads in PLA_{50}-mes that Proteinase K was preferred to degrade LL, LD and DL bonds, but DD bonds were excepted. Therefore, the limited content of DD (or LL) bonds in PLA_{50}-mes induced the faster degradation rate of the PLA_{50}-rac. Thus, the large amounts of absorbed water increased the free volume in polymer matrix and facilitated the enzymatic attack. Therefore, Proteinase K was effective to degrade PLA_{50}-mes and $PLA_{62.5}$ than PLA_{50}-rac of lactide units.

Ohkita and Lee (2006) studied the biodegradation of PLA and PLA/corn starch (PLA/CS) blends with and without lysine diisocyanate (LDI) by using enzyme Proteinase K at 38^{o}C in the Tris-HCl buffer (pH 8.6). LDI was used as a coupling agent to improve the miscibility between PLA and CS. The results showed that the degradation of the neat PLA was 40% weight loss within 6 days that was slower than that of PLA/CS blends with and without LDI composites because the higher CS content provided a faster degradation rate. It was observed that the PLA/CS blends without the addition of LDI could achieve 100% weight loss within 6 days of degradation period (PLACS-5). This was faster than PLA/CS blends with the addition of LDI (30% weight loss in 6 day (PLACS-5)). Thus, the improvement of interfacial adhesion by using LDI coupling agent induced the difficulty of PLA degradation.

Huang, Zhang et al. (2013) studied the hydrolytic degradation of PLA and PLA/natural rubber (NR) blends in the presence of distilled water at 58^{o}C. It was found that NR increased the hydrophobicity of PLA surface, but NR did not decrease water absorption in PLA. Moreover, the hydrolysis rate of PLA was not interrupted by NR. The scanning electron microscopy (SEM) image (Figure 2.8) shows the fracture of PLA and PLA/NR blends at different time of hydrolysis. The fracture surface of PLA was more homogenous than PLA/NR blends at the first day of hydrolysis test. After 9 days of hydrolysis test, the holes was formed in PLA and PLA/NR. After 20 days, the holes was distributed throughout the fracture surface of both PLA and PLA/NR blends. This indicated that NR did not change the erosion mechanism of PLA; although, NR could enhance the hydrophobicity of PLA which was confirmed by the change of residual mass (%) of PLA and NR/PLA in the hydrolysis. At the first 15 days of hydrolysis test, that amount of mass loss was rarely occurred in PLA and PLA/NR. After 35 days of hydrolysis, the mass was rapidly decreased (about 20%) in both PLA and PLA/NR.

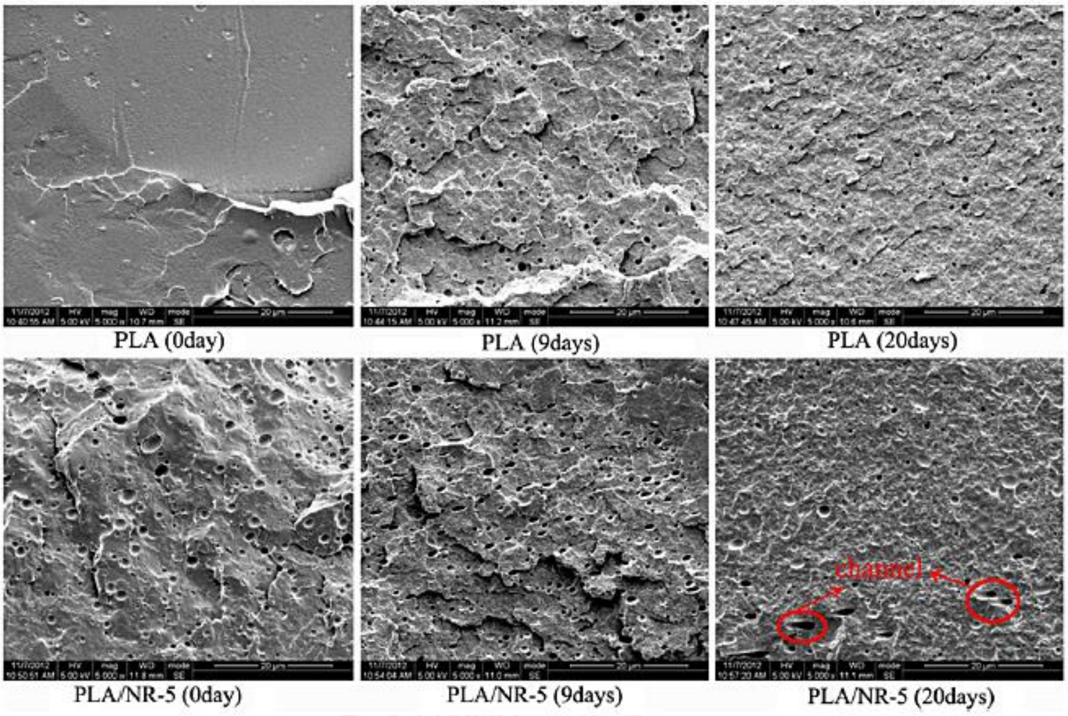

PLA (0day) PLA (9days) PLA (20days)
PLA/NR-5 (0day) PLA/NR-5 (9days) PLA/NR-5 (20days)

Figure 2.8 SEM images of fracture surfaces of PLA and PLA/NR blends at different hydrolysis time (Ohkita and Lee, 2006).

2.2 Natural Rubber

Natural rubber (NR) (Figure 2.9) is naturally organic product obtained from the *Hevea brasiliensis* tree. The rubber latex is the colloid solution containing spherical rubber particles. The NR latex obtained from *Hevea* has the chemical structure as *cis*-1,4-polyisoprene with its molecular weight in the range of 100,000 – 1,000,000. NR is an elastomer that can be vulcanized to form the thermoset materials. The most of NR used in various applications is vulcanized rubber such as rubber ball, boot, glove, O-ring. etc (Haper, 1975).

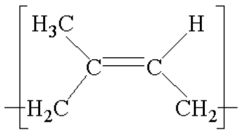


Figure 2.9 Chemical structure of NR.

2.2.1 Functionalization of NR with maleic anhydride

NR is one of engineering materials with highly elastic properties at room temperature. To extend its application, the chemical modification can induce NR with desired special properties. The chemical modification generally applied for NR was hydrogenation, halogenation, epoxidation and graft copolymerization.

The chemical modification of NR by using maleic anhydride (MAH) is one of the interesting reactions. The MAH molecules are added into the NR backbone to increase NR polarity and improve both hydrophiliicity and adhesion of NR. The four basic reactions involved with the functionalization of MAH onto NR was shown in Figure 2.10 (Mark, Erman et al., 1994):

Figure 2.10a indicates the intermolecular addition of MAH to the double bond within the isoprene chain.

Figure 2.10b shows the intermolecular addition of MAH to the double bonds of NR in different chains in this group.

Figure 2.10c shows the addition of MAH to α -methylenic carbon atoms of the polyisoprene chain.

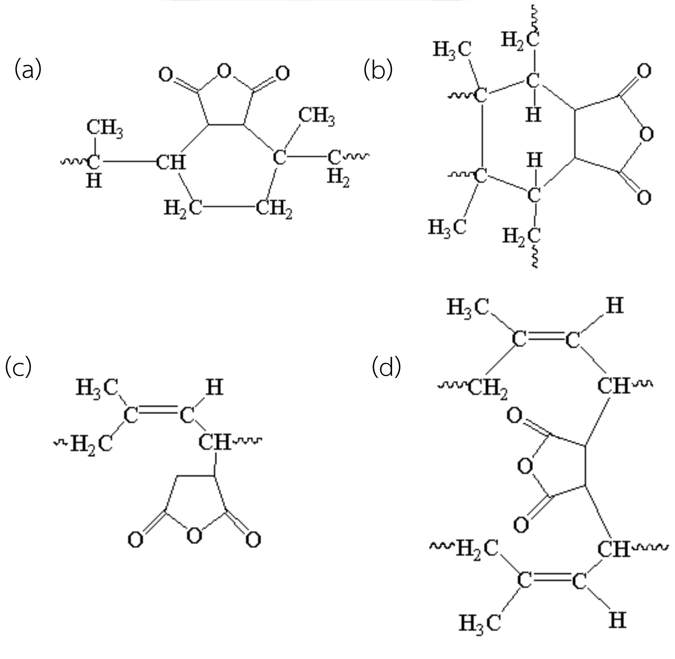


Figure 2.10 The modification of NR with MAH (Mark, Erman et al., 1994).

Figure 2.10d expresses the intermolecular addition of MAH to α-methylenic carbon atoms in adjacent chains.

Generally, the reaction rates increased with increasing reaction temperature. However, the increase in the reaction rates leaded the gel formation (Mark, Erman et al., 1994).

Moreover, there are many research works reported the graft copolymer of MAH onto NR (NR-MAH) and other elastomers as follows:

Nakason, Kaesaman et al. (2004) studied the synthesis of NR-MAH via the solution method using benzoyl peroxide (BPO) as an initiator (Figure 2.11). The effect of NR and BPO concentrations, time and temperature on the amount of grafted MAH onto NR backbone was investigated. It was found that the %grafted MAH content increased with increasing MAH and BPO concentrations. The optimized condition to obtain the maximum grafted MAH content (3.3%grafted MAH) was 10 phr (parts per hundred rubber) MAH loading and 3 phr BPO content at 80 °C for 2 h. The degree of MAH grafted on NR backbone was quantitatively determined by using titration method.

Nakason, Saiwaree et al. (2006) studied the preparation of NR-MAH by blending NR with MAH at 135 °C for 10 min. It was observed that the increase in the MAH contents increased the %grafted MAH content in NR. However, the %grafted MAH content in the solution system was only 3.5 wt% (at condition: [MAH] = 10 phr, [BPO] = 3 phr at 80 °C for 2h). This was lower than that obtained from the blending method (grafted MAH content = 5 wt%, at condition: [MAH] = 10 phr at 135 °C for 10 min).

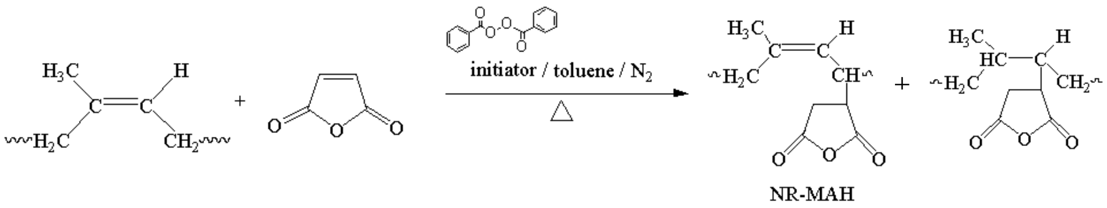


Figure 2.11 The possible free radical reaction of NR and MAH (Nakason, Kaesaman et al., 2004).

2.3 Polymer Blends

2.3.1 Introductions of polymer blends

Polymer blends are remarkable composite materials used in various applications. They are made up by mixing two or more polymers. There are three main reasons to produce polymer blend (Mark, Erman et al., 1994):

1. To improve the chemical or physical properties of original polymer
2. To achieve the better processing behavior
3. To reduce the material cost

The strategy of polymer blends is more convenient than discover the new materials. Furthermore, polymers blends is wide range of properties by changing blend compositions (Koning, Duin et al., 1998). The dissimilar structure or molecular weight of polymer induces immiscible blends resulting in phase separation and poor mechanical properties.

2.3.2 The immiscible blends

The main purpose of blending polymers is to improve the properties of polymers. However, the most polymeric constituents in the blends are incompatible due to the thermodynamic rule (Eq. 2.1) (Koning, Duin et al., 1998).

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{2.1}$$

The homogeneous miscibility requires the negative free energy of mixing (ΔG_{mix}). The addition of polymers which are macromolecules gains the entropy of mixing (ΔS_{mix}). Therefore, the ΔG_{mix} can only be negative if the heat of mixing (ΔH_{mix}) is negative (exothermic). In the other words, the blending of polymers requires specific interactions between polymer components (Koning, Duin et al. 1998). Moreover, the different molecular weight and weight distribution of polymeric constituents, blending condition, composition of blends, processing method and morphology of blends etc. can cause the immiscible blends (Paul and Bucknall, 2000).

2.3.3 PLA/NR blends

Due to the high brittleness of PLA (shown in Table 2.1 and 2.2) that limits its application, several research works have been reported to improve the brittleness of PLA by blending with elastomers. For examples,

Ho, Wang et al. (2008) studied the properties of thermoplastic polyolefin elastomer (TPO)/PLA blends using TPO-PLA as a compatibilizer. The results showed that the TPO-PLA copolymer significantly improved the compatibility of TPO/PLA blends and increased the mechanical properties of TPO/PLA blends. For example, the tensile toughness of TPO/PLA (20/80 (w/w)) was increased from 34.7 MPa to 35.6 MPa when the TPO-PLA compatibilizer (1 wt% based on wt of TPO/PLA blend) was applied. Moreover, the increase in the amount of TPO-PLA compatibilizer to 2.5 wt% based on TPO/PLA content increased the elongation at break of the TPO/PLA blends without the addition of the compatibilizer from 15% to 182%.

Bitinis, Verdejoa et al. (2011) studied the morphology and physical properties of PLA/NR blends. It was found that the elongation at break of PLA/NR blends increased from 5 to 200% by adding 10 wt% NR. Figure 2.12 shows fracture surfaces of the PLA/NR blends. It was observed that the droplet size of NR in PLA

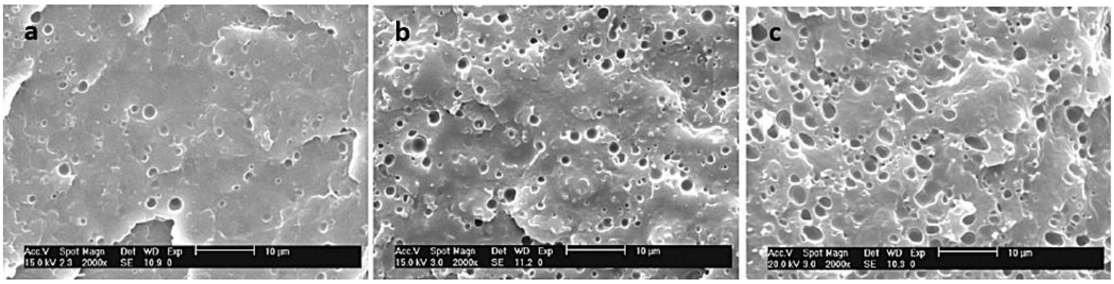


Figure 2.12 Morphology of NR droplet in PLA/NR blends: (a) 5 wt% NR, (b) 10 wt% NR and (c) 20 wt% NR (Bitinis, Verdejoa et al., 2011).

matrix increased from 1.15 to 2.03 µm with increasing NR contents from 5 to 20 wt%. This indicated that the larger droplet and low dispersed phase led immiscibility in the PLA/NR blends.

Ma, Hristova-Bogaerds et al. (2012) studied the mechanical properties of PLA/ethylene-*co*-vinyl acetate (EVA) blends with different vinyl acetate (VA) contents. The compatibility of PLA/EVA blend was controlled by ethylene and vinyl acetate composition. The impact toughness of PLA/EVA blends increased from 3 to 60 kJ/m^2 with increasing VA contents in EVA from 0 to 50 wt% at the PLA/EVA wt ratio of 80/20.

From the previous literatures, the key to improve the physical and mechanical properties of the PLA blends by using elastomeric materials was the enhancement of the compatibility between the polymeric constituents in the blends. Since NR is a non-polar aliphatic hydrocarbon, the modification of NR was required to increase the miscibility in the PLA matrix in the blends.

2.4 Chemical modification of polymers via graft copolymerization for using as compatibilizers

Compatibilizers are used as an additive to increase the miscibility of the blends resulting in the improvement of the physical and mechanical properties of the obtained products. One of the excellent agents to synthesize the compatibilizers is the maleic anhydride (MAH) and poly(methyl methacrylate) (PMMA). The graft copolymers obtained by using MAH or PMMA significantly enhanced the properties of blends; especially, the blends which are consisted of constituents with dissimilar polarity as reported in the previous literatures:

Oommen, Groeninckx et al. (2000) studied the preparation of NR grafted with PMMA (NR-*g*-PMMA) as the compatibilizer for NR/PMMA blends. SEM image showed that the immiscibility of NR and PMMA blends (Figure 2.13a) decreased when 15 wt% NR-*g*-PMMA compatibilizer was added into the blends (Figure 2.13b). Moreover, the increase in the NR-*g*-PMMA from 0 to 15 wt% in the NR/PMMA blends at 50/50 wt ratio

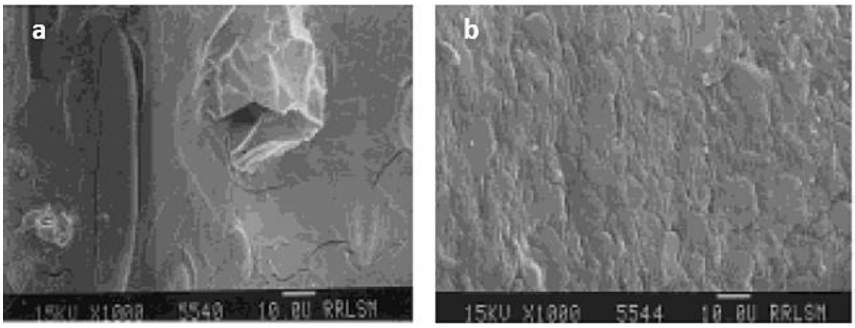


Figure 2.13 Morphology of NR/PMMA blends at 50/50 wt ratio: (a) 0 wt% NR-g-PMMA and (b) 15 wt% NR-g-PMMA (Oommen, Groeninckx et al., 2000).

enhanced their tensile strength from 3.14 MPa to 13.37 MPa and the tear strength from 12.80 N/mm to 23.47 N/mm. Moreover, the NR/PMMA blends containing the NR-*g*-PMMA had higher thermal stability than ones without the addition of the compatibilizer.

Thiraphattaraphun, Kiatkamjornwong et al. (2001) studied the NR-*g*-PMMA/PMMA blends. The NR was grafted with PMMA (NR-*g*-PMMA, GNR) in the emulsion polymerization using potassium persulfate as an initiator. The GNR/PMMA blends (60/40 (w/w)) was prepared by melt mixing system. The mechanical properties of the blends were improved by increasing MMA content in the GNR from 60 phr (GNR60, grafting efficiency = 42.6%) to 100 phr (GNR100, grafting efficiency = 64.1%) such as tensile strength increasing from 5.3 to 11.5 MPa, tear strength increasing from 16.3 to 46.1 N/mm and hardness (shore D) increasing from 35.8 to 56.1. Figure 2.14 shows the tensile fractural surface of the GNR60/PMMA and GNR100/PMMA blends at various blend ratios. For the GNR60/PMMA blend, the cavitation of sample decreased with increasing the GNR content in the blends (Figure 2.14a and 2.14b). In addition, the fracture surface of GNR100/PMMA (Figure 2.14c) was smoother than GNR60/PMMA (Figure 2.14b) at the same GNR/PMMA blend ratio (50/50 (w/w)). This means that the higher grafting efficiency of GNR100 provided the better interfacial adhesion between the PMMA and GNR phases in the blends than the use of GNR60.

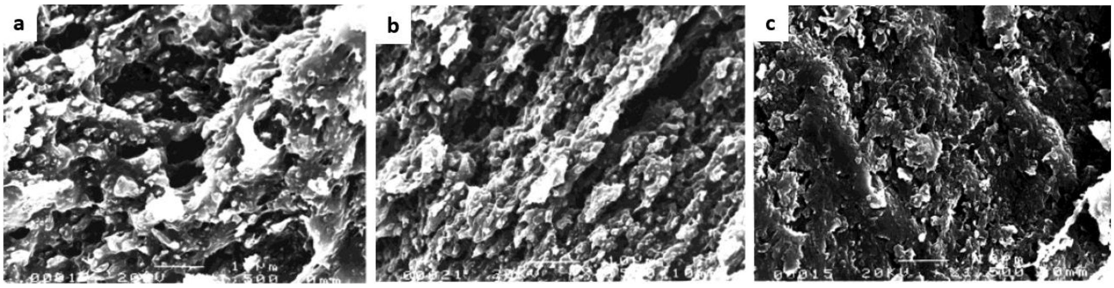


Figure 2.14 The fracture surface of GNR/PMMA (x1500): (a) GNR60/PMMA at 70/30 wt ratio, (b) GNR60/PMMA at 50/50 wt ratio and (c) GNR100/PMMA at 50/50 wt ratio (Thiraphattaraphun, Kiatkamjornwong et al., 2001).

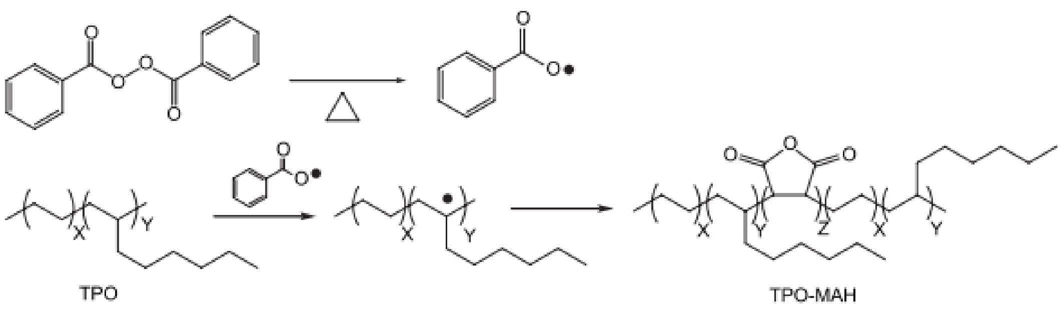
Arayapranee, Prasassarakich et al. (2004) studied the graft copolymerization of poly(styrene-*co*-MMA) onto the NR backbone (NR-*g*-(styrene-*co*-MMA)) for blending with poly(vinylchloride) (PVC). The NR-*g*-(styrene-*co*-MMA) was prepared in the emulsion state by using the redox initiator. It was found that the impact strength of the blends increased from 12 to 14 kJ/m^2 with increasing the graft copolymer content to 10 wt%.

Abacha and Fellahi (2005) studied the preparation of polypropylene-*g*-maleic anhydride (PP-*g*-MAH) for using as the compatibilizer for nylon 6/polypropylene blends. The PP-*g*-MAH was synthesized in the molten state in an internal mixer. It was applied in the nylon 6/PP blends (30/70 w/w) with various PP-*g*-MAH contents (2.5-10 wt%). It was found that the tensile modulus of nylon 6/PP blends increased from 2.38 to 2.75 GPa when PP-*g*-MAH content increased from 0 to 7.5 wt%.

Ho, Wang et al. (2008) studied the use of the TPO-PLA compatibilizer in PLA/TPO blends. The TPO-PLA compatibilizer was prepared by functionalized MAH onto TPO structure by using benzoyl peroxide (BPO) as an initiator. Then, the functionalized TPO (TPO-*g*-MAH) was grafted with PLA (TPO-PLA) via esterification using 4-dimethylaminopyridine (DMAP) as a catalyst (Figure 2.15). It was found that the miscibility between PLA and TPO phases improved by TPO-PLA compatibilizer was attested by the Molau test in the ethyl acetate solution as shown in Figure 2.16 and SEM (Figure 2.17). The PLA/TPO blends (80/20 (w/w)) without the addition of compatibilizer showed a phase separation between PLA and TPO. When 5 wt%

TPO-PLA was add into the PLA/TPO blends, the homogeneous phase of PLA/TPO blends was appeared. The compatibilization of PLA/TPO blend was also confirmed by SEM image (Figure 2.17). The size of TPO droplet was decreased by adding the TPO-PLA compatibilizer. The elongation at break of TPO/PLA/TPO-PLA blends (80/20/2.5 (w/w)) was 182%, which was higher than that of pure PLA (elongation at break = 6%).

A. Functionalization of TPO with maleic anhydride



B. Esterification of TPO-MAH with PLA

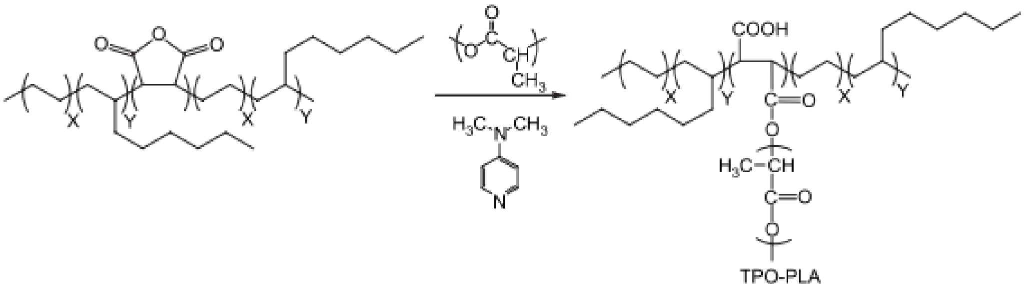


Figure 2.15 The synthetic route of TPO-PLA copolymer (Ho, Wang et al., 2008).

Figure 2.16 Molau test in ethyl acetate solvent: (a) PLA/TPO (80/20) and (b) PLA/TPO/TPO–PLA (80/20/5) (Ho, Wang et al., 2008).

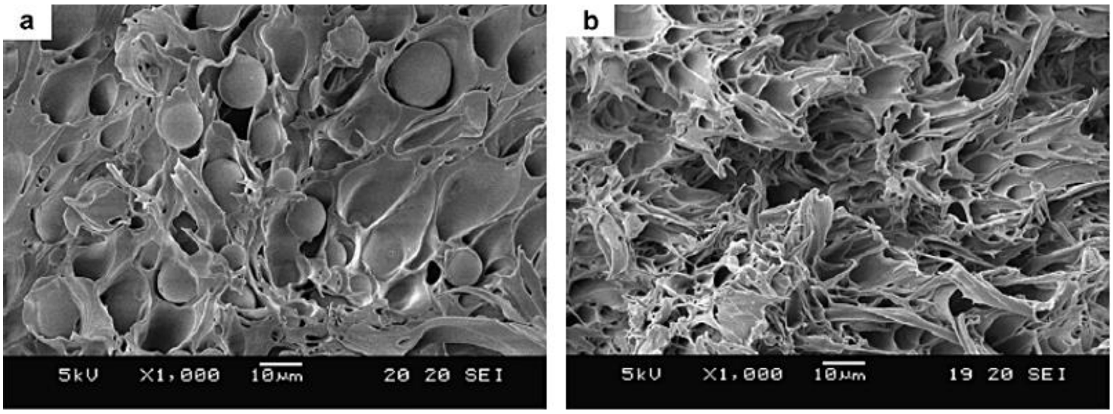


Figure 2.17 Morphology of tensile-fractured surface of PLA/TPO (80/20) blends: (a) without TPO-PLA and (b) with 5 wt% TPO-PLA (Ho, Wang et al., 2008).

For this research, it was found the similarity between TPO and NR structure. They were nonpolar elastomers and have unsaturated carbon-carbon double bonds in their backbones. Therefore, it was possible to graft NR with PLA (NR-PLA) for using as the compatibilizer in order to enhance the mechanical properties and miscibility of PLA/NR blends. Firstly, NR was prepared by functionalization with MAH (NR-MAH) via the solution method using BPO as the initiator. The PLA was then grafted at anhydride ring in the NR-MAH by using DMAP catalyst via esterification.

CHAPTER 3
EXPERIMENTAL

3.1 Materials

The solid natural rubber (NR) in the grade of STR-5L was obtained from PAN Innovation Industry Co.,Ltd. (Thailand). Poly(lactic acid) (PLA) 4043D was produced by NatureWorks® LLC. Maleic anhydride (MAH) was obtained from Sigma-Aldrich. Benzoyl peroxide (BPO) used as an initiator was purchased from Merk Schuchardt. 4-(Dimethylamino)pyridine (DMAP) used as a catalyst in the esterification step was obtained from Sigma-Aldeich. Toluene, acetone, methanol, benzyl alcohol, potassium hydroxide (KOH) and sodium hydroxide (NaOH) were obtained from Quality Reagent Chemical Co.,Ltd (Thailand). Phenolphthalein used as an indicator for titration to evaluate the level of grafted MAH was received from Riedel-Dehaen. In the bio-degradation, enzyme Proteinase K obtained from *Tritirachium album*, Tris-HCL buffer and sodium azide were purchased from Sigma-Aldrich.

3.2 Functionalization of NR by grafting with MAH

NR grafted with MAH (NR-MAH) was prepared in the solution state. NR was dissolved in toluene (0.9 M). Then, NR solution was poured into a two neck round-flask and heated in oil bath until 60 ^{o}C under nitrogen atmosphere. The solution of various MAH contents (5-20 phr) and 0.3 phr BPO in toluene was then added into the NR solution and stirred for 2 h at 80 ^{o}C. The NR-MAH product was precipitated in acetone and dried at 40 ^{o}C until the constant weight was received. The level of grafted MAH in the NR-MAH was determined by the titration method (Nakason, Kaesaman et al., 2004). The NR-MAH (1 g) was dissolved in 100 mL toluene and hydrolyzed by using 0.2 mL distilled water under reflux at 110 ^{o}C for 2 h. The amount of carboxylic group obtained from hydrolysis of NR-MAH was determined by titration with 0.025 N KOH in methanol/benzyl alcohol (1/9 (v/v)) and 1% vol phenolphthalein in methanol was used as the indicator. The amount of grafted MAH in the NR-MAH was calculated by using Eq. 3.1:

$$\text{Grafted MAH (wt\%)} = \frac{(V_0 - V_1)N}{2w} \times 98 \times 100\% \qquad (3.1)$$

Where V_0, V_1 = volumes of KOH in a blank and a sample (L), respectively

N = KOH concentration (M)

w = sample weight (g)

3.3 Esterification of PLA into NR-MAH

NR-MAH solution (prepared from 15 phr MAH and 0.3 phr BPO) and PLA pellets (PLA/NR-MAH = 2/1 (w/w)) was added into the reactor containing 0.4 M DMAP using as a catalyst for esterification in the presence of toluene (150 mL). The reaction was carried out in a stainless steel reactor consisting of a magnetic bar and placed on an electrical hot-plate stirrer. Nitrogen gas was purged into the reactor for 15 min to ensure that air was removed. The esterification of NR-MAH was then proceeded under vigorous stirring at 140 ^{o}C for 16 h. The variation of esterification parameters was shown below:

- DMAP concentration (M): 0, 0.05, 0.1, 0.2, 0.4 and 0.8
- Amount of grafted MAH in NR-MAH (wt%): 1.63, 2.26, 2.66 and 3.68
- PLA/NR-MAH (w/w): 1.0/0.5, 1.0/1.0, 1.0/2.0, 1.0/3.0, 1.0/4.0 and 1.0/5.0
- Temperature (^{o}C): 120, 130, 140 and 150
- Time (h): 8, 12, 16, 20 and 24

The obtained PLA grafted on NR-MAH (NR-PLA) solution was poured into an aluminium tray and placed in a hood to evaporate toluene. The level of PLA grafted on the NR-PLA was evaluated from the mass loss obtained from soxhlet extraction by using the solution of NaOH dissolved in methanol (0.38 M) for 24 h. Then, the extracted

NR-PLA was dried at 40 °C in the vacuum oven for 24 h. The grafted PLA in the NR-PLA was calculated by using Eq. 3.2:

$$\text{Grafted PLA (\%wt)} = \frac{W_{after}}{W_{before}} \times 100\% \tag{3.2}$$

where W_{before} and W_{after} are the weights of NR-PLA before and after soxhlet extraction

3.4 Gel fraction of NR-MAH

The gel fraction of NR-MAH was tested following ASTM D-3616. 0.40 g of NR-MAH was cut as pieces less than 1 mm thickness and about 5 mm long. The sample was placed on the screen of gel test apparatus. When 100 mL toluene was transferred into the bottle and capped, the bottle was allowed to stand in dark for 20 h at room temperature. Sample solution (25 mL) was pipetted and put in each aluminum dish for 3 times. Then, the dishes were placed in a fume hood to evaporate solvent until a constant weight was received. The gel content was determined as follows:

$$A \times 4 = B \tag{3.3}$$

$$\text{Gel (\%)} = \left(\frac{C - B}{C}\right) \times 100 \tag{3.4}$$

where A = average mass of the dry sol from 25 mL solution (g),

B = mass of the total dry sol (g)

C = mass of the original sample (g).

3.5 Structural characterization of NR-MAH and NR-PLA

3.5.1 Attenuated total reflectance fourier transform infrared (ATR-FTIR)

The ATR-FTIR spectra of PLA, NR and the modified NRs (10 mg) were recorded using Perkins-Elmer spectrometer over the wavelength in the range of 4,000 to 515 cm^{-1} with 64 scans at a resolution of 4 cm^{-1} at room temperature.

3.5.2 Proton nuclear magnetic resonance (^{1}H NMR)

The ^{1}H NMR spectra of NR, NR-MAH and NR-PLA were acquired at 25 ˚C using Varian Inova 500 MHz Spectrometers with 32 scans. The sample (10 mg) was dissolved in an NMR tube in the presence of 5 mL deuterated chloroform ($CDCl_3$).

3.6 Preparation of PLA/NR blends

PLA pallets was dried in an oven at 100 ^{o}C for 24 h before use and then it was kept in desiccators at room temperature. NR was masticated by using internal mixer (HAAKE Polydrive, Japan) at 120 ^{o}C for 3 min before blending with PLA. Then, PLA, NR (PLA/NR = 80/20 (w/w)) and NR-MAH or NR-PLA with various contents (0.5-5 wt%) were blended in an internal mixer at 190 ^{o}C with a rotor speed of 80 rpm for 8 min. The polymer blends were milled by ZERMA granulator, China to small pieces of 5×5×5 mm^3 and kept them in the desiccator at room temperature. The blends were sheeted (3 mm thickness) by using an electrical compression mold at 190 ^{o}C for 20 min.

3.7 Mechanical properties of the PLA/NR/NR-MAH or PLA/NR/NR-PLA blends

3.7.1 Tensile properties testing

The tensile properties of the blends were evaluated by using a Universal Testing Machine (Shimadzu DSS-10T) according to ASTM D638 type I at room temperature. The crosshead speed was controlled as 10 mm/min and 50 mm gauge length was used. The sample sheets (ca. 3 mm thickness) were cut by laser as the dumbbell shape. All tests were considered at least 5 times and the mean value was reported.

3.7.2 Impact strength testing

The notched Izod impact strength was investigated by using v-notched specimens according to ASTM D256 by using an Impact Ceast Resil impactor. The specimens were hit by 1 J impact hammer at a constant speed of 3.46 m/s at room temperature. The dimensions of a standard specimens are 63.5 × 12.7 × 3.2 mm. An average value obtained from five specimens was reported.

3.7.3 Hardness testing

The hardness of samples (ca. 6 mm thickness) was measured by using a Shore type B Lever Loader (REX GAUGE 2000 & OS Stand) according to ASTM D2240 at room temperature. The measurements were taken from five different points distributed over the sample and reported the mean value of five measurements was recorded.

3.8 Thermal properties of NR-PLA and PLA blends

3.8.1 Thermal gravimetric analysis (TGA)

The degradation temperatures of PLA, NR, modified NRs and PLA/NR blends with and without the addition of the compatibilizer were determined by using TGA technique (Perkin-Elmer Pyris Diamond TG/DTA). The sample (10 mg) was placed into a platinum pan and heated from 40 to 1,000 ^{o}C with a heating rate of 10 ^{o}C/min under nitrogen atmosphere at a flow rate of 50 mL/min. The degradation temperatures of the sample was calculated from thermogravimetry (TG) and differential thermogravimetry (DTG) plots.

3.8.2 Differential scanning calorimeter (DSC)

The glass transition temperature (T_g) of PLA, NR, modified NRs and PLA/NR blends with and without the addition of the compatibilizer were determined by using DSC (Netzsch 204-F1 Phoenix). The sample (10 mg) was sealed in 40 μL aluminum pan and heated from -50 to 300 ^{o}C with a heating rate of 10 ^{o}C/min under nitrogen atmosphere at a flow rate of 50 mL/min.

3.9 Morphology of PLA/NR blends

The morphology of PLA and PLA/NR blends with and without the addition of the compatibilizer was examined by using scanning electron microscopy (SEM, JEOL model JSM-6400) operated at 15 kV. The fractural surfaces after impact testing of each sample was coated with osmium vapor for 24 h before coating again with gold. The particle size of rubber phase in the blends was observed from the cross sectional area of specimens.

3.10 Degradation testing of PLA/NR blends

To study the effect of modified NRs used as the compatibilizer on the degradation of PLA/NR blends, there were three degradation methods:

3.10.1 Enzymatic degradation (Ebeling, Hennrich et al., 1974, Li, Tenon et al., 2000)

The specimens were prepared in a square shape with a dimension of 10×5×1 mm^3 by using the electrical compression mold at 190 ^{o}C for 20 min. Each of specimens was placed in a vial filled with the enzyme solution containing 0.5 mg Proteinase K and 0.5 mg sodium azide in 2.5 mL Tris-HCl buffer solution. The degradation process was allowed to proceed in a water bath at 37 ^{o}C. The enzyme solution was changed every 24 h to stabilize enzyme activity. The three samples were collected from enzyme at each time interval then thoroughly washed with distilled water and dried in an oven at 40 °C for a week. The weight loss of each specimens was calculated from Eq. 3.5:

$$\text{Weight loss (\%)} \qquad = \qquad \left(\frac{W_b - W_a}{W_b}\right) \times 100 \qquad (3.5)$$

Where W_b and W_a were the weights of specimens before and after degradation, respectively.

3.10.2 Hydrolysis degradation (Huang, Zhang et al., 2013)

For the hydrolysis study, the specimens were prepared in the same shape used in the enzymatic degradation as described above. Each sample was immersed in a vial containing 2.5 mL distilled water and all vials were placed in the water bath at a constant temperature of 58 °C. Three specimens were picked out every week, washed with distilled water and dried in an oven at 40 °C for a week. The weight loss was also calculated from Eq. (3.5).

CHAPTER 4

RESULTS AND DISUSSION

This research studied the preparation of natural rubber (NR) grafted with poly(lactic acid) (PLA) (NR-PLA) for applying as a compatibilizer in PLA/NR blends. The chemical structures were examined by using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy. The parameters influencing on the grafting efficiency of PLA onto NR-MAH and the gel content were investigated. The morphology, mechanical and thermal properties of PLA/NR blends with and without the addition of NR-PLA compatibilizer were studied. Moreover, the degradation of PLA/NR blends with and without the addition of NR-PLA was compared to the neat PLA.

4.1 Structural characterization of natural rubber before and after chemical modification

The chemical structures of NR before and after functionalization with maleic anhydride (MAH) and esterification with poly(lactic acid) (PLA) were comparatively investigated by using ATR-FTIR. For PLA (Figure 4.1a), the intense absorption band of carbonyl group was found at 1,738 cm^{-1} (Ho, Wang et al., 2008). The NR before modification (Figure 4.1b) showed the asymmetric and symmetric C-H stretching peaks between 2,851 – 2,960 cm^{-1}. After functionalization with MAH (Figure 4.1c), the NR grafted with MAH (NR-MAH) synthesized by using 15 part per hundred rubber (phr) MAH and 0.3 phr benzoyl peroxide (BPO) as an initiator showed the peak intensity at 1,849 and 1,782 cm^{-1} attributed to C=O stretching vibration of succinic anhydride ring of MAH grafted on the NR structure (%grafted MAH = 2.7 wt%) (Nakason, Kaesaman et al., 2004, Nakason, Saiwaree et al., 2006). After esterification of NR-MAH to produce NR-PLA, Figure 4.1d showed the higher peak intensity of C=O bond at 1,748 cm^{-1} in the NR-PLA structure reflecting the carbonyl group of the PLA grafted on the NR-MAH.

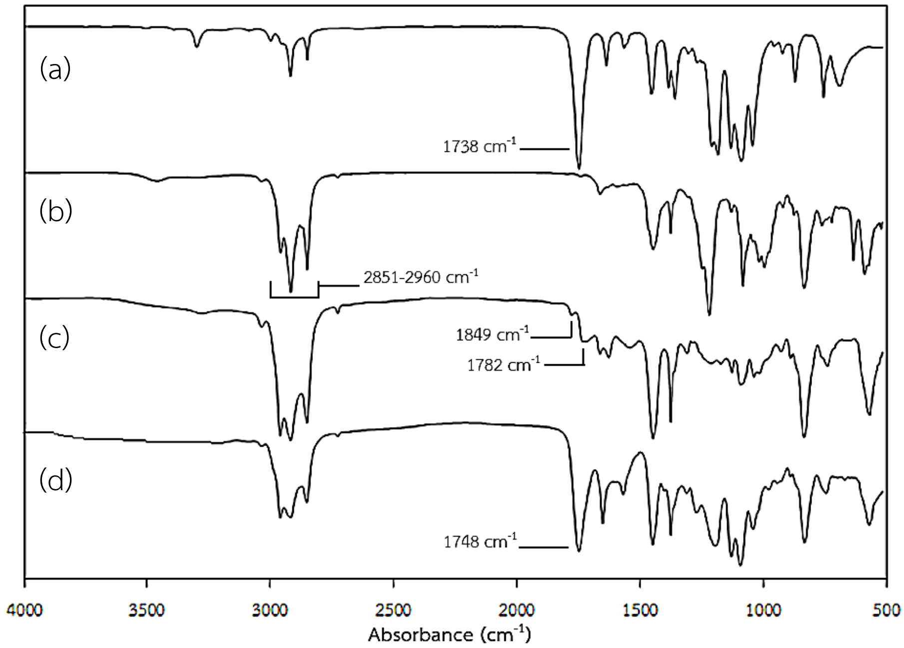


Figure 4.1 ATR FT-IR spectra of (a) PLA, (b) NR, (c) NR-MAH (%grafted MAH = 2.7 wt%) and (d) NR-PLA (%grafting PLA = 37 wt%).

To confirm the ATR-FTIR results, ^{1}H NMR spectroscopy technique was applied. Figure 4.2a showed the characteristic peaks of PLA appeared at 1.56 (a) and 5.14 (a’) ppm attributed to methyl and methyne protons in PLA, respectively (Choi and Choi et al. 2013). For the typical spectra of NR, Figure 4.2b indicated the peaks at 5.12 (b), 2.09 (b’) and 1.68 (b’’) ppm for the olefinic proton, methylene protons and the methyl protons, respectively (Oliveira, Oliveira et al., 2005). After grafting with MAH to produce NR-MAH, Figure 4.2c indicated the new signal at 3.49 ppm (c’) generated from –CH in the methylene protons of anhydride group (Miyauchi and Saito, 2012). When NR-MAH was grafted with PLA via esterification, Figure 4.2d showed the new peaks at ca. 5.17 (d’) and 1.59 (d’’’’) ppm attributed to the methyne proton and methyl protons of grafted PLA on the NR-MAH. The methyne proton peaks were shifted from 5.14 to 5.17 ppm because the shielding of NR molecule. Moreover, the peak intensity at 3.49 ppm (c’) in Figure 4.2c. The reaction mechanism to prepare NR-PLA via functionalization of NR with MAH and esterification was proposed as shown in Figure 4.3.

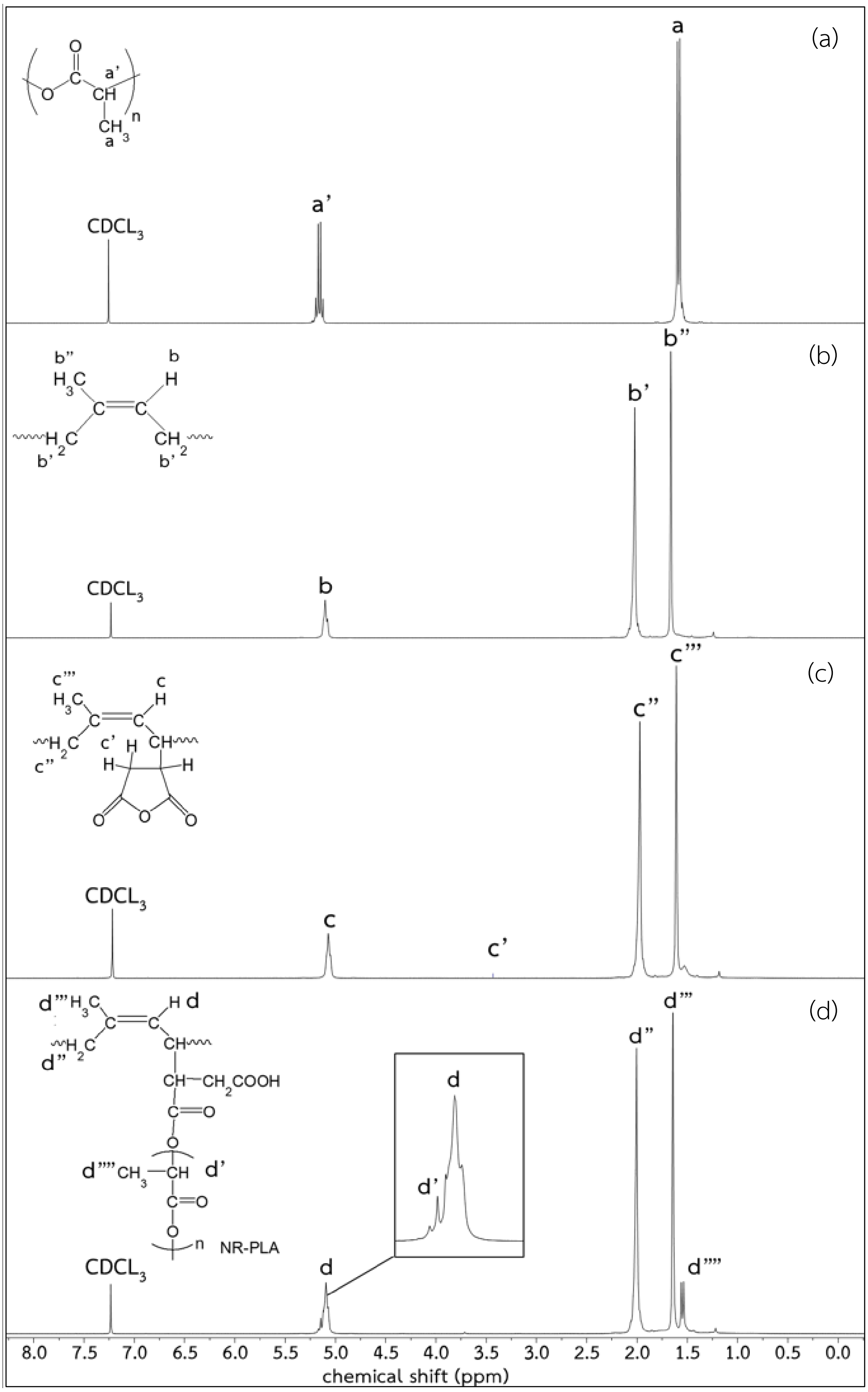


Figure 4.2 ^{1}H NMR spectra of (a) PLA, (b) NR, (c) NR-MAH (%grafted MAH = 2.66 wt%) and (d) NR-PLA (%grafting PLA = 37%).

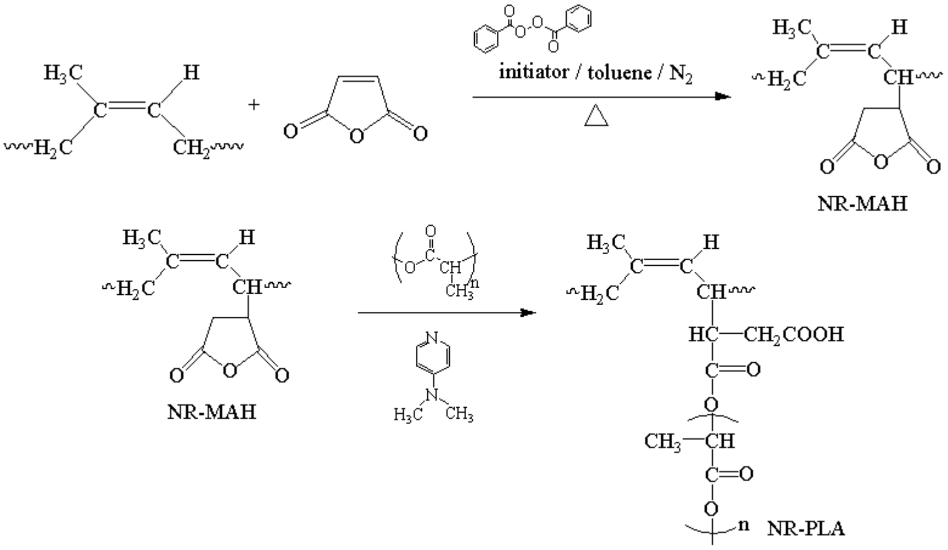


Figure 4.3 Proposed reaction mechanism of NR-PLA preparation.

4.2 Effect of MAH loading on the grafted MAH and gel contents in NR-MAH

The various MAH contents (5 – 20 phr) was grafted onto the backbone of NR dissolved in toluene (0.9 M) by using BPO (0.3 phr) as the initiator at 80 °C for 2 h. Table 4.1 presented the effect of MAH content on the degree of grafted MAH in the NR-MAH structure. The results obtained from the titration indicated that the amount of grafted MAH in the NR-MAH increased from 1.63 to 3.68 wt% when the MAH content increased from 5 to 20 phr because the higher loading of MAH increased the possibility for MAH radicals to react with NR molecules (Nakason, Saiwaree et al., 2006). It could be observed that the gel contents in the NR-MAH were in the range of 72 - 75%, which was higher than that in NR (11.7%). This could be explained that the increase in the MAH content in the presence of BPO used as the initiator provided more free radicles that could initiate both grafted sites and crosslink formation resulting in the gel inside the obtained grafted copolymer (Nakason, Kaesaman et al., 2004).

Table 4.1 The effect of MAH loading on the grafted MAH and gel contents in NR-MAH

Sample	MAH loading (phr)	Grafted MAH content (wt%)	Gel content (%)
NR	-	-	11.7
NR-MAH*	5	1.63	72.3
	10	2.26	75.1
	15	2.66	74.1
	20	3.68	71.9

* Condition: [BPO] = 0.3 phr, temperature 80 °C for 2 h.

4.3 Effect of reaction parameters in esterification of PLA onto NR-MAH on grafted PLA content

In this study, the effects of grafted MAH content in the NR-MAH, DMAP concentration, PLA/NR-MAH wt ratio, reaction time and reaction temperature were individually investigated at the central condition: [MAH] = 15 phr (%grafted MAH in NR-MAH = 2.7 wt%), [DMAP] = 0.2 M, PLA/NR-MAH = 1/2 (w/w) at 140 °C for 14 h.

Figure 4.4 showed the effect of the grafted MAH content in the NR-MAH structure on the amount of grafted PLA in the NR-PLA. The grafted MAH content in the NR-MAH was varied in the range of 1.63 to 3.68 wt% based on the MAH loading. It could be observed that the increase in the content of grafted MAH in the NR-MAH from 1.63 to 3.68 wt% obtained from the functionalization of NR using 5 - 20 phr MAH content enhanced the level of grafted PLA in the NR-PLA from 27.5 to 46.4 wt%. This indicated that the increase in the grafted MAH in the NR-MAH increased the sites for grafting with PLA via esterification. The effect of the grafted MAH content on the gel content in NR-PLA was also shown in the Figure 4.4. It was found that the gel content in the NR-PLA slightly decreased from 71.8 to 68.1% when the amount of grafted MAH increased from 1.63 to 3.68 wt%. To compare with Table 4.1, it was also observed that the grafting of PLA via esterification could slightly reduce the gel content in the NR-MAH (71.9 – 75.1%) at the same range of applied MAH concentration. This was

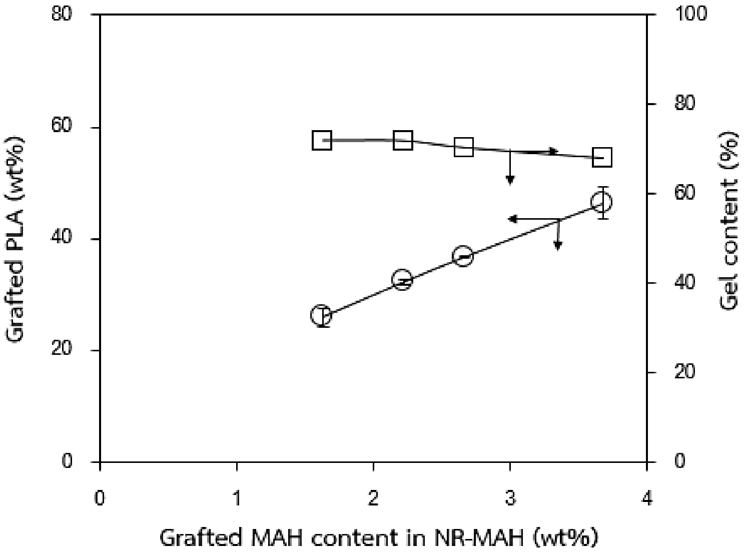


Figure 4.4 Effect of the grafted MAH content in the NR-MAH on the level of grafted PLA and gel content in NR-PLA (Condition: [BPO] = 0.3 phr at 80 °C for 2 h).

possible that the esterification provided the anhydrous ring opening of NR-MAH to graft with PLA resulting in the reduction of possibility to promote the gel formation (Nakason, Saiwaree et al., 2006).

For the effect of PLA/NR-MAH wt ratio on the level of grafted PLA in the NR-PLA, Figure 4.5a indicated that the increase in the amount of PLA in the PLA/NR-MAH mixture from 0.5-1.0 increased the level of grafted PLA in the NR-PLA from 34.0 to 51.1 wt% because the higher PLA loading could provide higher possibility to react with MAH group in the NR-MAH. However, the increase in the PLA content above 1.0 (w/w) PLA/NR-MAH declined the level of grafted PLA due to the limitation of the grafting sites obtained from the ring opening of anhydride group in the NR-MAH structure via esterification.

To consider the effect of DMAP concentration on the degree of grafted PLA, Figure 4.5b showed that the esterification could not occur without the addition of DMAP as the catalyst (Ho, Wang et al., 2008). The increase in the DMAP content from 0 to 0.05 M drastically increased the amount of grafted PLA in the NR-PLA from

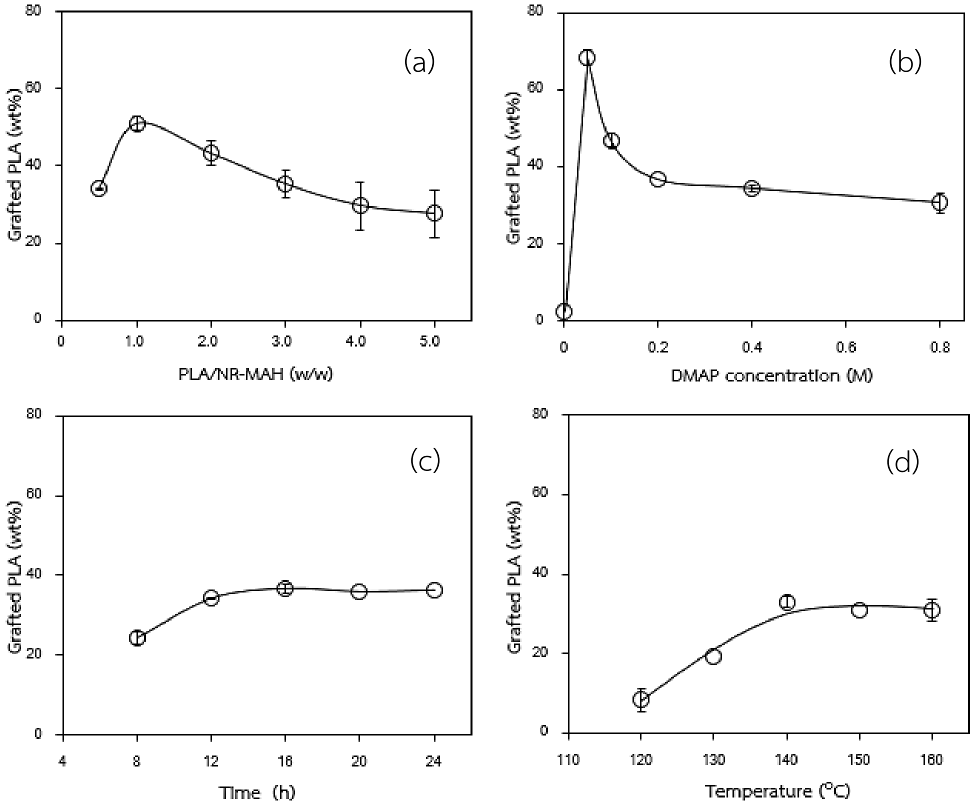


Figure 4.5 Effect of reaction parameters on the level of PLA grafting in NR-PLA: (a) PLA/NR-MAH wt ratio, (b) DMAP concentration, (c) reaction time and (d) reaction temperature (central condition: MAH content for NR-MAH preparation = 15 phr (%grafted MAH in NR-MAH = 2.66%), PLA/NR-MAH wt ratio = 2, [DMAP] = 0.2 M at 140 °C for 16 h).

2.35 to 65.3 wt%. For the role of DMAP in the previous research (Ho, Wang et al., 2008), the DMAP was used as a nucleophile catalyst for grafting PLA onto TPO grafted with MAH (TPO-MAH) via esterification of terminal hydroxyl groups of PLA with the succinic anhydride groups of TPO-MAH. Similarly to this study, the possible reaction mechanism of DMAP to catalyze NR-PLA and PLA was shown in Figure 4.6. The DMAP was formed as an ion pair to react with NR-MAH at the succinic anhydride groups to break the anhydride ring and produced species (1). Then, the electron of acetate groups from species (1) attacked the terminal hydroxyl group of PLA resulting in the removal of proton from the PLA and form species (3). The PLA with lone pair electron (species (4)) reacted with species (3) and form covalent bond with tertiary carbon near the DMAP and deprotonated the DMAP to release NR-PLA (species (5)) and DMAP for using as the catalyst again (Xu, Held et al., 2005). However, the increase in the DMAP concentration to 0.8 M decreased the level of grafted PLA in the NR-PLA to 30.7 wt%. This could be explained that the high loading of DMAP promoted the depolymerization of PLA at high reaction temperature (Ho, Wang et al., 2008).

Figure 4.5c exhibited the effect of reaction time on the level of grafted PLA in the NR-PLA structure. It was observed that the increase in the reaction time from 8 to 12 h significantly increased the grafted PLA in the resulting product from 24.5 to 34.2%. The amount of the grafted PLA in the NR-PLA was levelled off when the reaction time was longer than 24 h. This might be due to the steric hindrance effect obtained from the PLA grafted onto the NR-MAH at the earlier stage (Zhang and Duhamel, 2004). Thus, the optimum reaction time for esterification to produce NR-PLA for further experiments was controlled as 16 h.

For the effect of reaction temperature on the degree of grafted PLA in the NR-PLA, Figure 4.5d showed that the increase in the reaction temperature from 120 to 140 °C increased the level of grafted PLA in the NR-PLA from 8.3 to 36.7%. However, the level of grafted PLA at the reaction temperature (higher than 140 °C) tended to be constant due to the limited functional MAH group content on the NR-MAH structure.

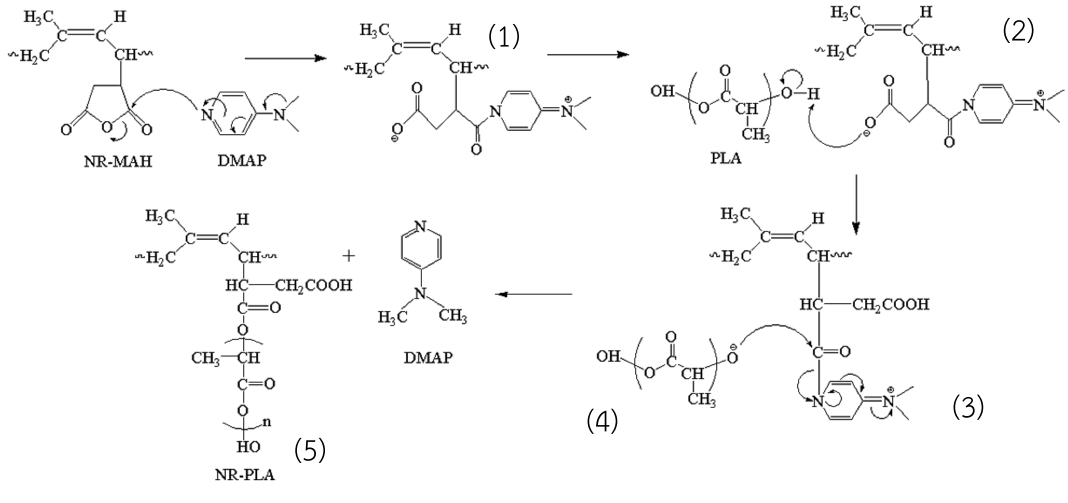


Figure 4.6 The possible mechanism of DMAP in the esterification step for the preparation.

4.4 Mechanical properties and morphology of PLA/NR blends

4.4.1 Effect of NR and NR-MAH on the mechanical properties of PLA blends

In this part, NR or NR-MAH (%grafted MAH = 2.66 wt%) was blended with PLA at various blend ratios and the mechanical properties of the blends were comparatively reported. Without the addition of NR, the tensile strength of PLA was 56.1 MPa (Figure 4.7a) with 11.2% elongation at break (Figure 4.7b). When NR or NR-MAH was applied into the PLA in the range of 3 – 10 wt% based on the PLA content, both tensile strength and elongation at break of blends decreased. In the case of PLA blended with NR (PLA/NR), the reduction of the tensile properties of PLA/NR blends

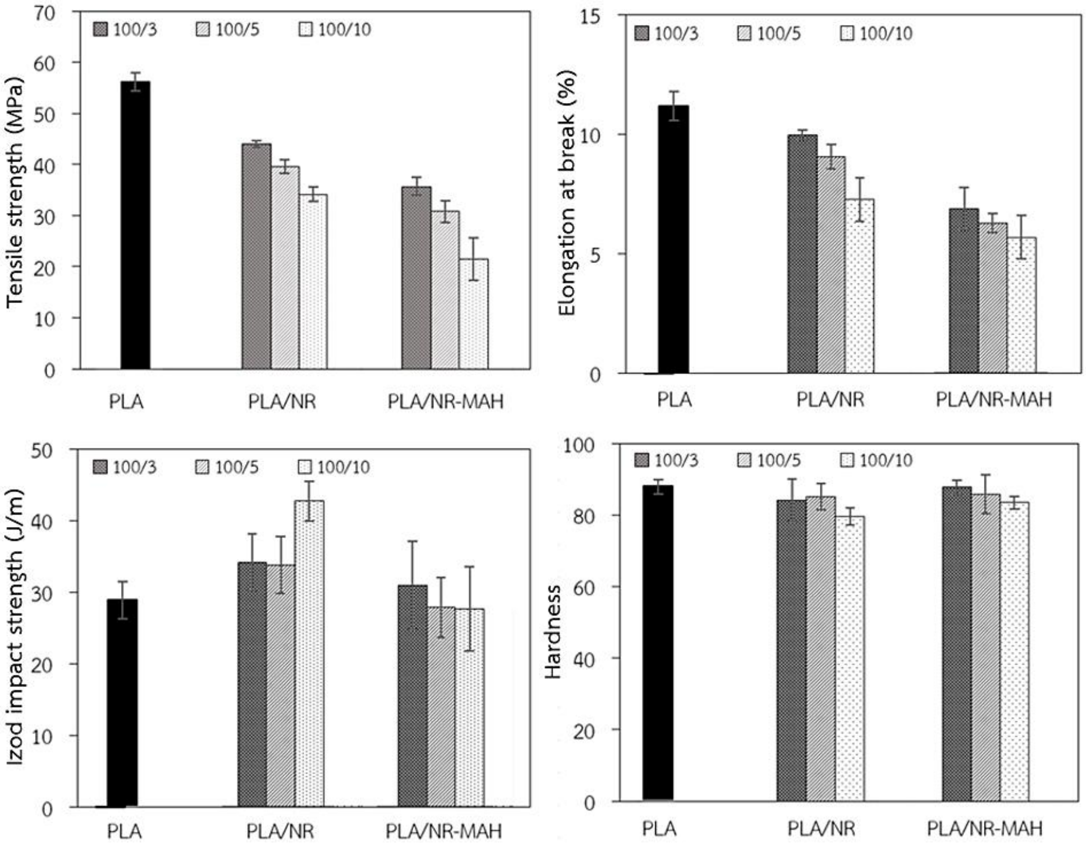


Figure 4.7 The effect of NR and NR-MAH (grafted MAH content = 2.66 wt%) contents on the mechanical properties of PLA/NR and PLA/NR-MAH blends: (a) tensile strength, (b) elongation at break, (c) Izod impact strength and (d) hardness.

was resulted from the polarity difference between PLA containing carbonyl group inducing the higher polarity and NR, which its structure was non-polar aliphatic hydrocarbon. This provided the more immiscibility and phase separation between PLA and NR phases when the NR content was higher in the NR/PLA blends. To compare the use of NR and NR-MAH for blending with PLA, it was found that the tensile strength and elongation at break of PLA/NR-MAH blends were lower than those of PLA/NR blends for all compositions. This could be explained that the shear viscosity of NR-MAH might be higher than that of NR resulting in the poor distribution of NR-MAH in the PLA phase. This phenomenon was also observed in the previous literature, which reported that the increasing grafted MAH content in the NR-MAH led the increasing apparent shear viscosity in NR-MAH. Besides, the trend of the Moony viscosity, the chemical interaction and crosslinks between polar groups in the NR-MAH molecules increased when grafted MAH content increased (Nakason, Saiwaree et al., 2006).

To consider the Izod impact strength of the blends (Figure 4.7c), it was noticed that the increase in the NR content in the PLA/NR to a wt ratio of 100/10 increased the Izod impact strength of the PLA/NR blends from 34.2 J/m to 42.7 J/m. This indicated that the increase in the NR portion could enhance the impact energy absorption of the brittle material (García, Lamannac et al., 2012). However, the increase in the NR-MAH content slightly decreased the Izod impact strength of the blends because of the immiscibility between PLA and NR-MAH phases as described above for tensile strength and elongation at break.

For the hardness of the blends, Figure 4.7d showed that the increase in the NR or NR-MAH in the blends caused slight reduction of hardness of both PLA/NR and PLA/NR-MAH due to the soft segment of NR dispersed in the brittle PLA phase.

For the PLA/NR-PLA blends, it was found that the PLA blended with NR-PLA could not be sheeted. Therefore, the NR-PLA was used as a compatibilizer for PLA/NR blends and the results of the mechanical properties of blends were compared to ones containing NR-MAH at the same content.

4.4.2 Effect of NR-PLA and NR-MAH used as a compatibilizer on meachanical properties and morphology of PLA/NR blends

The effect of NR-PLA (grafted PLA content = 36.7 wt%) and NR-MAH (grafted MAH content = 2.66 wt%) used as compatibilizers in the PLA/NR blends (80/20 (w/w)) was shown in Figure 4.8. For the tensile properties (Figure 4.8a and 4.8b), it was found that the neat PLA had tensile strength and elongation at break as 56.1 MPa and 11.2%, respectively. When PLA was blended with NR without the addition of the compatibilizers, the tensile properties of the blends decreased due to the phase separation resulting from the polar dissimilarity of NR and PLA phases as described

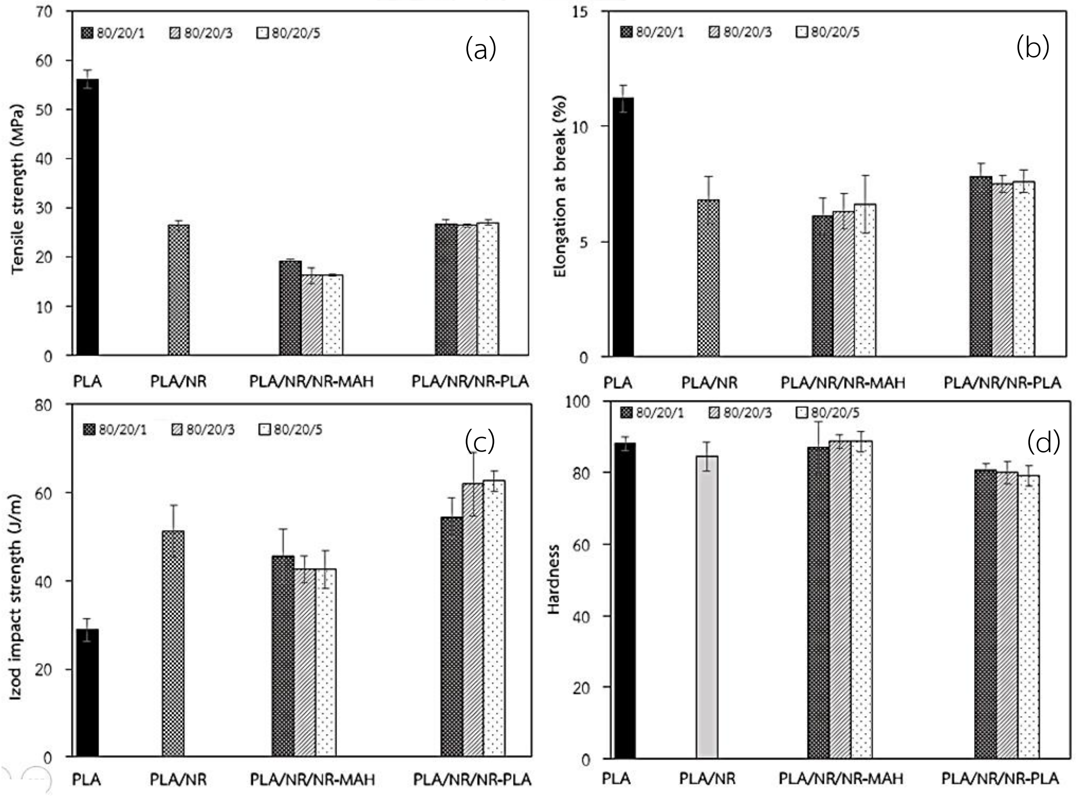


Figure 4.8 The effect of NR-PLA (grafted PLA content = 36.7 wt%) and NR-MAH (grafted MAH content = 2.66 wt%) used as the compatibilizer on the mechanical properties of PLA/NR blends (80/20 (w/w)): (a) tensile strength, (b) elongation at break, (c) Izod impact strength and (d) hardness.

above. However, it was observed that the addition of NR-MAH or NR-PLA with various contents in the PLA/NR blends could not enhance the tensile properties of the PLA/NR blends. Although these modified NRs decreased the tensile properties of PLA/NR blend NR-PLA provided the higher these properties than NR-MAH. This implied that NR-PLA might be higher compatible with PLA/NR blends than NR-MAH for all compositions.

To consider the Izod impact strength (Figure 4.8c), it was observed that the Izod impact strength of PLA (28.8 J/m) was improved to 51.27 J/m when PLA was blended with NR (PLA/NR (w/w) = 80/20). To compare the efficiency of NR-MAH and NR-PLA for using as the compatibilizer of PLA/NR blends, Figure 4.8c indicated that the addition of NR-PLA as the compatibilizer from 1 to 5 wt% based on the weight of PLA/NR increased the Izod impact strength of PLA/NR blends from 54.3 to 62.7 J/m. This was higher than that of PLA/NR blends containing NR-MAH as the compatibilizer (PLA/NR/NR-MAH) because the structure of NR-PLA had both PLA and NR phases that could be distributed in both phases higher than NR-MAH. The fractural morphology of the blends after impact testing was attested by scanning electron microscopy (SEM) at a magnifying power x1000. The smooth and sharp fractural surface of pure PLA shown in Figure 4.9a indicated the high strength and hardness of brittle PLA. Figure 4.9b exhibited the PLA/NR blends (80/20 (w/w)) without NR-PLA compatibilizer. It showed the phases separation between dark gray matrix of PLA phase and black spherical NR droplets. The fractural surface of PLA/NR blend without NR-PLA compatibilizer also exhibited the numerous cavities and crazes formed throughout the fractural surface. Figure 4.9c - 4.9d presented the fractural surfaces of PLA/NR blends containing 1 and 5% NR-PLA compatibilizer, respectively. They showed the smaller NR droplets size dispersed in the fractural surface of the blends when the NR-PLA content increased from 1 to 5%. Furthermore, the roughness and rupture of fractural surface morphology of PLA/NR/NR-PLA presented the enhancement of ductility of PLA/NR blends. To compare with PLA/NR/NR-MAH (80/20/5 (w/w)) in Figure 4.9e, the fractural surface of PLA/NR/NR-MAH blends showed the immiscibility between PLA and NR phases with the numerous cavities. The NR droplets in PLA/NR/NR-MAH (Figure 4.9e) was bigger than those in PLA/NR/NR-PLA (Figure 4.9d) at the same quantity of compatibilizer.

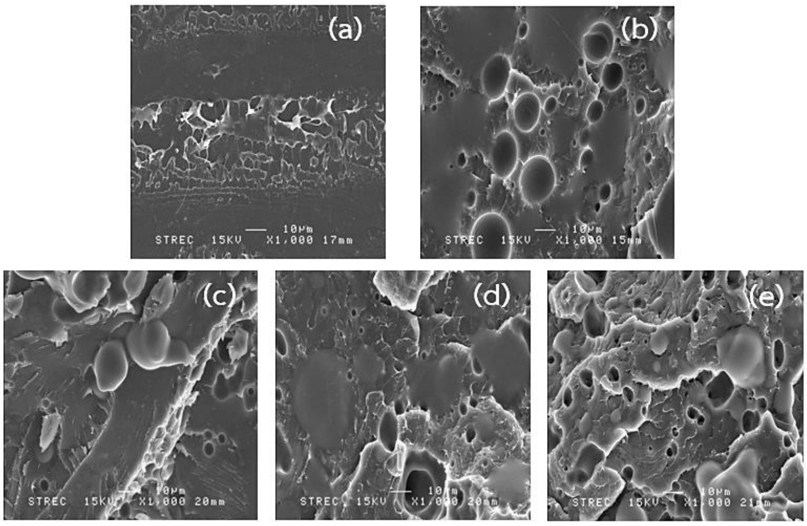


Figure 4.9 SEM images of fractural surface of specimens after impact testing: (a) PLA, (b) PLA/NR (80/20 (w/w)), (c) PLA/NR/NR-PLA (80/20/1 (w/w)), (d) PLA/NR/NR-PLA (80/20/5 (w/w)) (NR-PLA containing %grafted PLA = 36.7 wt%) and (e) PLA/NR/NR-MAH (80/20/5 (w/w)) (NR-MAH containing %grafted MAH = 2.66 wt%).

For the hardness of the PLA/NR blends, Figure 4.8d showed that the hardness of PLA/NR blends with NR with or without the addition of NR-MAH was not different from the neat PLA specimens. However, that addition of 1 – 5 wt% NR-PLA into the PLA/NR blends significantly decreased the hardness of samples. This implied that the NR-PLA could compatibilize the brittle PLA and soft NR phases inducing the lower hardness value of PLA/NR blends.

The effect of %grafted PLA in the NR-PLA on the mechanical properties of PLA/NR/NR-PLA blends (80/20/1 (w/w)) was shown in Table 4.2. The %grafted PLA was controlled by increasing the MAH content (5 – 20 phr) to obtain the %grafted PLA in the range of 27.5 - 46.4%. The results showed that the increase in the %grafted PLA in the NR-PLA from 27.5 to 36.7% increased the tensile strength and elongation at break from 23.3 to 26.8 MPa and from 5.7 to 7.5%, respectively. Above this point (%grafted PLA = 46.4 wt%), the tensile strength and elongation at break of the blends

Table 4.2 Effect of %grafted PLA in NR-PLA compatibilizer on the mechanical properties of PLA/NR/NR-PLA blends (80/20/1 (w/w))

Sample	%Grafted PLA in NR-PLA (wt%)	Tensile strength (MPa)	Elongation at break (%)	Izod impact strength (J/m)	Hardness (shore B)
PLA/NR/NR-PLA	27.5	23.3 (0.85)*	5.3 (0.45)	56.5 (3.7)	76.8 (4.3)
	32.3	22.9 (0.67)	5.1 (0.41)	55.9 (4.0)	82.4 (4.1)
	36.7	26.8 (0.82)	7.5 (0.60)	54.3 (4.4)	80.6 (2.1)
	46.4	22.8 (0.53)	6.5 (0.36)	56.0 (5.6)	81.2 (4.6)

*( ) standard deviation

was decreased because the enhancement of %grafted PLA increased the miscibility between PLA and NR-PLA phase than NR and NR-PLA phase. Hence, the heterogeneity of PLA/NR/NR-PLA was increased by the immiscibility from NR phase. Whereas, the increasing %grafted PLA in the NR-PLA insignificantly affect the Izod impact strength of the blends. For the hardness of PLA/NR/NR-PLA blends, it was found that the increasing %grafted PLA in the NR-PLA increased the hardness of PLA/NR/NR-PLA blends from 76.8 to 80 - 82 when the %grafted PLA in the NR-PLA was in the range of 32.3 – 46.4 wt% due to the higher amount of the brittle PLA segment in the graft product.

4.5 Thermal properties of modified NRs and PLA/NR blends with and without the addition of compatibilizers

4.5.1 Degradation temperature of NR before and after modification

The TG and DTG curves of NR, PLA, NR-MAH (grafted MAH content in NR-MAH = 2.26, 2.66 and 3.68 wt%) and NR-PLA (grafted PLA content in NR-PLA = 32.3, 36.7 and 46.4 wt%) was investigated by using thermo gravimetric analysis (TGA) technique. Figure 4.10 and Table 4.3 showed that the initial decomposition temperature (T_{id}) and maximum decomposition temperature (T_p) of NR were 358 and

387 °C, respectively which were slightly higher than those of PLA (T_{id} = 340 °C, T_p = 365 °C). Therefore, the NR had slight thermal stability than PLA.

To consider the decomposition temperature of NR-MAH (Figure 4.10a – 4.10b and Table 4.3), the NR-MAH was prepared by 0.3 phr BPO at 80 °C for 2 h. The increase in the %grafted MAH in the NR-MAH from 2.26 to 3.68 wt% slightly decreased T_{id} and T_p of NR to 350 – 352 °C and 380 °C, respectively. This implied that the modification of NR by using MAH might not affect the decomposition temperature of NR.

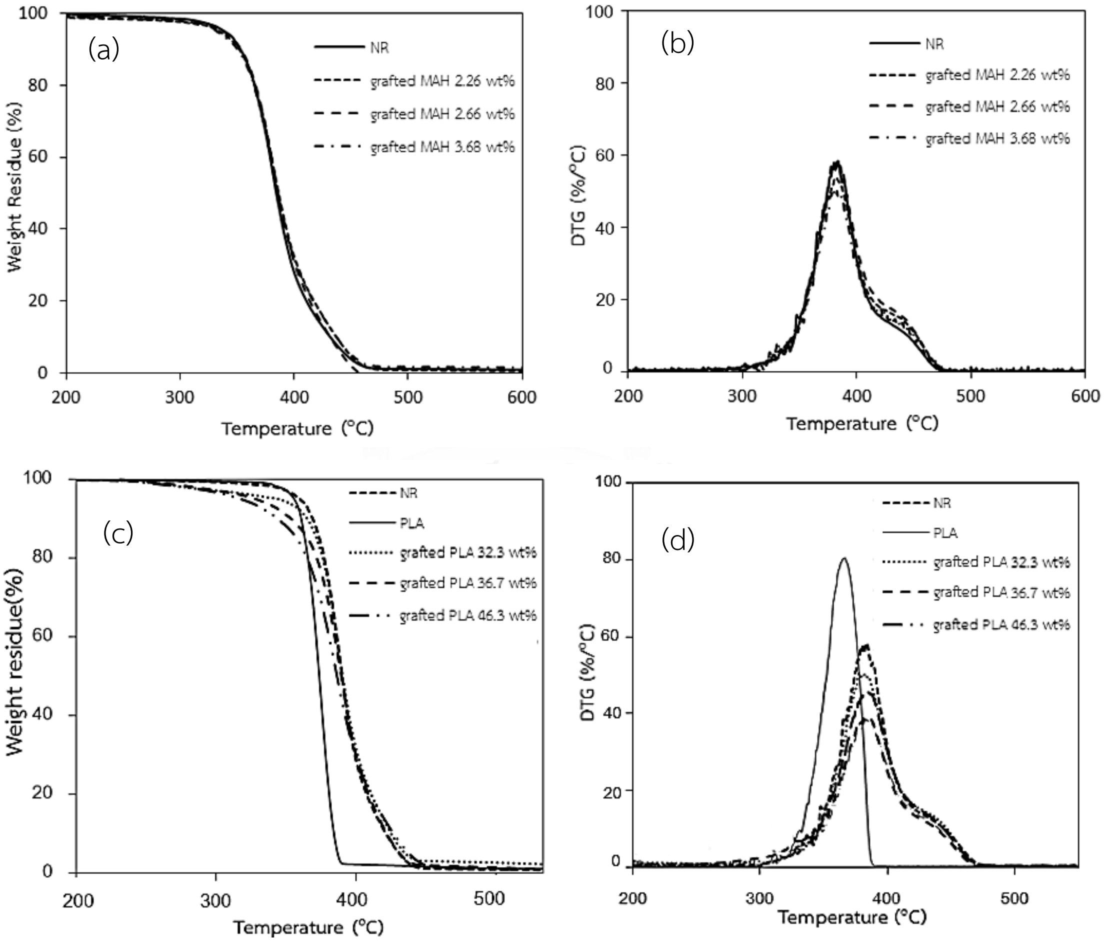


Figure 4.10 Thermograms of NR, PLA, NR-MAH and NR-PLA: (a) TG of NR-MAH, (b) DTG of NR-MAH, (c) TG of NR-PLA and (d) DTG of NR-PLA.

Table 4.3 Decomposition temperature of NR, PLA, NR-MAH and NR-PLA with various levels of grafting

Sample	%Grafted MAH (wt%)	T_{id}^1 (^{O}C)	T_p^2 (^{O}C)	Rate of thermal decomposition (%/min)
NR	-	358	387	58
PLA	-	340	365	80
NR-MAH[3]	2.26	350	380	57
	2.66	350	380	51
	3.68	349	380	51
Sample	**%Grafted PLA (wt%)**	**T_{id}^1 (^{O}C)**	**T_p^2 (^{O}C)**	**Rate of thermal decomposition (%/min)**
NR-PLA[4]	32.3	332	388	48
	36.7	330	388	45
	46.4	329	383	38

[1] Initial decomposition temperature [2] Maximum decomposition temperature

[3] Condition: MAH content = 10, 15 and 20 phr, [BPO] = 0.3 phr at 80 °C for 2 h.

[4] Condition: [MAH] = 10, 15 and 20 phr, [BPO] = 0.3 phr, PLA/NR-MAH wt = 2/1 (w/w), [DMAP] = 0.2 M at 140 °C for 16 h.

For the effect of %grafted PLA on the decomposition temperatures of NR-PLA as shown in Figure 4.10c – 4.10d and Table 4.3, the NR-PLA was synthesized following the central condition ([BPO] = 0.3 phr, PLA/NR-MAH = 2/1 (w/w), [DMAP] = 0.2 M at 140 °C for 16 h) with various MAH content (10-20 phr). The enhancement of %grafted PLA from 32.3 to 46.4 wt% decreased the both T_{id} and T_p values from 332 to 329 °C and from 388 to 383 °C, respectively. This could be explained by the condition of esterification step that it was operated at high reaction temperature (140 °C) and long reaction time (16 h) resulting in the chain scission of NR and reduction of the thermal stability of NR-PLA. Moreover, the DTG curve (Figure 4.10d) exhibited that the rate of thermal decomposition of PLA was decreased after grafting onto NR structure to produce NR-PLA. This indicated that PLA having high thermal decomposition rate had lower thermal stability than NR.

4.5.2 Glass transition temperature of NR before and after modification

DSC thermograms used to analyze the glass transition temperature (T_g), melting temperature (T_m) of PLA and NR before and after modification were shown Figure 4.11 and Table 4.4. For the neat PLA, the T_g and T_m were 65.9 and 155.7 °C, respectively; whereas, the T_g of NR was -62.3 °C without the melting point. When NR was grafted with MAH to produce NR-MAH containing %grafted MAH as 2.66 wt%, T_g of NR slightly increased to -59.9 °C reflecting the lower chain mobility and flexibility due to the interaction between polar group of anhydride in graft copolymer and the hydrogen bond of MA providing the rigid structure (Nakason, Kaesaman et al., 2004).

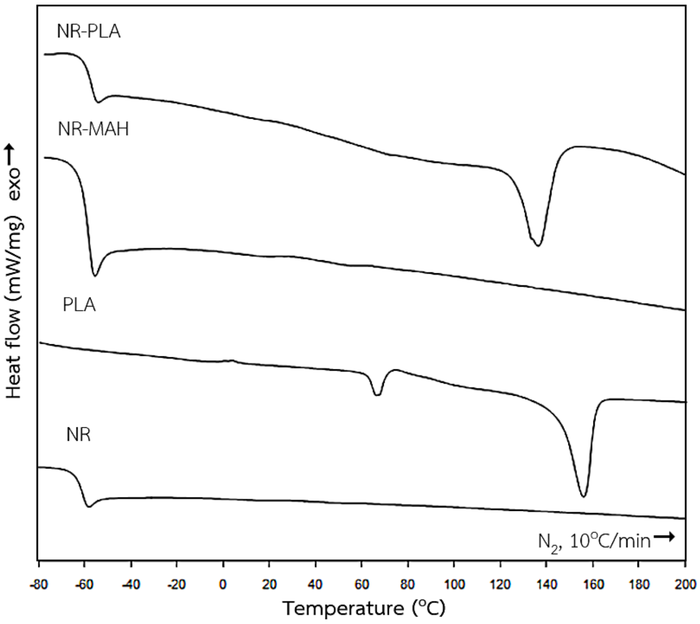


Figure 4.11 DSC thermograms of PLA and NR before and after modification with MAH (NR-MAH, %grafted MAH = 2.66 wt%) and esterification to produce NR-PLA (%grafted PLA = 36.7 wt%).

Table 4.4 Glass transition temperature and melting temperature of PLA and NR before and after modification

Sample	T_g[1] (^{O}C)	T_m[2] (^{O}C)
NR	-62.3	-
PLA	65.9	155.7
NR-MAH[3] (%grafted MAH = 2.66 wt%)	-59.9	-
NR-PLA[4] (%grafted PLA = 3.67 wt%)	-59.7	133.9

Testing condition: 40 – 800 ^{o}C, heating rate = 10 ^{o}C/min under N_2 atmosphere

[1] Glass transition temperature [2] Melting temperature

[3] Condition: [MAH] = 15 phr, [BPO] = 0.3 phr at 80 ^{o}C for 2 h.

[4] Condition: [MAH] = 15 phr, PLA/NR-MAH = 2/1 (w/w), [DMAP] = 0.2 M at 140 ^{o}C for 16 h.

After esterification of NR-MAH to synthesize the NR-PLA containing %grafted PLA as 36.7 wt%, it was observed that the T_g of NR-PLA was insignificantly different from that of NR-MAH. However, the T_m of NR-MAH was lower than that of PLA due to the effect of the soft NR segment to decrease the T_m of the PLA.

4.5.3 Degradation temperature of PLA/NR blends compatibilized by NR-MAH or NR-PLA

The thermogram of PLA/NR blends (80/20 (w/w)) with and without NR-PLA compatibilizer (grafted PLA content in NR-PLA = 36.7 wt%) was shown in Figure 4.12a – 4.12b and Table 4.5. It was found that the T_{id} (320 ^{o}C) and T_p (349 ^{o}C) of PLA/NR blend without NR-PLA compatibilizer was lower than those of NR (T_{id} = 358 ^{o}C, T_p = 387 ^{o}C) and PLA (T_{id} = 340 ^{o}C, T_p = 365 ^{o}C). Moreover, the thermal decomposition rate (DTG) of NR and PLA was higher than that of PLA/NR blend without NR-PLA compatibilizer as seen in Figure 4.12b. The thermal stability of PLA/NR blend was lower than that of NR and PLA. It was possible that the NR and PLA chains were degraded by heat and shear force during blending in the internal mixer.

To consider the PLA/NR blends compatibilizerd by 1.0, 3.0 and 5.0 wt% NR-PLA, the results indicated that the addition of NR-PLA compatibilizer increased the decomposition temperature of PLA/NR blends (T_{id} = 339 – 342 ^{o}C and T_p = 359 – 367 ^{o}C). This indicated that the NR-PLA could enhance the thermal stability of PLA/NR blends because NR-PLA increased the homogeneity between NR and PLA phases resulting in the higher T_{id} and T_p values. Moreover, the thermal decomposition rate of the PLA/NR blends containing NR-PLA at various content were similar to that of NR.

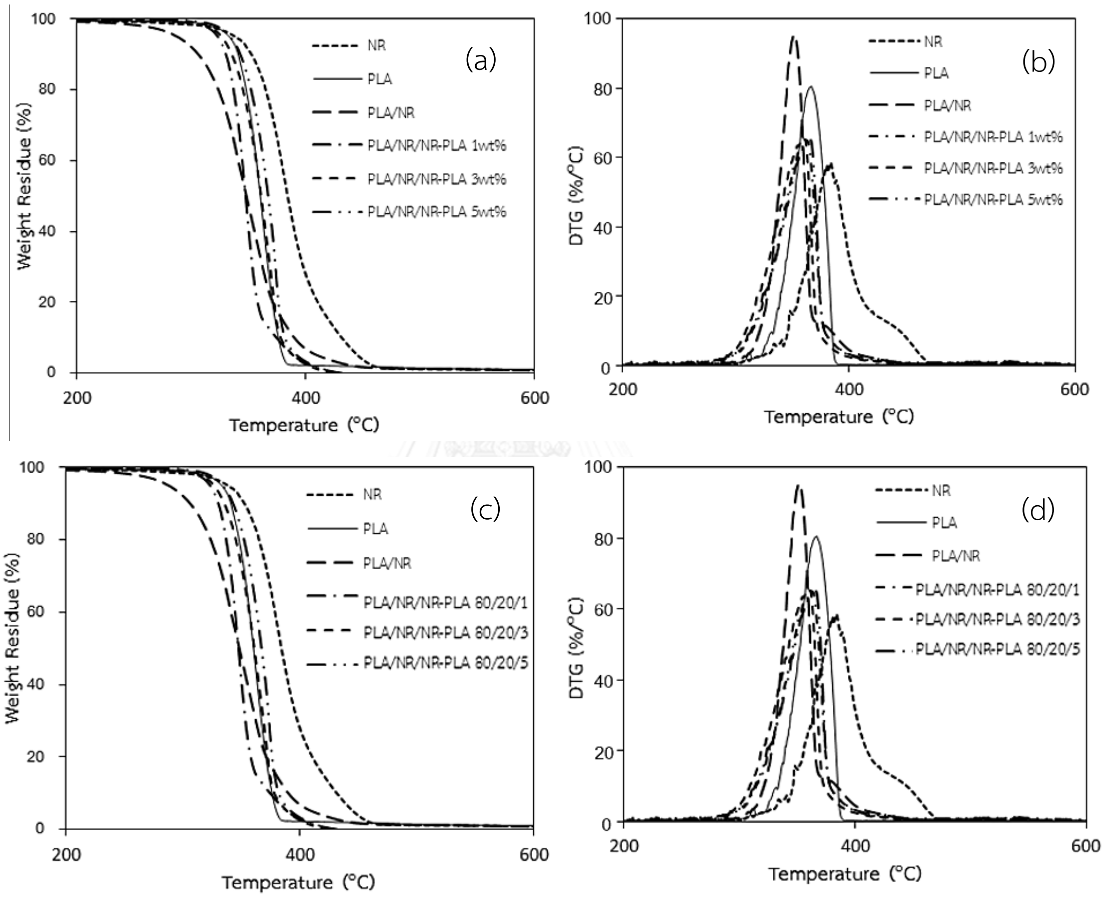


Figure 4.12 Thermograms of PLA/NR blends (80/20 (w/w)): (a) TG of PLA/NR/NR-PLA, (b) DTG of PLA/NR/NR-PLA, (c) TG of PLA/NR/NR-MAH and (d) DTG of PLA/NR/NR-MAH and PLA/NR/NR-PLA (%grafted MAH in NR-MAH = 2.66 wt% , %grafted PLA in NR-PLA = 36.7 wt%).

Table 4.5 The decomposition temperatures of PLA/NR blends (80/20 (w/w)) compatibilized by various NR-PLA contents

Sample	Blend composition	T_{id} (^{O}C)	T_p (^{O}C)	Rate of thermal decomposition (%/min)
PLA/NR	80/20	320	349	94
PLA/NR/NR-MAH[1]	80/20/1.0	324	350	53
PLA/NR/NR-PLA[2]	80/20/1.0	339	359	63
	80/20/3.0	342	363	65
	80/20/5.0	342	367	66

Testing condition: 40 – 800 °C, heating rate = 10 °C/min under N_2 atmosphere

[1] %grafted MAH in NR-MAH = 2.66 wt%, condition: [MAH] = 15 phr, [BPO] = 0.3 phr at 80°C for 2 h.

[2] %grafted PLA in NR-PLA = 36.72 wt%, condition: [MAH] = 15 phr, PLA/NR-MAH = 2/1 (w/w), [DMAP] = 0.2 M at 140 °C for 16 h.

To compare with the NR-MAH (grafted MAH = 2.66 wt%) as shown in Figure 4.11c and 4.11d, it was found that the T_{id} (324 °C) and T_p (350 °C) of PLA/NR/NR-MAH blends compatibilizer slightly increased from the PLA/NR blends without tha addition of compatibilizer.

4.5.4 Glass transition temperature of PLA/NR blends compatibilized by NR-MAH or NR-PLA

DSC thermograms of PLA/NR blends (80/20 (w/w)) with and without NR-PLA compatibilizer (%grafted PLA in NR-PLA = 36.7 wt%) were shown in Figure 4.13 and Table 4.6. To consider the PLA/NR blend without NR-PLA compatibilizer, it showed T_g of both NR (-67.9 °C) and PLA (66.6 °C) phases. The T_g of NR phase increased from -67.9 to -59.8 °C and T_g of PLA phase decreased from 66.6 to 61.5 °C when the amount of NR-PLA compatibilizer increased from 1.0 to 5.0 wt%. The shift of T_g for both phases indicated the enhancement of chemical compatibility between PLA and NR phases (Kumar, Mohanty et al., 2010). It was also found that and cold crystallization temperature (T_{cc}) peak appeared between T_g and T_m of PLA/NR blends at 112.7 °C. The previous research detected cold crystallization after quenching the melted sample. The kinetics of overall cold crystallization was separately controlled by the nucleation and crystal-growth regions. The increase in the temperature accelerate crystallization in the crystal-growth region, but it decreased the crystallization in the nucleation-controlled region (Yu, Liu et al., 2008). The T_{cc} of PLA in PLA/NR blends was explained by two aspects. Firstly, the rubber may acted as nucleating PLA during blending. Secondly, the molecular weight of PLA decreased after mixing in an internal mixer resulting in the chain scission of PLA that could be able to crystallize during heating above T_g (Jaratrotkamjorn, Khaokong et al., 2012, Pongtanayuta, Thongpina et al., 2013). For the PLA/NR blends with 0.5, 1.0, 3.0 and5.0 wt% NR-PLA compatibilizer, it was observed that the increasing NR-PLA

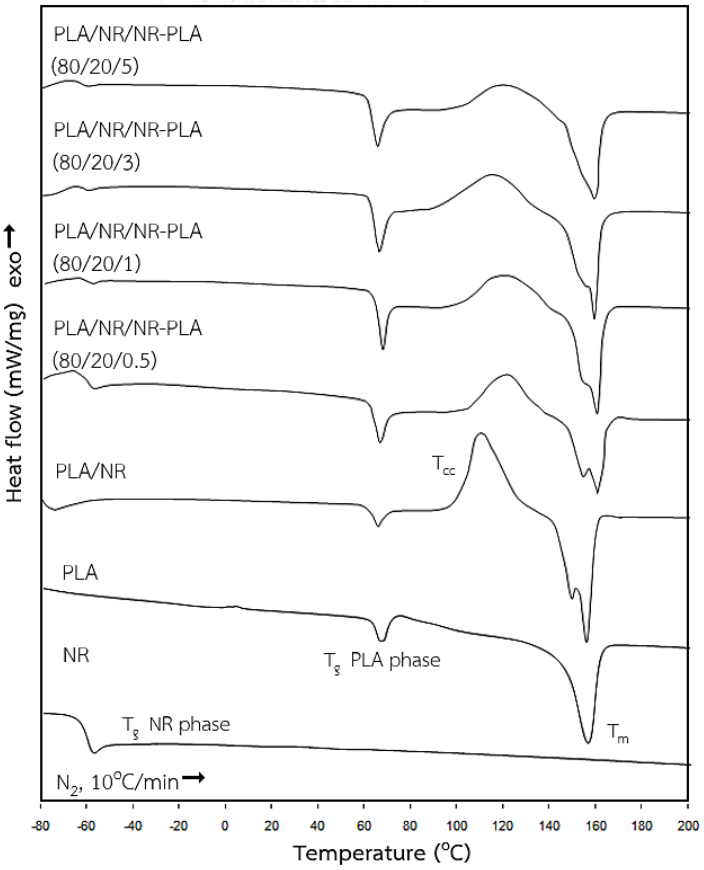


Figure 4.13 DSC Thermograms of PLA/NR blends (80/20 (w/w)) with and without NR-PLA compatibilizer (%grafted PLA = 36.72 wt%).

Table 4.6 Thermal properties of PLA/NR blends with and without NR-PLA compatibilizer

Sample	Blend composition	T_g[1] ($^{\circ}$C)		T_{cc}[2] ($^{\circ}$C)	T_m[3] ($^{\circ}$C)
		NR phase	PLA phase		
PLA/NR	80/20	-67.9	66.6	112.7	157.5
PLA/NR/NR-PLA[4]	80/20/0.5	-61.6	63.7	122.3	159.3
	80/20/1.0	-61.7	62.3	113.5	157.5
	80/20/3.0	-61.0	63.4	114.5	157.5
	80/20/5.0	-59.8	61.5	118.7	157.7

Testing condition: 40 – 800 $^{\circ}$C, heating rate = 10 $^{\circ}$C/min under N_2 atmosphere

[1] Glass transition temperature [2] Crystallization temperature [3] Melting temperature

[4] grafted PLA in NR-PLA = 36.72 wt%, condition: [MAH] = 15 phr, [BPO] = 0.3 phr, PLA/NR-MAH ratio = 2/1 wt%, [DMAP] = 0.2 M at 140 $^{\circ}$C for 16 h.

compatibilizer decreased T_g of PLA phase in the PLA/NR blends from 66.6 $^{\circ}$C (at 0 wt% NR-PLA) to 61.5 $^{\circ}$C (at 5 wt% NR-PLA) and also decreased the cold crystallinity of blend according to the enhancement of compatibility and chain mobility between PLA and NR by the NR-PLA compatiblizer (García, Lamannac et al., 2012). Furthermore, the T_m of PLA/NR/NR-PLA blends did not significantly change when the amount of NR-PLA compatibilizer increased (157-159 $^{\circ}$C) and also the double peaks of T_m representing the two crystalline structures induced from NR, but the crosslink from NR did not significantly affect the thermal properties of blends. The double endothermic also showed that the less perfect crystals had sufficient time to melt then reorganize into crystal with higher structure perfection by remelting again at high temperature (Kumar, Mohanty et al., 2010, García, Lamannac et al., 2012). The bimodal melting peak was slightly disappeared by the addition of the NR-PLA due to the combination of the crystallinity of PLA and NR.

4.6 Degradation of PLA/NR blends

The study of biodegradation of PLA and PLA/NR/NR-PLA blends (80/20 (w/w)) with and without the addition of NR-PLA (grafted PLA content in NR-PLA = 36.7 wt%) was investigated by enzymatic degradation and hydrolysis processes.

4.6.1 Enzymatic degradation

The enzymatic degradation of PLA and PLA/NR/NR-PLA blends with and without NR-PLA compatibilizer was shown in Figure 4.14a and Table 4.7. The experiment was prepared by dissolving enzyme Proteinase K with sodium azide and Tris-HCl buffer solution with controlled pH at 8.6 and 37 °C. In the end of enzymatic degradation period, it was found that the degradation rates of PLA/NR blends without NR-PLA compatibilizer (0.34%/day) and the PLA/NR blends containing NR-PLA compatibilizer (0.32 – 0.35%/day) were less than that of PLA (0.36%/day) because the neat PLA sample did not have NR phase to interrupt the enzymatic degradation. However, the %weight loss was slightly decreased with increasing the NR-PLA compatibilizer from 0.35 – 0.32%/day due to the NR-PLA compatibilizer had the complex structure than PLA including the long chain NR molecules that could not digested by enzyme Proteinase K. This implied that the decreasing of enzyme Proteinase K efficiency was inhibited by the increasing of NR-PLA compatibilizer.

4.6.2 Hydrolysis

The hydrolysis degradation of PLA and PLA/NR blends (80/20 (w/w)) with and without NR-PLA compatibilizer was shown in Figure 4.14b. The hydrolysis experiment was conducted in the distilled water with constant temperature at 58 °C. At first week of hydrolysis, it was observed that weight loss of neat PLA was slower than that of PLA/NR blends. However, the %weight loss of neat PLA was significantly increased to 39.9% (1.07%/day) which was higher than that of PLA/NR blends (0.90 – 0.93%/day). For the PLA/NR blends with the NR-PLA compatibilizer, the increase in the

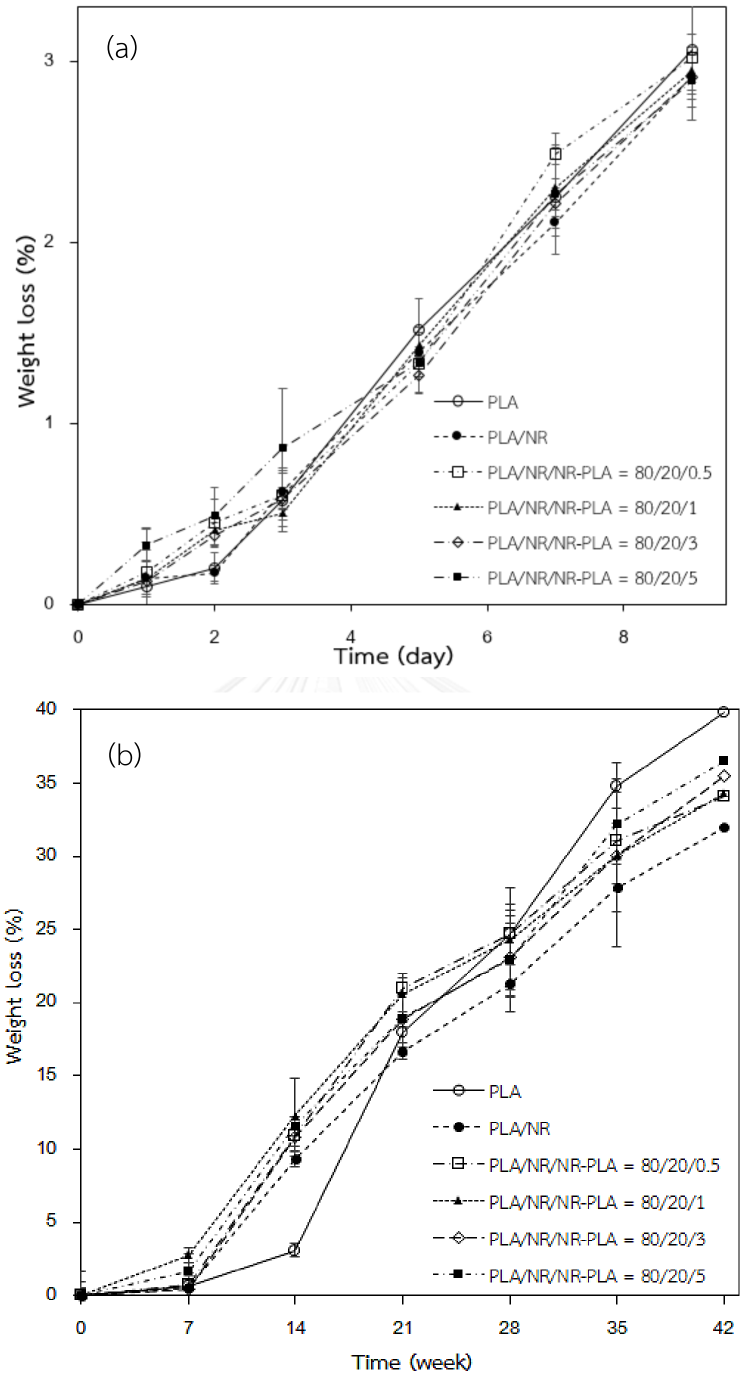


Figure 4.14 The degradation of PLA and PLA/NR/NR-PLA blend with and without NR-PLA compatibilizer: (a) enzymatic degradation and (b) hydrolysis (%grafted PLA in NR-PLA = 36.7 wt%).

Table 4.7 Degradation rate of PLA and PLA/NR blends with and without NR-PLA compatibilizer

Sample	Blend composition	dw/dt (%weight loss/day)	
	(w/w)	Enzymatic process[1]	Hydrolysis process[2]
PLA	-	0.36 (0.14)[4]	1.07 (0.61)
PLA/NR	80/20	0.34 (0.05)	0.83 (0.80)
PLA/NR/NR-PLA[3]	80/20/0.5	0.35 (0.11)	0.90 (1.18)
	80/20/1	0.35 (0.11)	0.87 (1.49)
	80/20/3	0.34 (0.10)	0.91 (0.97)
	80/20/5	0.32 (0.18)	0.93 (1.24)

[1] Condition: square shape with a dimension of 10×5×1 mm^3 in solution of 0.5 mg Proteinase K and 0.5 mg sodium azide in 2.5 mL Tris-HCl buffer with contstant pH at 8.6 and 37 °C

[2] Condition: square shape with a dimension of 10×5×1 mm^3 in distilled water with constant temperature at 58 °C

[3] %Grafted PLA in NR-PLA = 36.7 wt%, condition: [MAH] = 15 phr, [BPO] = 0.3 phr, PLA/NR-MAH ratio = 2/1 wt%, [DMAP] = 0.2 M at 140 °C for 16 h.

[4] standard deviation

NR-PLA content increased the %weight loss of samples. The PLA/NR blends containing 5 wt% NR-PLA had the highest %weight loss of 36.5%. It could be explained that the addition of NR-PLA provided higher compatibility between PLA and NR phases. The good dispersion of NR increased the water absorption of the blends to increase the hydrolysis rate (Huang, Zhang et al., 2013).

CHAPTER 5

CONCLUSIONS

5.1 Conclusions

This research work aimed to synthesize the natural rubber (NR) grafted with poly(lactic acid) (PLA) (NR-PLA) for using as a compatibilizer to enhance the compatibility of PLA/NR blends and improve the brittleness of PLA. NR-PLA compatibilizer was prepared by two steps. Firstly, NR was functionalized by various maleic anhydride (MAH) contents to produce NR grafted MAH (NR-MAH) having higher polarity than NR. Then, NR-MAH was grafted with PLA via esterification using 4-dimethyaminopyridine (DMAP) as a catalyst. The chemical structures of the NR-MAH and NR-PLA were examined by using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy. The quantities of the grafted MAH in the NR-MAH structure were determined by titration of the acidic group derived from the anhydride function. The parameters for grafting PLA onto NR-MAH such as DMAP content, NR/PLA wt ratio, reaction time and temperature were investigated. The morphology, mechanical and thermal properties of PLA/NR blends with and without the addition of NR-PLA compatibilizer were studied. Moreover, the degradation of PLA/NR blends with and without the addition of NR-PLA was compared to the neat PLA.

5.1.1 Structure characterization of NR-MAH and NR-PLA

The structural characterization of the NR-MAH and NR-PLA was confirmed by ATR-FTIR spectroscopy. The ATR-FTIR peaks of NR-MAH showed the peak intensity at 1,849 and 1,782 cm-1 attributed to C=O stretching vibration of succinic anhydride ring of MAH grafted on the NR structure. For ATR-FTIR peaks of NR-PLA, it was observed that the higher peak intensity of C=O bond at 1,748 cm-1 in the NR-PLA structure reflecting the carbonyl group of the PLA grafted on the NR-MAH. 1H NMR spectrum of NR-MAH showed the signal at 3.49 ppm generated from –CH in the methylene protons of anhydride group. For the NR-PLA structure, it exhibited the new peaks at ca. 5.17 and 1.59 ppm attributed to the methyne proton and methyl protons of grafted PLA on the NR-MAH, respectively.

5.1.2 Effect of reaction parameters on grafted PLA and gel content

The effect of MAH loading on %grafted MAH indicated that the increase in the MAH contents (5 – 20 phr) led the higher level of grafted MAH in the NR-MAH (%grafted MAH = 1.63 – 3.68 wt%) and it also induced the higher grafted PLA content in the NR-PLA (%grafted PLA = 27.5 - 46.4 wt%). For the effect of the grafted MAH content on the gel formation in the NR-MAH, it was found that the gel content in the NR-MAH was in the range of 72 - 75%, which was higher than that in NR (11.7%). The gel content in the NR-PLA slightly decreased from 71.8 to 68.1% when the amount of grafted MAH increased from 1.63 to 3.68 wt%. The suitable condition to increase the %grafted PLA was 1/1 (w/w) PLA/NR-MAH and 0.05 M [DMAP] at 140 ^{o}C for 16 h.

5.1.3 Mechanical properties and morphology of PLA/NR/NR-PLA blends

The addition of unmodified NR (3 – 10 wt%) in PLA blends increased the Izod impact strength of PLA/NR blends (34.2 – 42.7 J/m) and slightly increased the hardness of the blends due to the soft segment of NR. However, the tensile strength and elongation at break of the blends decreased when NR content increased. This was resulted from the immiscibility and phase separation between NR and PLA. The addition of NR-MAH (%grafted MAH = 2.66 wt%) decreased almost of the mechanical properties of the blends.

The effect of NR-PLA (%grafted PLA = 36.7 wt%) and NR-MAH (% grafted MAH = 2.66 wt%) used as the compatibilizers on the mechanical properties of the PLA/NR blends (80/20 (w/w)) was also investigated. For the tensile strength and elongation at break, it was found that the addition of NR-PLA and NR-MAH (0.5 – 5 wt%) decreased tensile strength and elongation at break of the blends. However, it was observed that the Izod impact strength of PLA (28.8 J/m) was significantly increased to 62.7 J/m when the PLA was mixed with NR and NR-PLA at 80/20/5 (w/w) PLA/NR/NR-PLA. At the same composition, the use of NR-MAH was provided the blends with lower Izod impact strength (42.6 J/m). From the scaning electron micrograph (SEM), it was found that the NR-PLA compatibilizer reduced the size of NR droplets in the blends and increased the NR phase distribution the NR-MAH.

5.1.4 Thermal properties

The increase in the grafted MAH content (5-20 phr) in the NR-MAH from 1.63 to 3.68 wt% decreased the initial decomposition temperature (T_{id}) to 349 – 352 ^{o}C and the maximum decomposition temperature (T_p) to 380 – 383 ^{o}C. The increase of %PLA grafted PLA (27.5 - 46.4 wt%) increased the decomposition temperature of NR-PLA (T_{id} from 329-350 ^{o}C and T_p from 383-389 ^{o}C) and it could be observed that the NR-PLA had higher T_p (365 ^{o}C) with lower rate of thermal decomposition than PLA. It could be explained by the condition of esterification step that it was operated under high reaction temperature at 140 ^{o}C and long reaction time (16 h) resulting in the chain scission of NR and decreased the thermal stability of NR-PLA. The glass transition temperature (T_g = -59.9 ^{o}C) of NR-PLA (%grafted PLA = 36.7 wt%) was insignificantly different from that of NR-MAH (%grafted MAH = 2.66 wt%) (T_g = -59.7 ^{o}C). However, the T_m of NR-MAH was lower than that of PLA resulting from the effect of the soft NR segment to decrease the T_m of the PLA.

The addition of NR-PLA compatibilizer (0.5 to 5.0 wt%) in the PLA/NR blends (80/20 (w/w)) increased the decomposition temperature of PLA/NR blends (T_{id} = 320 – 342 ^{o}C and T_p = 349 – 367 ^{o}C). These were between NR and PLA decomposition temperatures and they were higher 20 ^{o}C above PLA/NR blends without NR-PLA compatibilizer. It was shown that the thermal stability of PLA/NR/NR-PLA blends was improved by the chemical compatibilization of NR-PLA because of the increasing homogeneity of the PLA/NR/NR-PLA blends to increase the T_{id} and T_p. It was also also observed that the T_g of PLA and NR peaks was shifted together when NR-PLA was added reflecting the higher compatibility between PLA and NR phases.

5.1.5 Biodegradable of PLA and PLA/NR/NR-PLA blends

The enzymatic degradation of PLA and PLA/NR blends (80/20 (w/w)) with and without NR-PLA compatibilizer was examined by enzyme Proteinase K with sodium azide and Tris-HCl buffer solution for controlled pH at 8.6 and 37 °C. The result showed that in the end of enzymatic degradation period, the degradation rates of PLA/NR blends (0.34%/day) and the PLA/NR/NR-PLA (0.32 – 0.35%/day) were less than that of PLA (0.36%/day).

The hydrolysis degradation of PLA and PLA/NR blends (80/20 (w/w)) with and without NR-PLA compatibilizer was proceeded in the distilled water with a constant temperature at 58 °C. It was observed that the %weight loss of the neat PLA was significantly increased to 39.9% (1.07%/day) which was higher than that of PLA/NR blends (0.90 – 0.93%/day). For the PLA/NR blends with NR-PLA compatibilizer, the increase in the NR-PLA content increased the %weight loss of samples. The PLA/NR blends containing 5 wt% NR-PLA had the highest %weight lost at 36.5%. It could be explained that the addition of NR-PLA provided the higher compatibility between PLA and NR phases. The good dispersion of NR increased the water absorption in blends the increase the hydrolysis rate.

5.2 Recommendations

1. The effect of temperature and rotor speed of mixing on PLA/NR/NR-PLA with mechanical properties and morphology should be investigated.
2. The other kinds of plastic forming should be studied such as film blowing process.

REFERENCES

Abacha, N. and Fellahi, S. (2005). "Synthesis of polypropylene-*graft*-maleic anhydride compatibilizer and evaluation of nylon 6/polypropylene blend properties." Polymer International **54**: 909-916.

Arayapranee, W., Prasassarakich, P. and Rempel, G. L. (2004). "Blends of poly(vinyl chloride) (PVC)/natural rubber-*g*-(styrene-co-methyl methacrylate) for improved impact resistance of PVC." Journal of Applied Polymer Science **93**: 1666-1672.

Averous, L. (2008). Polylactic Acid: Synthesis, Properties and Applications. Monomers, Polymers and Composites from Renewable Resources. M. N. Belgacem and A. Gandini. London, Springer-Verlag.

Bitinis, N., Verdejo, R., Maya, E. M., Espuche, E., Cassagnau, P. and Lopez-Manchado, M. A. (2012). "Physicochemical properties of organoclay filled polylactic acid/natural rubber blend bionanocomposites." Composites Science and Technology **72**: 305-313.

Bitinis, N., Verdejoa, R., Cassagnau, P. and Lopez-Manchado, M. A. (2011). "Structure and properties of polylactide/natural rubber blends." Materials Chemistry and Physics **129**: 823-831.

Datta, R. and Henry, M. (2006). "Review Lactic acid: recent advances in products, processes and technologies – a review." Journal of Chemical Technology and Biotechnology **81**: 1119-1129.

Dorgan, J. R., Lehermeier, H. and Mang, M. (2000). "Thermal and rheological properties of commercial-grade poly(lactic acid)s." Journal of Polymers and the Environment **8**(1): 1-9.

Ebeling, W., Hennrich, N., Klockow, M., Metz, H., Orth, H. D. and Lang, H. (1974). "Proteinase K from *Tritirachium album Limber*." European Journal of Biochemistry **47**: 91-97.

García, N. L., Lamannac, M., D'Accorso, N., Dufresne, A., Arangurene, M. and Goyanes, S. (2012). "Biodegradable materials from grafting of modified PLA onto starch nanocrystals." Polymer Degradation and Stability **97**: 2021-2026.

Gramlich, W. M., Robertson, M. L. and Hillmyer, M. A. (2010). "Reactive compatibilization ofpoly(L-lactide) and conjugated soybean oil." Macromolecules **43**: 2313-2321.

Haper, C. A. (1975). Handbook of plastics and elastomers. New York, McGraw-Hill.

Hassouna, F., Raquez, J.-M., Addiego, F., Dubois, P., Toniazzo, V. and Ruch, D. (2011). "New approach on the development of plasticized polylactide (PLA): Grafting of poly(ethylene glycol) (PEG) via reactive extrusion." European Polymer Journal **47**: 2134-2144.

Henton, D. E., Gruber, P., Lunt, J. and Randall, J. (2005). Polylactic acid technology. Natural Fibers, Biopolymers, and Biocomposites. M. K. Mohanty, M. Misra and L. T. Drzal. Boca Raton, Taylor & Francis

Ho, C.-H., Wang, C.-H., Lin, C.-I. and Lee, Y.-D. (2008). "Synthesis and characterization of TPO–PLA copolymer and its behavior as compatibilizer for PLA/TPO blends." Polymer **49**: 3902-3910.

Huang, Y., Zhang, C., Pan, Y., Zhou, Y., Jiang, L. and Dan, Y. (2013). "Effect of NR on the hydrolytic degradation of PLA." Polymer Degradation and Stability **98**: 943-950.

Jaratrotkamjorn, R., Khaokong, C. and Tanrattanakul, V. (2012). "Toughness enhancement of poly(lactic acid) by melt blending with natural rubber." Journal of Applied Polymer Science **124**: 5027-5036.

Koning, C., Duin, M. V., Pagnoulle, C. and Jerome, R. (1998). "Strategies for compatibilization of polymer blends." Progress Polymer Science **23**: 707-757.

Kumar, M., Mohanty, S., Nayak, S. K. and Parvaiz, M. R. (2010). "Effect of glycidyl methacrylate (GMA) on the thermal, mechanical and morphological property of biodegradable PLA/PBAT blend and its nanocomposites." Bioresource Technology **101**: 8406-8415.

Li, S., Tenon, M., Garrenu, H., Braud, C. and Vert, M. (2000). "Enzymatic degradation of sterocopolymers derived from L-, DL- and meso-lactides." Polymer Degradation and Stability **67**: 85-90.

Ma, P., Hristova-Bogaerds, D. G., Goossens, J. G. P., Spoelstra, A. B., Zhang, Y. and Lemstra, P. J. (2012). "Toughening of poly(lactic acid) by ethylene-co-vinyl acetate copolymer with different vinyl acetate contents." European Polymer Journal **48**: 146-156.

Mark, J. E., Erman, B. and Eirich, F. R. (1994). Science and technology of rubber.

Martin, O., Schwach, E., Avérous, L. and Couturier, Y. (2001). "Properties of biodegradable multilayer films based on plasticized wheat starch." Starch/Stärke **53**: 372-380.

Mathew, A. P., Oksman, K. and Sain, M. (2005). "Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC)." **97**: 2014-2025.

Miyauchi, K. and Saito, K. (2012). "^{1}H NMR assignment of oligomeric grafts of maleic anhydride-grafted polyolefin." Magnetic Resonance in Chemistry **50**: 580-583.

Nakason, C., Kaesaman, A. and Supasanthitikul, P. (2004). "The grafting of maleic anhydride onto natural rubber." Polymer Testing **23**: 35-41.

Nakason, C., Saiwaree, S., Tatun, S. and Kaesaman, A. (2006). "Rheological, thermal and morphological properties of maleated natural rubber and its reactive blending with poly(methyl methacrylate)." Polymer Testing **25**: 656-667.

Ohkita, T. and Lee, S.-H. (2006). "Thermal degradation and biodegradability of poly (lactic acid)/corn starch biocomposites." Journal of Applied Polymer Science **100**: 3009-3017.

Oliveira, P. C. d., Oliveira, A. M. d., Garcia, A., Barboza, J. C. d. S., Zavaglia, C. A. d. C. and Santos, A. M. d. (2005). "Modification of natural rubber: A study by ^{1}H NMR to assess the degree of graftization of polyDMAEMA or polyMMA onto rubber particles under latex form in the presence of a redox couple initiator." European Polymer Journal **41**: 1883-1892.

Oommen, Z., Groeninckx, G. and Thomas, S. (2000). "Dynamic mechanical and thermal properties of physically compatibilized natural rubber/poly(methyl methacrylate) blends by the addition of natural rubber-*graft*-poly(methyl methacrylate)." Journal of Polymer Science: Part B: Polymer Physics **38**: 525-536.

Pongtanayuta, K., Thongpina, C. and Santawitee, O. (2013). "The effect of rubber on morphology, thermal properties and mechanical properties of PLA/NR and PLA/ENR blends." Energy Procedia **34**: 888-897.

Rasal, R. M., Janorkar, A. V. and Hirt, D. E. (2010). "Poly(lactic acid) modification." Progress Polymer Science **35**: 338-356.

Schmidt, S. C. and Hillmyer, M. A. (1999). "Synthesis and characterization of model polyisoprene-polylactide diblock copolymers." Macromolecules **32**: 4794-4801.

Thiraphattaraphun, L., Kiatkamjornwong, S., Prasassarakich, P. and Damronglerd, S. (2001). "Natural rubber-*graft*-methyl methacrylate/poly(methyl methacrylate) blends." Journal of Applied Polymer Science **81**: 428-439.

Tsuji, H. and Ikada, Y. (2009). Stereocomplexation Between Enantiomeric POly(lactide)s. Biodegradable polymer blends and composites from renewable resources. L. Yu.

Vink, E. T. H., Rabago, K. R., Glassner, D. A. and Gruber, P. R. (2003). "Applications of life cycle assessment to NatureWorks^{TM} polylactide (PLA) production." Polymer Degradation and Stability **80**: 403-419.

Xiao, L., Wang, B., Yang, G. and Gauthier, M. (2012). Poly(lactic acid)-based biomaterials: Synthesis, modification and applications. Biomedical Science, Engineering and Technology. D. N. Ghista.

Xu, S., Held, I., Kempf, B., Mayr, H., Steglich, W. and Zipse, H. (2005). "The DMAP-catalyzed acetylation of alcohols—A mechanistic study (DMAP=4-(dimethylamino)pyridine)." Chemistry - A European Journal **11**: 4751-4757.

Yamashita, K., Kikkawa, Y., Kurokawa, K. and Doi, Y. (2005). "Enzymatic degradation of poly(L-lactide) film by Proteinase K: Quartz crystal microbalance and atomic force microscopy study." Biomacromolecules **6**(2): 850-857.

Yu, L., Liu, H., Dean, K. and Chen, L. (2008). "Cold crystallization and postmelting crystallization of PLA plasticized by compressed carbon dioxide." Journal of Polymer Science Part B: Polymer Physics **46**(23): 2630-2636.

Zhang, M. and Duhamel, J. (2004). "Characterization by fluorescence of the distribution of maleic anhydride grafted onto ethylene-propylene copolymers." Macromolecules **37**: 1877-1890.

APPENDIX

APPENDIX A

CALCULATION OF %GRAFTED MAH AND GEL CONTENT IN NR-MAH

The %grafted MAH contents in NR-MAH was calculated by the following expression:

$$\text{Grafted MAH (wt\%)} = \frac{(V_0 - V_1)N}{2w} \times 98 \times 100\%$$

Where V_0, V_1 = volumes of KOH in a blank and a sample (L)

= 0.01075 L

V_1 = volumes of KOH in a sample (L)

= 0.00465 L

N = KOH concentration (M)

= 0.028 M

w = sample weight (g)

= 0.52 g

$$\text{Grafted MAH (wt\%)} = \frac{(0.01075 - 0.00465)0.028}{2(0.52)} \times 98 \times 100\%$$

$$= 1.63 \text{ wt\%}$$

Table A-1 The %grafted MAH contents in NR-MAH

MAH loading (phr)	%Grafted MAH content (wt%)			
	1	2	Avg.	SD
5	1.63	1.64	1.63	0.01
10	2.08	2.37	2.23	0.21
15	2.67	2.66	2.66	0.00
20	3.36	4.00	3.68	0.45

Condition: [BPO] = 0.3 phr at 80 °C for 2 h.

The gel contents in NR-MAH and NR-PLA was calculated by following expression (Nakason, Kaesaman et al., 2004):

$$A \times 4 = B$$

$$\text{Gel (\%)} = \left(\frac{C - B}{C}\right) \times 100$$

where A = average mass of the dry sol from 25 mL solution (g),
= 0.0287 g
B = mass of the total dry sol (g)
C = mass of the original sample (g)
= 0.3995 g

$$0.0287 \times 4 = 0.1148$$

$$= \frac{0.3995 - 0.1148}{0.3995} \times 100 = 71.26\ \%$$

Table A-2 Gel contents in NR-MAH and NR-PLA

Sample	MAH loading (phr)	Gel content (%)				
		1	2	3	Avg.	SD
NR	-	10.79	13.28	10.94	11.67	1.39
NR-MAH[1]	5	71.26	71.87	73.77	72.30	1.31
	10	75.36	74.86	75.11	75.11	0.25
	15	74.43	74.53	73.34	74.10	0.66
	20	69.75	72.74	73.14	71.88	1.86
NR-PLA[2]	5	71.42	72.31	71.92	71.88	0.45
	10	71.07	72.26	72.16	71.83	0.66
	15	70.35	69.37	71.39	70.37	1.01
	20	68.97	68.08	67.39	68.14	0.79

[1] Condition: [BPO] = 0.3 phr at 80 °C for 2 h.

[2] Condition: M[BPO] = 0.3 phr, PLA/NR-MAH wt = 2/1 (w/w), [DMAP] = 0.2 M at 140 °C for 16 h.

APPENDIX B

CALCULATION OF %GRAFTED PLA IN NR-PLA

The %grafted PLA in NR-PLA was calculated by the following expression:

$$\text{Grafted PLA (\%wt)} = \frac{W_{after}}{W_{before}} \times 100$$

where W_{before} = weight of NR-PLA before soxhlet extraction by 0.38 M NaOH in methanol.

= 4.47 g

W_{after} = weight of NR-PLA after soxhlet extraction by 0.38 M NaOH in methanol.

= 1.23 g

$$\text{Grafted PLA (\%wt)} = \frac{1.23}{4.47} \times 100$$

$$= 27.48\%$$

Table B-1 The effect of %grafted MAH in esterification of PLA on %grafted PLA

%grafted MAH in NR-MAH (wt%)	%Grafted PLA in NR-PLA (wt%)			
	1	2	Avg.	SD
1.63	26.00	28.32	27.16	1.64
2.23	32.29	33.04	32.67	0.53
2.66	36.72	36.50	36.61	0.16
3.68	46.36	42.23	44.30	2.92

Condition: MAH loading 5, 10, 15 and 20 phr, [BPO] = 0.3 phr, PLA/NR-MAH wt = 2/1 (w/w), [DMAP] = 0.2 M at 140 °C for 16 h.

Table B-2 The effect of PLA/NR-MAH ratio (w/w) in esterification PLA onto NR-MAH on grafted PLA content

PLA/NR-MAH ratio (w/w)	%Grafted PLA in NR-PLA (wt%)			
	1	2	Avg.	SD
0.5	34.14	33.85	34.00	0.21
1	49.85	52.31	51.08	1.74
2	41.23	45.53	43.38	3.04
3	32.75	37.88	35.32	3.63
4	25.37	33.95	29.66	6.07
5	23.28	31.95	27.62	6.13

Condition: MAH loading 15 phr, [BPO] = 0.3 phr, [DMAP] = 0.2 M at 140 °C for 16 h.

Table B-3 The effect of DMAP concentration in esterification PLA onto NR-MAH on grafted PLA content

DMAP concentration (M)	%Grafted PLA in NR-PLA (wt%)			
	1	2	Avg.	SD
0	2.36	-	2.36	-
0.05	68.31	65.34	66.83	2.10
0.1	46.82	44.31	45.57	1.77
0.2	36.72	-	36.72	-
0.4	34.43	35.68	35.05	0.88
0.8	30.73	34.38	32.56	2.59

Condition: MAH loading 15 phr, [BPO] = 0.3 phr, PLA/NR-MAH wt = 2/1 (w/w), at 140 °C for 16 h.

Table B-4 The effect of reaction time in esterification of PLA on %grafted PLA

Time (h)	%Grafted PLA in NR-PLA (wt%)			
	1	2	Avg.	SD
8	24.49	22.23	23.36	1.60
12	34.26	33.83	34.04	0.30
16	36.72	38.62	37.15	1.04
20	35.92	-	35.92	-
24	36.30	-	36.30	-

Condition: MAH loading 15 phr, [BPO] = 0.3 phr, PLA/NR-MAH wt = 2/1 (w/w), [DMAP] = 0.2 M at 140 °C

Table B-5 The effect of reaction temperature in esterification of PLA on %grafted PLA

Temperature (°C)	%Grafted PLA in NR-PLA (wt%)			
	1	2	Avg.	SD
120	8.33	12.32	10.32	2.82
130	19.43	-	19.43	-
140	33.00	31.21	32.11	1.26
150	30.82	-	30.82	-
160	30.92	34.65	32.79	2.64

Condition: MAH loading 5, 10, 15 and 20 phr, [BPO] = 0.3 phr, PLA/NR-MAH wt = 2/1 (w/w), [DMAP] = 0.2 M for 16 h.

APPENDIX C

DATA OF MECHANICAL PROPERTIES OF BLENDS

Table C-1 Data of mechanical properties of blends

Sample	Blend composition (by wt)	Tensile strength (MPa)	Elongation at break (%)	Izod impact strength (J/m)	Hardness (shore B)
PLA	100	56.1 ± 1.8[3]	11.2 ± 0.6	28.85 ± 2.57	88.1 ± 2.01
PLA/NR	100/3	44.1 ± 0.6	10.0 ± 0.2	34.16 ± 4.00	84.3 ± 5.85
	100/5	39.7 ±1.3	9.1 ± 0.5	33.77 ± 3.97	85.3 ± 3.66
	100/10	34.3 ± 1.4	7.3 ± 0.9	42.70 ± 2.80	79.8 ± 2.34
	80/20	26.4 ± 1.0	6.8 ± 1.0	51.27 ± 5.91	84.6 ± 4.04
PLA/NR-MAH[1]	100/3	35.9 ± 1.8	6.9 ± 0.9	30.88 ± 6.02	87.7 ± 1.98
	100/5	31 ± 2.1	6.3 ± 0.4	27.78 ± 4.16	85.8 ± 5.40
	100/10	21.7 ± 4.1	5.7 ± 0.9	27.58 ± 5.90	83.5 ± 1.73
PLA/NR/NR-MAH	80/20/1.0	19.1 ± 0.5	6.1 ± 0.8	45.07 ± 6.12	86.9 ± 7.22
	80/20/3.0	16.2 ± 1.6	6.3 ± 0.8	42.56 ± 3.01	88.8 ± 1.92
	80/20/5.0	16.3 ± 0.3	6.6 ± 1.3	42.58 ± 4.21	88.7 ± 2.77
PLA/NR/NR-PLA[2]	80/20/1.0	26.8 ± 0.8	7.8 ± 0.6	54.29 ± 4.41	80.6 ± 2.07
	80/20/3.0	26.4 ± 0.3	7.5 ± 0.4	61.86 ± 7.13	80.1 ± 3.13
	80/20/5.0	27 ± 0.6	7.6 ± 0.5	62.70 ± 2.29	79.2 ± 2.86

[1] Condition: [BPO] = 0.3 phr at 80 °C for 2 h.

[2] Condition: MAH loading 5 phr, [BPO] = 0.3 phr, PLA/NR-MAH wt = 2/1 (w/w), [DMAP] = 0.2 M at 140 °C for 16 h.

[3] Standard Deviation

APPENDIX D

CALCULATION OF WEIGHT LOSS IN PLA/NR BLENDS

The weight loss of NR-PLA after enzymatic or hydrolysis degradation was calculated by the following expression:

$$\text{Weight loss (\%)} = \left(\frac{W_b - W_a}{W_b}\right) \times 100\%$$

Where W_b = weight of specimens before degradation (g)

= 0.1556 g

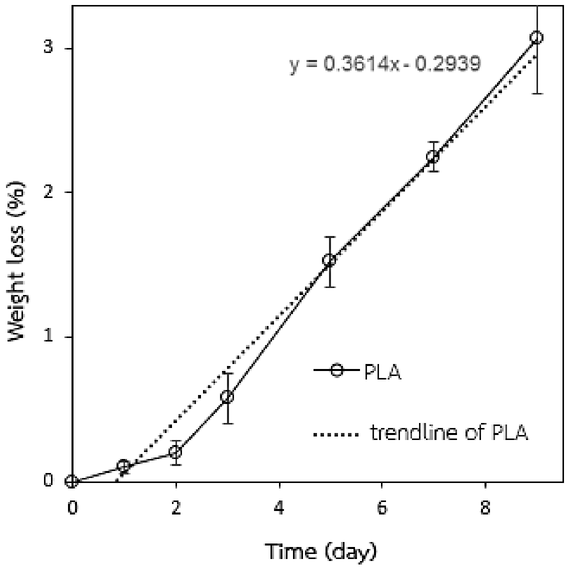
W_a = weight of specimens after degradation (g)

= 0.1554 g

$$\text{Weight loss (\%)} = \left(\frac{0.1556 - 0.1554}{0.1556}\right) \times 100\%$$

$$= 0.13\ \%$$

The weight loss rate of NR-PLA after enzymatic or hydrolysis degradation was calculated by the slope of weight loss vs. time plot as described below:



Where the weight loss rate of NR-PLA was calculated by slope of trend line

slope = 0.36

weight loss rate = 0.36%/day

VITA

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