ผลของเวลาในการบดและชนิดของยางธรรมชาติต่อสมบัติของฟิล์มเป่าพอลิแลคติกแอซิด/ยางธรรมชาติ

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EFFECTS OF MASTICATION TIME AND TYPE OF NATURAL RUBBER ON PROPERTIES OF POLY(LACTIC ACID)/NATURAL RUBBER BLOWN FILMS

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พิศวัส นุ่มพิบูรณ์มาน : ผลของเวลาในการบดและชนิดของยางธรรมชาติต่อสมบัติของฟิล์มเป่าพอลิแลคติกแอซิด/ยางธรรมชาติ. (EFFECTS OF MASTICATION TIME AND TYPE OF NATURAL RUBBER ON PROPERTIES OF POLY(LACTIC ACID)/NATURAL RUBBER BLOWN FILMS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.อนงค์นาฏ สมหวังธนโรจน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.กนกทิพย์ บุญเกิด, 85 หน้า.

งานวิจัยนี้ศึกษายางแผ่นผึ่งแห้ง (Air dried sheet) และ ยางก้อนมาตรฐาน 5 แอล (Standard Thai rubber 5L) เพื่อเพิ่มคุณสมบัติของฟิล์มเป่าพอลิแลคติกแอซิด (Poly(lactic acid) blown film) ในส่วนของยางมีการศึกษาปริมาณส่วนที่ไม่ใช่ยาง และสมบัติพลาสติกซิตีของยางทั้งสองชนิด พบว่าค่าพลาสติกซิตีภายหลังการอบ และดัชนีความคงสภาพพลาสติก (Plasticity retention index) ของยางก้อนมาตรฐาน 5 แอล มีค่าต่ำมากเมื่อเทียบกับยางแผ่นผึ่งแห้ง แสดงถึงยางก้อนมาตรฐาน 5 แอล มีความต้านทานความร้อนได้ต่ำกว่า กระบวนการบดยางเป็นกระบวนการทีมีประสิทธิภาพในการตัดสายโซ่โมเลกุลของยางจากความร้อนและแรงเฉือน โดยน้ำหนักโมเลกุลเฉลี่ยเชิงความหนืด และความหนืดมูนนี่ของยางที่ผ่านการบดลดลงเมื่อเพิ่มระยะเวลาการบดยาง โดยเฉพาะอย่างยิ่งยางก้อนมาตรฐาน 5 แอล หลังจากนั้นมีการศึกษาสมบัติของฟิล์มเป่าพบว่า ฟิล์มเป่าพอลิแลคติกแอซิดกับยางที่ผ่านการบดแสดงพื้นผิวของฟิล์มเรียบและโปร่งใสสูงขึ้นเมื่อใช้ยางที่ผ่านการบดยางที่เวลานานขึ้นเมื่อเปรียบเทียบกับฟิล์มเป่าพอลิแลคติกแอซิดกับยางที่ไม่ผ่านการบด เมื่อระยะเวลาในการบดยางนานขึ้น โดเมนของยางจะมีขนาดเล็กและกระจายตัวดีจากสัณฐานวิทยา ทำให้สมบัติเชิงกลโดยเฉพาะอย่างยิ่งความเหนียว ต้านทานการฉีกขาด และความต้านทานแรงกระแทกสูงขึ้นมาก ดังนั้นการผสมพอลิแลคติกแอซิดด้วยยางที่ผ่านการบดยาง เพื่อให้โมเลกุลยางสั้นซึ่งเป็นวิธีการที่มีประสิทธิภาพในการปรับปรุงสมบัติของฟิล์มเป่าเพื่อใช้ในงานบรรจุภัณฑ์เพื่อสิ่งแวดล้อมได้

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....
ปีการศึกษา 2556 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม ....

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PIDSAWAT NUMPIBOONMARN: EFFECTS OF MASTICATION TIME AND TYPE OF NATURAL RUBBER ON PROPERTIES OF POLY(LACTIC ACID)/NATURAL RUBBER BLOWN FILMS. ADVISOR: ASSOC. PROF. ANONGNAT SOMWANGTHANAROJ, Ph.D., CO-ADVISOR: ASST. PROF. KANOKTIP BOONKERD, Ph.D., 85 pp.

In order to enhance the properties of poly(lactic acid) (PLA) blown film, the different kinds of natural rubbers (NRs) were considered. Air dried sheet (ADS) and Standard Thai Rubber 5L (STR5L) were used in this research. Non-rubber content and plasticity of natural rubbers (NRs) were characterized before using. Plasticity after ageing (P30) and plasticity retention index (PRI) values of STR5L were much lower than those of ADS, indicating that STR5L is vary thermally sensitive. Mastication sufficiently induced the breaking up of the long rubber molecules into short ones via thermal oxidation and shear force. Viscosity average molecular weight and Mooney viscosity of masticated NRs intensely decreased with increasing mastication time, especially STR5L. The properties of PLA/NR blown films were then studied. Masticated NR/PLA blown film’s surface is much smoother and the film is much transparent than those of virgin NR/PLA blown films. As mastication time increased, numerous small rubber domains in PLA matrix were clearly evident by scanning electron microscope (SEM). The mechanical properties of blown films are outstandingly improved by the addition of masticated NRs into PLA matrix phase, especially toughness, tear strength and impact strength. Consequently, blending PLA with masticated NRs containing short rubber molecules is an effective approach to improve the properties of blown films for using in food and green packaging applications.

Department:	Chemical Engineering	Student's Signature ....
Field of Study:	Chemical Engineering	Advisor's Signature ....
Academic Year:	2013	Co-Advisor's Signature ....

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INTRODUCTION

1.1 General Introduction

Nowadays, the preservation of ecological systems has been more extensively considered owing to the increase of global warming and environmental pollutions. It is much widely accepted that the use of short-lived packaging made from long-lasting polymers is inadequate. Conventional plastics used in packaging application are produced from non-renewable petroleum-based materials. Although, some plastics can be recycled, they still need a large part of waste management. More greenhouse gases and toxic pollutants are also released from the incineration of them. Accordingly, a shift to bio-based plastics, which is made from biodegradable polymers, is enormous benefits for the environment and society.

One of the most distinguished bio-based plastics is poly(lactic acid) or PLA which is the most commercially available biopolymer. The currently marketed biopolymers are derived from renewable resources such as corn and cassava. PLA is mostly used in food and green packaging applications because of its good mechanical properties and transparency. However, PLA has inherent stiffness and brittleness at room temperature, limiting its use in many applications [1-3]. In previously works, brittle PLA was improved by blending with natural rubber (NR) because of its high elasticity and also biodegradable. It was found that the enhancement of PLA strongly depends on the properties of NR. There are many types of NRs whose composition, production process and storage conditions have a major influence on their properties. However, few studies have been investigated the effect of mastication, which is the important production process for PLA/NR blends, on the properties of NR and PLA/NR blends, especially PLA/NR blown films. Mastication directly affects the properties of NR, such as molecular weight and viscosity [4]. The effect of mastication of NR on the properties of PLA/NR blends was clearly observed.

Consequently, this research was designed to determine the intrinsic composition and properties of two types of NRs including Air dried sheet (ADS) and Standard Thai Rubber5L (STR5L). Mooney viscosity, viscosity average molecular weight and gel content of both NRs before and after various periods of mastication were also examined. Furthermore, PLA was blended with virgin NRs and masticated

NRs using twin screw extrusion and blown films of PLA/NR blends were then prepared using blown film extrusion. The morphology, mechanical properties and gas permeability of blown films were evaluated as well.

1.2 Objectives of the research

To investigate the effects of mastication time and type of rubber on the properties of NR and PLA/NR blown films

1.3 Scopes of the research

1. Clarify the intrinsic composition and properties of Air dried sheet (ADS) and Standard Thai Rubber5L (STR5L)

2. Elucidate the properties of masticated-NRs as a function of mastication time at 0, 5, 10 and 15 min

3. Prepare PLA-based blown films blended with 20wt% of virgin NRs and masticated NRs

4. Investigate the morphology, mechanical properties and gas permeability of blown films

CHAPTER II

THEORY AND LITERATURE REVIEWS

The first part describes general information of poly(lactic acid) (PLA) and natural rubber (NR). In the second part, mastication of NR as well as the effects of mastication on properties of NR is elucidated. In the final part, the effects of NR and modified NR on properties of PLA are discussed.

2.1 General information of PLA and NR

The information of PLA on this research includes resources and chemical structure as well as properties of PLA that were studied. Moreover, resources and categories of NR were discussed in this section.

2.1.1 Poly(lactic acid) (PLA)

PLA is linear aliphatic polyester that is produced from renewable resources such as corn, cassava, and potato. PLA is a biocompatible and biodegradable material which is decomposed to carbon dioxide and water [5, 6]. The chemical structure of PLA is shown in Figure 2.1 [1].

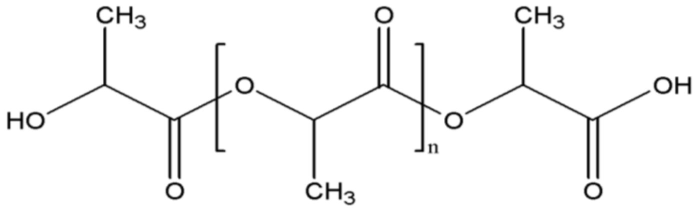

Figure 2.1 Chemical structure of PLA [1]

PLA is a semi-crystalline polymer whose properties depend on the ability to selectively incorporate L and D ratio and the molecular weight of PLA. In addition, the properties of PLA allow it to be tailored for specific applications. The ease of incorporation of various defects into PLA, allows controlling both crystallization rate and ultimate crystallinity. Therefore, PLA has various grades in which each grade is optimized in many applications. Properties of PLA grade 2003D for extrusion grades obtained from NatureWorks PLA, are shown in Table 2.1 [7].

Table 2.1 Properties of PLA grade 2003D [7]

Properties	value	ASTM Method
Physical Properties		
Specific gravity (g/cc)	1.24	D792
Melt index (g/10 min) (210 °C/2.16 kg)	6	D1238
Clarity	Transparent	
Mechanical Properties		
Tensile strength at break, psi (MPa)	7,700	D882
Tensile yield strength, psi (MPa)	8,700	D882
Tensile modulus, kpsi (GPa)	500	D882
Tensile elongation (%)	6.0	D882
Notched izod impact, ft-lb/in (J/m)	0.23	D256
Thermal Properties		
Glass transition temperature ($T_{g,}$ °C)	55-65	
Melt temperature (T_m, °C)	160-180	

The advantages of PLA exhibit high strength, modulus, transparency, biocompatibility, and degradability. However, the disadvantages of PLA are stiff and brittle at room temperature which limits the use in food packaging. NR is a good candidate to use as toughening agent in PLA.

2.1.2 Natural rubber (NR)

NR is linear polymer consisting of an unsaturated hydrocarbon called isoprene (2-methybutadiene) with molecular weights ranging from 100,000 to 1,000,000 g/mol. The chemical structure and particle of NR are shown in Figure 2.2. NR is obtained from the rubber trees existing in the form of colloidal suspension. Latex is the white milk-like fluid, including 30-40% of dry rubber content, which is obtained by wounding the rubber plant [8].

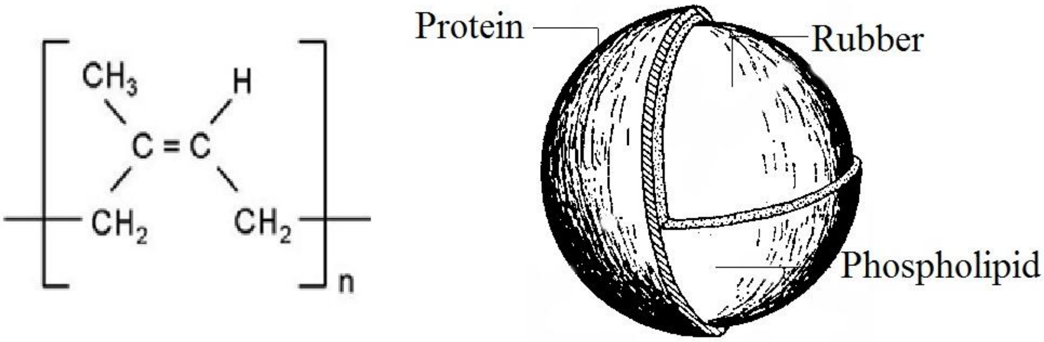

Figure 2.2 Chemical structure and NR particle [8]

There are many grades of NR sheet e.g. Ribbed smoke sheet, Pale Crape, Brown Crape, Air dried Sheet (ADS), Standard Thai Natural rubber (STR), Crumb Rubber. However in this research, only Air dried Sheet (ADS) and Standard Thai Natural rubber (STR) are considered in which both of rubbers are obtained from different processes and show different properties [9, 10].

Air dried Sheet (ADS) - if the sheeted rubber is dried in an open air, in place of drying in house, it is sold as ADS rubber (pale amber smoked sheet). This is a light colored sheet prepared under closely controlled conditions as ribbed smoke sheet but dried by air usually in a shed or tunnel without smoke. The grades of this rubber are classified by visual grading which must be considered variable such as cleanliness, color, dirt content, and moisture content. Generally, there are four grades of ADS which are grade that it is one to four. The grade ADS#1 is the top grade. Disadvantage of ADS is too hard to control the quality of rubber sheet because there is no exact universal standard to separate different rubber grades. Therefore, STR is developed to solve the problem by testing in the laboratory.

Technical Specifications for Natural rubber (TSR) – TSR is a standard of NR which is graded by its dirt content, ash content, nitrogen content, volatile matter content and Plasticity retention index. Common source of TSR include Standard Indonesian Rubber (SIR), Standard Sri Lanka Rubber (SSR), Standard Vietnam Rubber (SVR), Indian Standard Natural rubber (ISNR), Standard Malaysia rubber (SMR) as well as Standard Thai Rubber (STR). In STR grade, there are 8 categories and have clearly differentiate the properties of each category. These quality standards lay down the maximum permissible content of dirt content, ash content, nitrogen content, volatile matter content and Plasticity retention index allowed in NR as following in Table 2.2 [11].

Table 2.2 Specification of a STR grades [11]

Parameter	STRXL	STR5L	STR5	STR5CV	STR10	STR10CV	STR20	STR20CV
Produced from	latex		latex/ sheet		Cup lump / Sheet			
Dirt (max), % wt	0.02	0.04	0.04	0.04	0.08	0.08	0.16	0.16
Ash (max), % wt	0.40	0.40	0.60	0.60	0.60	0.60	0.80	0.80
Nitrogen (max), % wt	0.50	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile Matter (max), % wt	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Plasticity retention index (min)	60	60	60	60	50	50	40	40
Color (min) (lovibond color)	4.0	-	-	-	-	-	-	-

The conventional method of processing of ADS involves the removal of water from the latex coagulant to give a commodity which is marketable, convenient to handle and economic to ship. There are basic 3 main steps in making sheet rubber from latex [11].

The first step is coagulation which is aided by the addition of formic or acetic acid as shown in Figure 2.3 [12]. On a small scale produced by small-holder or co-operative, the latex is coagulated by the addition of the small amount of acid.

Figure 2.3 Coagulation which is aided by addition of formic or acetic acids [12]

In the second step, milling is done by passing slabs of coagulum through successive pairs of appropriately adjusted rollers as shown in Figure 2.4 [13]. The first two or three rollers are smooth and the final one is grooved so as to imprint on each sheet to increase the surface area for drying and to ensure that dried sheets do not stick together. The wet sheets are dried in the final stage of the process and passed through a mill which squeezes out most of the water.

Figure 2.4 Milling which is done by passing coagulum through successive pairs of adjusted rollers [13]

The third step is to dry the rubber sheets without smoke (ADS) in a smoke house. The arrangement of sheet making depends largely on the size of the holding or estate. After being dried, the sheets are inspected individually and the blemished parts are removed with scissors. Then sheets are graded, compressed, and picked into bales of about 113 kg.

In case of STR5L, the production process of STR5L is similar to production process of ADS but it is strict to control the quality of NR because production process of STR5L is cleaner than that of ADS. STR is to dry the rubber by hot air in the oven at 100-125°C, 3-4 hrs in which the moisture in the STR is higher than the moisture in ADS.

2.2 Mastication of NR and effect of mastication on properties of NR

NR is one of the most important rubbers to use in the rubber industry. It has a very high molecular weight portions and consequently has very high viscosity. In this condition, it cannot be processed or even mixed. Therefore, the reduction of viscosity by chain scission is called mastication. Characteristic and the effect of mastication on properties of NR were studied in this section.

2.2.1 Mastication of NR

The deformation of rubber in mastication process is related to the combination of a mechanical breakdown at low temperature and a thermo-oxidative mastication at high temperature[14]. Mastication efficiency increases at lower temperature, whereas, there is the same efficiency at a higher temperature as shown in Figure 2.5 (U-shaped curve), with a region of temperature around 80-100˚C where breakdown efficiency is low [15, 16]. At low temperature, the so-called mechanical mastication arises from shear forces applied to the polymer chains during the mixing, leading to a breaking of the chains and the formation of radicals. Mechanical mastication appears during deformation because chain molecules do not have time to relax and break by the action of stresses. The rate of scission depends upon the distribution of both shear and elongational stresses, the nature of the rubber and the temperature. When the temperature increases, the polymer chains are more mobile and relaxation times decrease which lower the mechanical breakdown. However, mastication at high temperature is useful and quicker than mastication at low temperature.

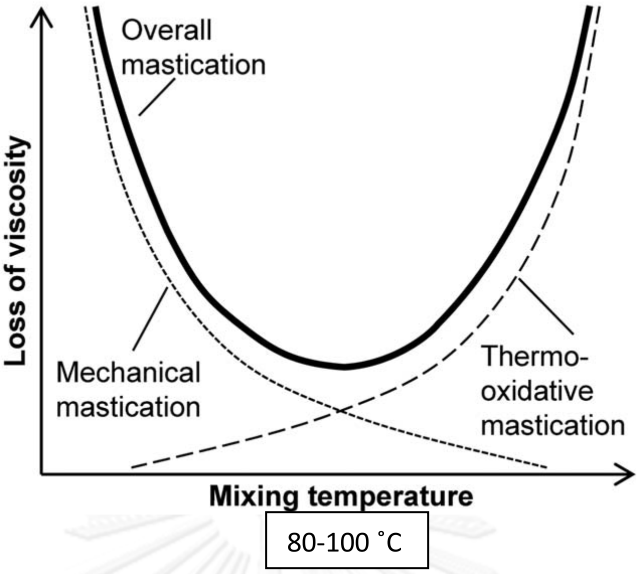

Figure 2.5 Effect of temperature and efficiency of NR breakdown during mastication [15]

At high temperature, the so-called thermal oxidative mastication is based on an oxidation of double bonds of a polymer backbone due to an oxidative reaction mastication process. It can reduce the chain length, depending on the amount of oxygen and temperature. Following the mastication of both low and high temperature, long-chained rubber molecules are splitted to form shorter chains with terminal free radicals. During mastication operating in a nitrogen atmosphere or other inert gases, these short chains recombine into long chain molecules, therefore molecular weights of the rubber is not reduced. Whereas if operating without inert atmosphere (oxygen atmosphere), free radicals that occur in the rubber rapidly react with oxygen to form peroxy radical and hydroperoxide or cyclic diperoxide which cannot recombine into long chain molecules as shown in Figure 2.6 [11]. Therefore, the mastication performance of rubber needs to be done in an oxygen atmosphere. In fact, the oxygen requirement for the breakdown process is so low that the amount presented in the air during processing in the internal mixer is usually sufficient [4].

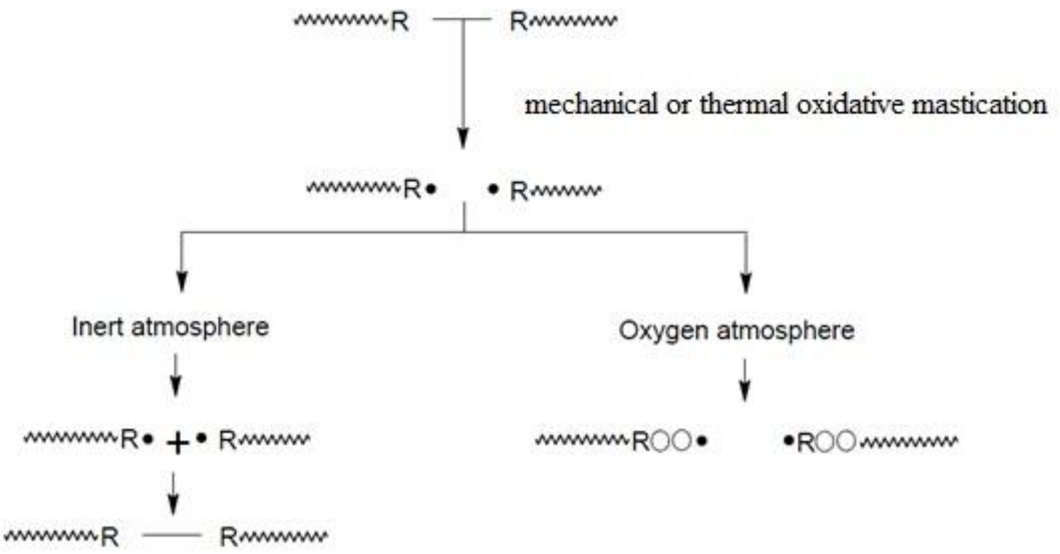

Figure 2.6 Mastication mechanism of rubber [17]

2.2.2 Effect of mastication on properties of NR

Many researchers have studied the effect of mastication on the properties of NR such as gel content, Mooney viscosity, molecular weight, and molecular weight distribution.

The gel content and Mooney viscosity of rubber samples at various time of accelerated storage hardening time before and after the mastication were studied [18]. It was found that gel content increased with the increasing accelerated storage hardening times, the different gel contents at ~0.5, ~4, ~6, ~12 and ~17% w/w were obtained. It was apparent that the gel content of rubber samples containing the highest gel content clearly decreased from 17% to 0% w/w after deproteinization and trans-esterification as shown in Figure 2.7, indicating that the gel was only soft gel occurring after accelerated storage hardening times since hard gel of rubber cannot be decomposed by trans-esterification. Moreover, 0% w/w gel content of all samples was obtained after mastication in an internal mixer at a rotor speed of 50 rpm at 50 °C for 15min (Figure 2.8). Reduction of gel content could be caused by two phenomena. The first one was random chain scission of the rubber as evidenced by obvious decrease of molecular weight and break down interactions of protein and phospholipids. The second one is the decomposed interaction of proteins and phospholipids at the chain end which was supported by the 0% w/w gel content of deproteinized trans-esterified natural rubber (DPTE-NR) (Table 2.3). The absence of gel fraction in DPTE-NR was due to the removal of proteins and phospholipids at the chain ends by deproteinization and, subsequently, by trans-esterification (0% w/w of N-content and 0 mmol/kg of ester content). It has been reported that the DPTE-NR comprised of linear molecules which was similar to the observation of linear cis-1,4-polyisoprene (IR). Furthermore, Mooney viscosity of all samples decreased to similar values after mastication.

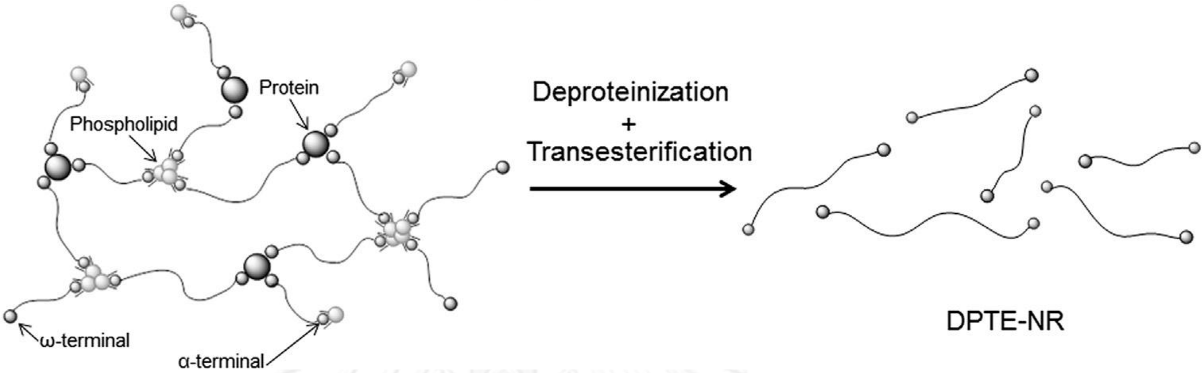

Figure 2.7 Schematic representations of NR gel and branching after deproteinization and subsequently by trans-esterification [18]

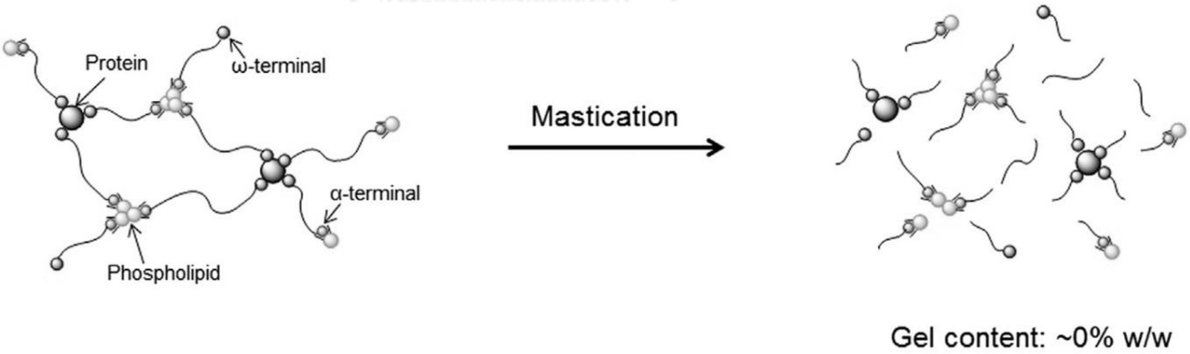

Figure 2.8 Schematic representation of natural rubber gel fraction after mastication [19]

Table 2.3 Gel content, Mooney viscosity and molecular weight of rubber samples before and after mastication for 15 min and Gel content, Mooney viscosity and molecular weight of DPTE-NR before mastication [18]

Storage time (h)	Before mastication			After mastication		
	Gel content (%w/w)	Mooney viscosity (ML1+4)	Mw x 10^5 (g/mol)	Gel content (%w/w)	Mooney viscosity (ML1+4)	Mw x 10^5 (g/mol)
0	~0.5	72.2	8.49	~0	22.4	2.49
6	~4	74.4	8.37	~0	22.6	2.53
12	~6	77.6	8.47	~0	23.5	2.48
24	~12	78.3	8.34	~0	22.9	2.59
48	~17	78.5	8.45	~0	22.5	2.47
DPTE-NR	~0	53.2	7.50	-	-	-

On the other hand, the result of gel content which was decreased to 0% w/w was not similar to the research titled *"High-temperature Mastication of Raw Natural rubber: Chances in Macrostructure and Mesostructure"*[4]. This research studied the formation of macrogel and microgel between non-viscosity-stabilized grade (TSR) as TSR3CV and TSR10 from both clones (PR107and PB217) after mastication at high temperature as shown in Figure 2.9. The macrogel contents of TSR10 were reduced very rapidly to a minimum of 4% after 4 min of mastication. Whereas for the TSR3CV, the macrogel contents was a very large in which they could be purported to limit of precision of the measurement. For microgel, all of the microgel of TSR3CV for clone PB217 was entirely absent, whereas for TSR3CV from clone PR107, a critical level (15%) was attained despite of long time mastication because the micro gel could be considered of intra-molecular crosslinked polymer molecules [20].

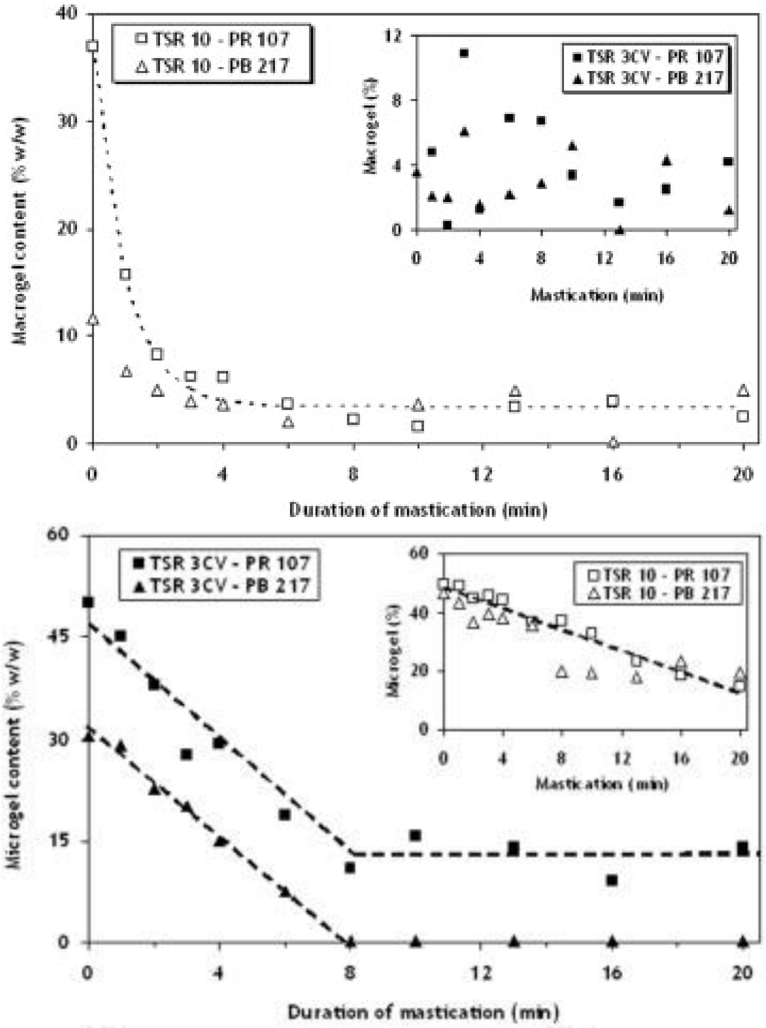

Figure 2.9 Effect of mastication on the macrogel and microgel content of TSR10 and TSR3CV natural rubber from clones PR107 and PB217 [4]

Effect of mastication of different grade and clone of NR on molar mass and molecular weight distribution (MWD) were investigated. Weight-average molar mass of the TSR3CV showed two distinct trends. The clone PB217 samples were degraded throughout the mastication period, while those of the clone PR107 seemed to be significantly degraded only during the early stages of mastication because of the effect of cold mastication which made short chain formed. Although in this report rubbers were masticated at higher temperature. MWD of NR of grade TSR10 and TSR3CV from both clones (PR107 and PB217) were shown in Figure 2.10.

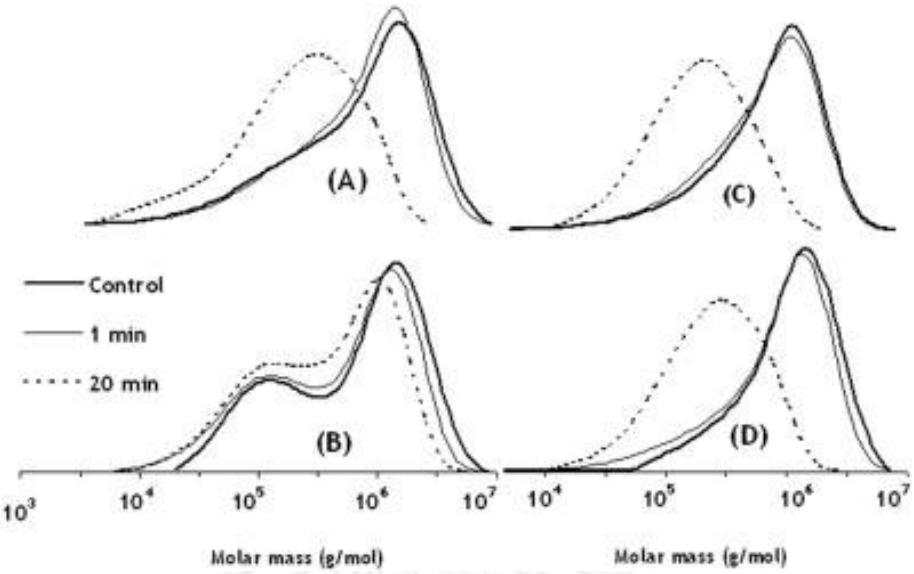

Figure 2.10 Effect of mastication on the MWD of NR of (A) grade TSR 10 from clone PR 107, (B) grade TSR3CV from clone PR107, (C) grade TSR 10 from clone PB217, and (D) grade TSR 3CV from clone PB217 [21]

In addition, effect of NR mastication with a two-roll mill was investigated by varying number of rubber mastication from 20 to 200[21]. The molecular weight distribution was shown in Figure 2.11. It was found that higher molecular weight part was destroyed and the average molecular weight shifted to the lower part. Molecular weight and Mooney viscosity of NR decreased with the increasing number of mastication.

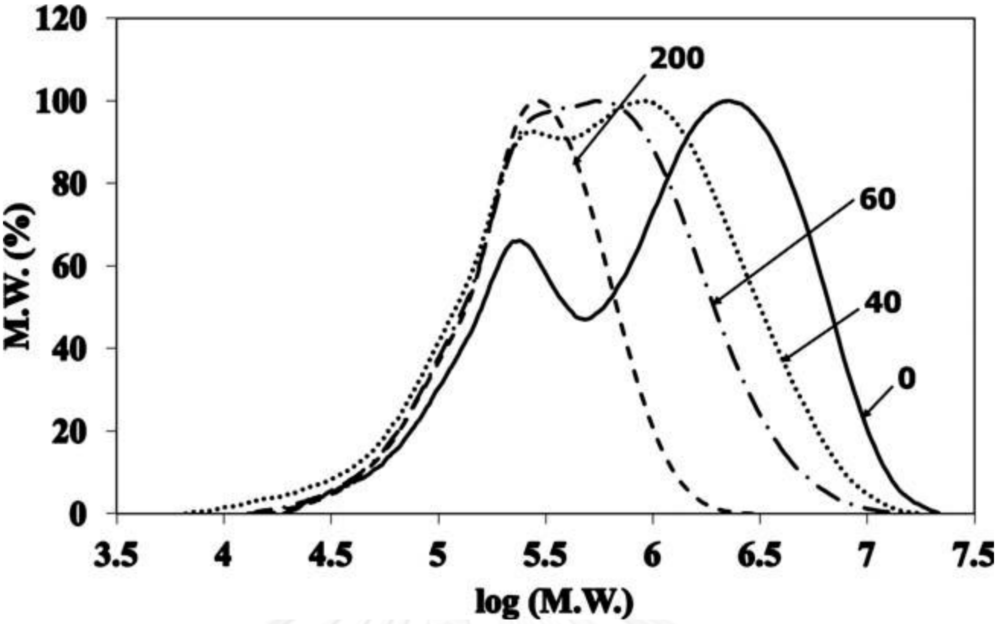

Figure 2.11 Molecular weight distribution of NR before and after mastication with number of passing as 20 to 200 [21]

2.3 Effect of NR and modified NR on properties of PLA

Melt blending PLA with NR and modified NR such as epoxidized natural rubber (ENR), natural rubber grafted maleic anhydride (NR-g-MA) and natural rubber grafted methyl methacrylate (NR-g-PMMA) have been investigated [3, 21, 22].

2.3.1 Mechanical properties

Considering chemical structure of NR and PLA, chemical-modified NR may provide more miscibility than the virgin NR. It has been reported that the toughness of the PLA/NR blend was improved by adding the NR grafted with maleic anhydride (MA) [22]. Adding 10 wt% natural rubber grafted with 1 phr of MA (MNR-1) enhanced the elongation at break from 3.44% for neat PLA blends and 17% for PLA/NR to 32% in machine direction (MD). PLA/MNR-1 blend had more compatibility than PLA/NR blend. However, an increase in MA content of MNR led to the decrease of plastic deformation zone and reduced elongation at break to 21% and 9% NR grafted with 3 and 5 phr of MA blends respectively, as shown in Figure 2.12.

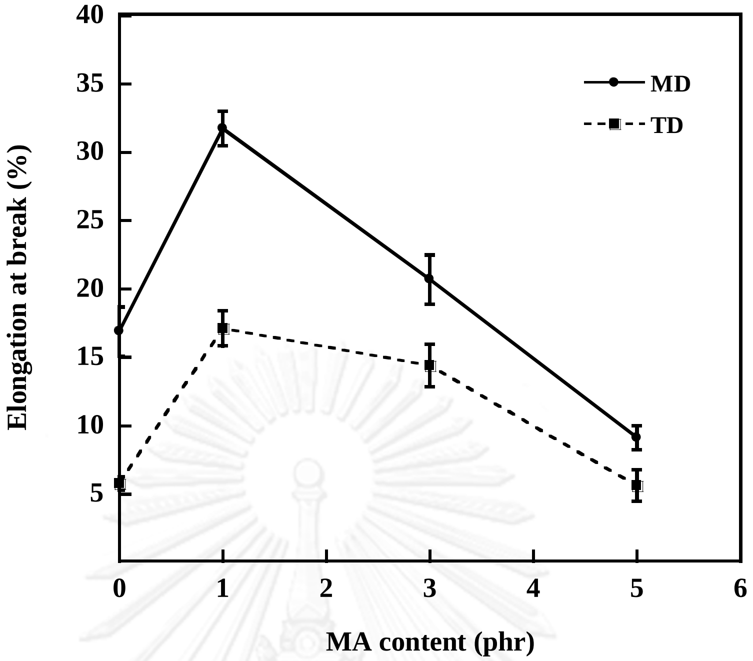

Figure 2.12 Tensile toughness of blown film of PLA with 10 wt% MNR at MA content of 0, 1, 3 and 5 phr in machine direction (MD) and transverse direction (TD) [22]

There are many factors affecting the toughness of the rubber toughened plastics. For instance, the blends should have high interfacial adhesion between the plastic matrix and the dispersed phase (the rubber domains) and the viscosity of both of molten polymers should be similar. Moreover, mechanical properties of all polymer blends are strongly dependent on the blending method and sample preparation [23]. Although the rubber toughened plastics are not a miscible blend, it is required to have low surface tension in the blends in order to obtain the appropriate rubber domain’s diameter [21].

However, some researchers found that blending PLA and NR led to the dramatic increase of elongation at break which was more effective than chemical modified NR such as NR grafted poly(methyl methacrylate) (NR-g-PMMA) and epoxidized NR (ENR) [21]. The results showed that interfacial adhesion between PLA and NR phase was not the key factor to improve mechanical properties of the blend because of low interfacial adhesion between two phases. Different mechanical properties of PLA blending with NR, NR-g-PMMA and ENR were investigated. Addition of NR-g-PMMA and ENR in PLA, the Young’s modulus of these blend were higher than that of PLA/NR blend due to PMMA and epoxide ring which are more rigid than virgin NR. PLA/NR blend gave higher tensile strength and ductility than the blend with NR-g-

PMMA and ENR, although they should be more compatible with PLA than NR because they were more polar than virgin NR. These results showed that polarity of rubber in NR-g-PMMA and ENR did not play an important role in mechanical properties of blends. One of many key factors that affected the toughness of the rubber toughened plastics is molecular weight. The molecular weight of chemical modified NR decreased its molecular weight. The more modification the rubber was performed, the more reduction of molecular weight it was observed as shown in Table 2.4. It might be expected that the molecular weight of NR attribute to higher mechanical properties of the blends. However, this hypothesis did not coincide with another key factor which was size of rubber domains in the blends. The smaller size of chemical modified NR indicated higher miscibility with PLA than virgin NR. However, the mechanical properties of the blend with modified NR was lower than those with virgin NR due to lower molecular weight of these rubbers in the blend, which might affect the particle size as well because of lower viscosity which was too small to act as toughening agent. In addition, NR-g-PMMA and ENR also had rigid structure comparing to NR.

Table 2.5 Molecular weight of the rubbers and average particle diameter in PLA/NR blend [21]

Rubber	M_n (g/mol)	M_w (g/mol)	Average particle diameter (μm) in blended PLA with 10wt%rubber
Natural rubber	1,485000 ± 32,000	2,702,000 ± 42,000	2.50 ± 1.16
G5 (NR-g-PMMA 5% grafted)	230,000 ± 8,000	849,000 ± 30,000	0.25 ± 0.17
G35 (NR-g-PMMA 35% grafted)	157,000 ± 12,000	618,000 ± 5,000	0.08 ± 0.02
ENR25 (25% degree of epoxidation)	309,000 ± 4,200	750,000 ± 12,000	0.45 ± 0.03
ENR50 (50% degree of epoxidation)	181,000 ± 15,600	558,000 ± 11,000	0.14 ± 0.09

To understand the effect of NR toughened PLA, Bitinis et al.[3] studied the fractured sections along the tensile direction of PLA and PLA blended with 10 wt% of rubber after stretching (Figure 2.13). PLA broke at the very low elongations and fractured section was smooth. The deformation mechanism of PLA was investigated by Ito et al [24] in which the uniaxial tensile deformation and formation of surface crazes occurred simultaneously with plastic deformation. However, addition of NR in PLA led to a large formation of a neck in plastic deformation because NR behaved as a stress concentrator. After the yield point, a typical neck started to form in order to release energy during deformation. Moreover, some whitening in the neck zone increased which reflects fine-scale cavities occurring. The un-deformed material contained cavities due to poor interaction between PLA and NR, which was clearly increased during the material deformation. Thus, the release of the strain was due to the formation of voids and relaxation of the toughness concentration, resulting significantly in the increase of the toughness of the material.

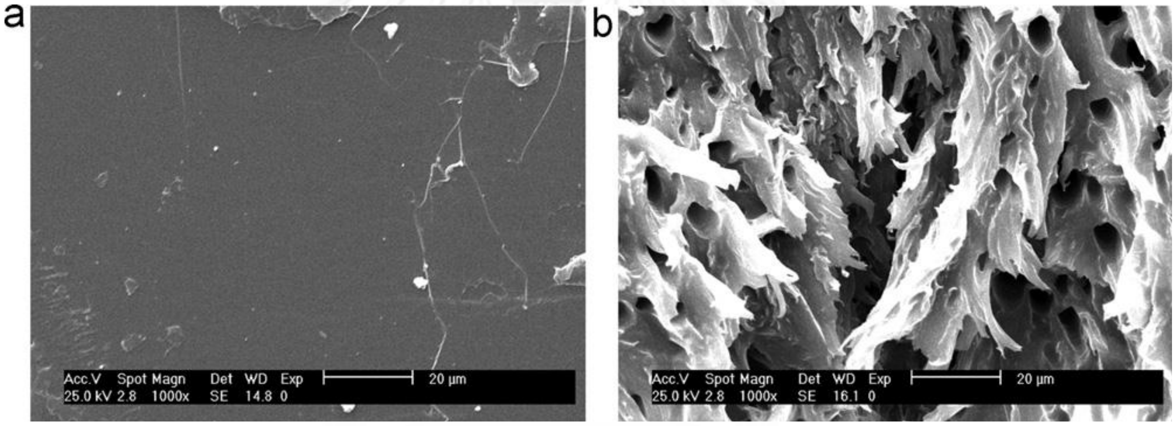

Figure 2.13 Fractured surface of stretched materials (a) PLA, (b) PLA/NR 10 wt% [3]

2.3.2 Gas permeation properties

Gas permeability is one of the most important factors in food packaging such as oxygen permeation (OP) and water vapor permeation (WVP). Suitable gas permeability of polymer film in food packaging can maintain the quality and extend life of food products. The permeation mechanism of gas in polymer consists of three mechanisms, i.e., absorption, diffusion and desorption.

Addition of NR in PLA matrix resulted in the increasing of the oxygen permeation and the water vapor permeation as shown in Figure 2.14 and Figure 2.15, respectively. The oxygen permeation of neat PLA film was 792 cc.mil/m^2.day.atm and the oxygen permeation of PLA/NR films were 946, 4693 and 7302 cc.mil/m^2.day.atm for the blends containing 5, 10 and 15 wt% NR, respectively. The water vapor permeation of the films showed similar trend to the oxygen permeation. The water vapor permeation of neat PLA film was 189 gm.mil/m^2.day.atm and the water vapor permeation of PLA/NR films were 194, 256 and 260 gm.mil/m^2.day.atm for the blends containing 0, 5, 10 and 15 wt%, respectively. The oxygen permeation and the water vapor permeation of these films increase because gas or vapor molecules can pass through the gaps or free volume in polymer.

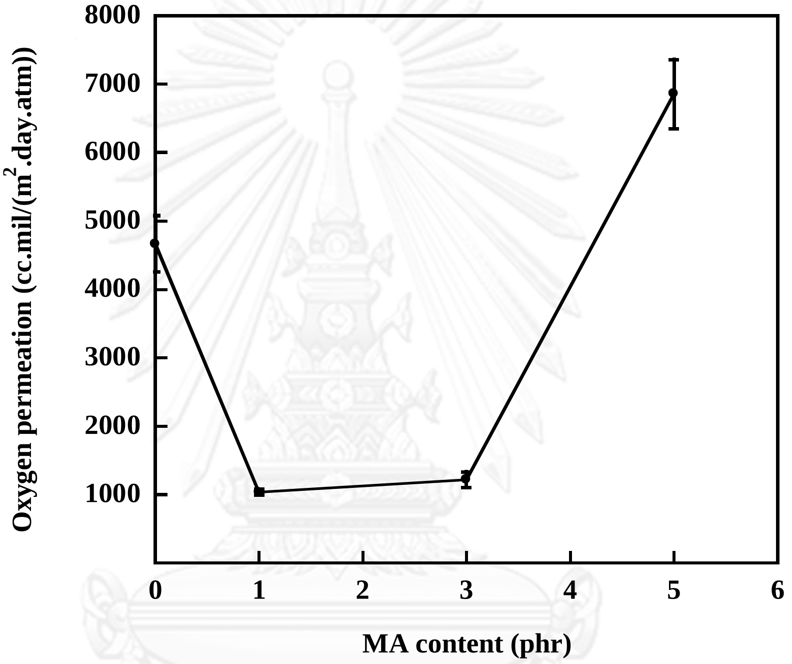

Figure 2.14 Oxygen permeability of blown film of PLA with 10 wt% MNR at MA content of 0, 1, 3 and 5 phr. [22]

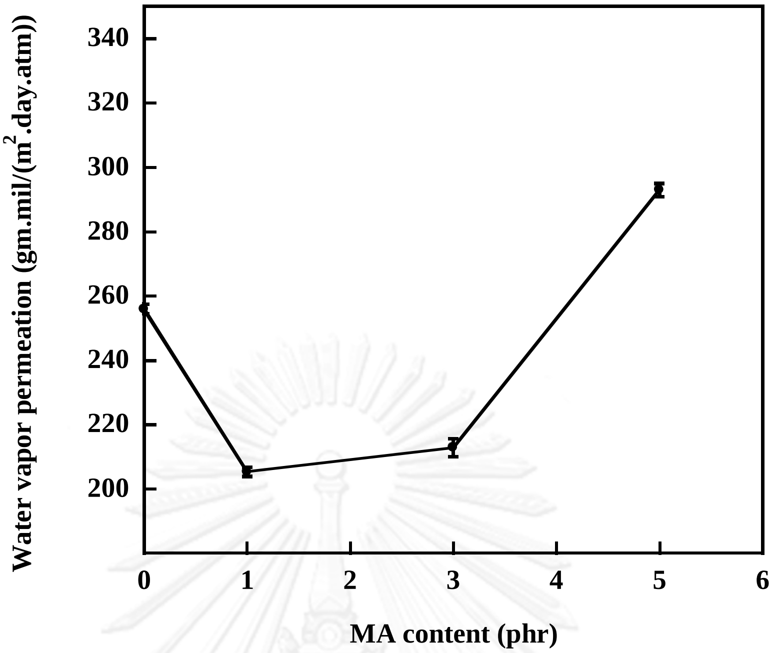

Figure 2.15 Water vapor permeability of blown film of PLA with 10 wt% MNR at MA content of 0, 1, 3 and 5 phr [22]

Moreover, the gas permeability of PLA/MNR films at various amount of MA was studied. The oxygen permeation and water vapor permeation of PLA/MNR at 0, 1, 3 and 5 phr were studied as shown in Figure 2.16 and Figure 2.17, respectively. The oxygen and water vapor permeation of PLA/MNR-1 and PLA/MNR-3 film decreased because of compatibility between PLA and MNR. In addition, gas permeation of PLA/MNR-5 film increased because of a presence of gel on the film surface and raised void content.

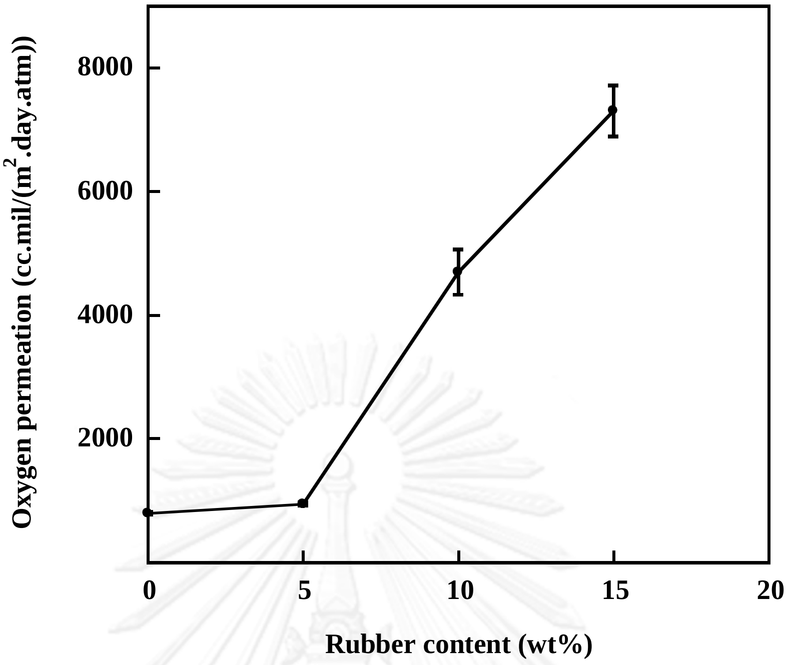

Figure 2.16 Oxygen permeability of PLA blown films at 0, 5, 10, and 15 wt% MNR [22]

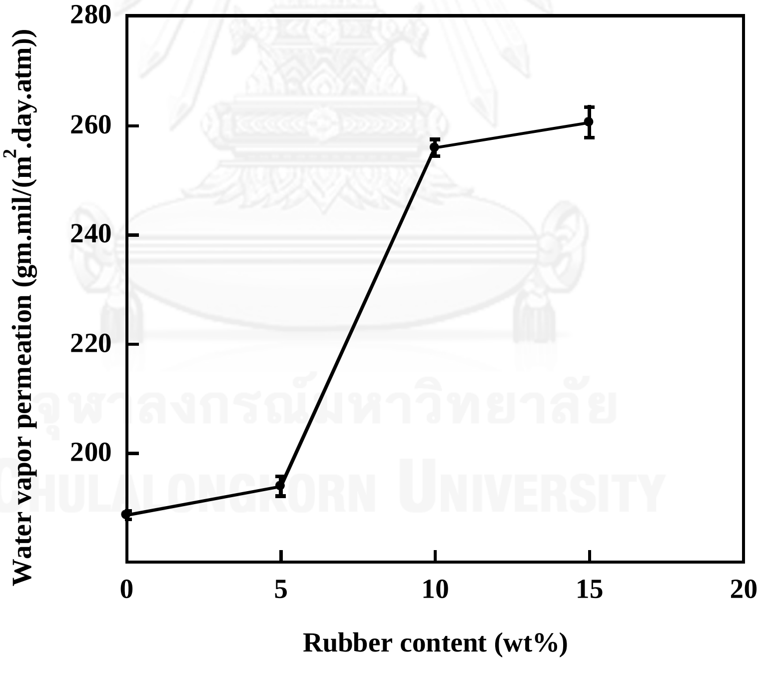

Figure 2.17 Water vapor permeability of PLA blown films at 0, 5, 10, and 15 wt% MNR [22]

CHAPTER III

EXPERIMENTS

This chapter contains materials, preparation of masticated NRs at various mastication time, PLA/virgin NRs and PLA/masticated NRs blends and blown films. ADS and STR5L were used in this research. The properties of virgin NRs and masticated NRs were characterized such as Mooney viscosity, viscosity average molecular weight and gel content. Non-rubber content and plasticity of rubber were only measured in case of virgin NR. The properties of PLA/masticated NRs blown films such as morphology, mechanical properties and gas permeability were also studied. The schematic diagram of experimental procedure along with analytical instrument used in this work is demonstrated in Figure 3.1

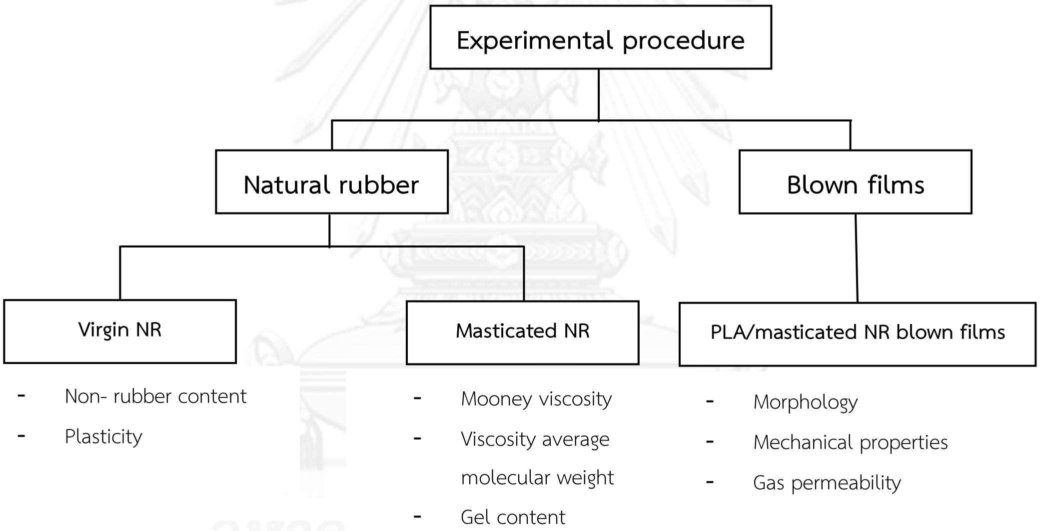

Figure 3.1 The experimental procedure

3.1 Materials

Poly(lactic acid) (PLA) grade 2003D was purchased from Nature Works. Air dried sheet natural rubber (ADS) was purchased from Hi Yangpara company, Rayong, Thailand. Standard thai rubber grade 5L (STR5L) was purchased from Thai Rubber Latex Corporation (Thailand) Co.,Ltd.

3.2 Preparation of masticated NRs

Masticated ADS and masticated STR5L were carried out by using internal mixer (Brabender Plasticoder EHT50, Germany) at135 °C with a rotor speed of 60 rpm. In this study, mastication time of rubber was varied with 5, 10 and 15 min.

3.3 Characterization of virgin NRs and masticated NRs

In this research, the virgin ADS and STR5L were characterized in non-rubber content and plasticity of virgin NR including dirt content, ash content, volatile matter content, nitrogen content, initial plasticity (P_0), plasticity after aging (P_{30}) and plasticity retention index (PRI). Mooney viscosity, viscosity average molecular weight, and gel content of both virgin NR and masticated NRs were also measured.

3.3.1 Non-rubber content

The non-rubber content in term of virgin NRs of ADS and STR5L were characterized in dirt content, ash content, volatile matter content (ASTM 1278-91a) and nitrogen content (ASTM D3533). Office of Agricultural Research and Development Region 8 (Songkhla province) performed all those measurement.

3.3.2 Plasticity characterization

Plasticity characterization in term of virgin NRs of ADS and STR5L were characterized in initial plasticity (P_0), plasticity after aging (P_{30}) (ISO R2007) and plasticity retention index (PRI) (ASTM D3194-04). Office of Agricultural Research and Development Region 8 (Songkhla province) performed all those measurement.

3.3.3 Mooney viscosity

Mooney viscosity (ML1+4,100 °C) of virgin NRs and masticated NRs were measured via a TECHPRO Mooney viscometer according to ASTM D1646 at Rubber Technology Research Centre (Mahidol university).

3.3.4 Viscosity average molecular weight

The molecular weight of virgin NRs and masticated NRs were determined by measuring viscosity of polymer solution using Ubbelohde viscometer. The viscosity of a polymer solution is related to the molecular weight of the polymer by the Mark-Houwink equation.

$[\eta] = KM_v^a$ where $[\eta]$ is the intrinsic viscosity, M_v is the viscosity average molecular weight, K and a are Mark-Houwink constants for particular polymer-solvent system at a given temperature. For isoprene-toluene system at 25 °C, K = 5.02×10^{-2} and a = 0.667 [25]. Ubbelohde viscometer is a suspended level viscometer. Hence measurement of a series of solutions with five concentrations can be made by successive dilution within the viscometer. The viscometer was suspended in a thermostat regulated within ± 0.02 °C.

3.3.5 Gel content

The gel content of ADS and STR5L masticated at various time (0, 5, 10 and 15 min) that was carried out in accordance with ISO/DIS 17278:2012. The rubber, approximately 1 mm^3 from a bale without milling, was weighed as M_0 (about 0.1 grams). Then, the prepared rubber was placed in the centrifuge tube and 30 ml of toluene was added, followed by shaking manually for a few seconds. The tube was allowed to stand for 20 hr at 25 °C without stirring. After soaking, the tube was shaken vertically by hand for 60 s to disperse the jelly-like fraction. The solution was centrifuged to precipitate the gel fraction at 14,000 rpm for 2 hr. The sol fraction was removed from the tube and 1 ml of acetone was added to the precipitate, the rubber gel into the bottom of the tube. It was subsequently transferred to a clean container which had been weighed as M_1. The container with the precipitate was dried in an oven at 110 °C for 1 hr and then weighed as M_2. The gel content was calculated as the following equation.

$$\text{Gel content (\%)} = \frac{M_2 - M_1}{M_0} x100$$

3.4 Preparation of PLA/virgin NR and PLA/masticated NR blown films

After mastication of NR, blended PLA/20 wt% ADS and PLA/20 wt% STR5L pellets masticated at various time (0, 5, 10 and 15min) that were obtained by twin-screw extruder (co-rotating, L/D = 40, D = 20 mm, Labtech Engineering, Thailand) at screw speed of 60 rpm. The effect of masticated NR on properties of PLA can be obviously observed when 20 wt% of NR was added in PLA. The compositions of blended PLA/ADS and PLA/STR5L (temperature range between 180-190 °C) are shown in Table 3.1 Moisture was eliminated from pellets in an oven overnight. Blown film process was performed by using single screw extruder attached to blown film die (L/D = 25, D =20 mm, Collin, Germany) at screw speed of 80 rpm. Operating temperature was varied from 180 - 200 °C. The speed of nip roll was adjusted to produce a film with thickness of 40 μm.

Table 3.1 The compositions of blended PLA/ADS and PLA/STR5L

Sample	Mastication time (min)	Blend composition (wt%)		
		PLA (wt%)	ADS (wt%)	STR5L (wt%)
PLA/ADS0 (PLA/virgin ADS)	0	80	20	-
PLA/ADS5	5	80	20	-
PLA/ADS10	10	80	20	-
PLA/ADS15	15	80	20	-
PLA/STR0 (PLA/virgin STR5L)	0	80	-	20
PLA/STR5	5	80	-	20
PLA/STR10	10	80	-	20
PLA/STR15	15	80	-	20

3.5 Characterizations of PLA/virgin NR and PLA/masticated NR blown films

The effects of mastication time and rubber type on the properties of PLA/ADS and PLA/STR5L blown films such as morphology, mechanical properties and gas permeability were characterized as follows.

3.5.1 Morphology

The morphology of neat PLA, PLA/masticated ADS and PLA/ masticated STR5L blown film in machine direction (MD) and transverse directions (TD) were investigated by scanning electron microscope (SEM: JEOL, JSM 5800LV, Japan) at an acceleration voltage of 10 kV. The samples were immersed in liquid nitrogen and cut. The fractured surfaced sample was coated with gold prior to SEM observation.

3.5.2 Mechanical properties

The tensile strength, young's modulus, and elongation at break of blown film samples were performed according to ASTM D882 by universal testing machine (Instron: model 5567, USA). The crosshead speed of this tensile testing was 12.5 mm/min at 1 kN of load cell. The sample films were measured in both machine and transverse directions.

The tear strength of blown film samples were performed according to ISO 6383 by tear testing machine (Digital Elmendorf type tearing tester model SA, SA-W, Toyoseiki, Japan). The specimens were prepared in dimension of 75 x 63 mm.

The impact resistance of blown film samples was evaluated according to ASTM D3420 by using film impact testing machine (Digital impact tester, Toyoseikai, Japan). The specimens were prepared in dimension of 10 x 10 cm.

3.5.3 Gas permeability properties

Oxygen permeation (OP) of blown film samples was measured according to ASTM D3985 by Mocon OX-TRAN model 2/21 with an oxygen flow rate of 40 cm^3/min at 0 %RH and 23°C. The area of specimens was 100 cm^2. Water vapor permeation (WVP) of the blown film samples was measured according to ASTM D398 by Mocon PERMATRAN-W model 398. All measurements were tested under nitrogen flow rate of 250 cm3/min at 90%RH and 37.8°C. The area of specimens was 50 cm2.

CHAPTER IV

RESULTS AND DISCUSSION

In order to improve the properties of poly(lactic acid) (PLA) blown films, Air dried sheet (ADS) and Standard Thai rubber grade 5L (STR5L) are used as toughening agents in this research. The general properties of both types of natural rubbers are firstly characterized in this section. The effects of mastication time and type of NR on their properties are subsequently investigated. Thenceforth, blown films of PLA blended with virgin and masticated NRs are successfully prepared. The properties of blown films are further discussed.

4.1 Intrinsic properties of natural rubbers

Generally, NR contains about 94% rubber hydrocarbons and 6% non-rubber contents such as proteins, lipids, carbohydrates [19]. As well-known, the properties of resulting rubber products mainly depend on the NR composition. Thus, it is reasonable to clarify the composition of both virgin NRs.

4.1.1 Non-rubber content of virgin NRs

In this part, non-rubber content of virgin ADS and STR5L as shown in Table 4.1 is firstly examined to ensure the quality of raw materials before using. The contents of dirt, ash, volatile matter and nitrogen are determined according to ASTM D1278-91a. As seen in Table 4.1, ADS and STR5L have very low non-rubber contents such as dirt and ash because both NRs are commercial rubber grades which are generally produced under the industry standard process. The nitrogen contents of them are also similar which could be due to the fact that both NRs are produced from fresh natural rubber latex. However, volatile matter of virgin ADS and STR5L is obviously different. Virgin ADS has higher content of volatile matter which indicates that ADS has higher moisture content than STR5L. This is mainly because ADS is dried in drying room by natural air drying, whereas STR5L is dried by hot air drying.

Table 4.1 Non-rubber content of natural rubbers used in this research

Composition	Natural rubber	
	ADS	STR5L
Dirt, % wt.	0.024	0.004
Ash, % wt.	0.38	0.20
Nitrogen, % wt.	0.40	0.37
Volatile Matter (VM), % wt.	0.49	0.30

Note: Standard of STR5L must be limited as follows: % Dirt =0.04%; Ash =0.40%; VM =0.50%; Nitrogen =0.50% [17]

4.1.2 Plasticity of natural rubbers

Plasticity parameters of natural rubbers are shown in Table 4.2. Plasticity is an important factor referring to the flow ability of rubber. Therefore, this factor is related to the difficulty of rubber processing. Initial Plasticity (P_0) of virgin ADS is higher than that of virgin STR5L, implying that flow ability of virgin ADS is lower than that of virgin STR5L. After aging in hot oven at 140°C for 30 min, Plasticity after ageing (P_{30}) of rubber is investigated. It is found that P_{30} of virgin ADS and STR5L are dramatically different. Plasticity of virgin STR5L is intensely decreased after ageing at high temperature. Besides, Plasticity retention index (PRI) associated with thermal resistance of rubber was evaluated. The PRI of virgin STR5L is much lower than that of virgin ADS. It was indicated that virgin STR5L has quite low thermal resistance.

Table 4.2 Plasticity of natural rubbers used in this research

Plasticity parameter	Natural rubber	
	ADS	STR5L
Initial Plasticity (P_0)	43.8	40.0
Plasticity after ageing (P_{30})	39.1	16.0
Plasticity retention index (PRI)	89.2	40.0

4.2 Mastication of natural rubbers

The mastication of ADS and STR5L is performed by using an internal mixer for 5, 10 and 15 min The properties including Mooney viscosity, viscosity average molecular weight and gel content of these masticated NRs are characterized. The effect of mastication time on their properties is discussed in this section and the results are displayed below.

4.2.1 Gel content

The rubber hydrocarbon is usually consisted of a long-chain branched polymer and the gel fraction. The gel in NR is possibly formed by the intermolecular interaction of proteins and phospholipids at chain-ends via hydrogen bonding [17]. It is well known that the level of gel fraction also affects the properties of NR. High protein content can provide a high rate of gel content and the increase of overall viscosity of NR, resulting in the difficulty of processing. The protein content can be calculated from the nitrogen content in NR as a following equation;

Protein content (%) = 6.25 × Nitrogen content (%)

Therefore, the protein content of virgin ADS and STR5L is 2.50% and 2.31%, respectively. This result indicates that the gel content of virgin ADS might be higher than that of virgin STR5L. As seen in Figure 4.1, gel content of virgin ADS and virgin STR5L is 10.75±0.13% and 9.46±0.01% respectively. After mastication for 5 min, gel content decreases to 6.47±0.02% and 5.88±0.08% for ADS and STR, respectively. It might be due to the decomposition of gel content into a sol fraction by shear force during mastication. This result is consistent with the observation in Figure 4.2 [18] that the gel of NR is decomposed by mastication. However, for higher mastication time at 10 and 15 min, the gel content of both ADS and STR5L slightly decreases. At 10 and 15 min of mastication, gel content of ADS is 6.15±0.04% and 5.16±0.07%, respectively. STR5L shows the similar trend as ADS that the gel content at 10 and 15 min of mastication time is 5.64±0.23% and 5.52±0.18%, respectively. As the study of Ehabe et al. [4] shows that the mastication of NR at high temperature could not decompose all gel content. The decreasing of gel content depends on the initial gel content of NR. In this study, the mastication temperature is 135°C. At initial state, the temperature of NR sample in mixer is around room temperature that causes high shear stress during mastication. Shear stress is inversed proportional to temperature [17]. Increasing of temperature can imply the decreasing of shear stress in system.

Lower shear stress could not decompose all of gel in NR. The reduction of gel content of NR at 5, 10, 15 min of mastication time is slightly different.

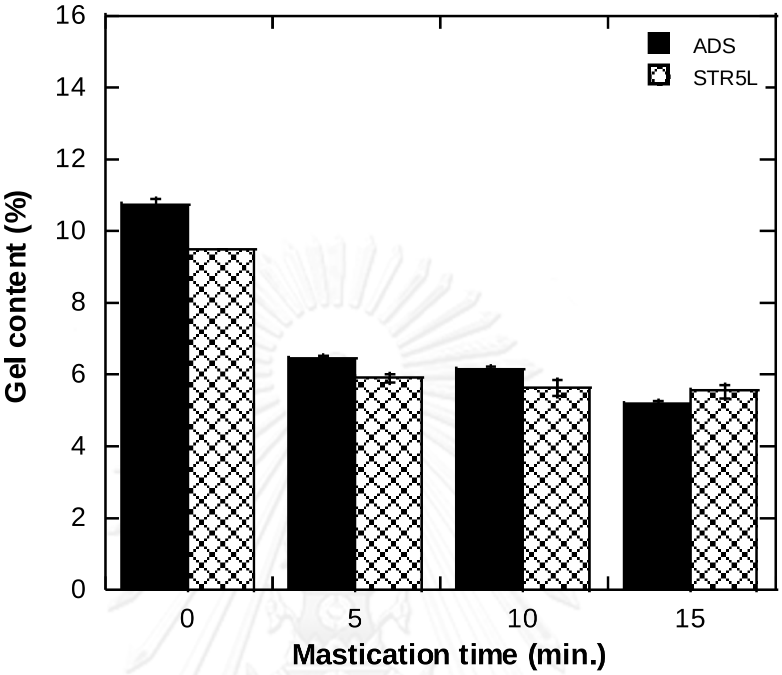

Figure 4.1 Gel content of ADS and STR5L by various mastication time

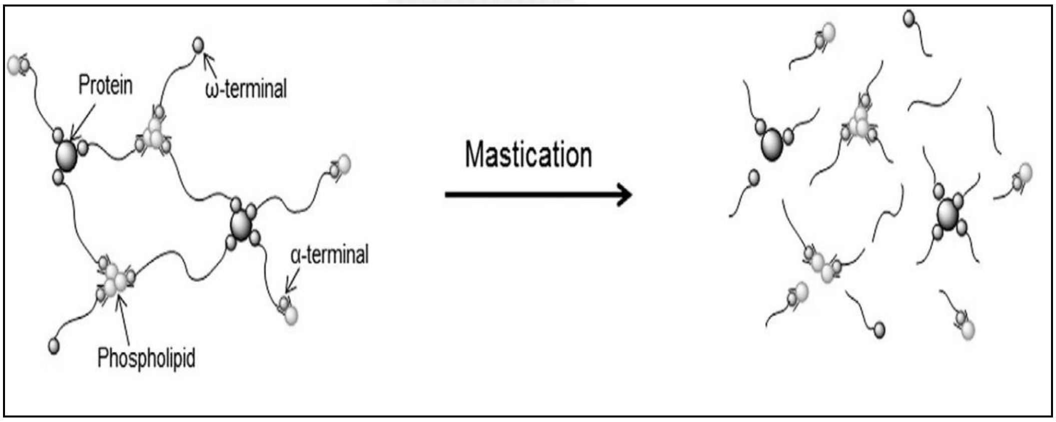

Figure 4.2 Schematic representation of gel content of NR after mastication [18]

4.2.2 Viscosity average molecular weight

The viscosity average molecular weight of virgin ADS and STR5L before and after the mastication process are examined using Ubbelohde viscometer is illustrated in Figure 4.3. Considering virgin NRs, ADS has higher viscosity average molecular weight than STR5L. For masticated samples, viscosity average molecular weight of all samples reduces as a function of mastication time. It is associated with the chain scission of rubbers caused by a mechanical mastication via shear stress and a thermo-oxidative mastication. It is notable that viscosity average molecular weight of STR5L extremely decreases from $5.89\text{x}10^5$ g/mol for virgin STR5L to $1.35\text{x}10^5$ g/mol at 5 min of mastication time. While viscosity average molecular weight of ADS gradually decreases from $6.44\text{x}10^5$ g/mol for virgin ADS to $4.90\text{x}10^5$ g/mol at 5 min of mastication time. It is mainly because the rubber chains of STR5L are easily broken to form shorter chains at high temperature by thermal oxidative mastication. This can be explained by inherent low PRI of STR5L. For ADS that has higher PRI than STR5L, viscosity average molecular weight of ADS after mastication is lower reduction when compared with that of STR5L. Comparing of masticated ADS at 5, 10 and 15 min, the obtained viscosity average molecular weight of STR5L reduces from $1.35\text{x}10^5$ for 5 min to $1.13\text{x}10^5$ and $0.81\text{x}10^5$ for 10 and 15 min of mastication time, respectively. While viscosity average molecular weight of ADS reduces from $4.90\text{x}10^5$ for 5 min to $2.43\text{x}10^5$ and $2.10\text{x}10^5$ for 10 and 15 min of mastication time, respectively. The reduction rate of viscosity average molecular weight in STR5L is lower than that of ADS. According to the low oxidative resistance of STR5L, most of rubber chains are broken up from initial to 5 min of mastication. Therefore, longer mastication time at 10 and 15 min results in lower reduction rate of viscosity average molecular weight for STR5L. On the other hand, 5 min of mastication time is not enough to break up most of rubber chains of ADS due to the high oxidative resistance of ADS. Thus, it is observed that the difference of viscosity average molecular weight at mastication time at 5 and 10 min of ADS is more than that of STR5L. The calculation of viscosity average molecular weight is explained in Appendix A.

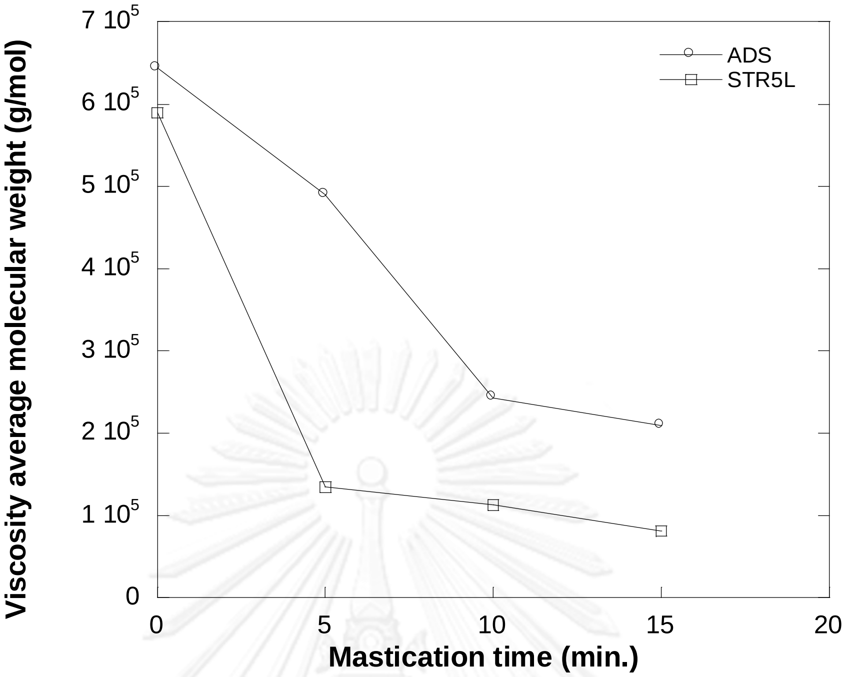

Figure 4.3 Viscosity average molecular weight of ADS and STR5L at various mastication time

4.2.3 Mooney viscosity

Mooney viscosity is an important property that is commonly characterized to monitor the quality and process-ability of NRs. Figure 4.4 shows Mooney viscosity of ADS and STR5L **at various mastication times**. Before mastication, Mooney viscosity of virgin ADS and STR5L were 80.81±0.99 ML(1+4, 100°C) and 78.24±0.10 ML(1+4, 100°C), respectively. This result is consistent with the result of viscosity average molecular weight as described in section 4.2.2. After mastication, it is found that the Mooney viscosity of both rubber types after mastication decreases as a function of mastication time. The decrease of Mooney viscosity in both NRs is associated with the reduction of viscosity average molecular weight during mastication process. The shorter chains increased free volume and reduced chain entanglement. Thus, obtained Mooney viscosity clearly decreases. Dramatically reduced Mooney viscosity can be observed for masticated STR5L, whereas those for masticated ADS gradually decrease. A rapid reduction in viscosity of STR5L is attributed to lower thermal oxidative resistance, leading to the ease of thermal oxidation of rubber chains as aforementioned. Moreover, the Mooney viscosity technique also affects the value of viscosity. Rubber sample was preheated at 100 C for 1 min and applied shear stress for 4 min before measurement. It is clearly seen that Mooney viscosity of STR5L decreases to 43.57±1.76 ML(1+4, 100°C), 21.35±0.18 ML(1+4, 100°C) and 10.11±0.28 ML(1+4, 100°C) at 5, 10 and 15 min of mastication time, respectively. Mooney viscosity of ADS decreases to 66.19±0.54 ML(1+4, 100°C) and 61.40±0.26 ML(1+4, 100°C) and 54.51±1.00 ML(1+4, 100°C) at 5, 10 and 15 min of mastication time, respectively.

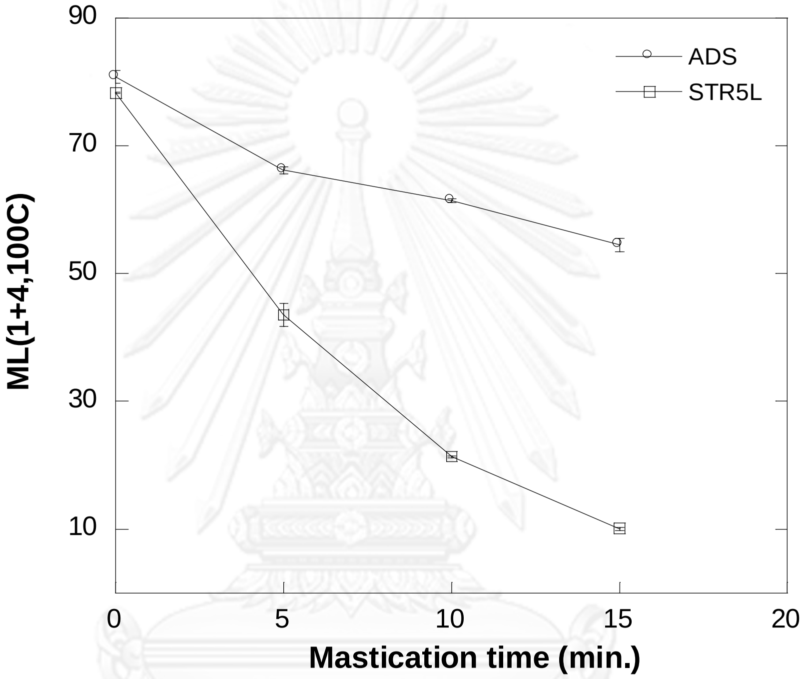

Figure 4.4 Mooney viscosities of ADS and STR5L at various mastication times

4.3 PLA-based blown films blended with virgin and masticated natural rubbers

The ADS and STR5L natural rubbers masticated at 5, 10, 15 min are used as toughening agents. Blending PLA with 20 wt% NR is carried out using a twin screw extruder. The 40.12±0.59 μm thick-films are then blown using a single screw extruder. The properties of PLA-based blown films blending with NRs masticated at various time are evaluated comparing with that of neat PLA blown film. The appearance, morphology, mechanical properties and gas permeability are discussed as follows.

4.3.1 Appearance Properties

As shown in

Table 4.3 , the surface smoothness and opacity of the neat PLA blown film and PLA films blended with different NRs masticated at various times are investigated by visual observation. Neat PLA film commonly has smooth surface and transparence. Blown film of PLA blended with virgin NRs has rougher surface and more opaque or translucent as seen in appearance properties of PLA/ADS0 and PLA/STR0. It is due to heterogeneous dispersion of large NR domains in PLA phase.

However, it is found that the blown film surface of PLA blended with masticated NRs was smoother than with virgin NRs. When considering the effect of mastication time. It can be explained by the difference in thermal oxidative break down between these two rubbers during mastication process. In previous section, it was shown that STR5L has much lower viscosity and molecular weight than ADS. Therefore, blending PLA with STR5L with low viscosity, STR5L can break down and form small domain, leading to smoother and more transparent blown film.

Owing to reduced molecular weight and lower viscosity of NRs resulting from mastication effect, the dispersion of rubber domains in PLA matrix achieved and the interfacial adhesion between phases also enhanced. Considering the addition of NRs masticated at different times, it can be observed that smoother and more transparent blown films are obtained by increasing mastication time. However, blown films from blends of PLA and masticated ADS appear surface rougher and more translucent than those of the other. It can be explained by considering the fact that mastication process has strong effect on properties of STR5L due to its high thermal sensitivity. Thus, the molecular weight and viscosity of STR5L extremely decrease as increasing mastication time, thereby improving appearance properties of their blown films.

Table 4.3 Appearance of PLA-based blown films

Blown film	Visual appearance	
	Surface smoothness	Transparency
Neat PLA	Smooth	Transparent
PLA/ADS0	Rough	Translucent
PLA/ADS5	Rough	Translucent
PLA/ADS10	Moderate	Transparent
PLA/ADS15	Smooth	Transparent
PLA/STR0	Rough	Translucent
PLA/STR5	Moderate	Transparent
PLA/STR10	Smooth	Transparent
PLA/STR15	Smooth	Transparent

4.3.2 Morphology

Cross-sectional fracture surfaces of blown films from neat PLA, PLA blended with ADS (PLA/ADS) and PLA blended with STR5L (PLA/STR) in both machine direction (MD) and transverse direction (TD) are observed by SEM technique. SEM micrographs of cross-sectional fracture surface of blown films from neat PLA film and blends of PLA with virgin NRs in MD and TD are displayed in Figure 4.5. Neat PLA film shows relatively smooth fracture surface because of its inherent stiffness and brittleness. For PLA blended with virgin NRs, the greater roughness of fracture surface is observed which indicated that the addition of virgin NRs enhanced the toughness of PLA blown films. Nonetheless, PLA and NRs is immiscible because a lack of interfacial interaction between phases and the difference in solubility between components [6, 26, 27]. The dispersed rubber domains are often pulled out during sample preparation for SEM analysis, resulting in the formation of cavities in the PLA matrix. Therefore, the large cavities can be clearly observed in SEM images of cross-sectional fracture surfaces for all blends.

The SEM micrographs of cross-sectional fracture surface of blown films from the PLA blended with masticated NRs in MD and TD are displayed in Figure 4.6 and Figure 4.7, respectively. Almost spherical or oval cavities of rubber domains can be seen in SEM images of cross-sectional fracture surface of blown films in MD. The size of cavities decreases when mastication time increases. Clearly, the PLA blended with masticated STR5L provides smaller size of cavities and better distribution in PLA matrix phase than those films with masticated ADS at the same mastication time. It is attributed to the effect of mastication on the reduction of molecular weight of NRs and the difference of their plasticity as mentioned in section4.1. STR5L having lower viscosity and higher flow ability could provide smaller size of rubber domains in PLA phase. The dispersion of rubber domains in the PLA matrix is also improved. These results are consistent with the previous work [28].

During blown film extrusion process, the molten polymer is generally drawn down to a thin film in MD and expanded outward in TD. The MD force is applied by the pulling speed of nip-roll unit, whereas the TD force is air pressure introduced into the bubble tube. The polymer chains are more oriented in MD than TD. The dispersed rubber domains often exhibit the different characteristic shape for cross-sectional fracture surface in MD and TD. In this work, the dispersed rubber domains are highly stretched and elongated along the same direction of polymer chain orientation in MD as displayed in Figure 4.8. Therefore, a dramatic shape change from a spherical cavity to an elongated cavity can be observed in cross-sectional fracture surface of films in TD. The cavities of stretched rubber domains are evident as thin layers. As mastication time increased, very thin layers are greatly formed and the space between thin layers reduces as well. It implies when NR is masticated before addition into PLA, better dispersion and smaller rubber domains are obtained after

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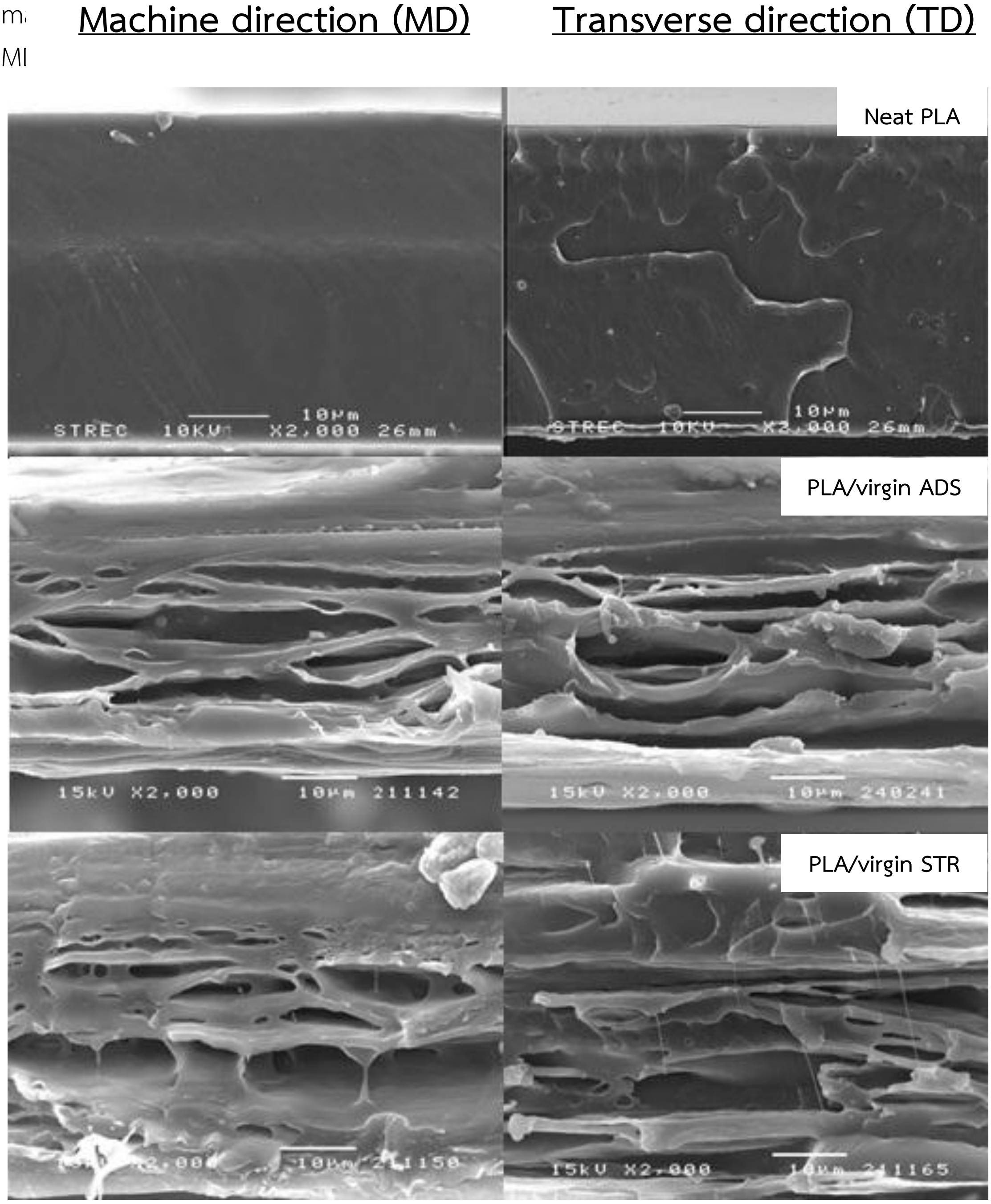


Figure 4.5 SEM micrographs of cross-sectional fracture surfaces in MD and TD of blown films from neat PLA as well as PLA blended with virgin ADS and virgin STR5L

Machine direction (MD)

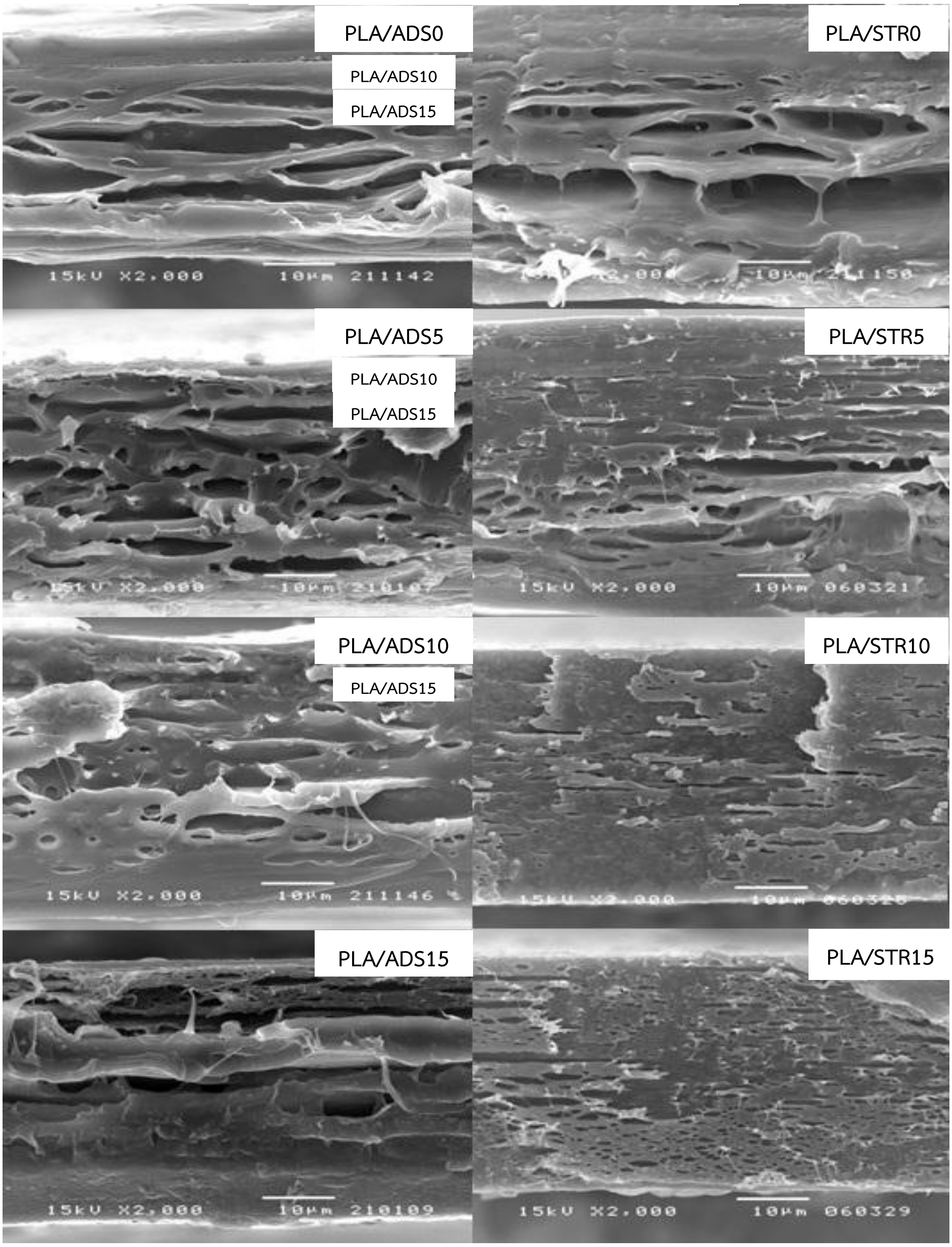


Figure 4.6 SEM micrographs of cross-sectional fracture surfaces in MD of blown films from PLA blended with ADS and STR5L masticated of different time

Transverse direction (TD)

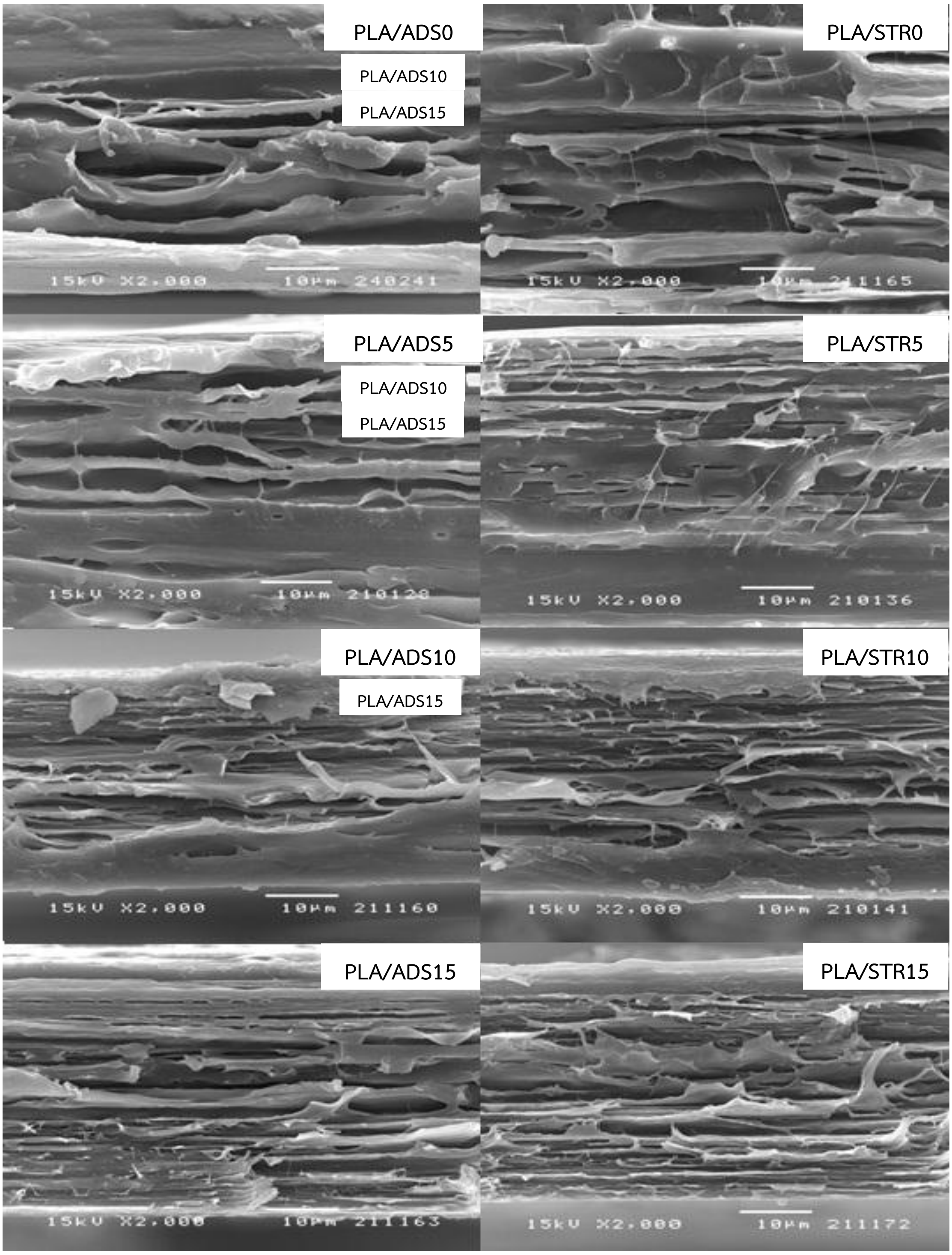


Figure 4.7 SEM micrographs of cross-sectional fracture surfaces in TD of blown films from PLA blended with ADS and STR5L masticated at different time

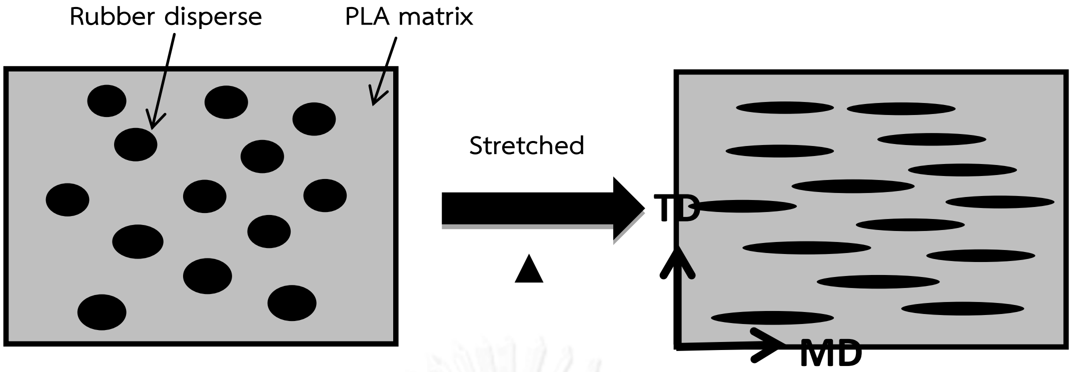


Figure 4.8 Schematic drawing of rubber domains stretching in blown film process

4.3.3 Mechanical properties

It is well known that the incorporation of second phase into PLA matrix phase has a strong effect on the properties of resulting products. Thus, the influence of virgin NRs and masticated NRs on blown film properties is evaluated and then discussed in this section. Tensile strength, Young's modulus, tensile toughness, and elongation at break can be determined from the stress-strain curve. Figure 4.9 represents the stress-strain curves of blown films in MD for neat PLA and PLA/virgin NR blown films. Neat PLA film commonly shows high tensile strength and modulus, but its elongation at break is very low due to the rigidity and brittleness of PLA. The stress-strain behavior obviously changes with adding virgin NRs into PLA. Tensile strength and Young's modulus of PLA/virgin NR blown films decrease, whereas their elongation at break increases. The elongation at break of blown films increased from 4.07 % for neat PLA film to 8.64 % and 16.08 % for PLA/ADS0 and PLA/ STR0 films, respectively. Tensile toughness also increased from 41.39 mJ for neat PLA film to 55.29 mJ and 187.64 mJ for PLA/ADS0 and PLA/ STR0 films, respectively. This result reveals that the incorporation of virgin NR could enhance the toughness of PLA blown films because of its very high elasticity. The difference in tensile properties between PLA/ADS0 and PLA/STR0 films could be caused by different intrinsic properties of virgin NRs. Owing to lower viscosity average molecular weight and viscosity of STR5L, smaller domain size of rubber is obtained Therefore, two toughening mechanisms (crazing and shear yielding) can be used to explain the behavior of these blown films as follows.

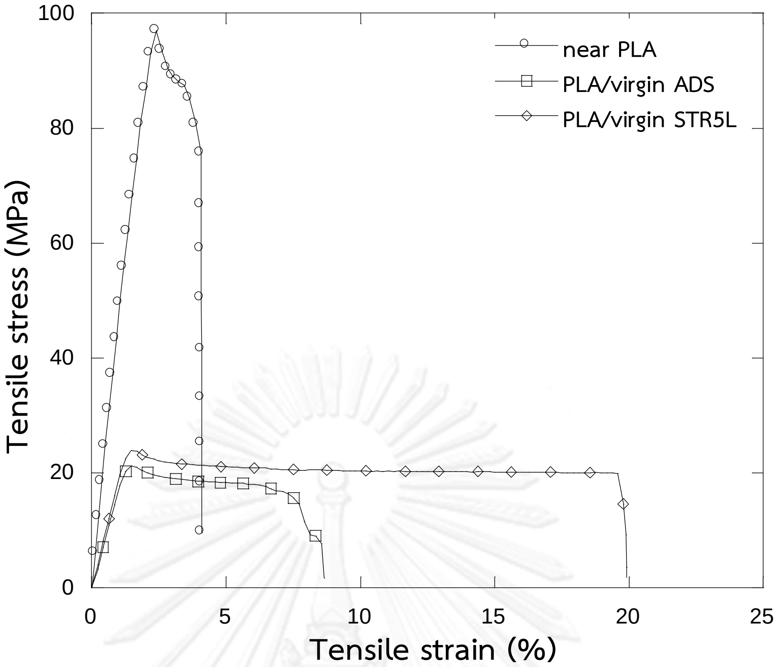


Figure 4.9 The tensile stress-strain curves of neat PLA, PLA/virgin ADS, and PLA/virgin STR5L blown films in MD

Crazing and shear yielding are the important mechanisms to improve toughness of polymers. Crazing is a phenomenon for the fracture of glassy polymer. In the craze formation process, numerous micro-voids will develop. At a certain stress, the fibrils can no longer bear the load. The micro-voids will coalesce and the craze becomes a crack, which will eventually grow and reach other cracks, so that it could result in fatal fracture. In rubber toughening polymer, crazes are initiated at the point of maximum applied stress although interactions between the particles‘stress fields can introduce deviations. Craze growth is terminated when rubber domain is encountered, preventing the growth of very large crazes. The result is a large number of small craze that suits to improve energy absorption of the matrix in the blend as shown in schematic drawing in Figure 4.10

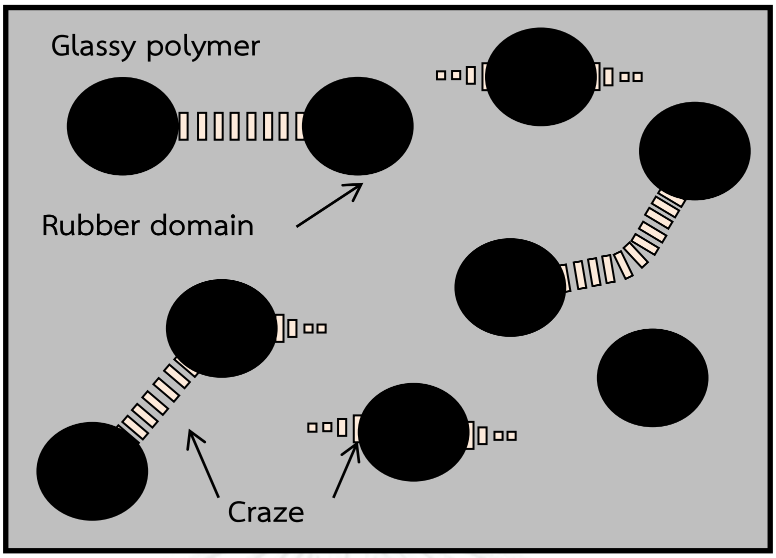


Figure 4.10 Schematic drawing of role of rubber domain in crazing mechanism

Shear yielding in the matrix phase also plays a major role in the mechanism of the rubber toughening in polymer blends as shown in schematic drawing in Figure 4.11. Shear yielding, as localized shear bands, usually occurs in addition to elastic deformation. This mechanism is always accompanied by the cavitation of the dampening particle (apparition of voids) absorbing also the energy. However, the apparition of shear bands absorbs most of the energy. Not only does this phenomenon act as an energy absorbing process but the shear band also presents a barrier to the propagation of crazes, hence crack growth; therefore, delaying failure of the material.

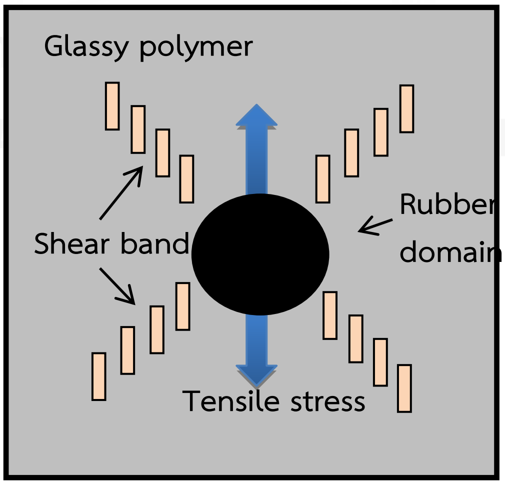


Figure 4.11 Characteristics of the shear yielding

Stress-strain curves of PLA/masticated ADS and PLA/masticated STR5L blown films in MD as shown in Figure 4.12 and Figure 4.13. All tensile properties especially, the elongation at break of PLA/NR films increased as a function of mastication time.. The elongation at break of PLA/masticated ADS films slightly increased with increase mastication time whereas the elongation at break of PLA/masticated STR5L films dramatically increased. The elongation at break of PLA/ADS0 films in MD increased from 19.90 % to 27.93 % for PLA/ADS5 film whereas it is very interesting that the elongation at break of PLA/STR5 film dramatically increases to 163.04 %. PLA/STR15 film shows the highest elongation at break which is 274.30 %.

The effect of masticated NR on PLA blown film can be explained in terms of characteristic of the rubber phase of NR. The films with well dispersed and small-sized rubber domains can be formed small cavities and led to large plastic deformation. Small-sized of rubber domain is effective for improving the toughness of film. The rubber domain toughness brittle polymer by acting as a stress concentrators, enhancing shear yielding, then inducing cavity and dissipating energy. Moreover, all tensile properties of PLA/masticated NR blown film in TD show the same trend with those in MD but lower tensile properties because the orientation of chain molecule that is explained in Figure 4.14.

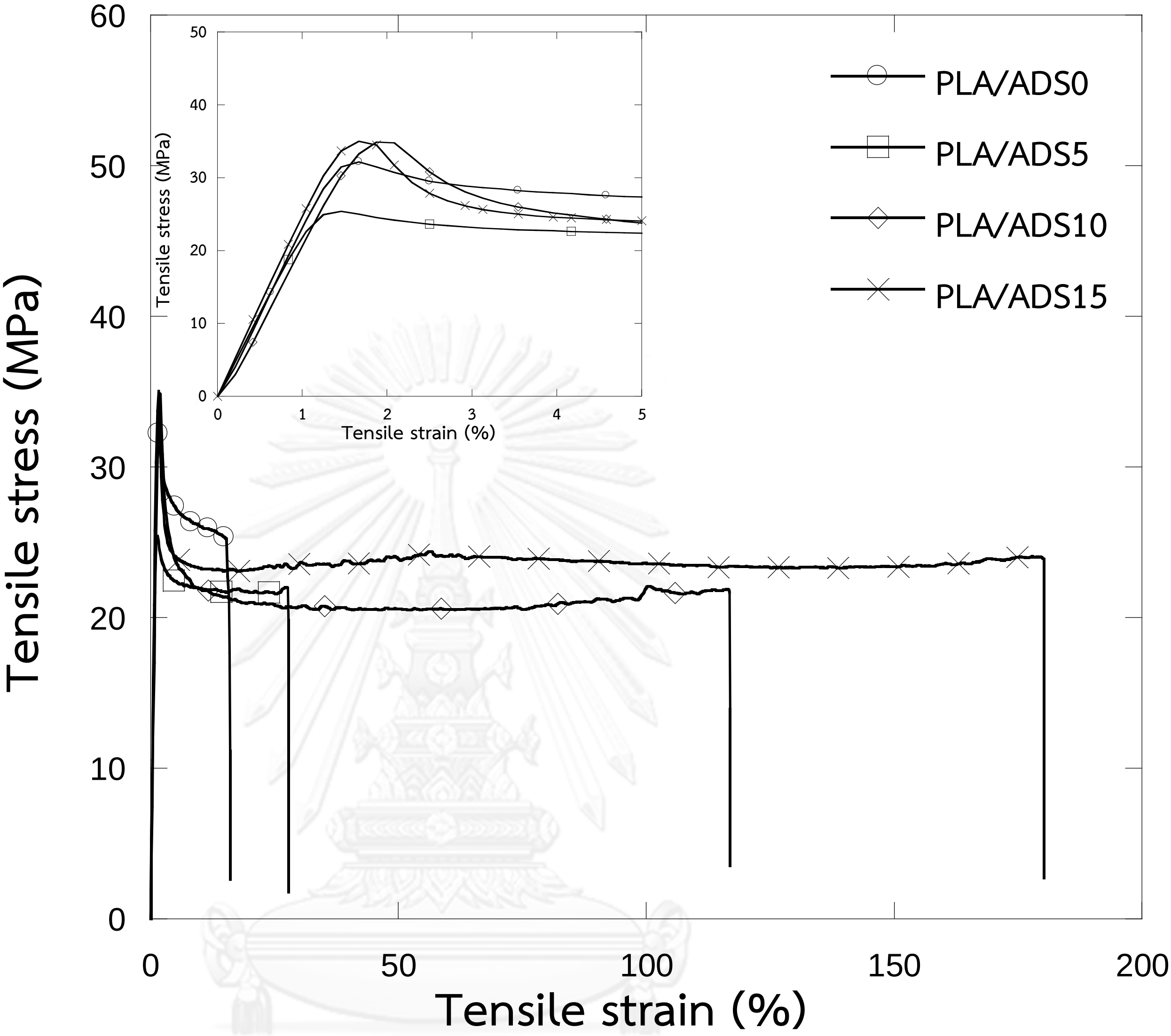


Figure 4.12 The tensile stress-strain curves and enlarge image caption in MD of PLA/ADS0, PLA/ADS5, PLA/ADS10 and PLA/ADS15 blown films

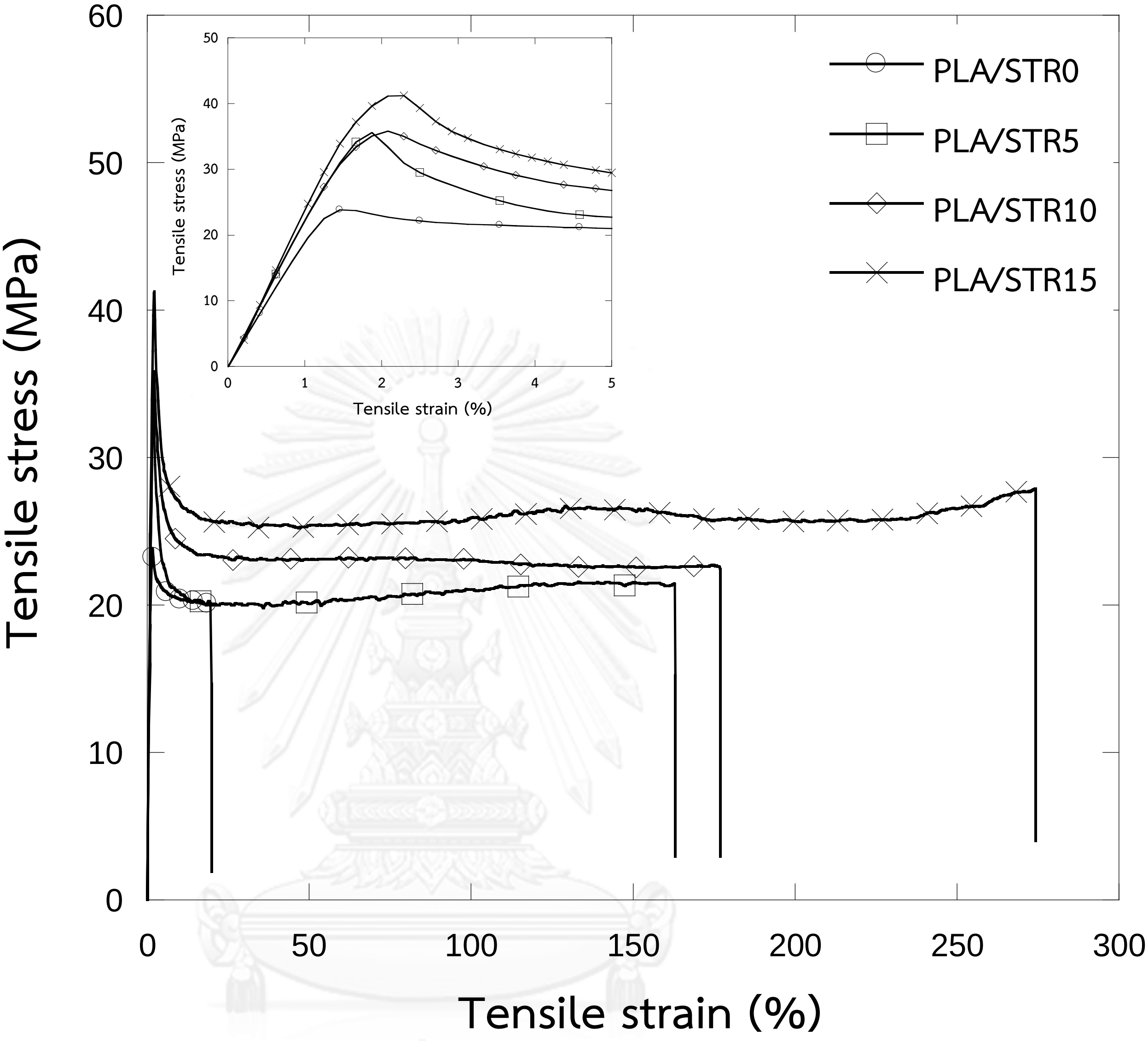


Figure 4.13 The tensile stress-strain curves and enlarge image caption in MD in MD of PLA/STR0, PLA/STR5, PLA/STR10 and PLA/STR15 blown films

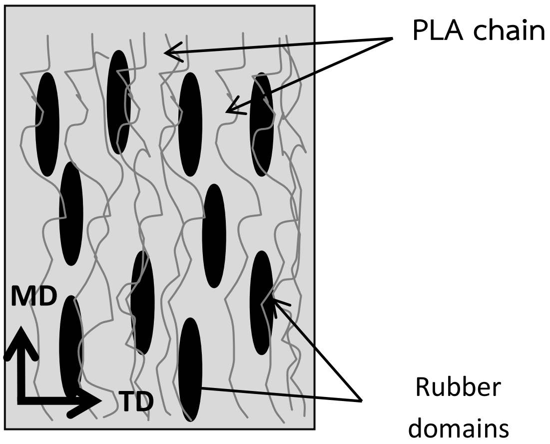


Figure 4.14 Schematic drawing of orientation of PLA chain and NR domains

The tear strength in MD and TD of neat PLA, PLA blended with virgin NRs and PLA blended with NRs at different time are shown in Figure 4.15 and Figure 4.16. Tear strength of neat PLA film in MD and TD are 456.60 and 304.5 N/m, respectively. Addition of virgin ADS (PLA/ADS0) and STR5L (PLA/STR0) into PLA matrix tends to increase the tear strength in both directions.

However, the tear strength in MD is lower than that in TD for all films (Figure 4.17) because tearing along TD in which the force acts in the region perpendicular to PLA molecular chain and NR elongated domains. The molecular chain molecule of PLA and rubber domains is oriented along the MD during film blowing due to the speed of nip roll.

From the tear strength of PLA/masticated ADS and PLA/masticated STR5L blown films, these results are consistent with the characteristic of rubber domains in PLA matrix. The tear strength of both PLA/NR films increases with increasing mastication time. In addition, the tear strength of PLA/STR5L blown films are higher than those of PLA/ADS blown films which can be explained by the domain size of rubber in the film as schematically illustrated in Figure 4.18 which is confirmed by the SEM images of films. At long time of mastication, the domain size of NR becomes smaller than short mastication In tearing mechanism, the internal force occurs at the edge of the film and then cracks through NR domains to the other edge. Tear resistance depends on the size and phase characteristic of NR, in which small-sized of NR domains and more rubber domains require higher force to tear the film. Therefore, PLA/STR5L films show higher tear strength than PLA/ADS films at the same mastication time due to good distribution of smaller dispersed rubber domains and compatibility of PLA and rubber domain phase, thereby achieving better interfacial adhesion between PLA phase and dispersed NR domains

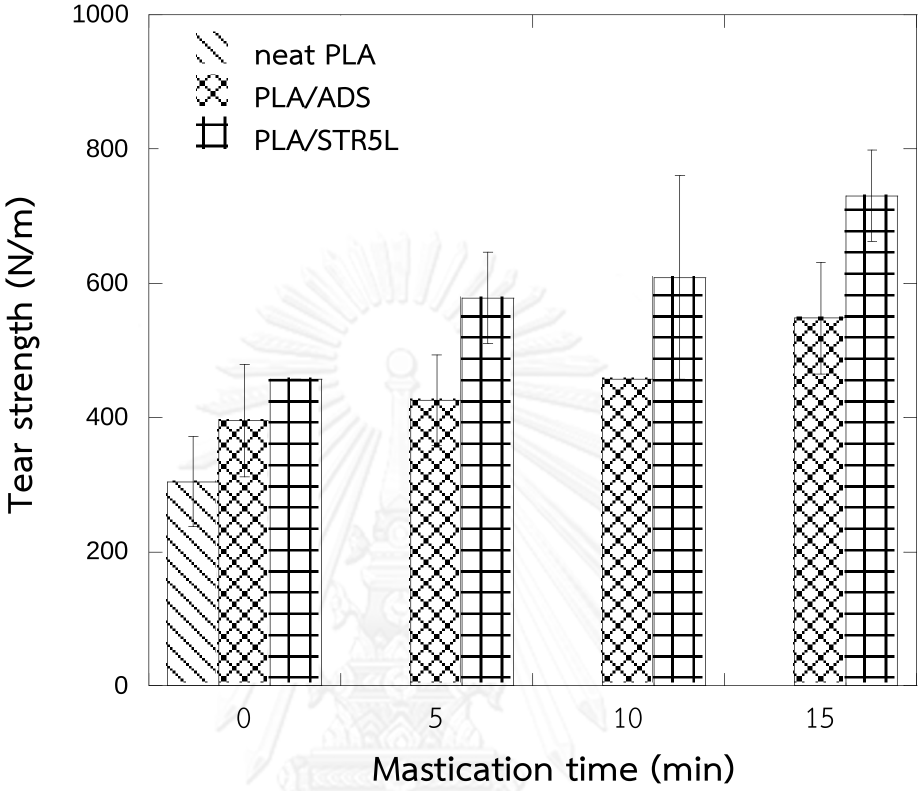


Figure 4.15 Tear strength in MD of neat PLA , PLA blended with virgin NRs and PLA blended with NRs at different time

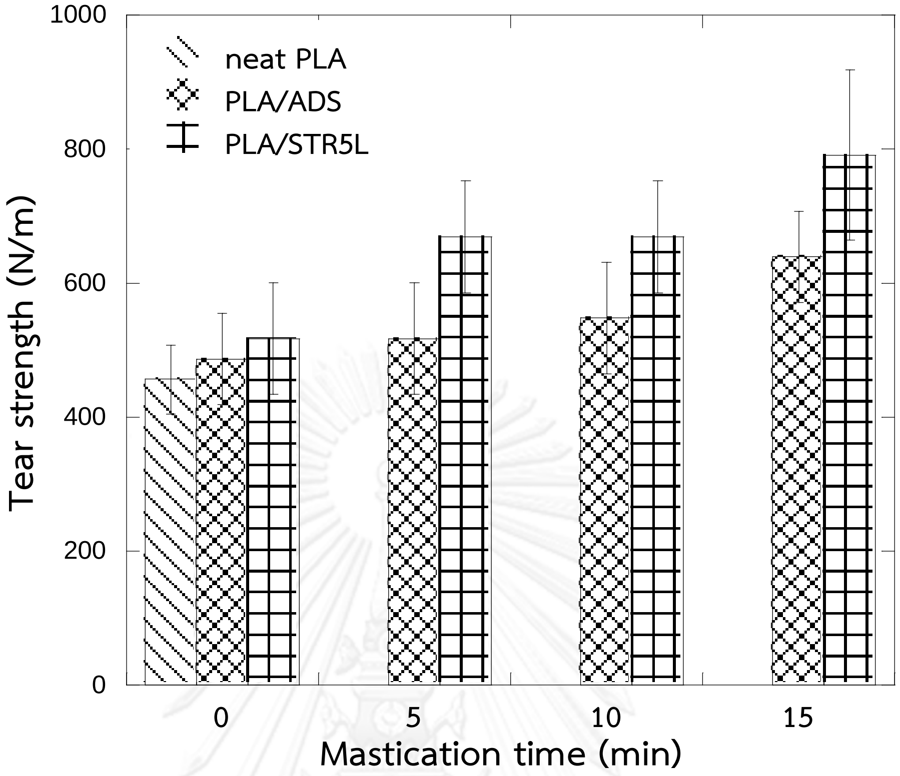


Figure 4.16 Tear strength in TD of neat PLA, PLA blended with virgin NRs and PLA blended with NRs at different time

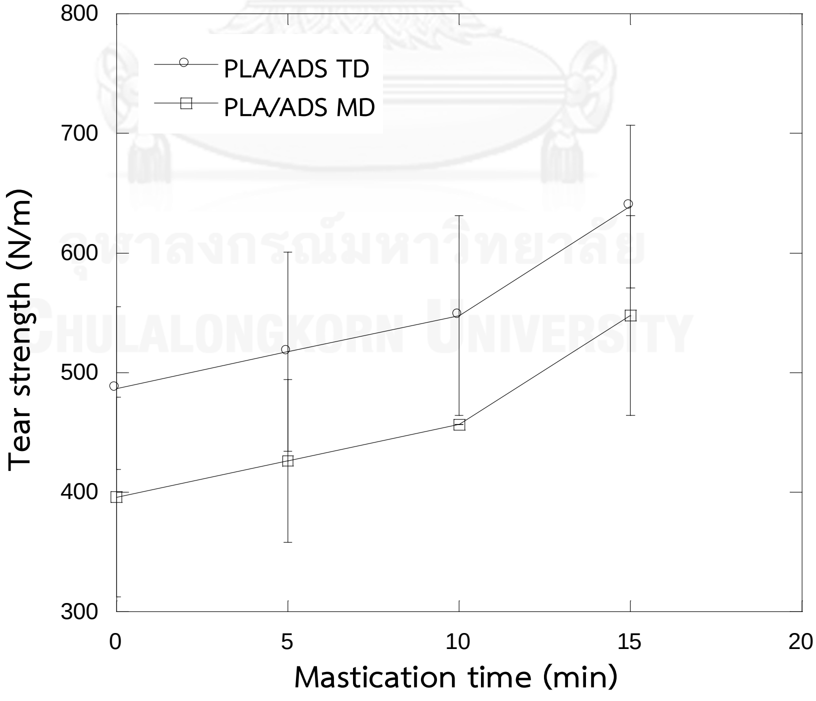
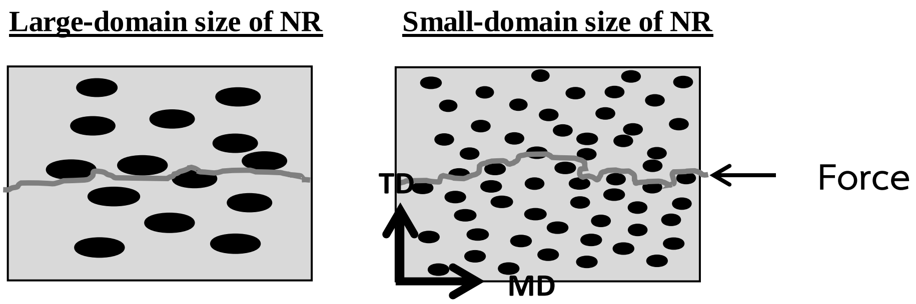


Figure 4.17 Tear strength in TD and MD of PLA blended with virgin ADS at different time



Large-domain size of NR

Small-domain size of NR

Figure 4.18 Schematic drawing to illustrate tear mechanisms for PLA film with large-sized and small-sized of rubber domains

The Impact strength of neat PLA film, PLA blended with virgin NRs and PLA blended with NRs at different time are shown in Figure 4.19. Addition of virgin NRs and masticated NRs are successfully increased impact resistance of PLA film. The impact strength increased from 3.02 J/cm for neat PLA film to 19.31 J/cm and 18.77 J/cm for PLA film blended with virgin ADS and virgin STR5, respectively.

For the PLA blown film blended with masticated NR, it is found that the Impact strength of the blown film increases with the increasing mastication time. The impact strength of PLA/masticated ADS films slightly increases with increasing mastication time whereas PLA/masticated STR5L films dramatically increases (Figure 4.19). The impact strength of PLA/ADS0 films in MD increases from 19.31 J/cm to 40.29 J/cm, 65.17 J/cm, and 73.12 J/cm for PLA/ADS5, PLA/ADS10, PLA/ADS15 film, respectively. Whereas it is very interesting that the impact strength of PLA/STR5 films dramatically increased to 90.12 J/cm.

From morphology of small domain as shown in previous section, it can be implied that small-sized rubber domain in the PLA matrix can absorb impact energy, then giving high impact strength. [26]. Schematical illustration of small-sized and large-sized rubber domain in PLA matrix is shown in Figure 4.20. Moreover, the impact strength dramatically increases with the PLA blended with masticated STR5L.

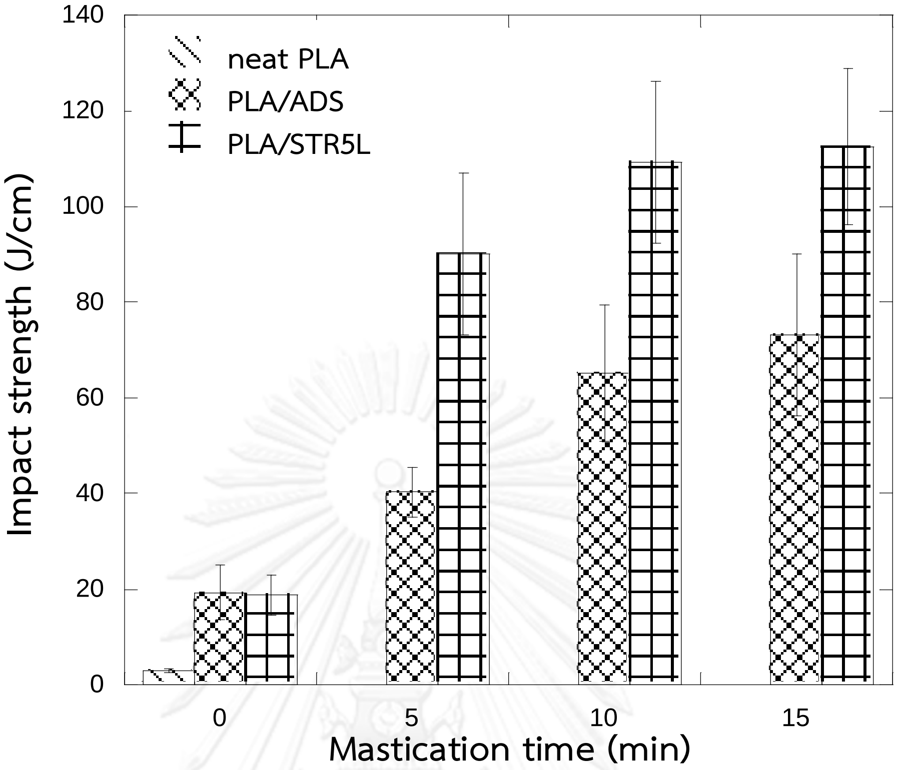


Figure 4.19 Impact strength of neat PLA, PLA blended with virgin NRs and PLA blended with NRs at different time

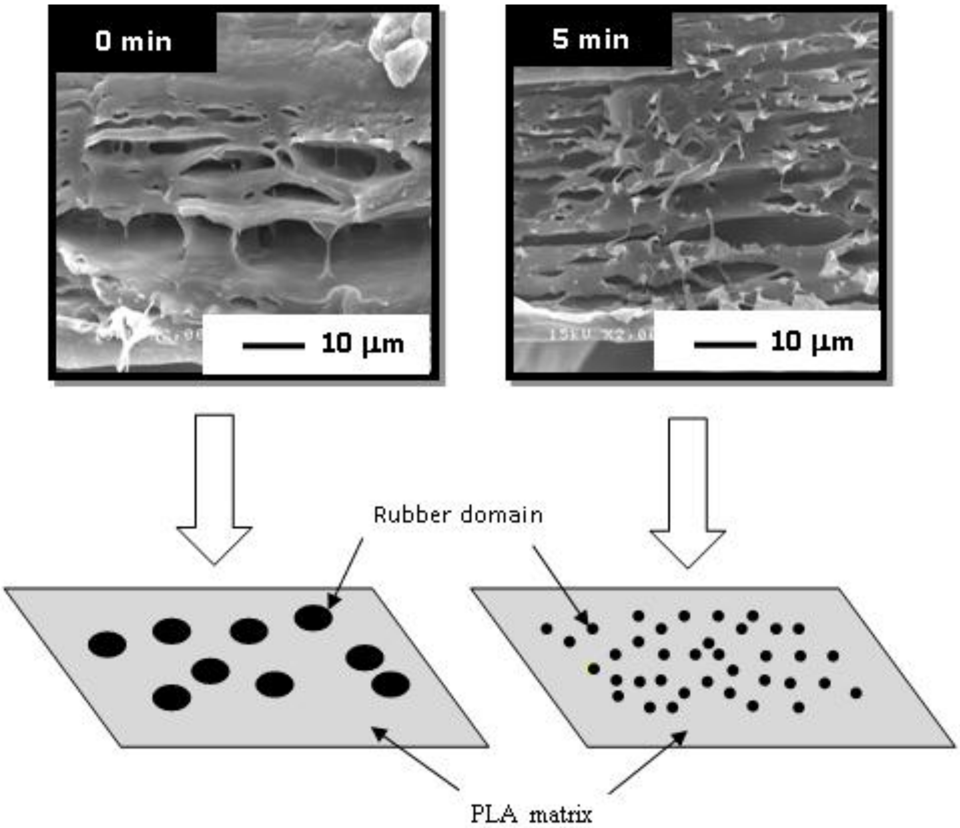


Figure 4.20 Schematic drawing to illustrate impact mechanism of large and small domain size of rubber in PLA film

4.2.4 Gas permeability

Gas permeability is an important property of films when using for food and product packaging applications. In this work, oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) of all blown films are evaluated using Mocon OX-TRAN model 2/21 and Mocon PERMATRAN-W model 398, respectively. Generally, the transmission of gas molecules in heterogeneous polymer blend can be explained by two characteristics as demonstrated in Figure 4.21. Gas molecules can mainly pass through the free volume in polymer when the interfacial adhesion between components is strong. While the interfacial adhesion between phases is not good, it can result in the formation of gap at interface thus gas molecules can easily pass through this way. According to the results of oxygen transmission rate (OTR) as shown in Figure 4.22, the addition of both types of virgin NRs into PLA film extremely enhances the oxygen permeability of blown films. The OTR increased from 564.57 ±

32.16 cc/m2day for neat PLA film to 1501.83 ± 4.76 cc/m2day and 1281.55 ± 44.82 cc/m2day for PLA/ADS0 and PLA/STR0 films, respectively. It is primary due to the fact that blends of PLA and virgin NRs is heterogeneous that often provided poor interfacial adhesion between phases. Therefore, oxygen molecules could pass through the gap formed at the interface between PLA and NR phases. Obviously, the OTR of PLA/ADS0 film is higher than that of PLA/STR0 film. This can be explained by the gap between PLA and rubber which are formed during blown film process. When the molten plastic from die is pulled by nip roll, the rubber domain and PLA matrix are stretched. After plastic is cooled down, the rubber domain is shrunk to the original form. Elasticity of rubber is determined the ability to stretch and shrink of rubber domain. The high elasticity of rubber can be more stretched and more shrunk when the rubber domain is shrunk, it would create gap between PLA matrix and rubber domain in film. Higher molecular weight of virgin ADS led to higher elasticity because this rubber has more rubber chain entanglement than lower molecular weight of virgin STR5L. Therefore, the rubber domain of ADS would shrink and leave larger empty space between PLA matrix and rubber domain than that of STR5L. The schematic drawings of different size of gap from NR are shown in. Therefore, incorporation of ADS into the PLA matrix leads to larger gap between PLA and rubber domain, thus leading to higher OTR when compared with incorporation of STR5L.

The compatibility and interfacial adhesion between PLA and STR5L improved, reducing the gap formation at interface. Considering PLA blended with masticated NRs, the OTR decreased as a function of mastication time. It is due to decreasing of elasticity of rubber that led to smaller gap between PLA and rubber.

ผิดพลาด! ไม่พบแหล่งการอ้างอิง illustrates the water vapor permeability of samples in term of WVTR. The WVTR increased from 95.13 ± 1.02 gm/m^{2}day for neat PLA film to 122.98 ± 8.39 gm/m^{2}day and 119.14 ± 1.94 gm/m^{2}day for PLA blended with virgin ADS and virgin STR5L, respectively. The water vapor permeability of blown films slightly decreases with the addition of masticated NRs into PLA matrix. These results are consistent with those of oxygen transmission rate as previously mentioned.

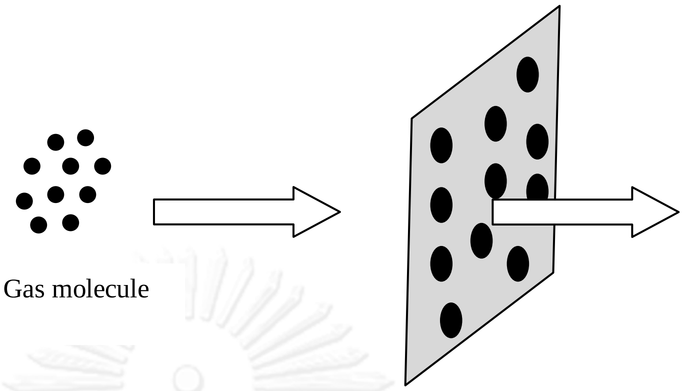


Figure 4.21 Schematic of gas permeability in a heterogeneous polymer blend

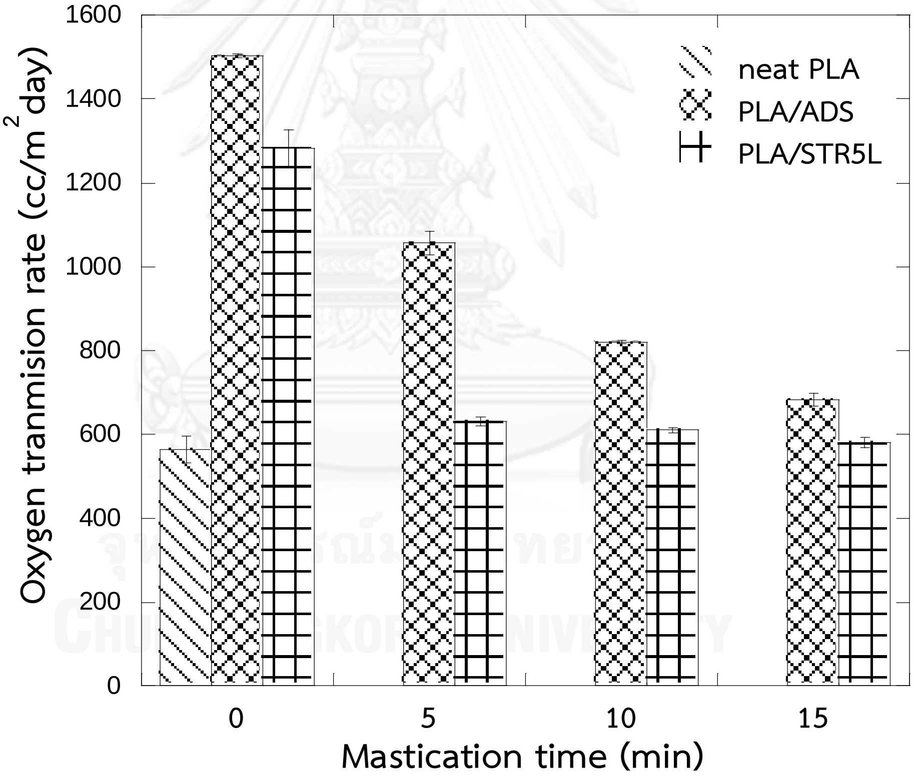


Figure 4.22 Oxygen transmission rate of PLA/NR blown films

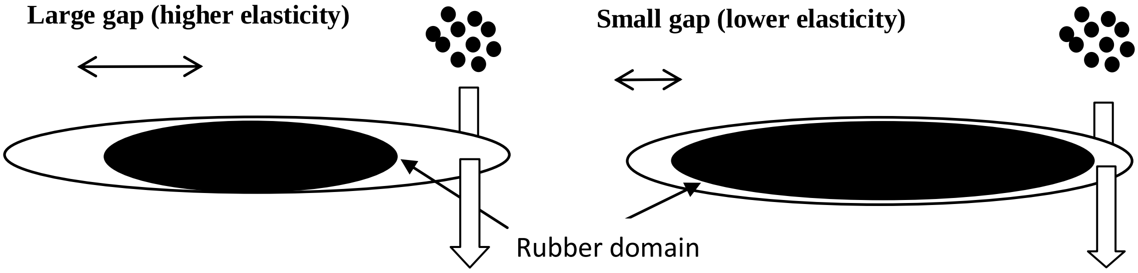


Figure 4.23 Schematic drawings of different size of gap from NR

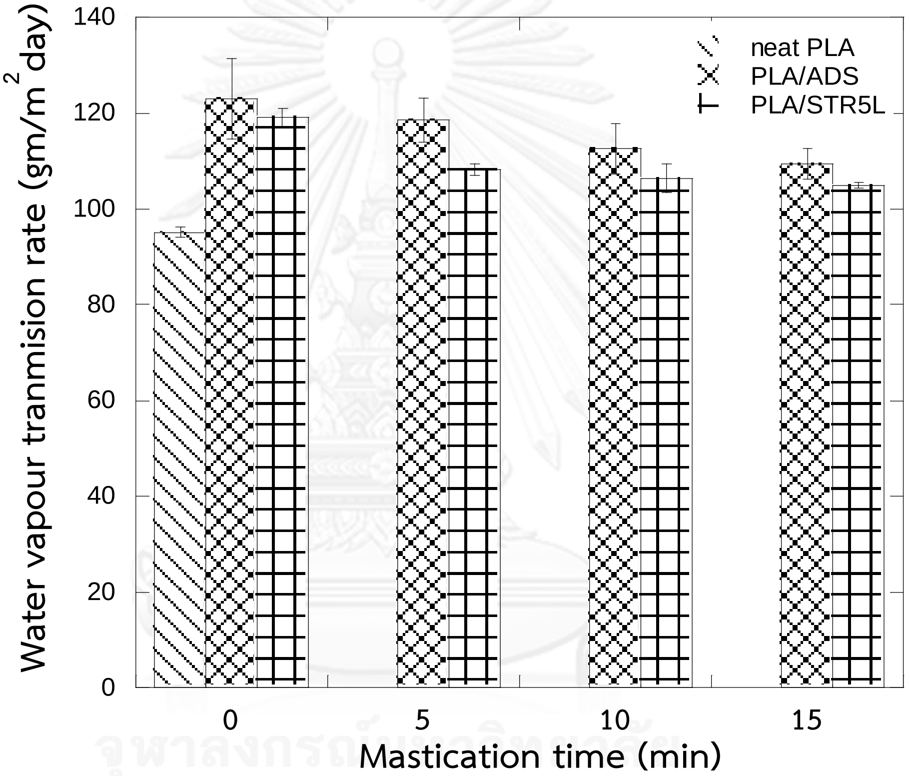


Figure 4.24 Water vapor transmission rate of PLA/NR blown films

CHAPTER V
CONCLUSIONS

5.1 Conclusions

Air dried sheet (ADS) and Standard Thai Rubber5L (STR5L) rubber were used in this work in order to improve the properties of poly(lactic acid) or PLA blown film. Non-rubber content and plasticity of natural rubbers (NRs) were investigated before usage. The values of non-rubber content and Initial Plasticity (P_0) for both NRs were similar. While Plasticity after ageing (P_{30}) and Plasticity retention index (PRI) of STR5L were much lower than those of ADS.

NRs were masticated at various in times of which the chain scission in NRs is strongly induced via thermal-oxidation mastication, resulting in the breaking up of the long rubber molecules into shorter ones. Viscosity average molecular weight and Mooney viscosity of masticated NRs intensely decreased with increasing mastication time, especially STR5L.

Blown films of PLA blended with virgin NRs and masticated NRs were successfully accomplished. Blown films showed smoother surface and more transparent when blending with masticated NRs as compared with blown films of PLA blended with virgin NRs. According to SEM observation, the size of dispersed rubber domains decreased with increasing mastication time as observed in the reduction of cavity size in fracture surface of blown films. Good distribution of numerous smaller rubber domains in PLA matrix is clearly observed.

Therefore, toughness, tear strength and impact strength of blown films outstandingly enhanced by the addition of masticated NRs into PLA matrix phase. The results of PLA blended with masticated ADS and masticated STR5L were different. At same mastication time, the toughness, tear strength and impact strength of PLA/ masticated STR5L blown film is higher than that of PLA/masticated ADS film because STR5L exhibits low thermal oxidative resistance that led to smaller rubber domain size. The mastication of NR before adding into PLA matrix is one of the effective methods to adjust the properties of NR when using a toughening agent of the PLA blown film.

Moreover, oxygen permeation rate of blown films obviously reduced, possibly due to the smaller gap between PLA matrix and rubber phases.

From this result, the mastication process is sufficient to reduce rubber molecules and the viscosity. Consequently, blending PLA with masticated NRs with shorter rubber molecules is an effective approach to improve the properties of PLA blown films.

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APPENDIX

Appendix A
Characterization of NR and masticated NR

Mooney viscosity

Table A.1 Mooney viscosity of ADS with 0, 5, 10 and 15 min mastication time

Number	Mastication time (min)			
	0	5	10	15
1	79.56	65.85	61.71	55.11
2	81.97	65.76	61.08	55.33
3	80.91	66.95	61.42	53.1
Avg.	80.81	66.19	61.40	54.51
SD	0.99	0.54	0.26	1.00

Table A.2 Mooney viscosity of STR5L with 0, 5, 10 and 15 min mastication time

Number	Mastication time (min)			
	0	5	10	15
1	79.56	42.29	21.6	9.88
2	81.97	46.06	21.24	9.95
3	80.91	42.37	21.2	10.5
Avg.	80.81	43.57	21.35	10.11
SD	0.99	1.76	0.18	0.28

Viscosity average molecular weight

From Mark - Houwink equation. $[\eta] = \mathrm{KM}_{\mathrm{v}}^{\mathrm{a}}$, viscosity can be directly related to time required for flow through the capillary that can be determined by two equations

1. Huggins equation

inherent viscosity $= \frac{\eta_{sp}}{C} = [\eta] + \mathrm{k}'[\eta]^2\mathrm{C}$, $[\eta] = \lim_{c=0} \frac{\eta_{sp}}{C}$

2. Kramer equation

reduce viscosity $= \frac{\ln\eta_{rel}}{C} = [\eta] - \mathrm{k}''[\eta]^2\mathrm{C}$, $[\eta] = \lim_{c=0} \frac{\ln\eta_{rel}}{C}$

Where

η_{sp} = specific viscosity $=\eta_{\mathrm{rel}} - 1 = \frac{\eta-\eta_0}{\eta_0} \approx \frac{\mathrm{t}-\mathrm{t}_0}{\mathrm{t}_0}$,

η_{rel} = relative viscosity $=\frac{\eta}{\eta_0} \approx \frac{\mathrm{t}}{\mathrm{t}_0}$

η = viscosity of the solution

η_0 = viscosity of the solvent

t = flow time of solution from ubbelohde viscometor

t_0 = flow time of solvent from ubbelohde viscometor

C = polymer concentration

k' = Huggins constant

k'' = Kramer constant

$\mathrm{k}' + \mathrm{k}'' = 0.5$

Table A.3 Flow time of toluene

Number	Temperature (°C)	Flow time (sec)
1	25	117.93
2	25	117.73
3	25	117.7
Avg.	25	117.79
SD	0	0.10

Table A.4 Flow time of virgin ADS (ADS0)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	122.06
	2	25	122.18
	3	25	122.19
0.03	1	25	130.36
	2	25	130.8
	3	25	130.66
0.05	1	25	140.74
	2	25	140.84
	3	25	140.88
0.07	1	25	150.93
	2	25	152.03
	3	25	151.25

Table A.5 Flow time of masticated ADS at 5 min (ADS5)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	121.60
	2	25	121.59
	3	25	121.51
0.03	1	25	127.35
	2	25	127.53
	3	25	127.54

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.05	1	25	135.62
	2	25	136.32
	3	25	135.01
0.07	1	25	140.28
	2	25	140.18
	3	25	141.14

Table A.6 Flow time of masticated ADS at 10 min (ADS10)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	120.18
	2	25	120.18
	3	25	120.18
0.03	1	25	123.45
	2	25	123.95
	3	25	123.45
0.05	1	25	127.82
	2	25	127.92
	3	25	127.83
0.07	1	25	131.82
	2	25	131.84
	3	25	131.89

Table A.7 Flow time of masticated ADS at 15 min (ADS15)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	120.01
	2	25	119.96
	3	25	119.78
0.03	1	25	123.08
	2	25	123.1
	3	25	123.41
0.05	1	25	126.55
	2	25	126.88

	3	25	126.95
0.07	1	25	130.38
	2	25	130.03
	3	25	130.08

Table A.8 Flow time of virgin STR5L (STR0)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	122.27
	2	25	122.26
	3	25	122.2
0.03	1	25	131.32
	2	25	131.38
	3	25	131.15
0.05	1	25	139.37
	2	25	139.63
	3	25	139.7
0.07	1	25	149.78
	2	25	149.68
	3	25	149.73

Table A.9 Flow time of masticated STR5L with 5 min (STR5)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	119.36
	2	25	119.31
	3	25	119.18
0.03	1	25	122.35
	2	25	122.98
	3	25	122.86
0.05	1	25	124.62
	2	25	124.66
	3	25	124.64
0.07	1	25	127.71
	2	25	127.71

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
	3	25	127.51
0.10	1	25	131.88
	2	25	131.92
	3	25	131.82

Table A.10 Flow time of masticated STR5L at 10 min (STR10)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	119.36
	2	25	119.31
	3	25	119.18
0.03	1	25	122.35
	2	25	122.98
	3	25	122.86
0.05	1	25	124.62
	2	25	124.66
	3	25	124.64
0.07	1	25	127.71
	2	25	127.71
	3	25	127.51
0.10	1	25	131.88
	2	25	131.92
	3	25	131.82

Table A.11 Flow time of masticated STR5L at 15 min (STR15)

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
0.01	1	25	118.88
	2	25	118.93
	3	25	119.12
0.03	1	25	120.79
	2	25	120.83
	3	25	120.95
0.05	1	25	122.79

Concentration (g/100 ml)	Number	Temperature (°C)	Flow time (sec)
	2	25	122.89
	3	25	122.8
0.07	1	25	124.74
	2	25	124.81
	3	25	124.85
0.10	1	25	128.26
	2	25	128.9
	3	25	128.3

Table A.12 Relative viscosity and specific viscosity of masticated ADS and STR5L at various concentrations

Sample	Concentration (g/100 ml)	Relative viscosity	Specific viscosity
ADS0	0.01	1.0370	0.0370
	0.03	1.1088	0.1088
	0.05	1.1956	0.1956
	0.07	1.2874	0.2874
ADS5	0.01	1.0321	0.0321
	0.03	1.0822	0.0822
	0.05	1.1517	0.1517
	0.07	1.1942	0.1942
ADS10	0.01	1.020	0.0203
	0.03	1.0502	0.0502
	0.05	1.0855	0.0855
	0.07	1.1195	0.1195
ADS15	0.01	1.0181	0.0180
	0.03	1.0460	0.0459
	0.05	1.0765	0.0765
	0.07	1.1041	0.1041
STR0	0.01	1.0378	0.0378
	0.03	1.1146	0.1146
	0.05	1.1849	0.1849
	0.07	1.2710	0.2710

Sample	Concentration (g/100 ml)	Relative viscosity	Specific viscosity
STR5	0.01	1.0127	0.0127
	0.03	1.0420	0.0420
	0.05	1.0582	0.0582
	0.07	1.0834	0.0834
	0.10	1.1196	0.1196
STR10	0.03	1.0355	0.0355
	0.05	1.0581	0.0581
	0.07	1.0863	0.0863
	0.10	1.1192	0.1192
STR15	0.01	1.0101	0.0101
	0.03	1.0261	0.0261
	0.05	1.0428	0.0428
	0.07	1.0598	0.0598
	0.10	1.0908	0.0908

Table A.13 Intrinsic viscosity of masticated ADS and STR5L

Sample	Intrinsic viscosity (100 ml/g)			Viscosity average molecular weight
	From Huggins equation	From Kramer equation	Average Intrinsic viscosity	
ADS0	3.5351	3.5523	3.5437 ± 0.012	589,188
ADS5	3.1421	3.1243	3.1332 ± 0.013	489,870
ADS10	1.9681	1.9621	1.9651 ± 0.004	243,404
ADS15	1.7818	1.7752	1.7785 ± 0.0047	209,578
STR0	3.7649	3.7548	3.7599 ± 0.007	643,853
STR5	1.3894	1.3795	1.3845 ± 0.007	134,842
STR10	1.1767	1.1752	1.1760 ± 0.001	112,749
STR15	0.9647	0.9466	0.9557 ± 0.013	81,376

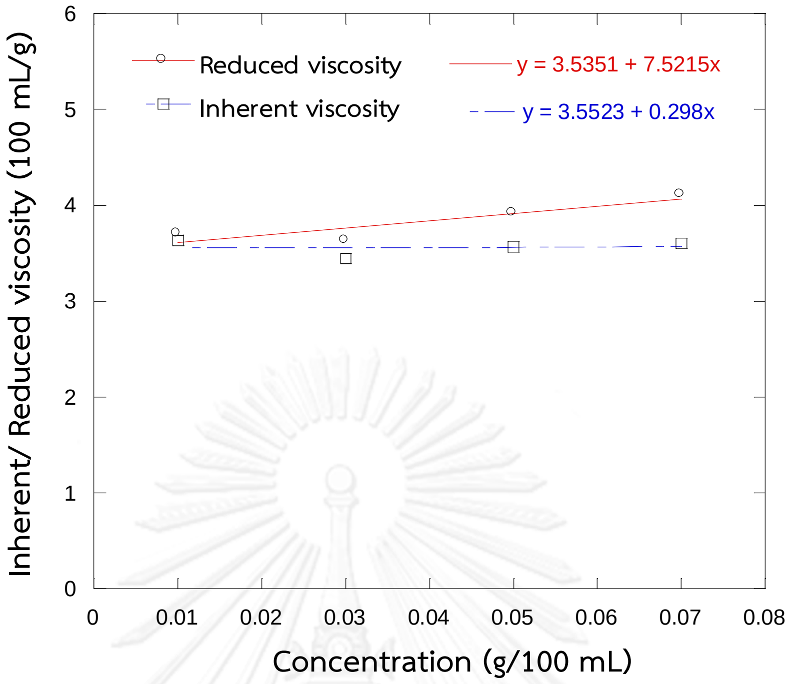

Figure A.1 Inherent and reduced viscosity of ADS0

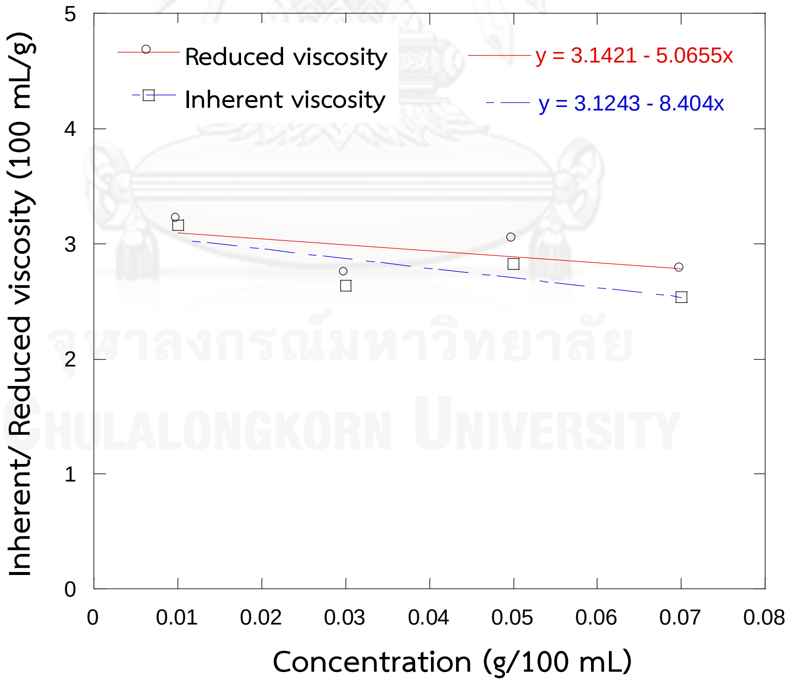

Figure A.2 Inherent and reduced viscosity of ADS5

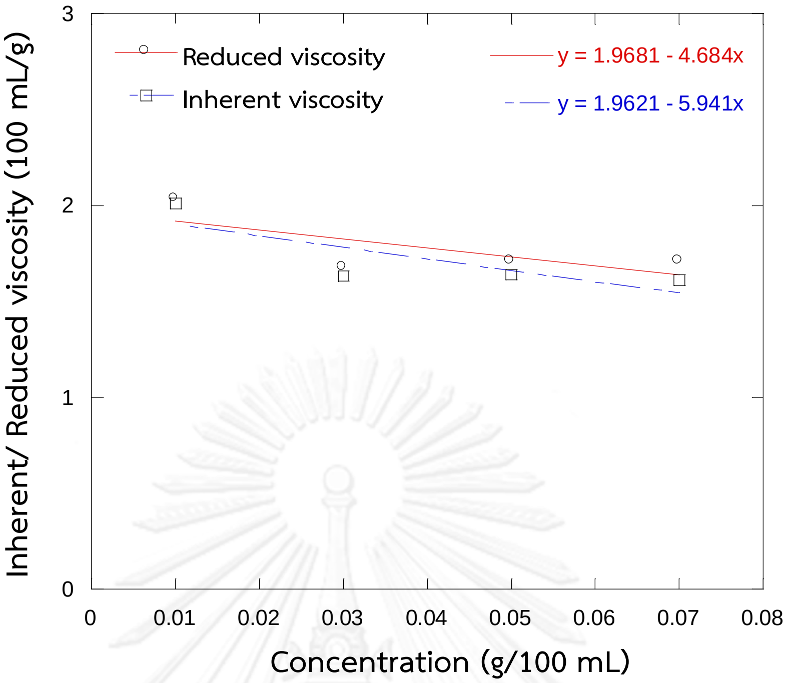

Figure A.3 Inherent and reduced viscosity of ADS10

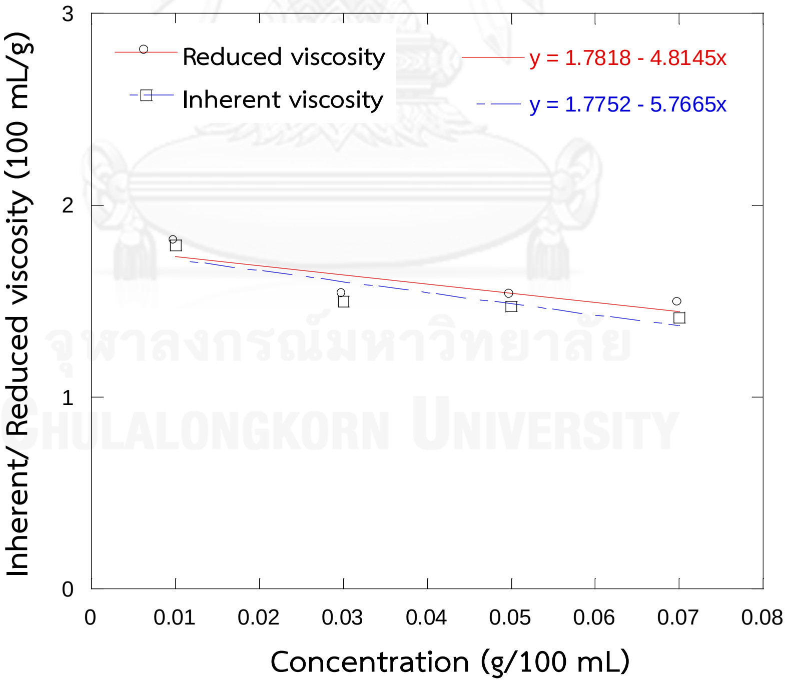

Figure A.4 Inherent and reduced viscosity of ADS15

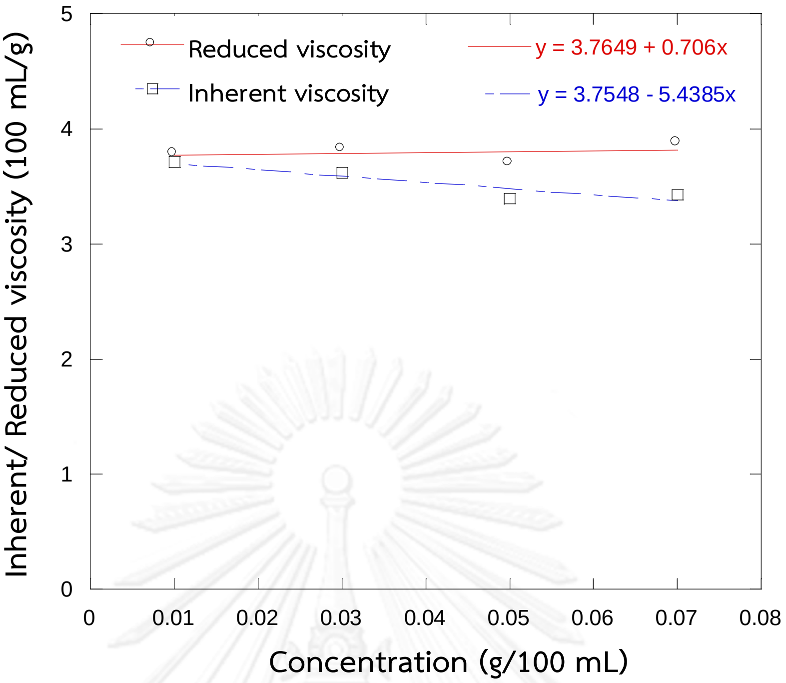

Figure A.5 Inherent and reduced viscosity of STR0

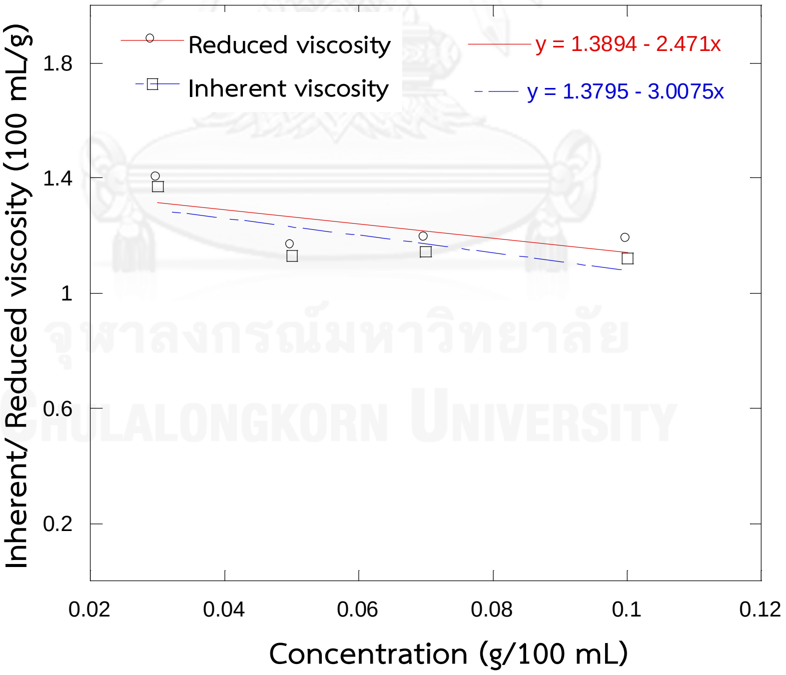

Figure A.6 Inherent and reduced viscosity of STR5

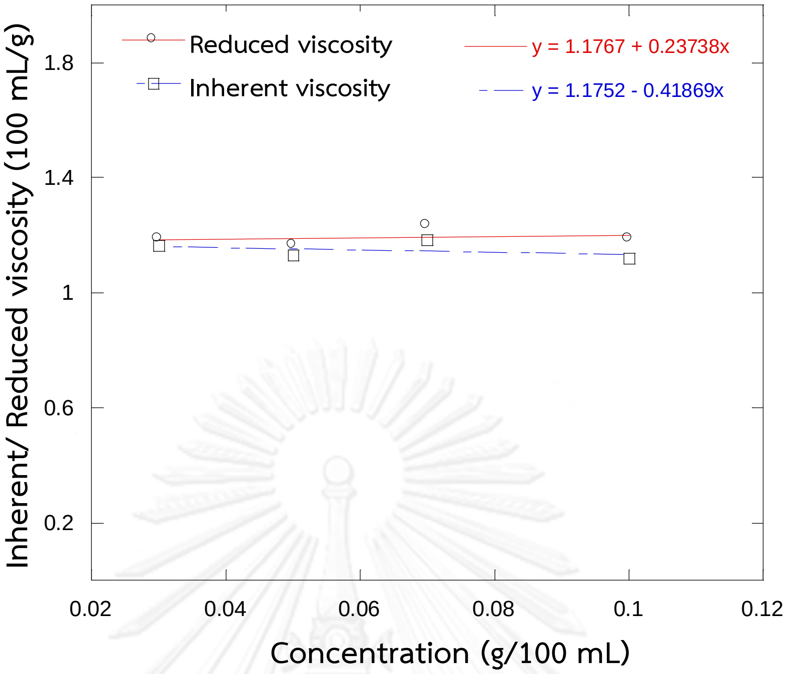

Figure A.7 Inherent and reduced viscosity of STR10

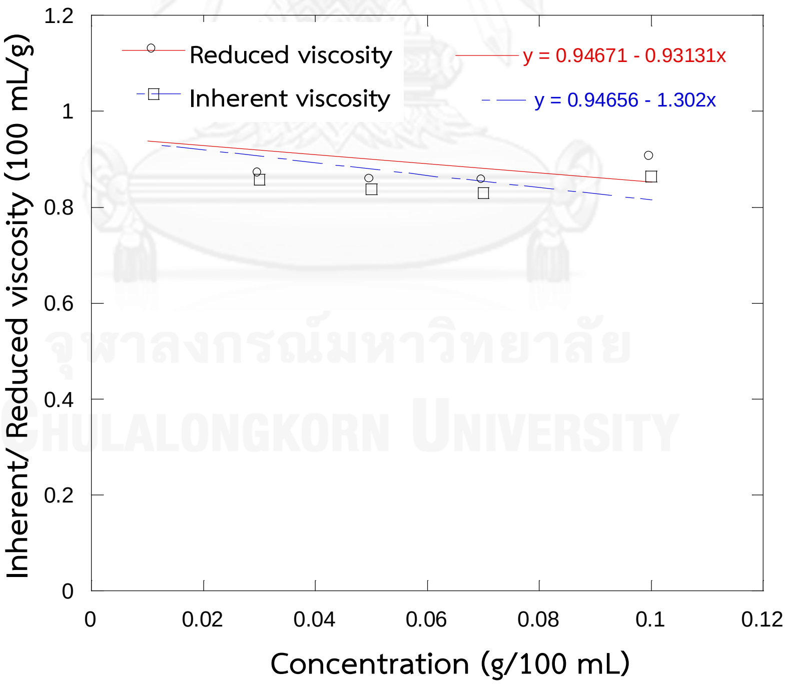

Figure A.8 Inherent and reduced viscosity of STR15

Table A.14 Gel content of masticated ADS and STR5L

Sample	Number	Mass of original test piece (M_0) (gram)	Mass of the empty container (M_1) (gram)	Mass of container containing dry precipitant (M_2) (gram)	Gel content (%)
ADS0	1	0.1026	1.0943	1.1052	10.62
	2	0.102	1.0937	1.1048	10.88
ADS5	1	0.1024	1.0904	1.097	6.45
	2	0.1032	1.0907	1.0974	6.49
ADS10	1	0.1018	1.103	1.1093	6.19
	2	0.1015	1.108	1.1142	6.11
ADS15	1	0.1002	1.0904	1.0955	5.09
	2	0.1012	1.0809	1.0862	5.24
STR0	1	1.0801	1.0898	1.0801	9.47
	2	0.1026	1.0805	1.0902	9.45
STR5	1	1.116	1.122	1.116	5.80
	2	0.1024	1.114	1.1201	5.96
STR10	1	1.1205	1.126	1.1205	5.41
	2	0.1017	1.11203	1.118	5.87
STR15	1	1.0902	1.0956	1.0902	5.34
	2	0.1018	1.0912	1.097	5.70

Appendix B
Mechanical properties

Table B.1 Tensile properties in MD of neat PLA

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	59.79	2798.49	2.56	36.80
2	68.66	3230.58	2.52	40.65
3	37.27	2472.46	2.05	19.54
4	61.78	2940.25	2.70	41.61
5	65.50	3304.48	2.44	38.56
Avg.	58.60	2949.25	2.69	35.43
SD	11.09	337.44	8.97	9.08

Table B.2 Tensile properties in TD of neat PLA

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	52.0	3152.54	2.29	29.62
2	55.2	3124.02	2.35	32.40
3	51.9	2971.06	2.23	28.32
4	56.4	3078.57	2.16	28.52
5	50.1	3070.24	1.89	21.81
Avg.	53.1	3079.29	2.18	28.13
SD	2.6	69.21	0.18	3.89

Table B.3 Tensile properties in MD of ADS0

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	28.22	2143.89	9.92	79.27
2	29.12	2130.78	8.37	77.17
3	21.17	1760.32	8.64	55.29
4	30.34	2384.22	9.02	86.18
5	21.49	1843.67	7.03	49.69
Avg.	26.07	2052.58	8.60	69.52
SD	3.93	251.74	0.94	14.33

Table B.4 Tensile properties in TD of ADS0

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	16.85	1808.74	7.12	39.95
2	15.26	1606.73	7.74	41.74
3	15.87	1709.68	9.77	52.31
4	17.50	1859.39	8.84	54.69
5	15.57	1649.46	8.39	46.20
Avg.	16.21	1726.80	8.37	46.98
SD	0.84	106.05	0.91	5.75

Table B.5 Tensile properties in MD of ADS5

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	25.88	2152.75	29.13	214.03
2	25.43	2243.76	27.92	211.98
3	28.13	2104.91	21.95	179.84
4	29.61	2293.55	28.17	246.68
5	26.29	2216.79	29.38	224.21
Avg.	27.07	2202.35	27.31	215.35
SD	1.57	74.49	2.73	21.61

Table B.6 Tensile properties in TD of ADS5

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	17.78	1901.68	8.08	45.30
2	19.37	1958.44	8.62	52.94
3	18.22	1922.64	9.61	56.50
4	20.80	2114.46	8.00	52.89
5	20.51	2025.70	7.88	47.27
Avg.	19.34	1984.58	8.44	50.98
SD	1.20	86.53	0.64	4.10

Table B.7 Tensile properties in MD of ADS10

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	34.89	2246.34	116.95	892.10
2	30.45	2083.39	102.29	747.91
3	39.43	2668.28	148.19	1321.72
4	30.51	2109.06	92.48	602.83
5	42.74	2734.54	195.62	1764.68
Avg.	35.61	2359.54	131.10	1065.85
SD	4.87	320.82	37.35	424.15

Table B.8 Tensile properties in TD of ADS10

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	15.45	1793.05	14.85	75.56
2	15.63	1802.75	15.96	82.93
3	16.29	1824.05	16.02	85.35
4	16.55	1840.68	15.58	84.91
5	14.81	1875.16	15.47	75.32
Avg.	15.74	1827.14	15.58	80.81
SD	0.62	32.62	0.42	4.46

Table B.9 Tensile properties in MD of ADS15

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	31.58	2738.89	186.43	1529.96
2	34.16	2093.26	146.17	1879.50
3	35.14	2254.30	176.90	2612.45
4	33.93	2486.92	274.30	1463.49
5	32.54	2615.03	183.54	2063.79
Avg.	33.47	2437.68	193.47	1496.73
SD	1.26	263.09	42.88	33.24

Table B.10 Tensile properties in TD of ADS15

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	16.89	1787.01	29.11	147.54
2	16.34	1819.58	25.58	121.33
3	17.73	1956.00	24.56	126.30
4	16.96	1860.50	33.54	169.68
5	17.75	1772.05	29.05	148.87
Avg.	17.13	1839.03	28.37	142.75
SD	0.54	73.68	3.17	17.41

Table B.11 Tensile properties in MD of STR0

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	23.84	1874.37	19.89	187.64
2	25.12	720.88	22.28	219.94
3	32.18	2384.48	33.19	409.32
4	29.75	2189.50	24.65	291.57
5	28.02	2162.17	23.39	258.21
Avg.	27.78	1866.28	24.68	273.34
SD	3.03	665.69	4.53	76.49

Table B.12 Tensile properties in TD of STR0

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	19.54	1845.15	14.77	125.556
2	19.47	1994.15	6.25	51.40
3	20.52	1900.52	10.87	92.82
4	20.26	1925.15	16.04	140.30
5	20.37	1957.81	9.50	82.59
Avg.	19.97	1924.56	11.48	98.53
SD	0.37	56.64	3.56	31.57

Table B.13 Tensile properties in MD of STR5

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	31.68	2838.85	180.14	24.22
2	29.59	2613.47	184.12	195.84
3	31.56	2779.57	176.93	197.44
4	30.53	2706.52	184.45	200.74
5	28.05	2546.95	180.83	188.27
Avg.	30.28	2697.07	181.30	1425.36
SD	1.35	118.87	3.07	20.27

Table B.14 Tensile properties in TD of STR5

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	17.44	1781.62	15.24	92.92
2	17.95	1900.17	15.54	95.55
3	18.77	1954.71	12.50	80.78
4	16.67	1769.03	13.54	79.08
5	17.65	1871.17	16.54	100.03
Avg.	17.70	1855.34	14.67	89.67
SD	0.69	79.09	1.45	8.29

Table B.15 Tensile properties in MD of STR10

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	28.49	1910.39	201.69	1650.73
2	35.60	2205.03	163.04	1602.31
3	28.29	1782.58	161.88	1407.79
4	35.42	2196.10	228.71	2519.32
5	26.25	1732.93	149.63	1228.90
Avg.	30.81	2009.46	195.74	1681.81
SD	3.91	185.43	29.59	444.73

Table B.16 Tensile properties in TD of STR10

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	11.35	1184.66	21.71	108.36
2	11.26	1486.91	21.69	108.30
3	11.34	1569.28	19.07	95.92
4	10.86	1326.12	22.94	109.86
5	11.96	1307.78	19.17	100.51
Avg.	11.35	1374.95	20.91	104.59
SD	0.35	152.81	1.54	5.43

Table B.17 Tensile properties in MD of STR15

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	45.50	2232.10	227.49	2191.92
2	34.36	2432.07	249.74	1350.72
3	35.84	2460.14	337.08	1639.31
4	41.24	2275.93	216.00	2864.29
5	42.08	2353.75	302.68	1971.82
Avg.	39.50	2350.80	266.60	2003.01
SD	4.12	97.81	46.14	517.38

Table B.18 Tensile properties in TD of STR15

Number	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	15.80	1043.88	32.76	190.45
2	15.79	1502.09	28.04	164.24
3	16.86	1463.46	27.29	171.04
4	15.34	1301.66	28.33	161.21
5	17.00	1500.38	33.61	207.06
Avg.	16.16	1362.30	30.01	178.80
SD	0.65	196.16	2.63	17.41

Table B.19 Impact strength of PLA and PLA/masticated NR films at various mastication time

Sample	Impact strength (J/cm)
PLA	3.02 ± 0.388
ADS0	19.31 ± 5.79
ADS5	40.29 ± 5.25
ADS10	65.17 ± 14.24
ADS15	73.12 ± 16.96
STR0	18.77 ± 4.29
STR5	90.12 ± 16.96
STR10	109.30 ± 16.69
STR15	112.47 ± 16.35

Table B.20Tear strength of PLA and PLA/masticated NR films at various mastication time in MD and TD

Sample	Tear strength (Nm)	
	MD	TD
PLA	304.5 ± 66.94	517.4 ± 50.92
ADS0	456.6 ± 0.00	669.4 ± 83.25
ADS5	578.2 ± 67.98	669.4 ± 83.25
ADS10	608.6 ± 152.00	790.92 ± 83.25
ADS15	730.2 ± 83.31	487 ± 127.08
STR0	395.76 ± 68.02	517.4 ± 67.98
STR5	426.18 ± 0.00	547.8 ± 83.25
STR10	456.6 ± 83.25	639 ± 83.25
STR15	547.8 ± 83.25	517.4 ± 67.98

Appendix C
Gas permeation properties

Table C.1 Oxygen transmission rate (cc/(m^{2}day)) of PLA and PLA/masticated films at various Mastication time

Number	Samples								
	PLA	ADS0	ADS5	ADS10	ADS15	STR0	STR5	STR10	STR15
1	524.05	1497.07	1085.43	823.89	698.31	1326.37	619.06	621.00	586.46
2	569.53	1506.58	1028.04	817.48	667.45	1236.74	642.42	598.81	575.21
Avg.	546.79	1501.83	1056.74	820.68	682.88	1281.55	630.74	609.91	580.84
SD	32.16	4.76	28.69	3.20	15.43	44.81	11.09	5.62	11.68

Table C.2 Water vapor transmission rate (cc/(m^2.day)) of PLA and PLA/masticated films at various Mastication time

Number	Samples								
	PLA	ADS0	ADS5	ADS10	ADS15	STR0	STR5	STR10	STR15
1	96.24	126.12	120.5	116.36	112.85	124.82	109.14	109.24	105.12
2	94.80	118.21	114.36	109.23	108.66	122.00	107.12	105.32	104.25
Avg.	95.52	122.17	117.43	112.80	110.76	123.41	108.13	107.28	104.69
SD	1.02	5.59	4.34	5.42	2.96	1.99	1.43	2.77	0.62

VITA

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