

CHAPTER I

INTRODUCTION

1.1 General introduction

Currently, the increases in uses of plastic productions cause plastic disposals which have been attended as a serious environmental problem because they do not degrade easily in the natural environment. In recent years, the biodegradable polymers have thus received much attention as one of the approaches to solve this problem. They are made from renewable resources and are biodegradable in 0.5-2 years by suitable condition [1-3].

Poly(lactic acid) (PLA) is one kind of biodegradable polymer produced from renewable resources that has been widely applied for packaging applications. Because it shows high mechanical strength, moderate barrier, processability, transparency as well as biocompatibility. However, PLA has intrinsic shortcoming such as stiff and poor toughness. Therefore, brittle PLA is improved through blending with elastomeric disperse phase to improve toughness of PLA. Examples of biodegradable polymer which are used to blend with PLA are poly (butylene adipate-*co*-terephthalate) (PBAT) [4], poly (ϵ -caprolactone) (PCL) [5, 6] and poly (ethylene succinate) (PES) [7].

Toughness is a measure of ability of material to absorb energy and plastically deform without fracturing. Good dispersion of the small rubber particles in the polymer matrix is the basis of the improvement. Based on theories of rubber

toughened polymer, the blend morphology and characteristics such as average rubber particle size, the content of rubber and the mixing condition influence on the final mechanical properties [8-10].

Natural rubber (NR) latex acting as soft and elastic material is linear *cis*-polyisoprene in general form of a milky colloid obtained from *Hevea brasiliensis* tree [11]. Because it is a renewable polymeric material exhibiting excellent physical properties such as high elasticity, fracture resistance and flexibility so, NR matrix has been commonly widely used as a secondary polymer to improve toughness of many brittle thermoplastic polymer such as nylon6 (PA6)/Epoxidized natural rubber (ENR) [12] and PS/NR [13, 14]. However, NR latex is quite soft, tacky and backbone unsaturation which simplifies the certain types of chemical modification to yield a range of modified NR polymer. From this reason, most of NR should be prevulcanized by using sulfur, peroxide or γ -radiation systems to reduce its sticky properties and obtains stronger chain than un-vulcanized natural rubber [15, 16].

Films can be manufactured using different processes such as extrusion, co-extrusion, casting and extrusion coating. These processes have several advantages and disadvantages depending on material type, width and thickness of film and required film properties. However, blown film extrusion technique is the most suitable process for film production which offers economic advantages, the desired properties of the end products and ease of processing.

In this study, we focus on improving the toughness of PLA blown film which is enhanced by incorporating NR with and without vulcanization as toughening agent. To obtain this aim, this study is divided into 2 parts. First part is to find the optimal

NR contents on thermal, mechanical and barrier properties of PLA films. NR contents are varied from 0-7 wt%. Also, effects of vulcanized NR (VNR) with peroxide system on physical properties are examined at the optimal NR contents from previous study. A wide variety of peroxides can be used to crosslink most type of elastomers. Because the advantage of prevulcanized-peroxide system is short crosslinking time, simple compounding, good heat-aging resistance, less tension set and strain, no mold contamination and possible transparent rubbers [15, 17, 18].

The mechanical and thermal properties of blown film added with above-mentioned rubber are selected as the parameters which is appropriate for part two. The second part is to investigate the effect of morphology on the properties of PLA/rubber system. Rubbers, used in the second part, were coated with Gum arabic and spray-dried to obtain rubber powder. The mechanical and thermal properties of blown film in part 2 are also being compared with those of part 1. Differential scanning calorimetry (DSC) can be used to measure fusion, crystallization and glass transition temperature. Dynamic mechanical analyzer (DMA) is also particularly useful for qualitatively characterizing the glass transition temperature (T_g) of polymer and composite materials by determining the peak temperatures of the loss moduli or tan delta curves and storage modulus is measure of sample's elastic behavior. Gas barrier properties of PLA films with NR and VNR were examined by OTR and WVTR. In addition, tensile strength, Young's modulus and elongation of material can be obtained by Universal testing machine. Scanning electron microscope (SEM) used to characterize the morphology of sample.

1.2 Objectives

1. To examine effect of rubber contents on the mechanical and thermal properties of PLA/rubber blown films
2. To explore the effect of crosslinked natural rubber by vulcanization with peroxide system on the mechanical and thermal properties of PLA/rubber blown films
3. To investigate the effect of rubber powder on the mechanical and thermal properties of PLA/rubber powder blown films

1.3 Scopes of the research

1. Characterize natural rubber latex and natural rubber sheet
2. Vary the rubber loading in PLA matrix between 0 - 7 % by weight
3. Compare the properties of PLA blown film with un-vulcanized natural rubber (NR) and vulcanized natural rubber (VNR) in PLA matrix with optimal rubber content from previous part
4. Characterize the PLA/rubber blown film by means of thermal, mechanical, barrier properties and morphology
5. Compare properties of PLA containing NR and NR-Powder (NRP) at optimal rubber contents
6. Investigate effect of NRP on the mechanical and thermal properties of blown film

CHAPTER II

THEORY

2.1 Developments in poly(lactic acid)

Poly(lactic acid) is brittle thermoplastic polymer that is synthesized and developed from renewable sources. Its popularity is due to its good mechanical and biodegradable properties which are for producing the interesting packaging. However, the drawback of PLA is poor toughness. In the past, the properties of PLA was improved by plasticizers, toughening agents and fillers to obtain the desired properties [19, 20]. One of the most important aspects in the thermoplastic material development is to achieve the good combination of properties and processability at a moderate cost. As far as mechanical properties are concerned, the main objective is to strike a balance of stiffness, strength and toughness. Therefore, toughness is an important mechanical property and it is one of the important factors in the material selection. To enhance the toughness and impact strength of PLA, toughening agent was also blended with PLA. Toughening agent is substance that increases toughness for brittle polymer. In addition, natural rubber (NR) is an interesting material to use as secondary polymer to improve the toughness of polymer.

In this chapter, the chemistry, production, properties of PLA with application, characterization of natural rubber and prevulcanization process which acts as toughening agent, rubber toughening mechanisms in polymeric materials and process of blending as well as blown film are discussed.

2.2 Poly(lactic acid)

Poly(lactic acid) or PLA is the first commodity polymer produced from annually renewable resources. It is a rigid thermoplastic polymer that belongs to the family of aliphatic polyesters as shown in Figure 2.1 commonly made from lactic acid (primary monomer), which can be produced from sugar or starch. These exist as two optically active configurations, L(-) lactic acid and D(-)lactic acid isomer. L(-) lactic acid is natural and the most common form of the acid. PLA can be prepared by both direct condensation of lactic acid and by ring-opening polymerization of lactide dimer (ROC). Normally, commercial grade of PLA is a blend of PLLA and PDLA or copolymer PDLLA, obtained by polymerization of LLA and DLLA, respectively [21].

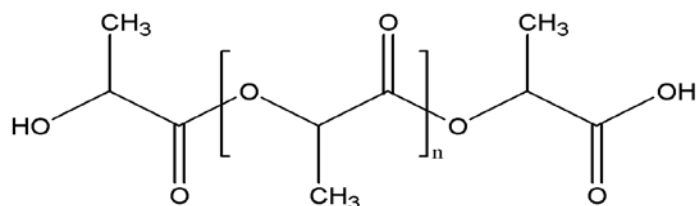


Figure 2.1 Chemical structure of PLA

2.2.1 Properties of PLA

PLA can be either amorphous or semicrystalline depending on the ability to selectively incorporate L-, D-, and meso-lactide stereoisomers into the polymer backbone 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 for both processing and performance in its intended applications. For instance, properties of

PLA grade 2002D for extrusion grades obtained from NatureWorks PLA, Cargill Dow LLC are shown in Table 2.1.

Table 2.1 Properties of PLA grade 2002D [22].

Properties	value	ASTM Method
<u>Physical Property</u>		
Specific gravity (g/cc)	1.25	D792
Melt index (g/10 min) (190 °C/2.16 kg)	4-8	D1238
Clarity	Transparent	
<u>Mechanical Properties</u>		
Tensile strength at break, psi (MPa)	7,700 (53)	D882
Tensile yield strength, psi (MPa)	8,700 (60)	D882
Tensile modulus, kpsi (GPa)	500 (3.5)	D882
Tensile elongation (%)	6.0	D882
Notched izod impact, ft-lb/in (J/m)	0.24 (0.33)	D256
<u>Thermal Properties</u>		
Glass transition temperature (T_g , °C)	55-65	
Melt temperature (T_m , °C)	160-180	

Generally, the advantages of PLA are high strength, high modulus, transparency, biocompatibility, degradable and processability. However, the disadvantages are poor toughness and expensive.

2.2.2 Applications of PLA

PLA can be used in many applications, including packaging, paper coating, container, fibers, films, biomedical science and a host of mold articles because PLA is environmentally friendly polymer and providing good mechanical properties. Commercially, available PLA films and its packages have been found to provide

better mechanical properties than polystyrene (PS) and their properties are comparable to those of PET [23]. However, PLA packaging is quite brittle. Commonly, PLA's properties can be modified by incorporation of plasticizer, filler, and toughening agent into PLA matrix [19].

2.3 Natural rubber

2.3.1 Basic information of natural rubber

Commercial natural rubber latex (NR) is mainly obtained from the rubber tree (*Hevea brasiliensis*). NR is a polymer of isoprene most often cis-1,4-polyisoprene with a molecular weight of 100,000 to 1,000,000. The chemical structure of cis-1,4-polyisoprene consists of 5 carbons and 8 hydrogen atoms (C₅H₈) as repeating unit with double bond along the backbone as demonstrated in Figure 2.2 [11].

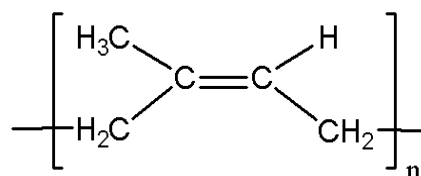


Figure 2.2 Chemical structure of cis-1,4-polyisoprene

2.3.2 Fresh natural rubber latex

Commonly, the rubber particle has spherical shape. Rubber particle displays colloidal stability due to presence of adsorbed proteins and lipids on the rubber particle surface, making surface of rubber particle displays negative charged which are polydisperse and have a range of particle size from 0.05 - 3 μm with average size between 0.25 and 0.8 μm, pH around 6-7 and density of 0.975-0.980 g/ml. Figure 2.3

shows the rubber latex particle [11]. The composition of fresh NR latex and dry rubber is given in Table 2.2.

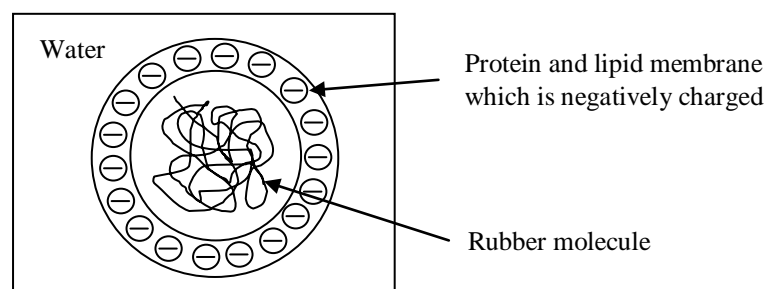


Figure 2.3 A negative charged rubber particle suspended in water

Table 2.2 Composition of fresh and dry natural rubber latex [11].

Composition	Fresh natural rubber	Dry natural rubber
Hydrocarbon rubber	36.0	93.7
Protein and amino	1.4	2.2
Neutral lipid	1.0	2.4
Glycolipids and phospholipids	0.6	2.4
Carbohydrates	1.6	0.4
Inorganic	0.5	0.2
others	0.4	0.1
water	58.5	-

Industrially, fresh NR latex (dry rubber content: DRC about 30-36%) was added by ammonia to protect coagulation of rubber after it was centrifuged at high speed (higher than 10,000 rpm) in order to obtain the concentrated latex (DRC about

60%). The centrifugation process also generates by-product liquid known as skim (DRC about 5%) [24]. Production process of NR latex is shown in Figure 2.4.

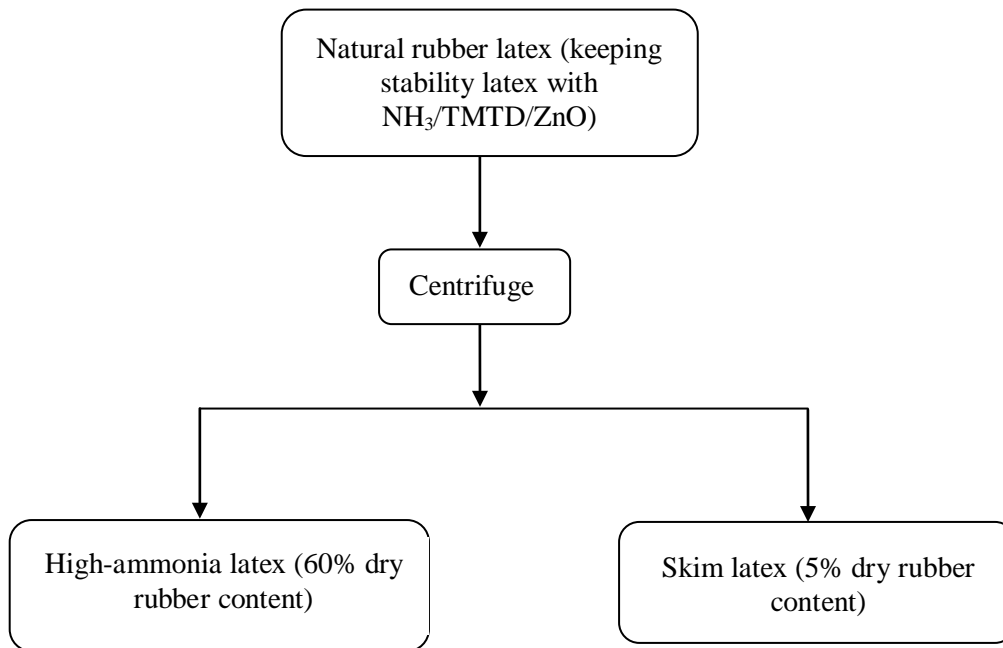


Figure 2.4 Production process of natural rubber

NR was studied for its use as an impact modifier in several polymers. Because NR is a renewable polymeric material, with excellent physical properties such as high elasticity, high tear resistance, high tack, high abrasion resistance, and no toxicity and low density [25]. However, the disadvantages are low chemical resistance, high aging, rigidity and instability. Therefore, the NR latex must be prevulcanized by sulphur, peroxide or γ -radiation system in order to achieve, (a) a toughened material that is more resistant to oxidation, (b) more elastic as the cross-linked chains can revert back to their original positions, (c) more heat resistant which means the vulcanized rubber is less soft and sticky on warming and (d) less soluble in organic solvent [26-28].

2.4 Pre vulcanization

Pre vulcanization, also called crosslinking process, involves heating raw NR latex with vulcanizing ingredient for initial crosslinking or forming a three-dimensional network structure from a linear polymer by a chemical or physical method within rubber particles [18]. Drying of the pre vulcanized rubber latex produces a crosslinked film without the need for further heating. However, the physical properties of the final product can be controlled by design of crosslink in particle during pre vulcanization. The effects of pre vulcanized rubber latex on properties depend on rate of pre vulcanization, pre vulcanization system, and the extent of pre vulcanization. Generally, NR latex can be pre vulcanized by systems based on sulfur, peroxide, or γ -radiation system [17, 27, 28].

Peroxide pre vulcanization is crosslinked within the rubber particle in latex by free radicals generated from peroxide and hydrogen peroxide system. The mechanism of peroxide is shown in Figure 2.5. The advantages of this system are high-temperature aging resistance, good elastic behavior, transparent, short crosslinking time, and no mold contamination [17].

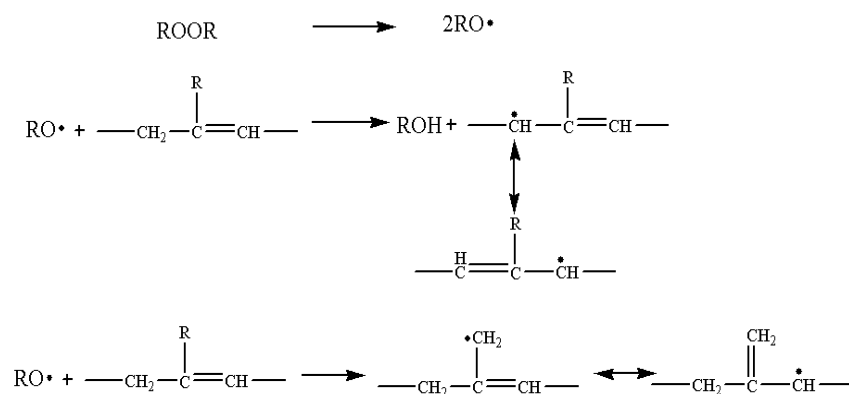


Figure 2.5 Peroxide crosslink mechanisms [17]

2.5 Processing of natural rubber sheet

Concentrated natural rubber latex (60%) is used for two formation referring sheet and powder, to facilities in using.

2.5.1 Natural rubber sheet from HA-NR

Concentrated natural rubber latex (60%) was dried by cast film method on glass plate. Rubber particle and non-rubber component is included in the rubber sheet. Latex can still coagulate if acids are not added. Normally, the latex will coagulate if it is left overnight. Bacteria from the air slowly attack the protein on the membrane to produce lactic acid. Ionisation of the lactic acid produces hydrogen ions. The hydrogen ions neutralize the negative charges to form neutral rubber particles, allowing coagulation to occur. Process film formation is shown in Figure 2.6.

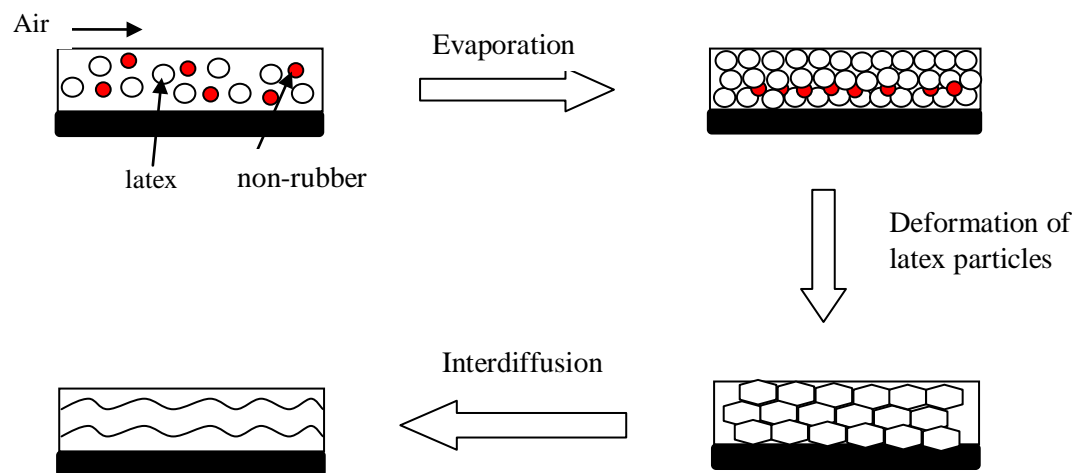


Figure 2.6 Process film formations

2.5.2 Commercial natural rubber sheet

Generally, dry rubber refers to the grades, which are marketed in the dry form such as rubber sheet, crepe rubber, and crumb rubber, whereas liquid rubber refers to the latex concentrate production in which the field latex is separated into concentrated latex containing about 60% dry rubber and skim latex with 4-6% of dry rubber content. Rubber sheet could be categorized as Air Dried Sheet (ADS) and Ribbed Smoked Sheet (RSS). The main difference of ADS and RSS depends on the procedure used for drying the sheet, in which ADS use air, whereas RSS uses smoke provided in a smokehouse with the temperature up to 60°C.

Rubber sheet processing is started from latex collection in the field. It is then diluted and screened before the addition of methanoic acid (formic acid) for coagulation process. Hydrogen ions from the acid neutralize charges on the surface of the membrane. A neutral rubber particle is formed. When these neutral particles collide with each other, their outer membrane layers break up and the rubber polymers are set free. The rubber polymers start to coagulate by combining together to form large lumps of rubber polymers which then precipitate out of the latex solution. Figure 2.7 displays the mechanisms of coagulated latex with acid. The wet sheet is sheeted off to a thickness of about 3 mm and finally passes an embossed two roll mill. The sheets are dried whether by air or in a smokehouse for about one. The process of natural rubber sheet was shown in Figure 2.8.

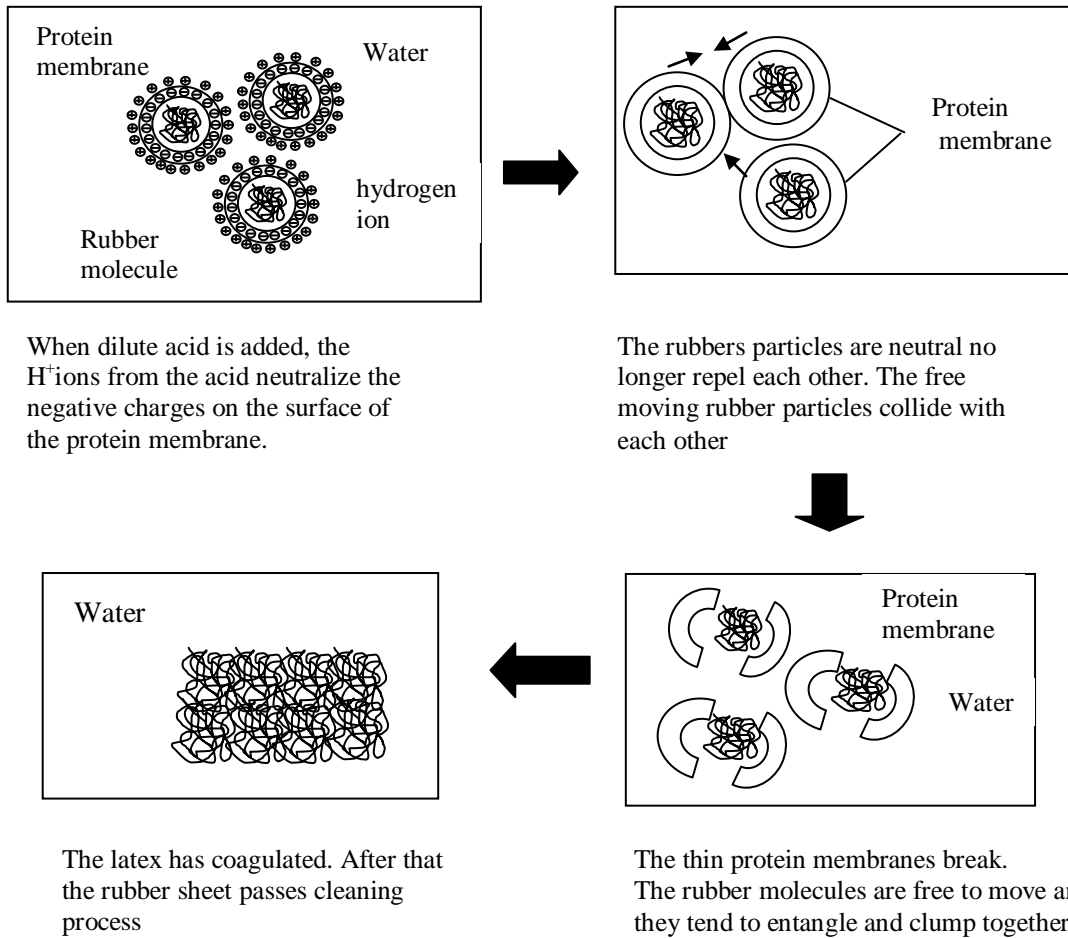


Figure 2.7 Mechanisms of coagulated latex with acid

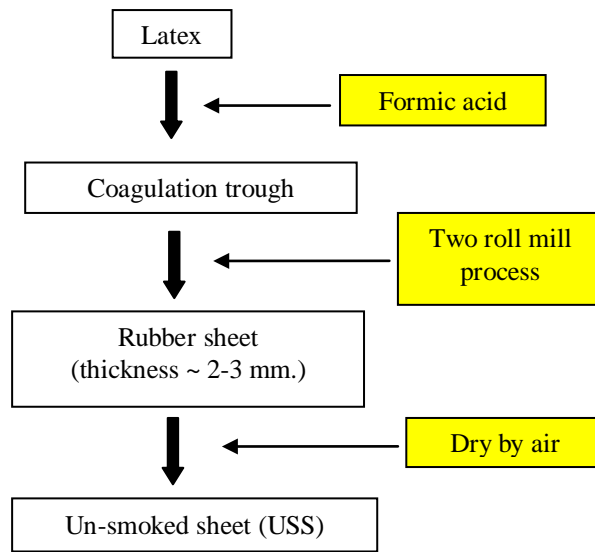


Figure 2.8 Process of natural rubber sheet (commercial grade) [29]

2.6 Rubber Powder

Rubber Powder was prepared with encapsulation method from spray drying process. Encapsulation is the process by which a substance or mixture to be coated with another type. The most common coated or entrapped substance is liquid but may be solid or gas which has various names such as core material or internal phase. The substance is brought to coat, so called wall material, carrier, membrane, shell or coating.

2.6.1 Type of coating

The type of coating will affect properties of product, stability of emulsion in feed line, flowing of material and shelf-life products. The required properties of coating are high water soluble, good emulsifier, makeable film and low viscosity in high water concentration. These can be distinguished to 5 types i.e., carbohydrate such as starch, maltodextrin, ester or cellulose ether such as

carboxymethyl cellulose, gum such as Gum arabic, lipids such as paraffin, wax and protein such as Gelatin [30].

2.6.2 Gum arabic

Gum arabic (GA), prepared from exudates of *Acacia senegal* and *Acacia seyal* trees, consists of the complex mixture of low molecular weight polysaccharides and high molecular weight glycoprotein. GA serves as an expensive hydrocolloid emulsifier and a stabilizer in the primary food and cosmetic industries. Generally, GA comprises of the major three parts as following:

(1) The first part (~89 wt % of the total) is a highly branched polysaccharide (MW = 3×10^5)

(2) The second part (~10 wt % of the total) is a higher molecular weight ($\sim 1 \times 10^6$ g/mol) arabinogalactan–protein complex (GAGP –GA glycoprotein) which is linked to the protein chain through serine and hydroxyproline groups.

(3) The third part is a glycoprotein as the smallest fraction (~1% of the total) having the highest protein contents (~50 wt %) [31]. The chemical structure of GA is shown in Figure 2.9.

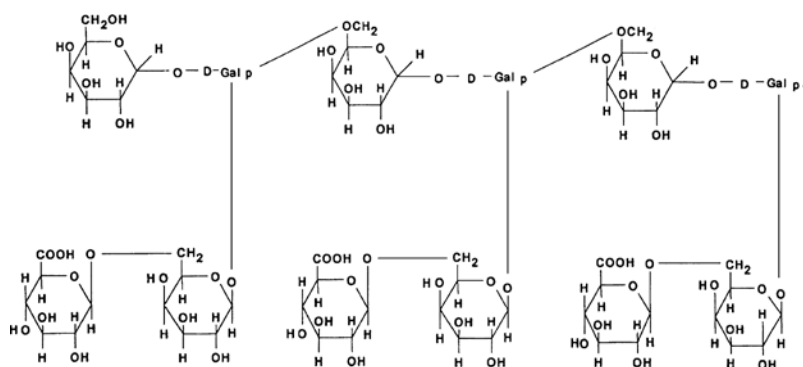


Figure 2.9 Chemical structure of Gum arabic [32]

2.6.3 Encapsulation techniques

There are many encapsulation techniques such as spray drying, spray, coacervation, fluidized bed coating, liposome entrapment and freeze drying. The most common technique that is used for coating the particles is spray drying due to its simple and reliability method [30].

2.6.4 Spray drying

Spray drying is a most widely used technique for producing particles and drying. The liquid are rapidly dried with hot gas becoming the dry powder with a controlled average particle size. Most of spray dryers require some type of atomizer (spray nozzle) to disperse the liquid into a controlled drop size spray. A spray dryer mixes a hot gas with a sprayed liquid within a drying chamber to achieve evaporation and produce a free flowing dry powder. The unit operation of spray drying includes the following components [33]:

1. A method for atomizing the solution or slurry
2. An gas heater or a source of hot air
3. A chamber for mixing hot gas and sprayed liquid with appropriate residence time and droplet trajectory distance to achieve the heat and mass transfer
4. A means for recovering the solids from the gas stream
5. A fan for inducing the required air or gas through the spray drying system

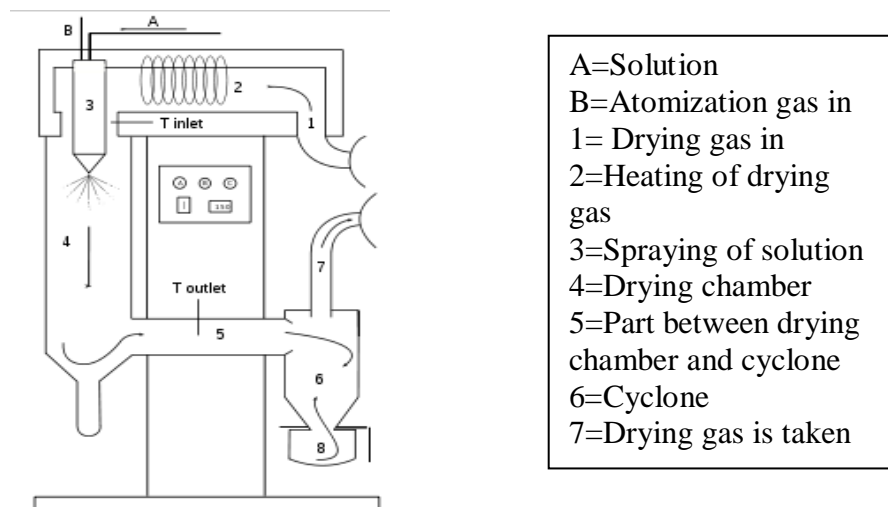


Figure 2.10 Laboratory-scale spray dryer [33]

2.6.5 The advantages of spray drying method

1. The dried particle size can be easily controlled with atomization and the design of the hot gas inlet.
2. Most of the shape of dried particles is sphere.
3. Spray drying can be used for producing multi-component solutions and slurries to the most homogeneous product.
4. The surface area of the liquid feed produced by atomization enables a short gas residence time which permits spray drying without thermal degradation [34].

2.7 Rubber toughened polymer

Toughness can be defined as the amount of energy a material can absorb before it fractures. The area below a stress-strain curve represents in fact the toughness per unit volume. Under impact loading conditions, embrittlement is a problem often encountered, therefore, impact resistance is an attribute required in the

plastic materials for using in many load-bearing applications. There are many techniques to improve toughness of brittle plastics. Among them, incorporating the brittle matrix with rubbery component is the most commonly used one. Combined the stiffness and processability of brittle polymer matrix with the fracture resistance of elastomers would be expected.

2.7.1 Toughening mechanisms

Toughening mechanisms in the laminate are characterized by two distinctly different processes, which are categorized by the propagation of the crack path. At the crack tip, processes in operation are crazing, matrix microcracking, plastic deformation, fibre or particle debonding, and phase transformation. As the crack propagates another set of toughening mechanism becomes operative. These can be summarized by fibre or particle bridging, matrix bridging, fibre pull-out and precipitate elongation. The interaction between processes can increase effective area for toughening mechanisms, and enhance toughness. The toughness enhancement carried out by the specific mechanism is produced by the energy change in volume element as a crack propagates through the composite. The toughening mechanisms produced in the polymer are presented in Figure 2.11 [9].

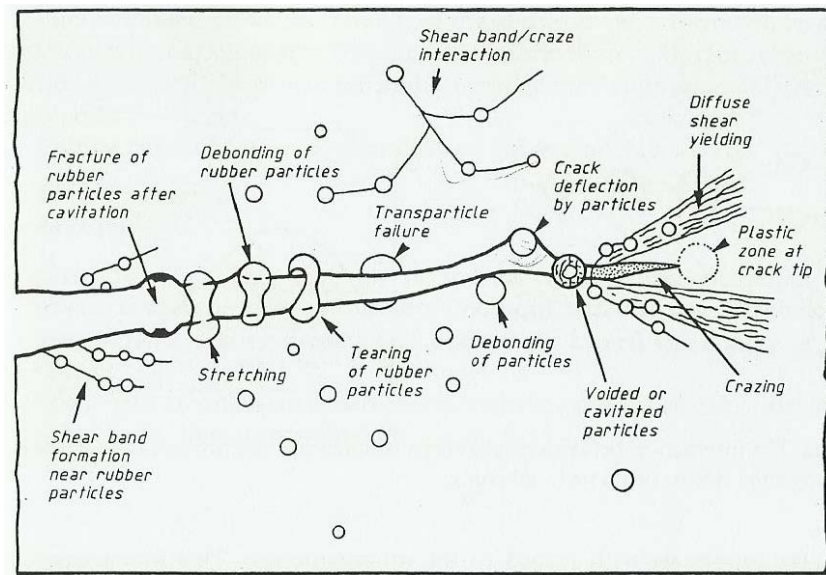


Figure 2.11 Crack toughening mechanisms in rubber filled modified polymers [9]

Generally, the major toughening mechanisms of brittle polymer are crazing and shear yielding or combination of shear yielding and crazing

2.7.2 Crazing

Crazes can be described as micro-cracks which are bridged by numerous nanoscale fibrils running across from one craze interface to the other. These fibrils are connected by thinner cross-tie fibrils. The fibrils comprise of the oriented chains which are drawn out of the craze interface. This is a main difference between a crack and a craze. Craze formation itself will therefore not necessary leading to a fracture of the material. However, the deformation is localized in a very small volume.

In the craze formation process, numerous microvoids will develop. This result in a macroscopic give the increase of the volume of the material.

Crazes are initiated at inhomogeneities, such as surface or interface damage, trapped bubbles or encapsulated particles. These kinds of initiation points are always existent in practice. The crazes develop in a plane perpendicular to the direction of the maximal applied stress.

At a certain stress the fibrils can no longer bear the load. 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. Although the fibrils themselves are drawn to the maximum, the macroscopic strain to break is generally small, due to more localized deformation. Therefore, the material shows brittle fracture [9, 35].

2.7.3 Shear yielding

The other important mechanism that can take place during glassy amorphous polymer deformation is shear yielding. This involves a plastic deformation, either locally or homogeneously. The volume of the material does not change while shearing, which implies an easily detectable difference with the crazing mechanism.

Shearing preferentially occurs in the densely entangled or crosslinked polymers, or in circumstances in which the competing crazing process is suppressed, such as under hydrostatic pressure. The polymeric chains are not broken, and often the material will regain its original shape upon annealing, due to the relaxation of the entanglement network.

Shear yielding takes place in so-called shear bands, in a direction approximately 45° to the plane of maximum applied stress (direction of maximum shear stress). There are existing different types of shear bands, mainly as a result of

the growth speed: microshear bands and diffuse shear zones [6]. The diffuse shear zones can extent through the whole material, until it is drawn maximally. Only then cracks originate and the material fractures [9, 35].

2.7.4 Cavitation

The occurrence of cavitation in the presence of shear yielding has been observed in rubber toughened polymers. Shear yielding is not accompanied by expansion of the matrix, but in rubber toughened blends. The presence of the rubber will rise to the increase of volume if the strain rate is sufficiently high. This expansion is caused by the cavitation of the rubber particles. The rubber particles dissipate the bulk strain energy by cavitation, leading to a reduction in local hydrostatic stress and a reduction in the yield stress of the blend. Thus shear band formation is enhanced by the voids in the matrix caused by the cavitated rubber particles [9, 35].

2.8 Mechanism of permeation

The diffusion of a gas is described by Fick's law which relates the diffusive flux to the concentration field [36]:

$$j_i = D_{ij} \cdot dc_i/dx \quad (2.1)$$

Where the variables are rate of diffusion (j) of matter (i), where $ij D$ is diffusion coefficient of the matter i in a medium j , and dc_i/dx describes the concentration gradient in the diffusion direction.

In the case of diffusion through a permeable material, its permeability P ($\text{g m}^{-1} \text{s}^{-1}$) is defined as:

$$F = P \cdot A \cdot \Delta p \quad (2.2)$$

where F (g s^{-1}) is the mass flux, Δp is the mass fraction gradient (percent), and A (m^2) is the area of the film. The mass fraction gradient can also be expressed by the partial pressure difference of the gas (Pa). As a result, permeability is also reported in $\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$. Alternatively, if volume flux is considered instead of the mass flux, permeability, P ($\text{m}^2 \text{s}^{-1} \text{Pa}^{-1}$), refers to the amount of gas, by volume, which penetrates unit thickness and area of the material per unit time, under constant temperature and unit partial pressure difference when permeation is stable. If partial pressure difference is given as mass fraction difference, permeability is expressed in the same units as diffusivity ($\text{m}^2 \text{s}^{-1}$).

When a thin film is considered, its gas transfer characteristics are described by the permeance, PR ($\text{g m}^{-2} \text{s}^{-1}$) or ($\text{g m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$):

$$F = PR \cdot A \cdot \Delta p \quad (2.3)$$

The permeability rate for a specific partial pressure difference Δp (Pa), TR , ($\text{g m}^{-2} \text{s}^{-1}$) is then defined as:

$$TR = PR \cdot \Delta p \quad (2.4)$$

2.9 Melt blending process

Melt blending process is by far the most widely adopted method for converting PLA resins into various end products. This process is performed by heating the polymer above its melting point, shaping the molten polymer into the

desired shapes, and then cooling to stabilize its dimension. In this section, the extrusion blow film process is discussed.

2.9.1 Extrusion process

The important technique converts thermoplastic pellets into a homogeneous melt that is extrusion. Several kinds of conventional processes, such as injection molding, single-stage stretch blow molding and film blowing.

During the plasticating process as shown in Figure 2.12, thermoplastic pellets are conveyed to the extruder from a hopper near the barrel. The screw, driven by an electric or hydraulic motor, transports and compresses the pellets which they move through the barrel and a die with laminar flow. The heater bands, around the barrel, required to raise the temperature above its T_m for melting thermoplastic pellets [21].

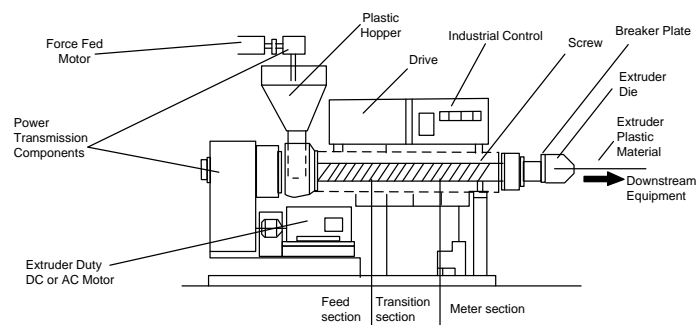


Figure 2.12 Scheme of the extruder

2.9.2 Extrusion blown film

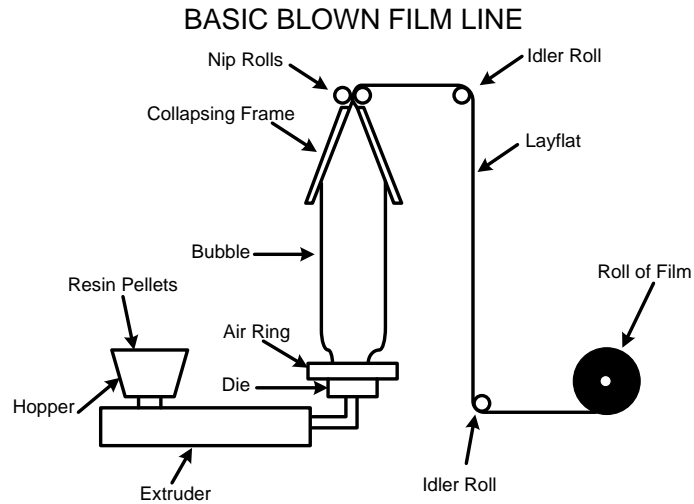


Figure 2.13 Scheme of blown film extrusion

Blow film extrusion as shown in Figure 2.13, is a highly efficient process to form thermoplastic film which also produces biaxially oriented film with enhancing mechanical properties. In the extrusion blown film process, polymer melt is extruded through an annular die to form a tube. By blowing air through the die head, the tube is pulled in a thin tubular bubble from the die vertically to nip roll. The size of bubble is maintained with the certain internal pressure. Then the bubble is flattened in two nip rolls into two flat layers and taken up by the winder. Generally, the die temperature about 190-200 °C have been used for extrusion blowing of films. The volume of air, speed of crew can be used to control film's width and thickness [21].

CHAPTER III

LITERATURE REVIEW

PLA is used in producing the packaging materials in order to replace petrochemical based polymer because it is a biodegradable polymer and the mechanical properties of PLA is compared to the petrochemical based polymer. However, PLA still has some limiting properties, especially, in term of poor toughness. Therefore, its properties were improved by incorporation of additive, such as toughening agent; so, it can be used in packaging applications at present. Many factors were considered for improving PLA blend's properties such as types, content, domain size of toughening agent and compatibilizer.

3.1 PLA blended with other polymers

PLA is blended with various polymers to improve its properties. Many researchers have studied the development of the toughness of PLA blended with toughening agent from petrochemical based bioplastic which is similar to rubber and has low glass transition temperature such as poly(butylenes adipate-*co*-terephthalate (PBAT) [4], poly(ϵ -caprolactone) (PCL) [5], poly(ethylene oxide) (PEO) [37], poly(ethylene-*co*-vinyl alcohol) (EVOH) [38], poly(butylene succinate) (PBS) [39]. In these blended PLA, some systems are immiscible or partial miscible; however, the elongation and toughness can be improved.

Jiang et al. [4] have studied the improvement of the toughness of PLA by filling PBAT, which is aliphatic-aromatic copolyester, using melt mixing method with corotating twin screw extruder. Thermal properties were measured by differential scanning calorimetry (DSC). It was found that the distinct phase separation of blended was observed while the glass transition temperature (T_g) remained unchanged when PBAT uniformly dispersed and formed about 300 nm domains in the PLA matrix which indicates that is the lack of significant molecular interaction between PLA and PBAT. Adding 5 wt% of PBAT increased the elongation at break more than 200% and the elongation at break increased with increasing the PBAT content while the impact strength of PLA increased about 1-2 folds at 20 wt% of PBAT. However, tensile strength and tensile modulus of blended PLA decreased about 24 - 25 % compared with that of neat PLA.

Broz et al. [5] blended PLA with PCL which is a rubbery polymer with low T_g and degradable. It was found that stress at yield and tensile modulus of PLA/PCL blend was decreased around 3 and 8 times, respectively. On the other hand, elongation at break of blend increased about 16 folds compared with that of neat PLA.

Nijenhuis et al. [37] showed that the miscibility of high molecular weight poly(L-lactide) (PLLA) with high molecular weight poly(ethylene oxide) (PEO) was obtained. Changes in mechanical properties were small in blends with less than 10 wt% PEO. At higher PEO concentrations, the materials became very flexible, an elongation at break of more than 500% was observed for a blend with 20 wt% PEO; however, the tensile strength of blend at same concentration increased about 3 times when compared with that of neat PLA.

3.2 Rubber Toughened Polymer

Numerous researches have studied the use of rubber, which is one of the toughening agents that can be used to develop the properties of various polymers such as polystyrene (PS) [13, 14, 40, 41], polypropylene (PP) [26, 42], nylon 6 [12, 43, 44], high density polyethylene (HDPE) [45], poly(methyl methacrylate) (PMMA) [46, 47], poly(ethylene terephthalate) (PET) [48], polyhydroxyalkanoate (PHA) [49] and so forth. Generally, the spherical rubber particles act as stress concentrators, initiating and terminating crazes in the brittle polymer matrices in which they are responsible for the enhanced fracture energy absorption [9, 14, 50]. So, these rubbers affect the impact strength and the toughness of polymer. There are two types of rubber, i.e., natural rubber (NR) and synthetic rubber. Both types of rubbers are used as the toughening agent, due to their high elasticity, high tear resistance and high impact strength [11].

Recently, the toughness of PLA was improved by adding synthetic rubber. Ishida et al. [51] blended PLA with four kinds of rubber component, i.e., ethylene-propylene copolymer (EPM), ethylene-acrylic rubber (AEM), acrylonitrile-butadiene rubber (NBR), and isoprene rubber (IR). All of the blend samples exhibited the distinct phase separation. Amorphous PLA constituted a topologically continuous matrix in which the rubber particles were dispersed. According, toughness was achieved only when PLA was blended with NBR at 20 wt% in which the impact strength increased nearly 2 folds because NBR showed the smallest domain size which is about 3 - 4 μm and the polarity of cyano groups make the mixture to be partially miscible blend. The elongation at break increased about 2 times when PLA

was blended with IR. However, the elongation at break of EPM and AEM melt-blends decreased about 2 folds. The tensile strength and Young's modulus decreased for all rubber blends.

Li et al.[52] studied PLA/rubber composite, two types of core-shell rubbers, namely, EXL2314 and EXL2330. The core and shell composition for both rubbers were poly(butyl acrylate) and poly(methyl methacrylate), respectively. The two types of core-shell rubber differed in their surface chemistry; i.e., the surface of the EXL2314 was grafted with an epoxy functional group whereas the surface of the EXL2330 was not treated. The impact strength and strain at break increased about 2 and 1.5 - 2 times, respectively, when adding 10 wt% of EXL2330. The strain at break of PLA added with 10 wt% of EXL2314 increased about 1.5 folds. Moreover, the tensile strength and tensile modulus also decreased about 1.5 folds when using both types of rubber.

Many researchers described the factors that influenced the mechanical and thermal properties of the rubber blended polymer such as types of rubber, rubber contents, domain size of rubber, degree of crosslink density of rubber and compatibilizer.

3.2.1 Effect of types of rubber on the properties of polymer

Many researchers discovered that all types of rubber can improve the properties of brittle polymers such as impact strength, elongation at break, and toughness. There are several types of rubber categorized by the chemical structure.

Loyens et al. [48] studied the properties of ethylene-co-propylene rubber (EPR) blended PET. The result showed that the impact strength of PET compound increased 30-40 times when adding 30 wt% of EPR and ethylene-co-propylene rubber-graft-glycidyl methacrylate (EPR-g-GMA8), as compatibilizer at 8 wt% GMA with ratio of EPR:GMA was about 0.25 by weight. Kaynak et al. [53] improved toughness of phenolic resin by incorporating it with acrylonitrile-butadiene particle and amino silane, which is compatibilizer. The blends demonstrated that impact strength increased about 63% compared with that of pure phenolic resin.

Furthermore, Li et al. [7] found that the elongation at break and impact strength of polystyrene (PS) increased 5 and 3 times, respectively, when adding 15 wt% of nano powder styrene-butadiene rubber (NPSBR) in PS matrices. Sae-Oui et al. [45] studied the behavior of HDPE blended with natural rubber powder (NRP), in which rubber was vulcanized by sulfur system before use. The elongation at break increased 347-478 % compared to neat HDPE when adding NRP about 60 - 70 wt%.

3.2.2 Effect of rubber content on the toughness and impact strength of polymers

Effect of rubber concentration as well as size distribution influences properties of the blends. Many works revealed that the content of second type of polymer is the important factor to improve the elongation at break, toughness and impact strength of the polymer matrices. In the past, many researchers tried to discover the appropriate content of rubber to improve the toughness of polymer matrices.

The research done by Tanrattanakul et al. [12] showed that adding 20 - 40 wt% of the epoxidized natural rubber (ENR), which is un-vulcanized rubber with epoxide functional group, in nylon6. The polymers were mixed by melt blending method in which the specimen is processed by compression molding. The elongation at break and the impact strength increased 20% and 4 - 10 folds compared to those of nylon6, respectively. Mathew et al. [54] found that the elongation at break of polystyrene increased about 100-140 times when the natural rubber was added about 70 wt%.

Zabaleta et al. [55] has described the improvement of the toughness of polyether imide (PEI). PEI at 80 wt%, polybutylene-terephthalate (PBT) at 20 wt%, and maleic anhydride 0.9 wt%-grafted-polyethylene-octene (mPEO) at 2.5 - 20 wt% were mixed. Young's modulus decreased about 3 times. The impact strength increased 10 folds when adding 15 wt% of mPEO because the domain size of rubber was about 1.01 μm . But they were decreased with high rubber content since some particle flocculation was observed, producing a large dispersed phase which has bad effect to the properties. For poly (ethylene terephthalate) (PET) toughened by natural rubber (NR), when NR content increased, the impact property increases while the Young's modulus decreases. This result may be due to the elastomeric nature of NR [85].

In conclusion, the rubber content is the important factor that affects the improvement of the properties of the polymer matrix including elongation at break and impact strength. The elongation and toughness properties tend to increase with increasing of rubber content. Furthermore, if the rubber content increases over the

optimal value, these properties decreased. However, it was found that the tensile strength and Young's modulus of the polymer matrix decreased when the polymer blended with any types of rubber and even decreased more with higher rubber content.

3.2.3 Effect of domain size of rubbers on the impact strength of polymers

Domain size of rubbers affects the impact strength of polymer blends because the rubber particles can absorb energy from stress of tension. Tanrattanakul et al. [12] reported the relationship between the domain size and impact strength of nylon 6 that if the domain size of rubber is in range of 0.1 - 0.5 μm , the impact strength of polymer blends will increase more than that the pure polymer matrix. But if the domain size is below 0.1 μm or above 0.5 μm , the impact strength will decrease. They also found that the optimal domain size of rubber for nylon 6 is about 0.2 μm , in which the impact strength of nylon 6 blended with rubber is higher than that of pure nylon 6.

Cho et al. [46] studied the toughness of poly(methyl methacrylate) (PMMA) by incorporating it with poly(n-butyl acrylate) (PBA). The core and shell composition for rubber were PBA and PMMA. The relationship between the impact strength and rubber particle size is represented by a bell shaped curve where toughness is maximum at an optimal rubber particle size. The impact strength increased 2 - 4.5 folds at optimum domain size of 0.25 μm of core rubber. If the core rubber was smaller than 0.25 μm , it will decrease. The impact strength was reported

as a function of the rubber content. The impact strength increased up to a certain (around 12 wt%) level of rubber content and decreases above that level.

In work done by Tangboriboonrat et al. [13] the toughness of PS was enhanced by natural rubber at average size particle about 0.7 μm the with the phase transfer technique. They found that the impact strength increased about 3 times compared with that of PS. Additionally, several researches reported the optimal size of rubber particle is in the range of 1-4 μm to improve the toughness of high impact polystyrene (HIPS).

Moreover, the dispersion of rubber particles is one of the important factor that influenced by the size of rubber particle. If the size of rubber particle is too small, it will be dispersed well in polymer matrix because it can insert between gaps in the polymer matrix. If it is too big, it will agglomerate causing the decreasing in mechanical properties of polymer.

3.2.4 Effect of the degree of crosslink density on the impact strength of polymers

The effect of degree of crosslink density on swelling and stiffness of rubber shows the improvement of mechanical properties. The tensile strength and Young's modulus of the polymer increased when the rubber was vulcanized [13, 40]. The particle size depends on the degree of crosslink density. The degree of crosslink density was measured by the swelling ratio. In previous research, the prevulcanized natural rubber is stiff and stable when the swelling ratio is lower 500% in sulfur system. The swelling ratio depends on system of vulcanization and time of

vulcanization [56, 57]. The degree of crosslinking of the rubber phase affects the impact strength properties of PS blends.

Tangboriboonrat et al. [40] studied the effect of the crosslink density of natural rubber (γ -irradiation) on impact resistance of polystyrene. The optimum crosslink density improves impact resistance at irradiation dose equal to 14 kGy. On the other hand, the impact resistance decreased when increasing irradiation dose.

3.2.5 Effect of the compatibilizer on the morphology

Numerous researchers found that the blends exhibited distinct phase separation between rubbers, which is a non-polar material and the biodegradable polymer that is hydrophilic polymer. Therefore, compatibilizer is used to increase dispersion of rubber in polymer matrix.

Sangribsub et al. [40] mixed 5 wt% radiation vulcanized natural rubbers (RVNR) latex (at irradiation dose equal to 14 kGy) by phase transfer/bulk polymerization technique in which this rubber was vulcanized by radiation system, RVNR polymerized by using benzoylperoxide (BPO) at 1 wt%, which is linker, and polystyrene-*block*-polyisoprene-*block*-polystyrene or KRATON at 5 wt%, which is interfacial agent, with HIPS. The unnotched Izod impact strength increased 2 folds compared to that of HIPS.

Nakason et al. [58] showed that the tensile strength and the elongation at break of PP increased about 2 MPa and 2 times when compared with those of PP without compatibilizer, respectively, when adding ENR 30 mole% by the ratio of ENR:PP to equal 25:75 with 5 wt% of Phenolic modified polypropylene (Ph-PP),

which is compatibilizer. The toughness of polybutylene terephthalate (PBT) was improved by adding ethylene propylene diene monomer (EPDM), un-epoxidized EPDM (uEPDM) and epoxidized EPDM (eEPDM) with particle size about 2 μm . The eEPDM could increase the impact strength of PBT about 23 times higher than that of uEPDM.[59]

Ismail et al.[42] reported the blends of recycled acrylonitrile butadiene rubber (NBRr):PP in weight proportion of 80:20 - 40:60 with diglycidyl ether of bisphenol-A epoxy resin (epoxy resin has epoxide group about 0.48-0.54) about 1 part, which is compatibilizing agent, in NBRr:PP 100 parts. The elongation at break, Young's modulus, and tensile strength of every ratio of PP: NBRr: epoxy resin increased around 1-2%, 100-200 MPa, and 1-2 MPa, respectively, compared with those of PP: NBRr.

Therefore, the compatibilizer is used to connect between non-polar and polar polymer which can improve the properties of blended polymer.

CHAPTER IV

EXPERIMENTAL METHODOLOGY

This chapter describes the materials and analytical instrument used in this research. Also, the experimental details of the preparation of vulcanized natural rubber, the preparation of natural rubber powder, blown poly(lactic acid) /rubber films technique were explained. Characterization of natural rubber (NR) latex such as particle size and swelling ratio were examined. The thermal, thermomechanical, mechanical and morphology analyses of films were also studied by differential scanning calorimeter (DSC), Dynamic mechanical analyzer (DMA), Universal testing machine and scanning electron microscope (SEM), respectively.

4.1 Materials and Chemicals

4.1.1 Materials

4.1.1.1 Poly (lactic acid)

Poly(lactic acid) (PLA) grade 2002D pellets were supplied by NatureWorksTM. It is a semicrystalline extrusion material with a specific gravity of 1.24 and melt index around 5-7 g/10 min. (210°C/2.16 Kg). The glass transition temperature (T_g) and the melting temperature (T_m) of PLA 2002D is 55-60 °C and 155-160 °C respectively, which is examined by Differential Scanning Calorimetry (DSC). Chemical structure of PLA is shown in Figure 4.1.

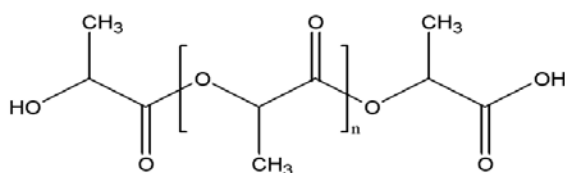


Figure 4.1 Chemical structure of PLA

4.1.1.2 Natural Rubber latex

Commercial high-ammonia natural rubber latex (60% dry rubber content) was purchased from Rayong Rubber Co., Ltd. (Thailand) that is filtered through a 250-mesh aluminium screen to remove impurity before uses. Chemical structure of cis-1,4-polyisoprene is shown in Figure 4.2

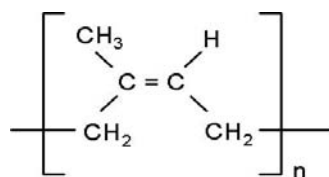


Figure 4.2 Chemical structure of cis-1,4-polyisoprene

4.1.1.3 Gum arabic

Gum arabic or Acacia for food grade was purchased from Nacalai Tesque (Kyoto, Japan). It is white to pale yellow-white powder form. It is soluble in water and emulsifier. Chemical structure of Gum arabic is shown in Figure 4.3

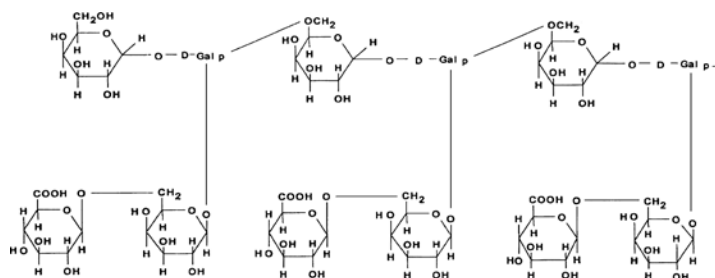


Figure 4.3 Chemical structure of Gum arabic [32]

4.1.2 Chemicals

Vulcanizing ingredients i.e. *tert*-butyl hydroperoxide (*t*-BuHP) 70 wt% in H₂O was obtained from Fluka, Aldrich Chemical (USA) and was used as initiator. Sodium dodecyl sulphate solution (SDS) was purchased from Fluka, Aldrich Chemical, (USA) and was used as surfactant without any purification. Tetraethylene pentamine (TEPA), gel permeation chromatography grade, used as activator, and toluene (commercial grade) were used as received from Fluka, Aldrich Chemical (USA). Also, glacial acetic acid was purchased from Merck (USA). Sodium Chloride was obtained from Aldrich Chemical (USA).

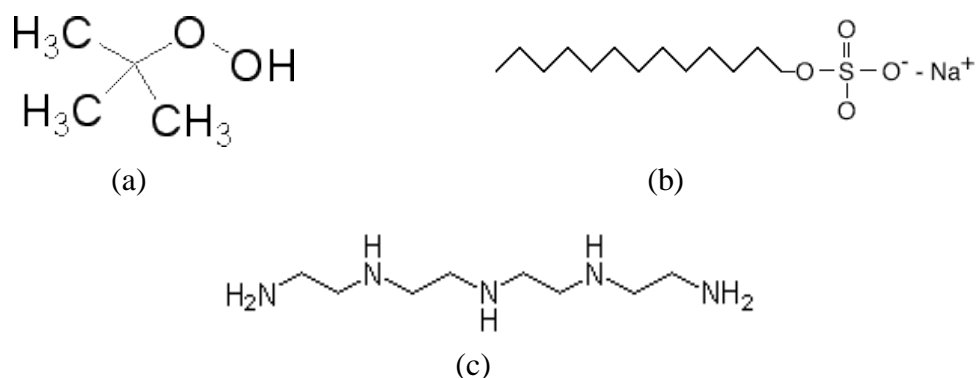


Figure 4.4 Chemical structure of (a) *tert*-Butyl hydroperoxide (*t*-BuHP), (b) sodium dodecyl sulphate solution (SDS) and (c) tetraethylene pentamine (TEPA)

4.2 Methodology

This experimental procedure comprised of 2 parts. The first part is to investigate the NR content and influence of crosslinked NR with vulcanization by peroxide system on the properties of PLA blown films. The properties of PLA blown films added with NR and crosslinked NR were compared with those of PLA/NR-

Commercial blown film. Firstly, rubber and PLA were blended with internal mixer and the films were prepared by extruder attached to blown film die. The properties of PLA/rubber blown films were studied. In the second part, the optimal NR content and type from the first part was brought to produce NR-Powder (NRP). Then, the powder after coating its surface with Gum arabic followed by spray dryer was prepared. The PLA/NRP blown films were prepared using blown film technique with twin screw extruder. The schematic of the entire experimental procedure is shown in Figure 4.5.

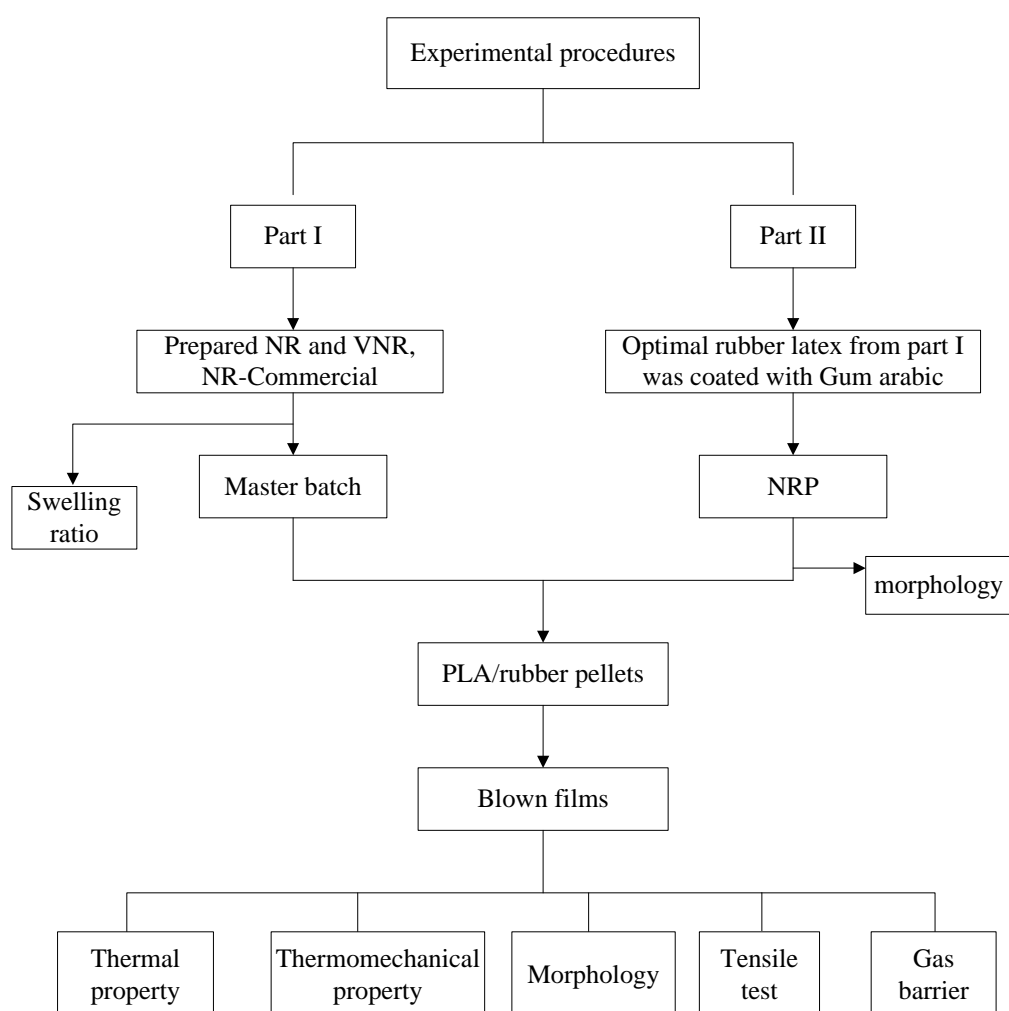


Figure 4.5 Methodology of this research

4.3 Experiment

4.3.1 Natural rubber sheet

4.3.1.1 Prevulcanized natural rubber latex by peroxide method

Commercial high ammonia preserved concentrated NR latex (60% dry rubber content (DRC)) was purchased from Rayong Bangkok Rubber Co., Ltd (Thailand). Before being used and characterized, NR latex was passed through a 250 mesh aluminium sieve to filter any rubber coagulum or dust.

NR was vulcanized by using the system based on peroxide. The formulation used to prepare peroxide vulcanized NR latex is given in Table 4.1.

Table 4.1 Formulation used for peroxide vulcanization of NR latex [47, 60]

Ingredients	Amount (g)
Concentrated NR latex (60%DRC)	250.00
Tetraethylene pentamine solution (10w/v%) (TEPA)	1.75
<i>tert</i> -Butyl hydroperoxide solution (70w/v%) (<i>t</i> -BuHP)	1.82
Sodium dodecyl sulfate solution (20w/v%) (SDS)	1.88
Distilled water	33.60

Peroxide emulsion was firstly prepared by mixing (*t*-BuHP) solution (1.82 g) with distilled water (16.8 g) and SDS solution (1.88 g). The emulsion was then added, while stirring into NR latex at room temperature. Then, 10 w/v% tetraethylene pentamine solution (1.75 g) was poured into the mixture followed by the rest of distilled water (16.8 g). Vulcanization was carried out at 60°C in the reaction

vessel equipped with a condenser and a thermometer. During vulcanization, a portion (about 5 g) of the compound latex was taken out every one hour for seven hours and rapidly cooled down to room temperature before being cast on a Petri dish and dried at room temperature for 1 week. After that, the swelling ratio of the rubber was calculated as described in section 4.4.5. At the end of heating stage, the vessel was quickly immersed in a water bath at room temperature to prevent further reaction.

4.3.1.2 Dried rubber

Dry natural rubber sheet was prepared from both un-vulcanized rubber latex (NR) and vulcanized rubber latex (VNR). They were dried by cast film method on glass plate. They were weighed 40 - 45 g and poured into the glass plate and dried at room temperature for about 1-2 weeks. The yellowish NR sheet was obtained. The NR sheet was dried again in a vacuum oven for one day and cut into small pieces before use.

4.3.2 Natural rubber Powder

NR latex having 60% total solid content (TSC) was diluted with deionised water to 10% TSC. An aqueous solution of Gum arabic was adsorbed onto the natural rubber latex surface (10% TSC, 60g) in weight ratio of NR: Gum equal to 1:2. After making the concentration of mixer in each batch equal to 5% TSC, it was added with deionised water, the mixture was stirred continuously for 30 min at room temperature. Furthermore, the mixture was then fed into a spray dryer (model B-190, Buchi, Switzerland) with inlet temperature of 160 °C, flow rate of feed equal to 6 ml/min,

flow rate of air equal to 700-800 cm³/s. The obtained natural rubber powder (NRP) was dried under freeze dry process for 2 days. Finally, morphology of the NRP was investigated by a scanning electron microscope (SEM).

4.3.3 Preparation PLA blends with rubbers

4.3.3.1 PLA blended with natural rubber

PLA was dried in an oven at 60 °C for 24 h before use and then kept in desiccators at room temperature. NR and VNR sheets were cut into small pieces of size 20x20x10 mm³. PLA blend with NR were prepared by using an internal mixer (350s, Barbender, Germany) at 180 °C with rotor speed of 50 rpm. The PLA was molten in a chamber of the internal mixer for 5-8 min followed by the addition of rubbers, and mixing was continued until the torque of the mixer became constant. The PLA blends were well-mixed for another 10 - 15 minutes. The total mixing time of this process was taken for 15 - 20 minute for all blends. Then, they were sheeted by using two-roll mill before cutting into small pieces. After that, the blending of PLA/rubber was performed in a twin-screw extruder (Thermo Hakke Rheomix, Germany) attached to rod capillary die at temperature of 180-185 °C. Screw speed, feed rate and torque depend on processing condition. The extrudate was subsequently quenched in a water bath at room temperature and pelletized. The pelletized samples were dried in an oven at 60 °C overnight and kept in desiccators at room temperature. Then, they were re-extruded by using blown film die of twin-screw extruder with similar thermal profiles. Furthermore, films were kept in container with silica gel and bring to test mechanical and thermal properties. The mixing ratio between PLA and

rubber were 99/1, 97/3 and 95/5 w/w and temperature profile was shown in Table 4.2 and 4.3.

Table 4.2 Operating condition of twin screw extruder for PLA blend with rubber

Rubber content (wt%)	TS-E1 (°C)	TS-E2 (°C)	TS-E3 (°C)	TS-E4 (°C)	TS-D1 (°C)	TS-D2 (°C)
1	180-185	180-185	180-185	180-185	180-182	180-182
3	175-180	175-180	175-180	175-180	172-177	172-177
5	170-175	170-175	170-175	170-175	167-172	167-172

*screw speed = 125 rpm, feeder speed = 80 rpm

Table 4.3 Operating condition of twin screw extruder for PLA/rubber blown film

Rubber content (wt%)	TS-E1 (°C)	TS-E2 (°C)	TS-E3 (°C)	TS-E4 (°C)	TS-D1 (°C)	TS-D2 (°C)
1	170-175	170-175	170-175	170-175	167-172	167-172
3	165-170	165-170	165-170	165-170	162-167	162-167
5	160-165	160-165	160-165	160-165	157-162	157-162

*screw speed = 125 rpm, feeder speed = 80 rpm, roll speed = 380 rpm, torque = 45-60 n.m

4.3.3.2 PLA blended with natural rubber powder

PLA was dried in an oven at 60 °C for 24 h before use and then kept in desiccators at room temperature. NR-Powder was mixed with PLA pellets before pouring into hopper. Then, the blending of PLA/rubber was performed in a twin-screw extruder (Thermo Hakke Rheomix, Germany) at 180-185 °C. Screw speed, feed rate and torque depend on processing condition. The extrudate was subsequently quenched in a water bath at room temperature and pelletized. The pelletized samples were dried in an oven at 60 °C overnight and kept in a desiccator at room temperature.

Then they were re-extruded by using blown film die of twin-screw extruder with similar thermal profiles. Furthermore, films were kept in container with silica gel and bring to test in properties such as mechanical, thermal ones.

4.4 Characterizations

4.4.1 Determination of total solid content (TSC)

TSC of latex is defined as percentage by weight of concentrated NR latex, which is non-volatile at a definite temperature in vented air oven. The %TSC of concentrated latex was determined by using the method described in ASTM D1076-97 [58, 61] and calculated by using the following equation:

$$\%TSC = \frac{W_x}{W_t} \times 100 \quad (4.1)$$

where,

W_x =weight of dry NR sample (g)

W_t =weight of NR latex sample (g)

4.4.2 Determination of dry rubber content (DRC)

DRC of latex is defined as percentage by weight of concentrated latex which is precipitated by 5% acetic acid. The %DRC of concentrated NR latex in this study was determined by using the method described in ASTM D1076-97 [58, 61].

$$\%DRC = \frac{W_r}{W_t} \times 100 \quad (4.2)$$

where,

W_r =weight of dry coagulum (g)

W_t =weight of NR latex sample (g)

4.4.3 Measurement of particle size

The particle size and size distribution of NR latex were measured by using Mastersizer (model 2000, Malvern, England) at 25°C. During continuous stirring, NR latex was dropped into the chamber containing deionized water slowly, until its concentration was in the range of 5 - 10%. Each measurement was repeated 3 times [60].

4.4.4 Measurement of zeta potential

The NR was diluted with sodium chloride solution (10^{-3} M), and pH of the latex was then adjusted by adding an aqueous solution (0.1 M) of sodium hydroxide or hydrochloric acid. The zeta potential of the dispersion was determined by using a particle microelectrophoresis apparatus (Zetasizer model Nano-Zs, Malvern, England), with measurements being carried out within 20 min after mixing and pH adjustment at 30 °C. The variation of the zeta potential of the NR with pH at a concentration of sodium chloride of 10^{-3} M is shown [62].

4.4.5 Determination of crosslink density

The crosslink density of rubber sheet, casted from un-vulcanized and vulcanized rubber latex at room temperature, was determined by using the swelling

method. The dry rubber sheet, cut into a known weight square piece (approximately 0.2 g), was immersed in toluene (40ml) at room temperature. At equilibrium swelling (about 7 days) in the dark cabinet, the weight of swollen rubber was recorded after blotting its surface with filter paper. %swelling ratio was calculated according to ASTM D471 by the following equation [58, 60, 61]:

$$\% \text{swelling ratio} = \frac{W_{\text{eq}} - W_{\text{o}}}{W_{\text{o}}} \times 100 \quad (4.3)$$

where,

W_{o} = initial weight of dry rubber (g)

W_{eq} = weight of swollen rubber at equilibrium (g)

4.4.6 Mechanical properties

4.4.6.1 Tensile testing

Tensile test of films were measured by universal testing machine (Instron 5567, NY, USA) operated under the tension mode at room-temperature. Standard tensile testing of films was examined following ASTM D882. All the specimen was prepared as rectangular shape and the dimension of films was, the thickness of 0.035 mm, the width of 10 mm, and the length of 100 mm. The condition of tensile testing was performed on 1 kN electronic load cell and the test was conducted at a crosshead speed of 12.5 mm/min. The data were acquired by a computer such as tensile strength, elongation at break and Young's modulus.

4.4.6.2 Impact testing

Films impact testing was examined following ASTM D1709. Samples were prepared by tubular blow film extrusion. The circle shape specimen with the thickness of 0.035 mm, the diameter of 100 mm² was used. Films impact testing was performed by using a film impact testing machine (Digital impact tester, Toyoseiki, Japan). The pendulum energy of 1.5J was used at room temperature. Minimum of ten specimens were tested for each condition.

4.4.7 Thermal properties

Thermal properties of the sample were determined by using a differential scanning calorimeter (DSC) (TA instruments model 2910, USA). The 5-10 mg samples were sealed in 40 μ L aluminum pan. All measurements were tested under nitrogen atmosphere and heated from 30 to 200 °C at heating rate of 10°C/min. Percentage of crystallinity of PLA in the blends was calculated by equation (4.4) according to the enthalpy obtained from the DSC curves.

The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), degree of crystallinity (X_c), and heat of fusion (ΔH_m), of PLA blends are collected.

$$X_c = \frac{(\Delta H_m - \Delta H_{cc})}{(\Delta H_o \times \Phi)} \times 100 \quad (4.4)$$

where, ΔH_m and ΔH_{cc} are the enthalpies of the melting and cold crystallization of blending PLA, and ΔH_o (93 J/g) is the melting enthalpy of 100% crystalline PLA.

A parameter Φ , the weight fraction of the matrix, is introduced to eliminate the weight contribution of rubber[63].

4.4.8 Thermomechanical properties

The thermomechanical properties of neat PLA and PLA/rubber blown films were measured by using dynamic mechanical analyzer (DMA) (NETZSCH, DMA-242 c instrument, Germany). Rectangular shape specimen with 10 mm long, the thickness of 0.035 mm, and the height of 30 mm was used. Measurement was operated in tension mode under inert nitrogen atmosphere with the temperature range from -100 to 100 °C. The heating rate and nominal frequency were set at 2°C/min and 1 Hz, respectively, using liquid nitrogen as a cryogenic medium and controlled by the flow of nitrogen gas of 20 ml/min. Prior to each measurement, the environment was kept at the set temperature for 10 min to ensure thermal equilibration. Storage modulus (E'), loss modulus (E''), and tan delta ($\tan \delta$) were recorded as a function of temperature.

4.4.9 Morphology

The morphology of the pure PLA and PLA/rubber blends was investigated with scanning electron microscope (SEM) (Hitachi VP-SEM S-3400N, Japan). Fracture surface of the samples were obtained by immersing sample in liquid nitrogen for 30 min and were then broken cryogenically. After that, the samples were sputtered with gold for 4-5 min prior examination. Gold coating electron microscope was used at an accelerating voltage of 10-20 kV. The particle size of rubber was measured in representative zone of cross section specimens from SEM image.

4.4.10 Gas barrier testing

4.4.10.1 Oxygen permeation

Oxygen permeation of neat PLA blown films and PLA/rubber blended blown films were measured using MOCON OX-TRAN model 2/21 with an oxygen flow rate of 40 cm³/min at 0% relative humidity and surrounding temperature of 23 °C. Standard oxygen permeation testing was examined following ASTM D3985. Circular shaped specimen with the thickness of 0.035 mm, the diameter of 100 cm² was prepared. Oxygen permeation was carried out at atmospheric conditions. OPC (cc·mil/m²·day·atm) of PLA and PLA blends films was calculated as

$$\text{OPC} = (\text{OTR} \times \Delta l) / \Delta p \quad (4.5)$$

where OTR was the measured oxygen transmission rate (cc/m²·day) through a film. Δl was the mean film thickness (m) and Δp was the difference in oxygen partial pressure across the film [64].

4.4.10.2 Water vapor permeation

Water vapor permeation of neat PLA blown films and PLA/rubber blended blown films were measured using MOCON PERMATRAN-W model 398 with a nitrogen flow rate equal to 250 cm³/min at 90 % of relative humidity and temperature of 37.8 °C. Standard water vapor permeation testing was examined following ASTM E96. All of samples for water vapor permeation test were required in circular shape with the diameter of 50 cm² and the thickness of 0.035 mm. Water vapor permeation test was carried out at atmospheric conditions. WVP (gm·mil/m²·day·atm) of PLA and PLA blends films was calculated as

$$WVP = (WVTR \times \Delta l) / \Delta p \quad (4.6)$$

where WVTR was the measured water vapor transmission rate ($\text{gm}/\text{m}^2 \cdot \text{day}$) through a film. Δl was the mean film thickness (m) and Δp was the difference in the water vapor partial pressure across the film [64].

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results of experiment on the blown films of PLA/NR, PLA/NR-Powder (NRP) and PLA/NR-Commercial (ADS grade) blends were discussed. The chapter comprises of four sections. First, the effect of natural rubber content on thermal, mechanical and barrier properties of PLA/rubber blends was studied in section 5.1. In section 5.2, the effect of un-crosslink and crosslinked natural rubber on thermal, mechanical, barrier properties and morphological of PLA/rubber blends was studied. The effect of dispersion of NRP compared with NR sheet on the properties of PLA blends and their physical properties are discussed in sections 5.3. Finally, the section 5.4 presents the properties of PLA/NR film compared with those of PLA/NR-Commercial blown films on mechanical and barrier properties.

5.1 Effects of natural rubber content on physical properties of PLA/NR blown films

In this work, the high ammonium natural rubber latex (HA-NR) was used. % total solid content (%TSC) and % dry rubber content (%DRC) are approximately 61% and 60%, respectively, in the HA-NR latex. %TSC was slightly higher than %DRC (about 1%) due to the presence of the non-rubber such as protein, fatty acid, organic salts in which the obtained data agrees with previously reported [65].

In this study, the rubber sheet casted from HA-NR with various content of rubber sheet were blended with PLA at 0, 1, 3, 5 and 7 wt% because the extrusion blown film process require only low content for producing films because sample with high rubber content cannot be blown to obtain film. Furthermore, using internal mixer followed by twin screw extruder attached to blown film die at suitable condition achieved PLA/NR blown films. Analytical techniques were used to identify the physical properties of blended PLA, i.e., differential scanning calorimetry (DSC), Oxygen transmission rate (OTR), Water vapor transmission rate (WVTR) and tensile testing.

PLA/NR blown films from extrusion blown film technique are yellowish films with the thickness of $35 \mu\text{m} \pm 0.05 \mu\text{m}$, width of 13 cm throughout experiment.

5.1.1 Thermal properties

Thermal properties of pure PLA (grade 2002D) and PLA/NR blown films were investigated by DSC which can be used for the evaluation of the phase behavior between components of polymer blend. The data are collected under nitrogen atmosphere in a temperature range from 30 to 200 °C at a heating rate of 10 °C/min. The results of DSC show the glass transition temperature (T_g) demonstrating the relaxation in polymer chain from glassy state to rubbery state. Above T_g is cold crystallization temperature (T_{cc}) where the molecular chains in the amorphous region can rearrange to form crystalline phase, this phenomenon is called crystallization. Beyond T_g and T_{cc} is melting temperature (T_m), where crystalline phase of polymer is

melted in this temperature. The properties of all samples are summarized in Appendix B.

As shown in Figure 5.1, the DSC thermograms of the first heating scan of neat PLA and PLA/NR obtained after processing in the blown films process. The T_g (which is calculated from slope of DSC profile) of PLA/NR blown films at 1, 3 and 5 wt% were observed at 57, 61 and 60 °C which were closed to that of neat PLA (63 °C). The glass transition temperature of PLA/NR was similar to that of neat PLA film. Because only small amount of NR was added into PLA, we cannot observe the change of PLA/NR's T_g .

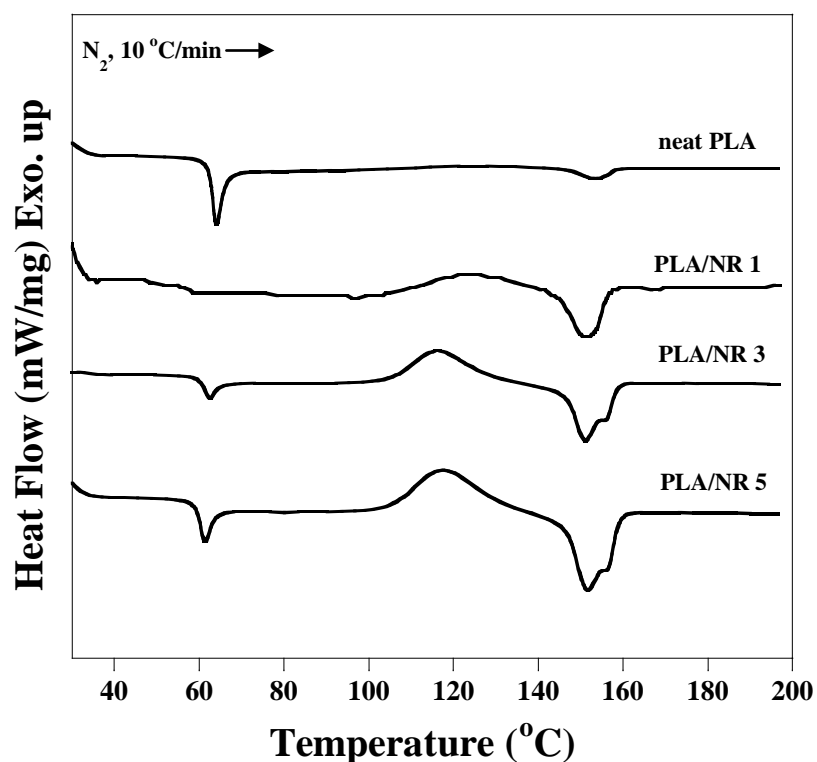


Figure 5.1 DSC first heating thermograms recorded at a heating rate of 10 °C/min under N₂ for PLA/NR blown films containing NR at 0, 1, 3, and 5 wt%

The T_{cc} of PLA/NR film at 0, 1, 3, and 5 wt% is 124, 122, 116 and 117, respectively. DSC showed that the T_{cc} of PLA/NR film was slightly lower than that of neat PLA. In addition, increasing the rubber content did not influence on the cold crystallization temperature. Broad peak of T_{cc} of PLA/rubber film is larger than that of neat PLA when rubber content increases. It indicates that the blends establish crystalline form. The enthalpy of T_{cc} and T_m which can be determined by the area under DSC curve of cold crystallization and melting peaks increases. Degree of crystallization (X_c) can be calculated by equation (4.4). The X_c of PLA/NR at 0, 1, 3, and 5wt% is 1.16, 0.08, 0.35 and 2.78, respectively. The X_c obtained from first heating thermograms increases slightly compared with that of neat PLA. Thus, rubber can be as the nucleating agent affecting chain mobility PLA and forming crystalline structure [66].

The T_m appeared around 153 °C for neat PLA film. In addition, Incorporation of rubber did not change T_m in comparison to that of neat PLA. Especially, the double-peak melting temperature was observed when incorporating rubber. The peaks at low temperature were approximately 1-2 °C lower than the peaks of neat PLA (Appendix B) suggesting the presence of new crystalline structure. However, the intensity of melting peak at lower temperature (T_{m1}) is higher than that at higher temperature (T_{m2}). These results could be explained that T_{m2} showed perfect crystalline structure than that at T_{m1} . The less perfect crystals have enough time to melt and reorganize into crystals with higher perfect structure and remelt at high temperature [67] The crystal structure at lower temperature is called α' form and that at higher temperature is called α form [68].

Therefore, the presence of rubber in PLA/NR blown films did not change T_g and T_m . In addition, T_{cc} of PLA films was decreased when adding NR, however; degree of crystallinity (X_c) of PLA/NR also increases with increasing rubber contents.

5.1.2 Mechanical properties

The effects of NR content on mechanical properties of PLA/NR blown films were investigated by universal testing machine (Instron 5567) according to ASTM D882. The mechanical results include tensile strength, Young's modulus, elongation at break and tensile toughness. The tensile strength of material is defined as the maximum tensile stress where material begins to deform. The tensile modulus is determined by the first linear slope of stress-strain curve which indicates the stiffness of material. The elongation at break is defined as the strain at maximum tensile strain at break or at the rupture of the specimen. All the mechanical properties of PLA/NR blown films are summarized in Appendix D.

Tensile behavior of PLA/NR blown films at 0, 1, 3 and 5 wt% in machine direction (MD) is shown in Figure 5.2. The tensile properties of PLA film, such as static modulus, tensile stress, and elongation at break, determined from these curves as shown in Table D.1-D.12. From Figure 5.2, neat PLA blown film showed brittle behavior of polymer due to the material breaks after yield without necking and its strain at break was only about 3%. The brittle fracture of PLA film to ductile fracture with formation and propagation of neck while stretching and the yield fracture was suppressed when adding NR in the PLA matrix.

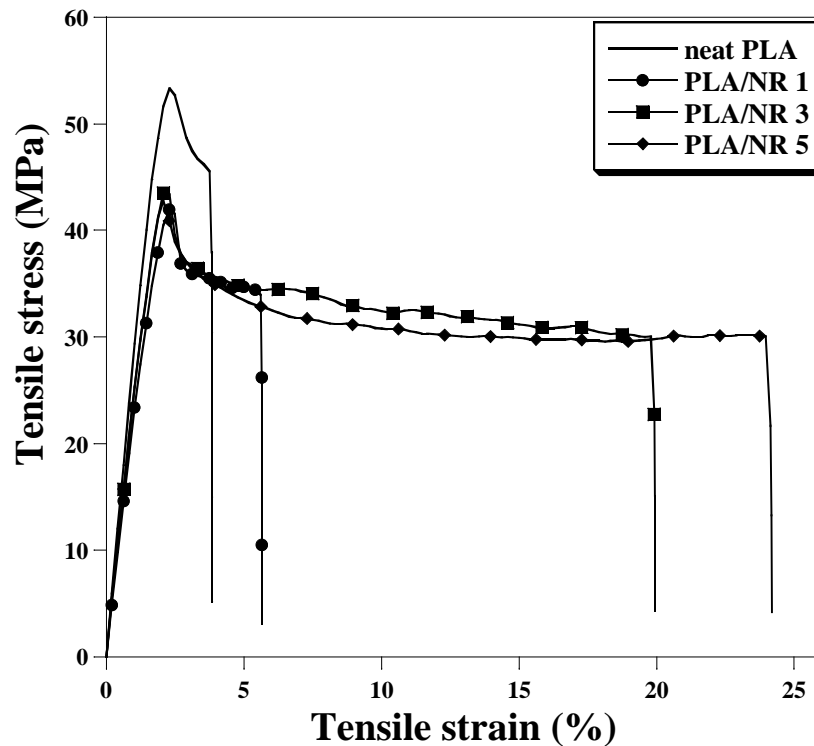


Figure 5.2 Stress-strain curve of the PLA/NR blown film at rubber content at 0, 1, 3 and 5 wt% NR in machine direction (MD)

The yield stress of PLA/NR is lowered than that of neat PLA but it increases the %tensile strain. The plastic deformation of PLA/NR in uniaxial tensile is brittle to ductile due to the major mechanisms of deformation (crazing and shear yielding of the matrix). These results suggest that the added NR acts as the stress concentrator and the debonding in the initial stage of stretching occurs at the particle–matrix interface due to the poor interfacial adhesion. This results in the formation of a yield point at which stable plastic deformation takes place. A necking starts to form and then extends in a “cold drawing” process after from the yield point which the material shows whitening in the necked zone that affects of a fine-scale cavitation process. Therefore, the release of the strain constraint due to the formation of voids and the

decrease of yield stress resulted in the relaxation of stress concentration, and in the significant increase of the toughness of the material which consistent with previous research [69].

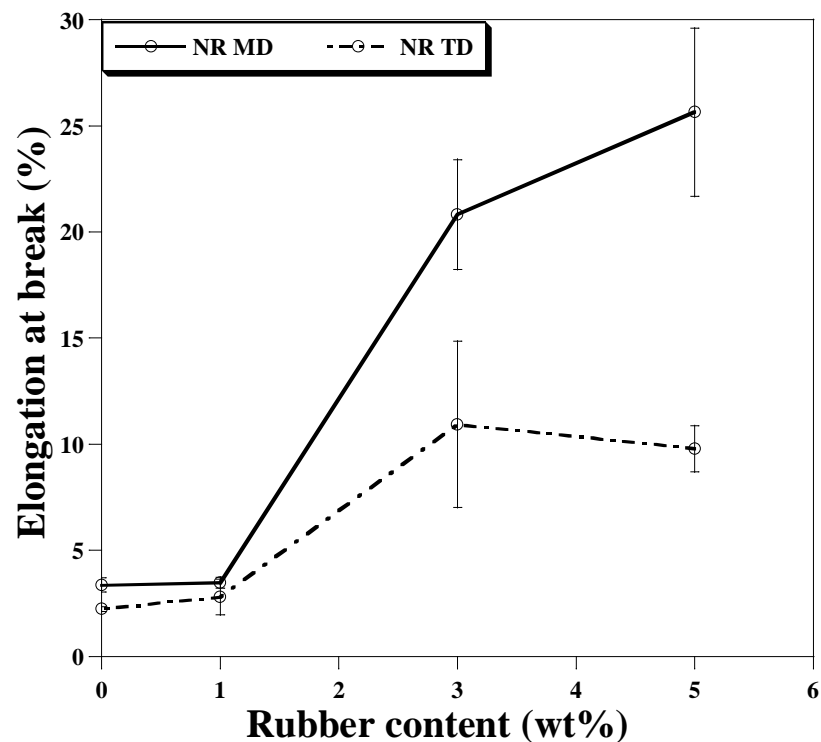


Figure 5.3 The elongation at break in machine direction (MD) and transverse direction (TD) of PLA/NR as a function of NR contents

The elongation at break of neat PLA and PLA/NR blown films in machine direction (MD) and transverse direction (TD) is shown in Figure 5.3. The elongation at break in MD of neat PLA is 3.3%, while the PLA/NR blown films in MD when adding NR at 1, 3 and 5 wt% was linearly raised to 3, 21 and 26 %, respectively. In contrast, the elongation at break in TD of neat PLA is about 2%, while PLA/NR blown films in TD when adding 1, 3 and 5 wt% NR is about 3, 11 and 10%,

respectively. However, the elongation at break of PLA/NR film in MD is higher than that in TD because orientation of polymer chain in transverse direction blown films in only depends on flow rate of air but that in machine direction depends on flow rate of air and pull rate of nip roll.

PLA/NR blown films displayed high elongation at break in MD and increased with increasing the rubber contents. This can be described by craze growth which is normal to the tension force and can see as stress whitening. The crazes include microfibrils of polymer which help resist the fracture of specimen. These microfibrils cause the high elongation at break in tensile test. Furthermore, the fracture of specimen also results from the shear yielding.

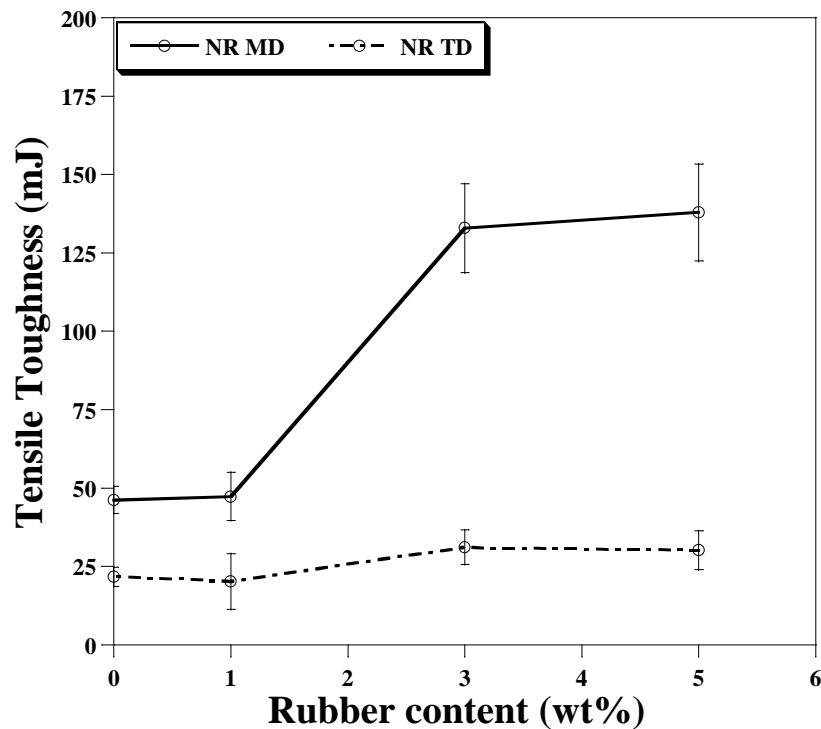
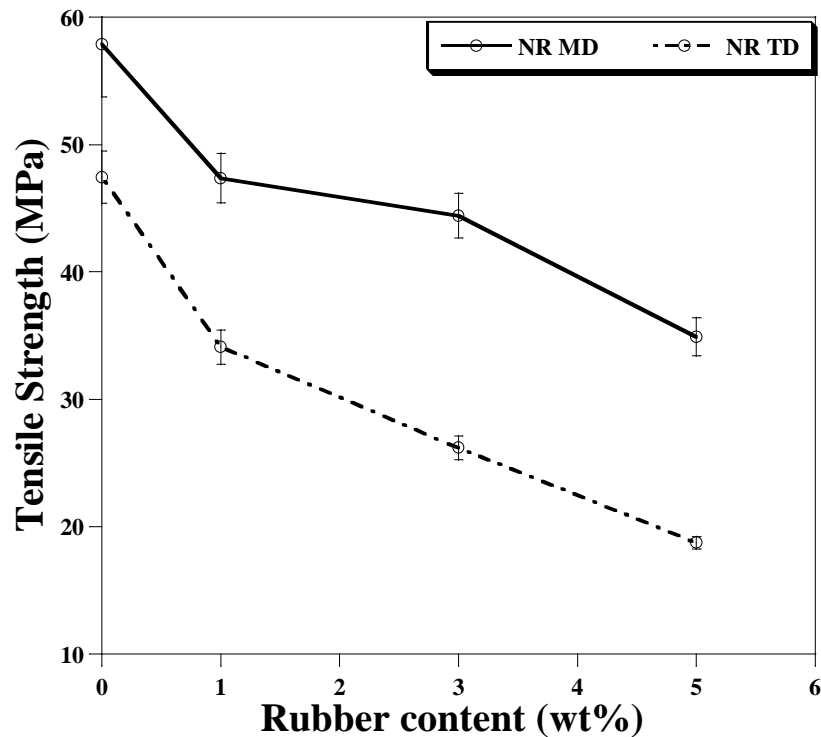


Figure 5.4 The tensile toughness in machinery direction (MD) and transverse direction (TD) of PLA/NR as a function of NR contents

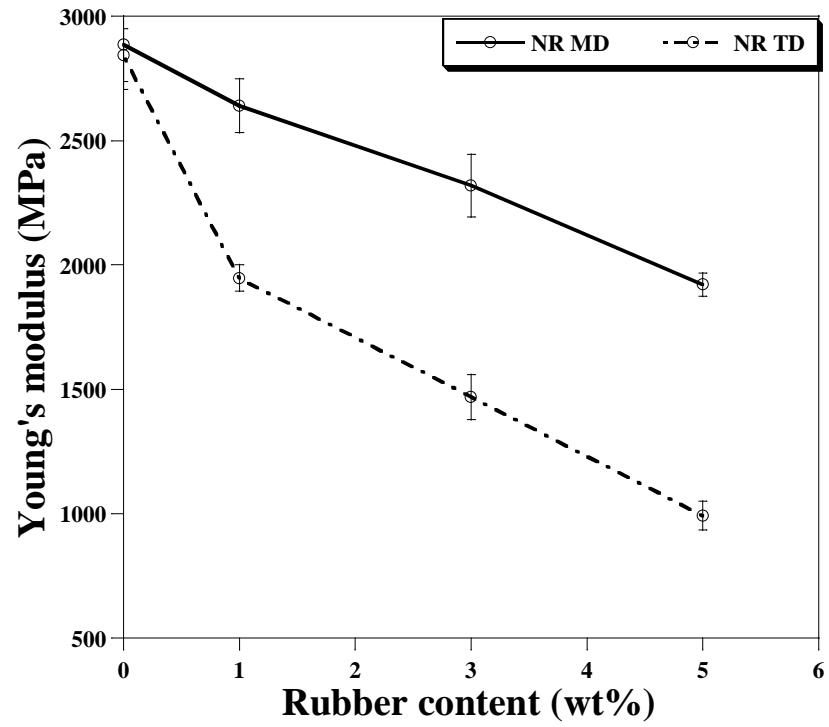
The tensile toughness of neat PLA and PLA/NR blown films is shown in Figure 5.4. Tensile toughness of specimens was calculated from the energy at break curve of universal testing machine. The tensile toughness of PLA/NR blown films in MD is about 46, 47, 135 and 138 mJ at rubber content of 0, 1, 3, and 5 wt%, respectively while the tensile toughness of PLA/NR blown films in TD is about 22, 21, 31 and 31 mJ at rubber content of 0, 1, 3, and 5 wt%, respectively. The tensile toughness in both MD and TD of PLA/NR blown films increased with rubber contents in which these results showed similar trend with the elongation at break of these films. However, the PLA/NR films in MD are tougher than film in TD due to arrangement of molecular chain. Because the development of crazing (with further elongation of the fibrils) is due to energy absorption of rubber domain at first cavity provoking locally a plane strain/plane stress transition in toughening mechanism. However, tensile toughness of PLA/NR film in TD slightly increased compared with that of neat PLA. The addition of 5 wt% NR shows the highest toughness of film in MD whose toughness increased three folds compared to that to neat PLA. Thus, this data indicated that the incorporating NR can improve the tensile toughness for PLA film.



(a)

Figure 5.5 (a) tensile strength and (b) Young's modulus in machine direction (MD) and transverse direction (TD) of PLA/NR as a function of NR contents

Figure 5.5 (a) and (b) shows the tensile strength and Young's modulus of PLA/NR blends in MD and TD at various NR contents. The tensile strength of neat PLA in MD and TD are 58 and 47 MPa, respectively. The Young's modulus of neat PLA films in MD and TD are 2886 and 2843 MPa, respectively. The tensile strength and Young's modulus in MD and TD of PLA blends decreased with increasing rubber contents because the rubber has high elasticity and decrease the strength of polymer. The Young's modulus in MD of PLA/NR blown films was less than neat PLA which was dropped from 2888 MPa to 1920 MPa the tensile strength in MD was decreased from 58 MPa to 34 MPa when the NR was added at 5 wt%.



(b)

Figure 5.5 *continue*

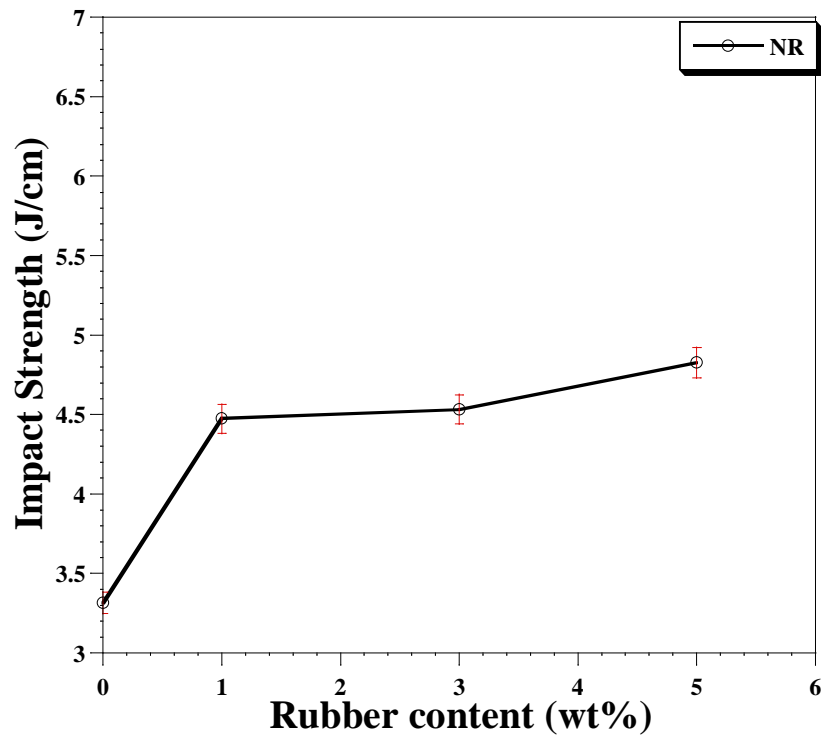


Figure 5.6 The impact strength of PLA/NR as a function of NR contents

Figure 5.6 depicts the impact strength of neat PLA and PLA/NR blown films as a function of rubber contents. The data is summarized in Table D.21 (Appendix D). The impact strength of PLA/NR was increased when compared with that of neat PLA film. The neat PLA film showed the most brittle behavior with the impact strength of 3.32 J/cm. When incorporated with NR at 1, 3 and 5 wt%, the impact strength is 4.47, 4.53 J/cm and 4.82 J/cm, respectively. The impact strength of PLA/NR blown films was increased with increasing rubber content because natural rubber let cavitation to occur. The cavitation and shear yield have been identified as the energy dissipation involved in the impact fracture of NR toughened PLA system. Thus, adding NR can improve the impact strength for PLA film.

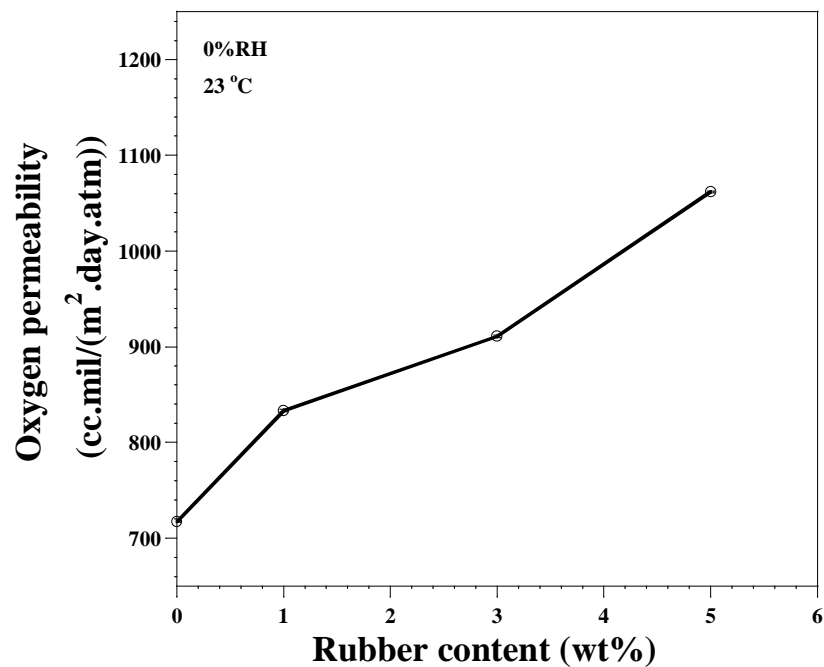
5.1.3 Gas barrier properties

Oxygen and water vapor permeability of blown films containing 0, 1, 3 and 5 wt% of NR contents are presented in Figure 5.7 (a) and (b), respectively. Oxygen permeability of PLA/NR blown films illustrated in Figure 5.7 (a) increased with increasing rubber contents. The oxygen permeability of PLA/NR at 3, 5 wt% increased about 23 and 48%, respectively, compared with that of neat PLA films. The data is listed in Table E.1-E.4 (Appendix E).

Diffusion through a polymer film occurs when the small molecules (permeant, diffusant) pass through voids and other gaps between the macromolecules. Natural rubber is amorphous polymer in the rubbery state, macromolecular fragments have high mobility and there is an appreciable “free volume” in the mass of the macromolecular compound. In addition, because of the fragments’ mobility, it is highly likely that a macromolecular fragment will at some stage move out of the way of a diffusant molecule; thus diffusion rates are higher in rubbers than in other types of polymers [36]. Therefore, the free volume of PLA/NR blown film is higher than neat PLA film that affects oxygen permeability.

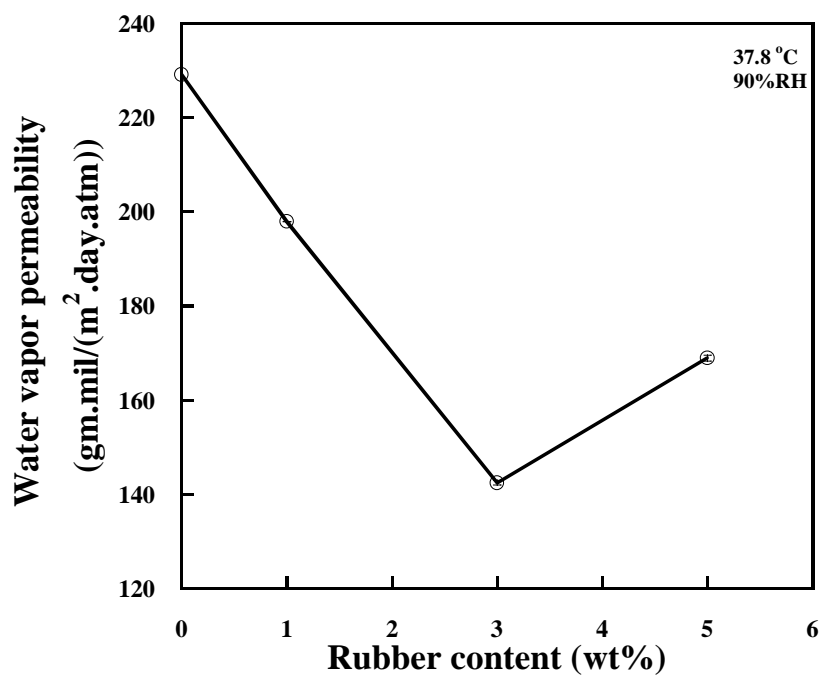
In the contrary, the water vapor permeability of the blended PLA films is presented in Figure 5.7 (b). It was found that adding 3 wt% of rubber into PLA matrix decreased the water vapor permeability approximately 37% compared with that of neat PLA film because the non-polar rubber did not allow water vapor to pass through the films. On the other hand, the water vapor permeability of PLA/NR at 5 wt% of rubbers is higher than that film with at 3 wt% NR due to larger size of the gap between PLA and NR (it has low interfacial adhesion).

Therefore, it can be concluded that adding the natural rubber in PLA matrix blown film did not suppress the oxygen permeability but to protect water vapor permeability in the suitable condition and amount of rubber. The data of both gas permeation properties of blended PLA blown film is shown in Table E.1 and E.3 (Appendix E).



(a)

Figure 5.7 (a) Oxygen permeability; and (b) water vapor permeability of PLA blown films containing 0, 1, 3 and 5 wt% of NR



(b)

Figure 5.7 continue

5.2 Effect of crosslinked natural rubber on physical properties of PLA/rubber blown films

In this section, the effects of NR and pre vulcanized NR (VNR) latex on the mechanical, thermal, thermomechanical and permeability properties were studied. VNR was prepared by peroxide-pre vulcanization (*t*-BuHP/ TEPA system).

5.2.1 Swelling ratio of VNR

The swelling ratios of VNR sheet casted from the peroxide-pre vulcanized natural rubber latex (*t*-BuHP/TEPA system) at various pre vulcanization times are shown in Figure 5.8. The swelling ratio of NR is initially about 3280%. At

pre vulcanization time of 1 h, the swelling ratio of VNR was about 2390% which is less than NR that indicates partially crosslink. It was also found that the swelling ratios (1950%) of VNR have a relatively small change which implies that the rubber is almost fully crosslinking after 6 h pre vulcanization time. It can be observed that the swelling ratios were inversely proportional to the degree of crosslinking and decreased with increasing reaction time in the initial period. Therefore, the swelling ratio of VNR could confirm that the crosslinking was obtained in this pre vulcanization. The data is listed in Table A.3 (Appendix A).

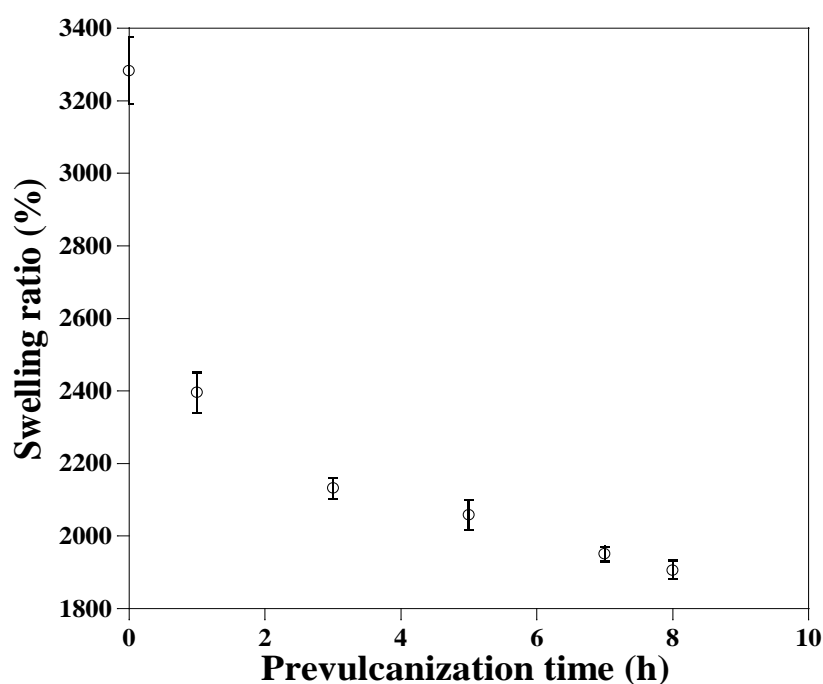


Figure 5.8 Swelling ratios of peroxide-pre vulcanized natural rubber sheet

5.2.2 PLA/NR and PLA/VNR blown films

In this study VNR at prevulcanization for 3 h whose swelling ratios is about 2130% was used to added into PLA matrix because it is partially crosslink that the network of natural rubber at this time is not too stiff and show light color of rubber sheet. From section 5.1 it was found that adding 3 and 5 wt% rubber can improve the elongation at break and tensile toughness of PLA films so in this section 3 and 5 wt% of VNR were blended with PLA and their properties were compared with those of PLA/NR blown film. The samples were prepared by using internal mixer followed by twin screw extruder attached to blown film die at suitable condition in order to make PLA/rubber blown films. Analytical techniques were used to identify the physical properties of blended PLA, i.e., differential scanning calorimetry (DSC), Dynamic mechanical analysis (DMA), scanning electron microscope (SEM), Oxygen transmission rate (OTR), Water vapor transmission rate (WVTR) and tensile testing.

5.2.2.1 Thermal properties

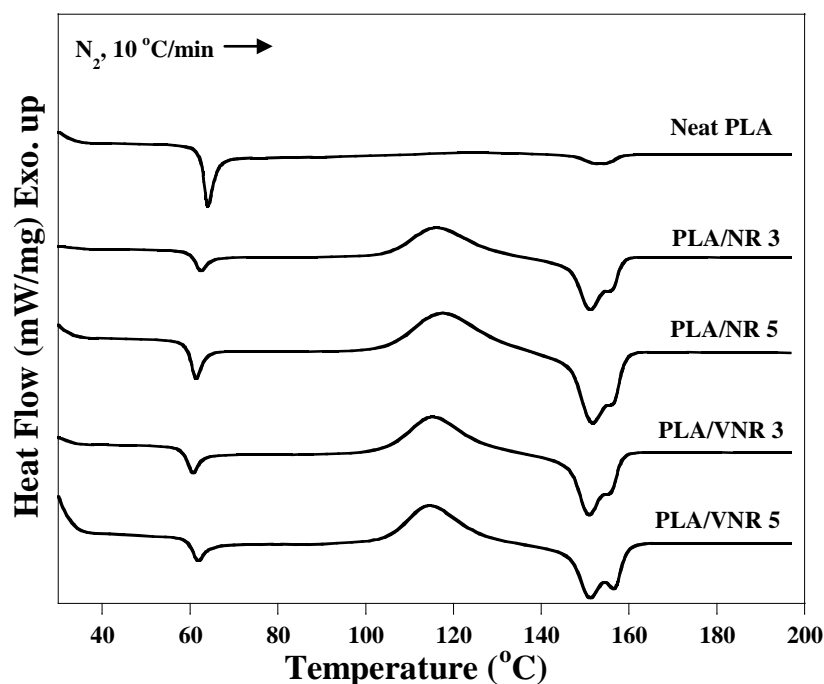


Figure 5.9 DSC first heating thermograms recorded at a heating rate of 10 °C/min under N₂ for neat PLA and PLA/rubber blown films containing NR and VNR at 3, and 5 wt%

DSC thermograms of the first heating scan of neat PLA, PLA/NR and PLA/VNR blown films are shown in Figure 5.9. For neat PLA, the T_g , T_{cc} and T_m is about 63, 124 and 153 °C, respectively. The addition of NR or VNR exhibited the same glass transition temperature as that of neat PLA (about 58 - 60 °C). Because only small amount of NR was added into PLA, we cannot observe the change of T_g of samples.

From Figure 5.9, the T_{cc} of PLA/NR and PLA/VNR blown films slightly decreased to 115-120 °C compared with that of neat PLA. Although, increasing the rubber content did not change the cold crystallization temperature. It was found that area under T_{cc} peak of PLA/NR and PLA/VNR blown films is larger than that of neat PLA when both NR and VNR content increases indicating that the blends establish crystalline form. Degree of crystallinity (X_c) of PLA/NR and PLA/VNR blown films is 0.34, 2.65, 2.52 and 3.49% at rubber content 3 and 5 wt%, respectively. X_c of the both blended films is increased with increasing rubber content. Furthermore, the degree of crystallinity of PLA/VNR blown films was slightly higher than that of PLA/NR blown films. The data from the DSC first heating thermograms is summarized in Table B.1 (Appendix B).

Furthermore, the T_m of blended PLA blown films did not change when increasing rubber content (about 150-160 °C). Especially, the double-peak melting temperature was observed when incorporating VNR in which this result is similar to thermal properties of PLA/NR blown film. Because the presence of two crystalline structures form (α' and α form) induced by NR and VNR that is mentioned. Therefore, the different of crosslinked natural rubber did not significant on the thermal properties of PLA blown films which is the same of PLA/NR.

5.2.2.2 Thermomechanical properties

The phase behavior of the blends was studied by Dynamic mechanical analysis (DMA). DMA is a thermal analytical technique used to measure the dynamic response of PLA/rubber blown films under a given set of condition. The results from

DMA exhibited phase behavior, reported as the storage modulus, loss modulus and tan delta ($\tan \delta$) curves as a function of temperature for neat PLA and PLA/rubber blown films. Storage modulus measures the elastic behavior as an in-phase component of sample. The $\tan \delta$, called damping factor, is ratio of the loss to the storage modulus or a measure of the energy dissipation of a material under cyclic load. DMA is also particularly useful for qualitatively characterizing T_g of polymer and composite by determining the peak of the loss modulus or $\tan \delta$ curves [70]. All thermomechanical properties of sample are summarized in the Table C.1 (Appendix C).

In this study, storage modulus (E') and $\tan \delta$ of neat PLA, PLA/NR and PLA/VNR blown films as a function of temperature are shown in Figures 5.10 and 5.11. The storage modulus at glassy state and T_g from $\tan \delta$ peak of all PLA/rubber (NR and VNR) blown films were slightly lower than those of neat PLA at all rubber contents. In Figure 5.10, the storage modulus of all samples is rather constant in glassy state, then it rapidly decreases during transition state in which this region is concerned with T_g , from slope of graph and the final region is rubbery plateau [71].

The storage modulus of the neat PLA and PLA/rubber blown films had high modulus approximately 2700-2800 MPa at glassy state. In addition, from storage modulus, it was found that T_g of neat PLA and PLA/rubber blown films (at 3 and 5 wt%) is approximate 77 and 70 °C, respectively. The T_g of PLA/rubber blown films did not significantly change compared with that of neat PLA. It implies that adding the rubbers did not affect T_g in every compositions. However, the storage modulus at

rubbery plateau of PLA added with NR and VNR at 5wt% were higher than those at 3wt% because of the increase in degree of crystallinity as evidenced by DSC.

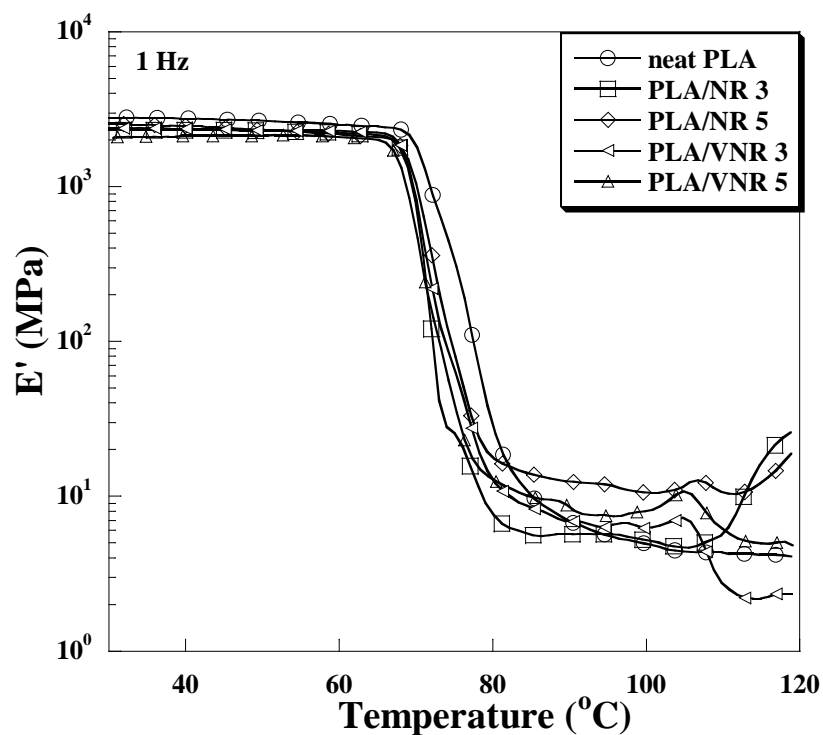


Figure 5.10 Temperature dependence of storage modulus (E') for neat PLA and PLA blown films containing 3 and 5 wt% of NR and VNR

Tan δ or damping factor is a measure of energy dissipation and it identifies the transition temperature in plastics or blends such as the glass transition temperature, as shown in Figure 5.11. The peak of tan δ peak is indicated as T_g of samples. The T_g of neat PLA is 80 °C. In addition, the T_g of PLA/NR and PLA/VNR blown films at 3 and 5 wt% are about 78, 77, 78 and 76 °C, respectively, which is slightly shifted from that of neat PLA. The height of tan δ peak exhibits the ability of forming the crystallinity of PLA that tan δ peak of PLA/rubber at 5 wt% rubber is

higher than PLA/rubber at 3 wt% rubber due to the increase in degree of crystallinity as evidenced by DSC.

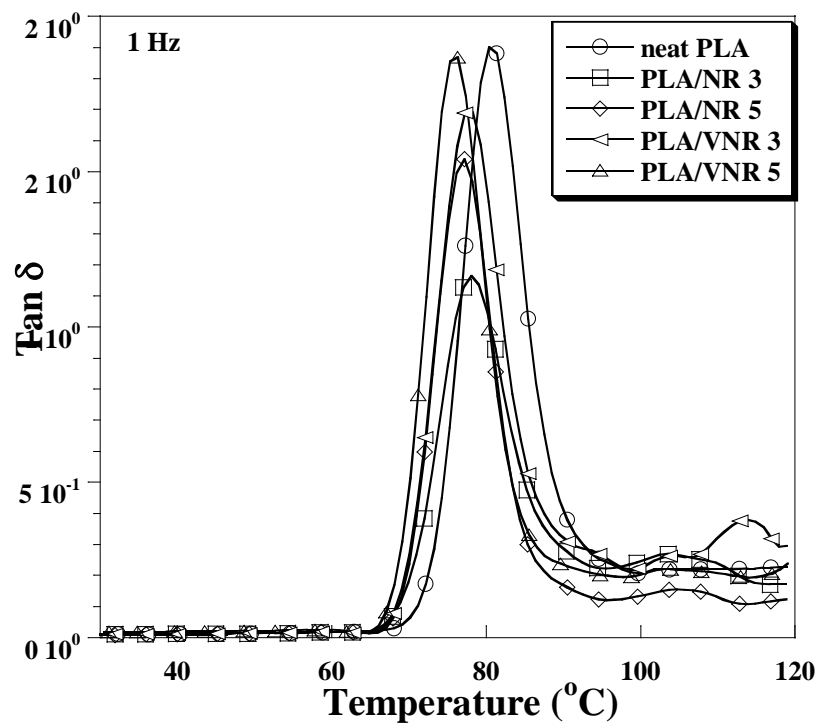
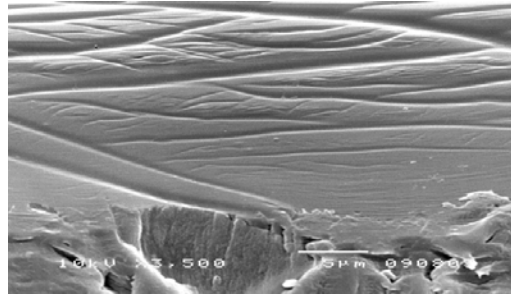
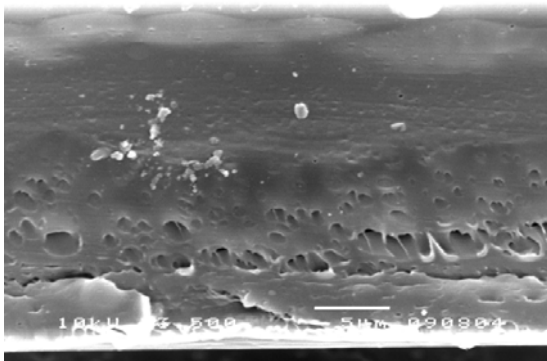


Figure 5.11 Temperature dependence of $\tan \delta$ for neat PLA and PLA/rubber blown films containing 3 and 5 wt% of NR and VNR

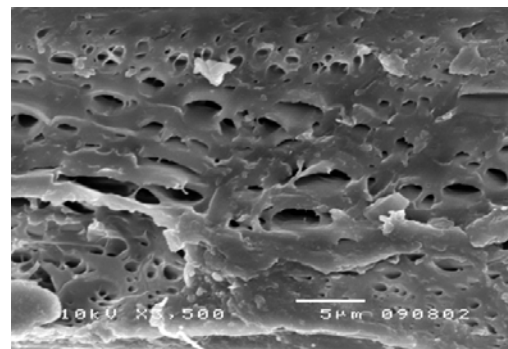
5.2.2.3 Morphology



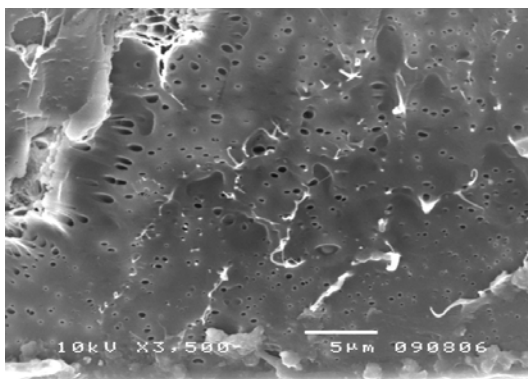
(a)



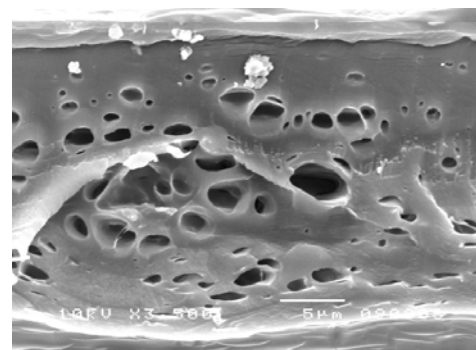
(b)



(c)



(d)



(e)

Figure 5.12 SEM micrographs of PLA/rubbers blown in the impact films testing: (a) neat PLA, (b) PLA/NR at 3wt%, (c) PLA/NR at 5 wt%, (d) PLA/VNR at 3 wt% and (e) PLA/VNR at 5 wt% (— 5 μm)

The fractured surfaces (cross section) of pure PLA and PLA/rubber blown films were analyzed using SEM, as shown in Figure 5.12. The results of mechanical properties can be explained by phase morphology.

Figure 5.12 (a) reveals the relatively smooth surface with small ridges of pure PLA, indicating the brittle fracture behavior. This smooth fractured surface agrees well with low impact strength and elongation at break. Fractured surfaces of PLA/rubber films became rough, as shown in Figure 5.12 (b-e). The immiscible phases between rubber and PLA matrix were observed due to low interfacial interaction between rubber and PLA. The size of spherical rubber phase became larger with the increase in rubber content. It was also seen that voids are created as a result of drop of dispersed rubber phases.

In addition, the rough fractured surface of PLA/NR blends indicated the ductile behavior and the impact fractured surface showed the spherical rubber particles evenly dispersed in PLA matrix up to 5 wt% of rubber content. This result indicated evenly dispersed of rubber phases in PLA matrix which increases impact strength of the blown film.

The effect of crosslinked rubber phase on the morphology of fracture surface of films can be observed by comparing Figure 5.12 (c) and (e). These images are SEM micrographs of PLA blown films containing the same amount of crosslinked and un-crosslinked natural rubber. Nearly all the incorporated particles were debonded from the matrix when the NR phase was crosslinked. Crosslinked rubber domain was not removed to form cavity and the crack went around the particle. On the other hand, most of the un-crosslinked domain ruptured and the crack propagated

through the NR core. Un-crosslinked NR domain were well integrated in the crazed matrix [14].

5.2.2.4 Mechanical properties

The effects of crosslinked natural rubber on mechanical properties of PLA blown films were investigated by universal testing machine (Instron 5567) according to ASTM D882. The mechanical results include tensile strength, Young's modulus, elongation at break and tensile toughness. The tensile strength of material is defined as the maximum tensile stress where material begins to deform. The tensile modulus is determined by the first linear slope of stress-strain curve which indicates the stiffness of material. The elongation at break is defined as the strain at maximum tensile strain at break or at the rupture of the specimen. All the mechanical properties of plasticized PLA blown films are summarized in Appendix D.

Tensile stress-strain curves of neat PLA, PLA/NR and PLA/VNR blown films at rubber content equal to 3 and 5 wt% in machine direction (MD) are shown in Figure 5.13. The tensile properties, such as static modulus, tensile stress, and elongation at break, determined from these curves are presented in Table D.1-D.12. Neat PLA blown film showed brittle behavior of polymer due to the matrix broken in strain hardening region. Tensile strength and Young's modulus of neat PLA were 58 MPa and 2840 MPa, respectively. Moreover, neat PLA specimens showed a smooth longitudinal fracture surface without necking and visible plastic deformation in which strain at break was only about 3%. It was also found that addition of rubber (NR and VNR) into PLA decreases tensile strength and Young's modulus but it

increases elongation at break in comparison with neat PLA blown film. PLA/VNR blown films were also brittle as same as neat PLA, whereas PLA/NR blends blown films were ductile, showing distinct yielding and stable neck growth in cold drawing region where fracture occurred. Since their stress-strain curves resemble that of typical natural rubber, showing a strain-induced crystallization phenomenon at high strains because the degree of strain-induced crystallization is more pronounced when adding NR [45].

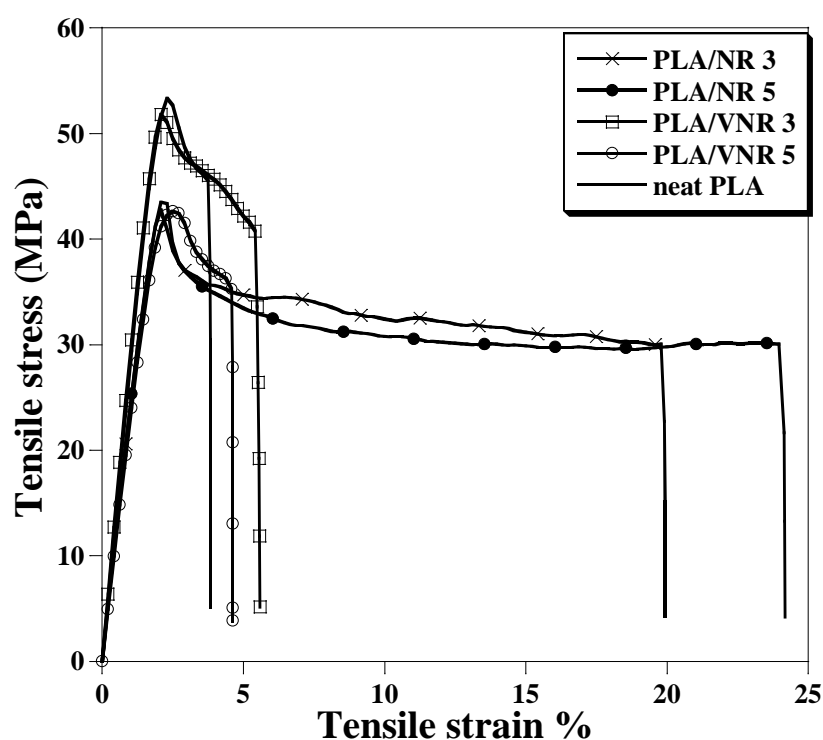


Figure 5.13 Tensile stress-strain curve of the PLA blends with different NR and VNR content at 3 and 5 wt% in machine direction (MD)

The elongation at break of neat PLA and PLA/rubber blown films in machine direction (MD) and transverse direction (TD) is shown in Figure 5.14. The

elongation at break in MD and TD of neat PLA was about 3 and 2%, respectively, while the NR modified PLA film in MD was linearly raised at 21% and 26% when the NR was incorporated at 3 and 5 wt%, respectively. PLA/NR blends displayed high elongation at break in MD and increased with increasing the rubber contents due to the toughening mechanism as mentioned. Nevertheless, the elongation at break of PLA/NR in TD was slightly decreased due to production process.

On the other hand, the elongation at break in MD and TD of PLA/VNR blends slightly increased because the crosslinked VNR is stiffer than un-crosslinked NR leading to higher polymer chains mobility and relaxation. Adding 5 wt% of VNR increases the elongation at break in MD about 2 times compared with neat PLA. The difference in the change of elongation at break of films taken place in the area of plastic deformation zone, where the appearance of tensile specimen after testing of the materials showed the stress whitening band perpendicular to tensile direction all over the gauge length. This explanation was confirmed by the fact that the NR blended samples showed larger plastic deformation zones near the fracture flank in comparison with the VNR blend. These results are similar with data of Ishida et al. [51]. Thus, the elongation at break depends on the type of rubber, crosslink density and the rubber contents.

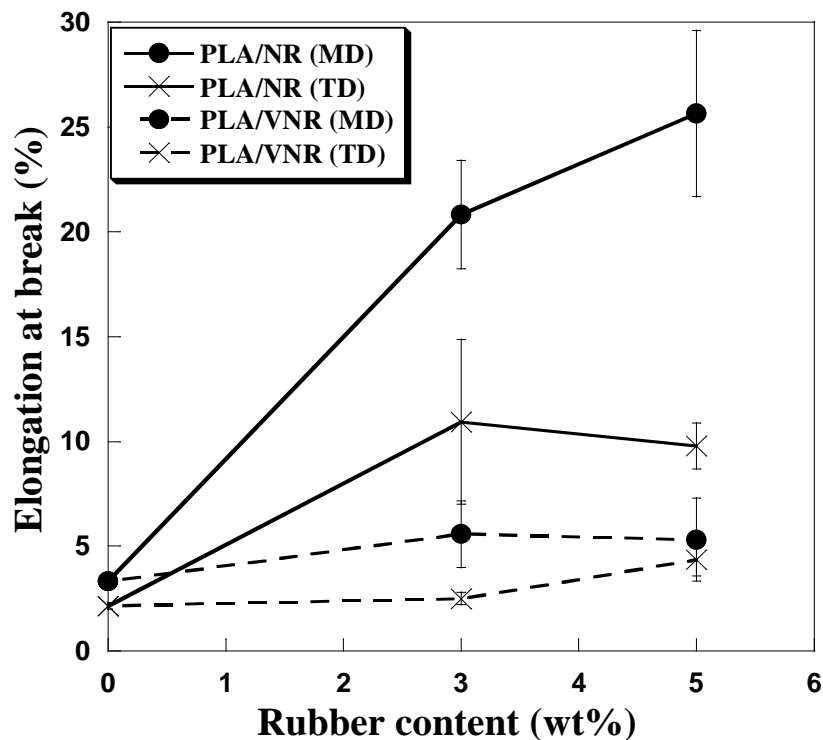


Figure 5.14 The elongation at break in machine direction (MD) and transverse direction (TD) of PLA blends as a function of NR and VNR contents

To improve tensile toughness of neat PLA and PLA/rubber blends blown films as shown in Figure 5.15. The tensile toughness of PLA/NR blown films in MD is 46, 133 and 138 mJ at NR content of 0, 3, and 5 wt%, respectively. The tensile toughness in MD and TD of NR increased with the rubber contents increased in which these results showed the similar trend as the elongation at break previously mentioned. This support the development of crazing (with further elongation of the fibrils) the ductility due to energy absorption of rubber domain at first cavity provoking locally a plane strain/plane stress transition in toughening mechanism. However, tensile toughness of PLA/NR in TD slightly increased compared with neat

PLA. The blend added 5 wt% NR in MD showed the highest toughness of film which increased three folds compared to neat PLA. In addition, the energy at break of PLA/VNR blends was lower than those of PLA/NR blends. Thus, this data indicated that the incorporating NR can improve the tensile toughness for PLA film.

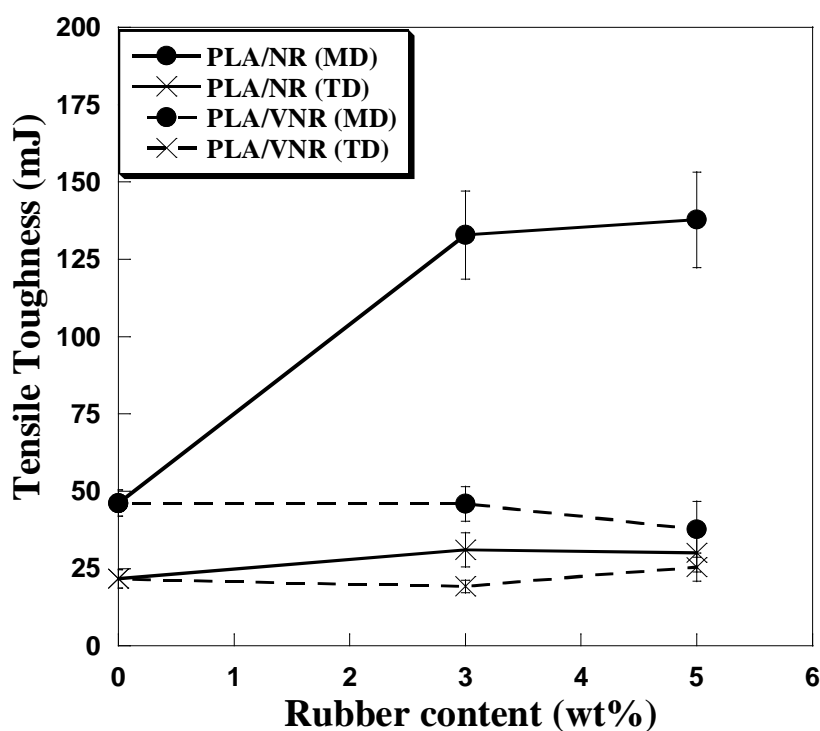


Figure 5.15 The tensile toughness in machine direction (MD) and transverse direction (TD) of PLA blends as a function of NR and VNR contents

Figure 5.16 and 5.17 show the tensile strength and Young's modulus of PLA blends in MD and TD at various NR and VNR contents. The tensile strength of neat PLA in MD and TD are 58 and 47 MPa, respectively. The Young's modulus of neat PLA films in MD and TD are 2886 and 2843 MPa, respectively. The tensile strength and Young's modulus in MD and TD of PLA/NR and PLA/VNR blown

films decreased with increasing rubber contents because the rubber has high elasticity in which it decreased the strength of polymer. The Young's modulus in MD of PLA/NR blown film dropped from 2888 MPa to 1920 MPa corresponding to the drop in the tensile strength in MD from 58 MPa to 34 MPa when 5 wt% NR was added. Furthermore, it was also found that tensile strength and Young's modulus of PLA/NR blown film were lower than those of PLA/VNR blown film, because VNR is the crosslinked rubber, thus, it has stronger chain than NR. Moreover, the increase in these properties of PLA/VNR blown film is due to higher degree of crystallinity of PLA/VNR blown film in comparison to that of PLA/NR as confirmed by DSC data.

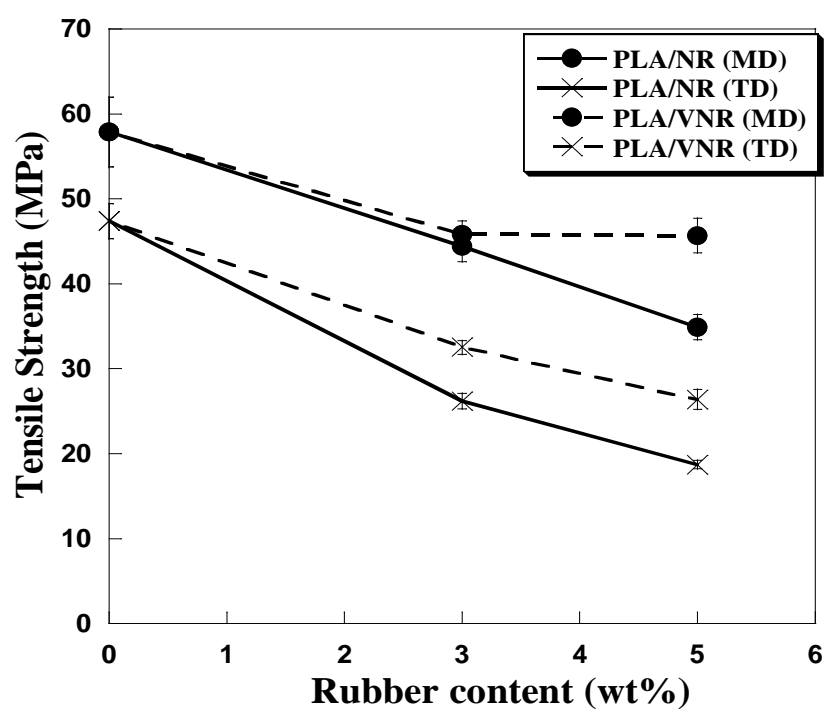


Figure 5.16 The tensile strength in machine direction (MD) and transverse direction (TD) of PLA blends as a function of NR and VNR contents

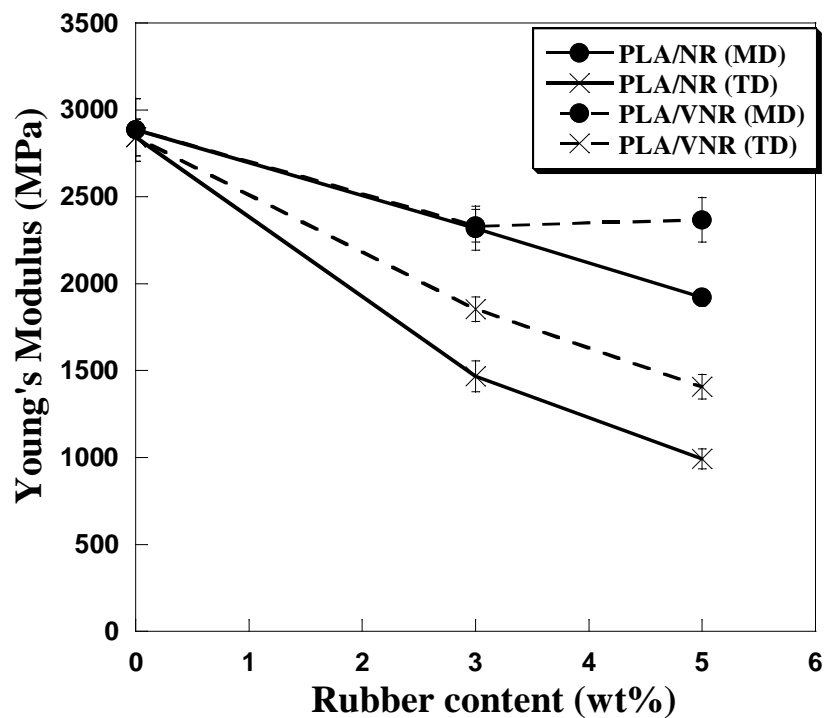


Figure 5.17 The Young's modulus in machine direction (MD) and transverse direction (TD) of PLA blends as a function of NR and VNR contents

Figure 5.18 depicts impact strength of neat PLA and PLA/rubber film as a function of rubber contents. The data are summarized in Table D.21 (Appendix D). The impact strength of film containing both NR and VNR increased compared with that of neat PLA films. The neat PLA showed the most brittle behavior with the impact strength of about 3.32 J/cm. When incorporated with NR and VNR at 3 and 5 wt%, the impact strength of film is 4.53, 4.82 J/cm, 4.09 and 4.67 J/cm, respectively. The impact strength of PLA/NR blown films was slightly higher than that of the PLA/VNR blown films at every studied compositions. Because the VNR is stiffer than NR that did not let cavitation occurred, the strain energy was released during

cavitation which is lower than the energy to form a void. Hence, no free surface is provided from which cessation can be nucleated.

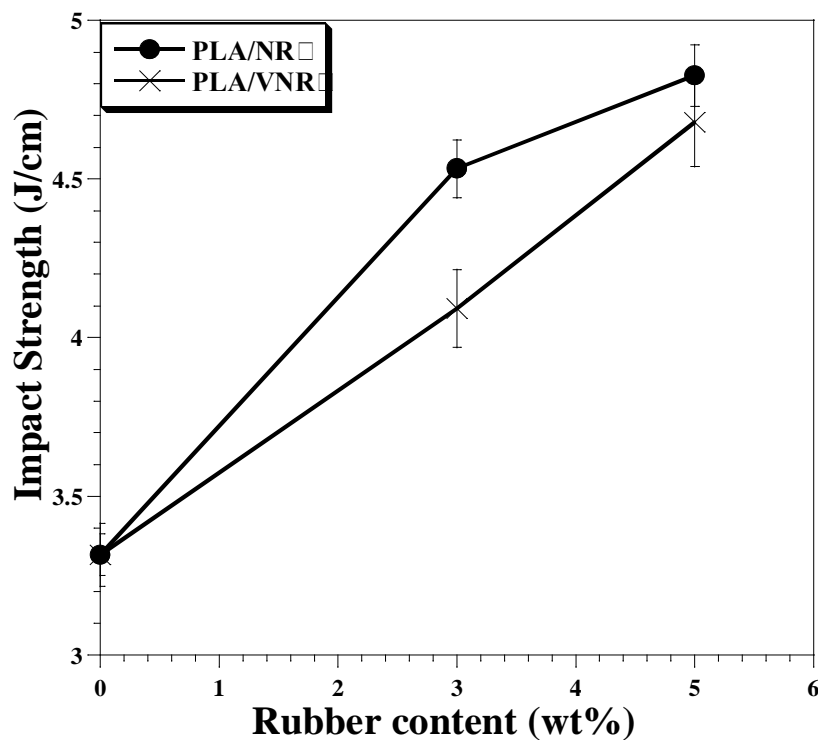


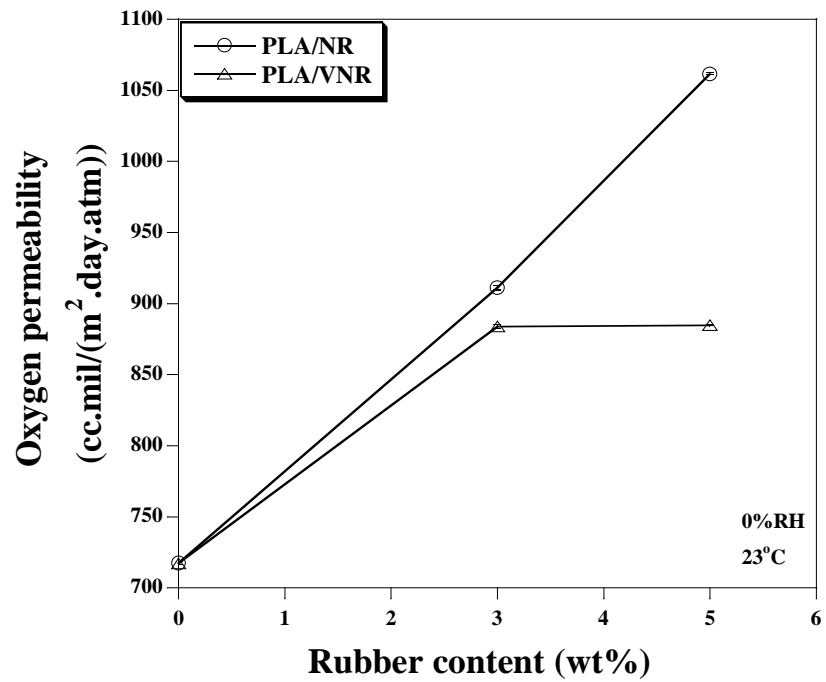
Figure 5.18 The impact strength of PLA blown film as a function of rubber contents

5.2.2.5 Gas barrier properties

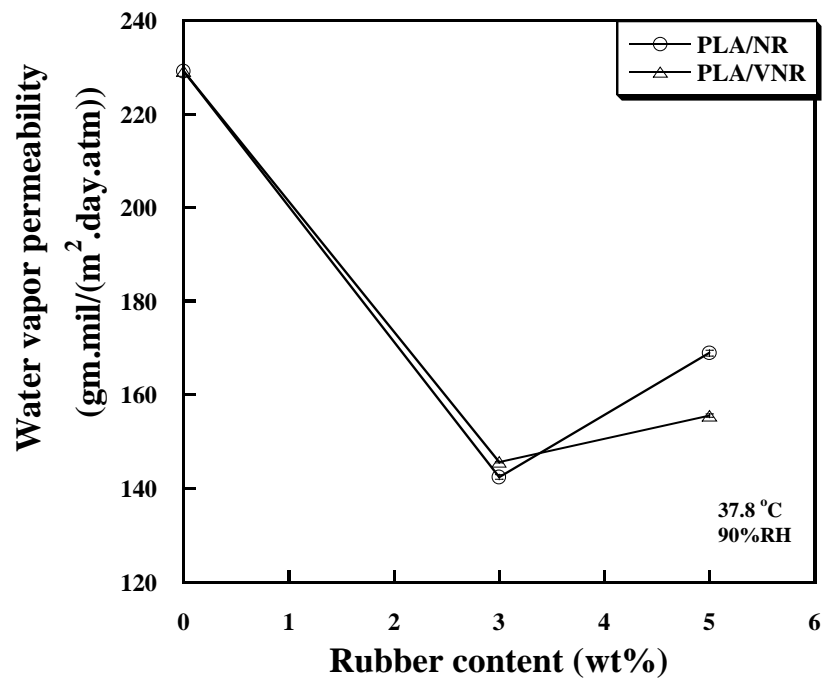
Oxygen and water vapor permeability of blown films containing 0, 3 and 5 wt% of rubber contents: NR and VNR are presented in Figure 5.19 (a) and (b), respectively. Oxygen permeability of PLA/NR and PLA/VNR blends blown films illustrated in Figure 5.19 (a) increased with increasing rubber contents. Because NR and VNR are non-polar secondary polymers which can increase free volume in PLA film, the rubbers tend to increase the mobility of the oxygen molecules in polymer matrix. Thus, the ability to allow oxygen gases pass through them is better than neat PLA film due to the diffusion rate in amorphous phase. The diffusion rate will

therefore depend to a large extent on the size of the small molecules and the size of the gaps. The one depends to a large extent on the physical state of the polymer that is, whether it is glassy, rubbery, or crystalline [36]. The oxygen permeability of NR and VNR at 3 wt% increased 23-27 %. However, the oxygen permeability of PLA/VNR films did not change significantly at rubber content of 5 wt% since it has higher crystallinity than other blended PLA, which generates more tortuous path for the permeation of oxygen molecules. The data is listed in Table E.1-E.4 (Appendix E).

In the contrary, the water vapor permeability of the blended PLA films is presented in Figure 5.19 (b). It was found that adding 3 wt% of rubber into PLA matrix decreased the water vapor permeability 37-39% compared with neat PLA film because of the non-polar rubber not allowing water vapor to pass through the films. On the other hand, the water vapor permeability at 5 wt% of rubbers is higher than at 3 wt% of rubbers due to high free volume in PLA matrix. Therefore, it can be concluded that adding the natural rubber in blends blown film did not suppress the oxygen permeability but to protect water vapor permeability in the suitable condition and amount of rubber. The data of the both permeation properties of blended PLA is shown in Table E.1 and E.3 (Appendix E).



(a)



(b)

Figure 5.19 (a) Oxygen permeability; and (b) water vapor permeability of PLA blown films containing 0, 3 and 5 wt% of NR and VNR

5.3 Effect of morphology of natural rubber on physical properties of PLA/NRP blown films

When compared between NR and VNR, the results indicate that NR can improve the toughness of PLA to be better than VNR. Thus, we also used NR for producing powder. In preparing NR-Powder, the rubber latex particle was coated by Gum arabic which is a soluble emulsifier and passes in spray dry process. The ratio of latex to Gum arabic is 1:2 (10%TSC of NR). Furthermore, we prepared PLA/NR-Powder at content 3 wt%. The PLA/NRP blown film is not smooth due to aggregation of NRP during spray dry.

5.3.1 Particle size distribution of natural rubber latex

The particle size distribution of natural rubber latex was reported by particle size distribution curves in Figure 5.20 that exhibits a broad particle size distribution of NR. The particle size distributions of the NR latex were observed in ranges of 0.04-2 μm which was measured by mastersizer. The average particle size of NR was about 0.8 μm . The data agreed well with the typical data indicating the naturally polydispersed latex particles [13, 16, 65, 72]. The data are summarized in Table A.1 (Appendix A).

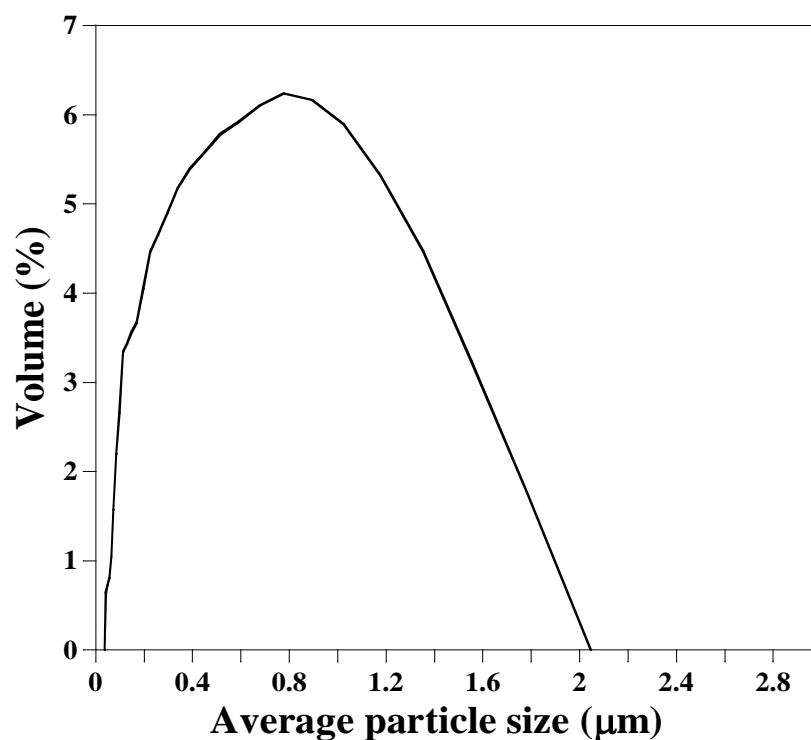


Figure 5.20 Particle size distributions of NR latex

5.3.2 Zeta-potential of natural rubber latex

The zeta-potential of NR latex at various pHs are displayed in Figure 5.21. The obtained results indicated that the surface of NR particles possessed positive charges when the pH was less than 4.7. Above pH 4.7, the zeta-potential was negative and rapidly changed with increasing pH. These data can confirm the amphoteric characteristic in nature of NR particles with an isoelectric point at pH about 4.7, which verifies the presence of amino acid moieties on the surface of NR [16, 41, 57, 62]. The data is listed in Table A.2 (Appendix A).

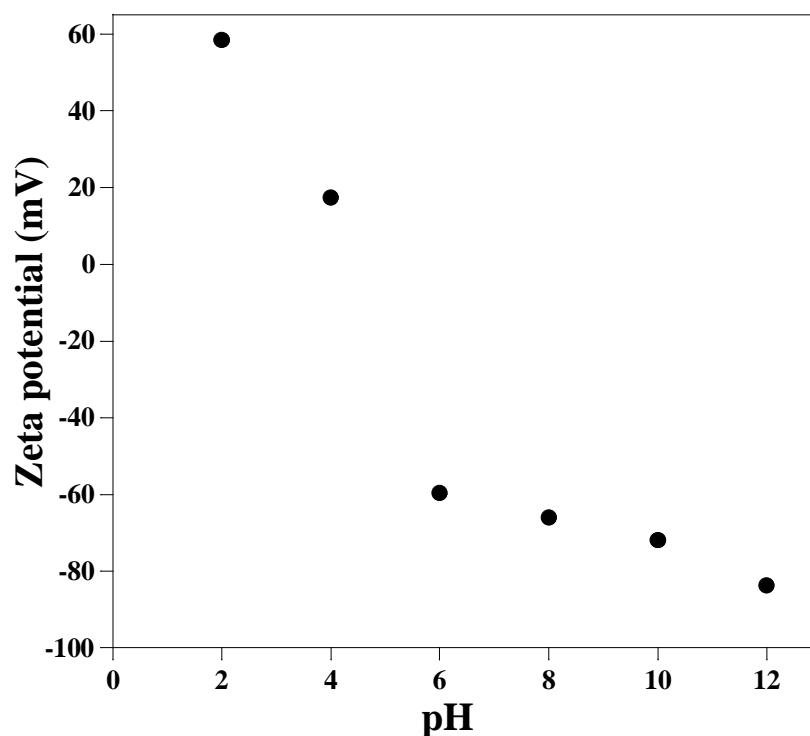
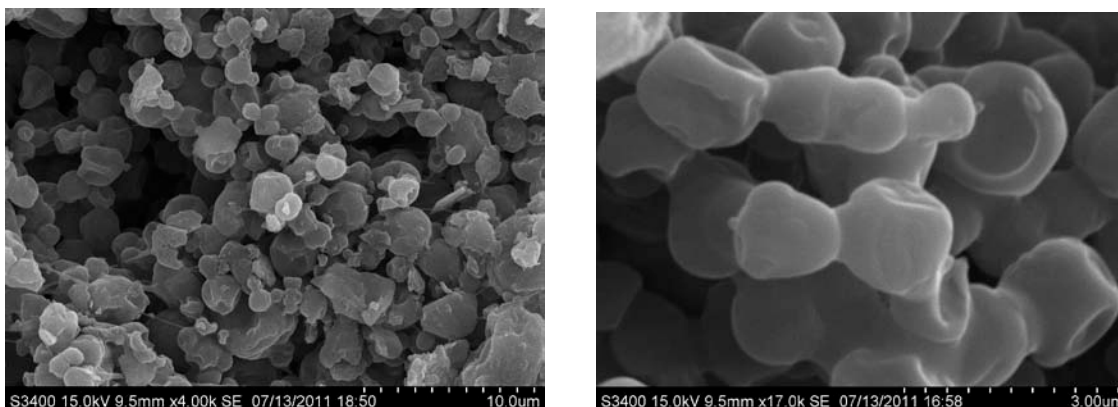


Figure 5.21 Zeta-potential of NR latex

5.3.3 Morphology of natural rubber powder

Figure 5.22 represents SEM micrographs of the natural rubber powder (NRP) at different magnifications which obtained from the spray drying technique. It revealed that the NRP has spherical shape and relatively large particle size distribution at low magnification (x4,000), i.e., the particle size ranges from 1 to 5 μm . At higher magnification (x17,000), it could be observed that these particles have a relatively rough surface and are partially interconnected.



(a)

(b)

Figure 5.22 SEM micrographs of the NRP at different magnification (a) x4,000

(b) x17,000

5.3.4 Thermal properties

Differential scanning calorimetry (DSC) data from Figure 5.23 shows the thermal properties of PLA/NR and PLA/NRP blown films at 3 wt%. Also, this technique can be used for the evaluation of the phase behavior between components of polymer blend. The specimens were measured under purged nitrogen atmosphere and a temperature range from 30 to 200 °C at a heating rate of 10 °C/min. The data from the DSC first heating thermograms is summarized in Table B.2 (Appendix B).

From the results, it was observed that the thermal behavior did not significantly change when adding NRP due to no interaction between polymer chains implying phase separation. The glass transition temperature (T_g) and the melting temperature (T_m) of PLA/NRP film were at 57 °C and 154 °C, respectively. Moreover, the T_m of the PLA/NRP film displayed single peak indicating the presence of NRP did not change the crystallization of PLA in which the reorganization of crystal structure

composed of α form (high thermodynamic stability) and β form (low thermodynamic stability) was not occurred [68].

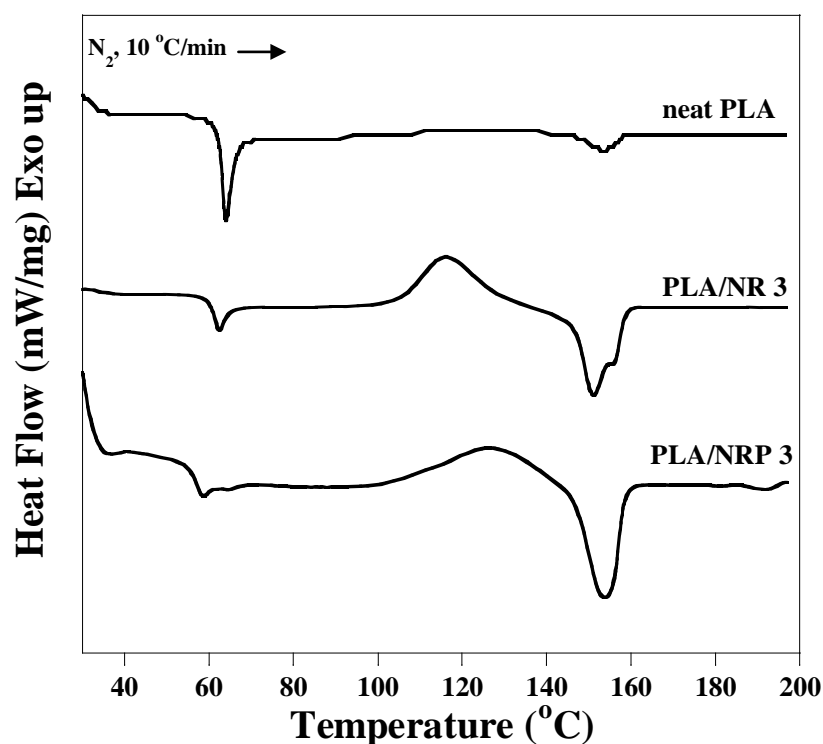


Figure 5.23 DSC first heating thermograms recorded at a heating rate of 10 °C/min under N₂ for (a) neat PLA; (b) PLA/NR ; and (c) PLA/NRP blown film at 3 wt% rubber content

By the way, the exothermic peak of cold crystallization temperature (T_{cc}) was at 127 °C and was broadened when adding NRP. Degree of crystallinity of PLA/NRP film was approximately 0.54 % in which it was slightly higher than that of PLA/NR film at 3 wt% (0.35%). In addition, the tensile strength and the Young's modulus of PLA/NRP film was similar to those of PLA/NR films. The data is listed in Table.B.2 (Appendix B).

5.3.5 Mechanical properties

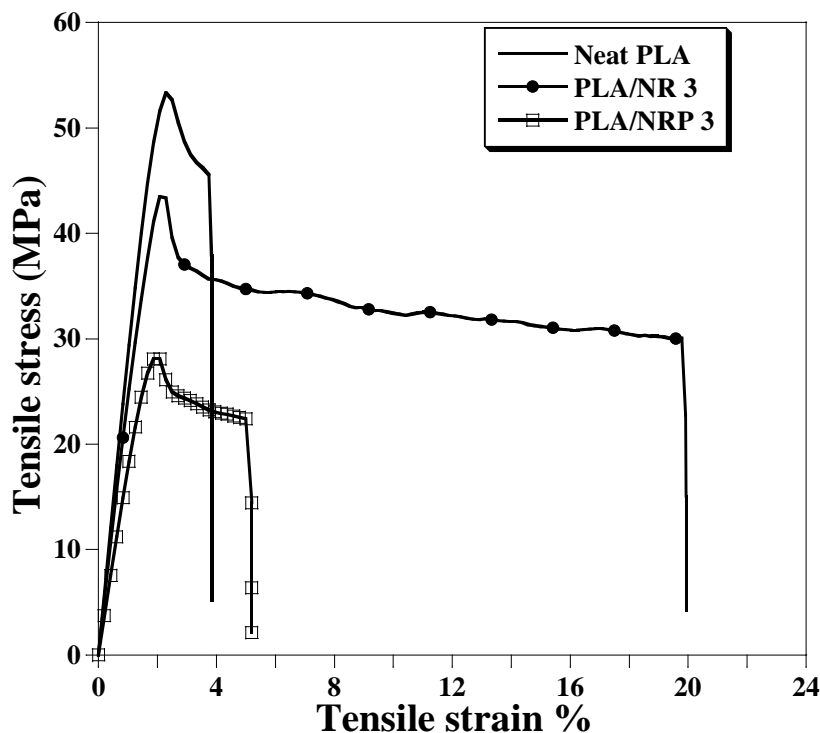


Figure 5.24 Tensile stress-strain curve in machine direction (MD) of the neat PLA and PLA/NRP blends at 3 wt%

The stress-strain behavior of tensile test in MD of neat PLA, PLA/NR and PLA/NRP blown films at 3 wt% is shown in Figure 5.24. The stress-strain curve displays the rate deformation of modified PLA film which changed the properties of blends from brittle to ductile. The data is summarized in Appendix D. From Figure 5.24, the neat PLA film exhibited highest stress, but its strain at break was only about 3.7%. On the contrary, strain at break of PLA/NR blends was remarkably increased.

The obtained results showed that the NRP did not enhance the mechanical properties of neat PLA when compared with NR. The NRP has large particle size in which it could be deboned from the PLA matrix. In addition, the NRP was coated

with Gum arabic which is not strong enough to improve interfacial adhesion between PLA and NR. However, the toughness calculated from the area under the stress-strain curve indicated that the presence of NR improved toughness better than NRP.

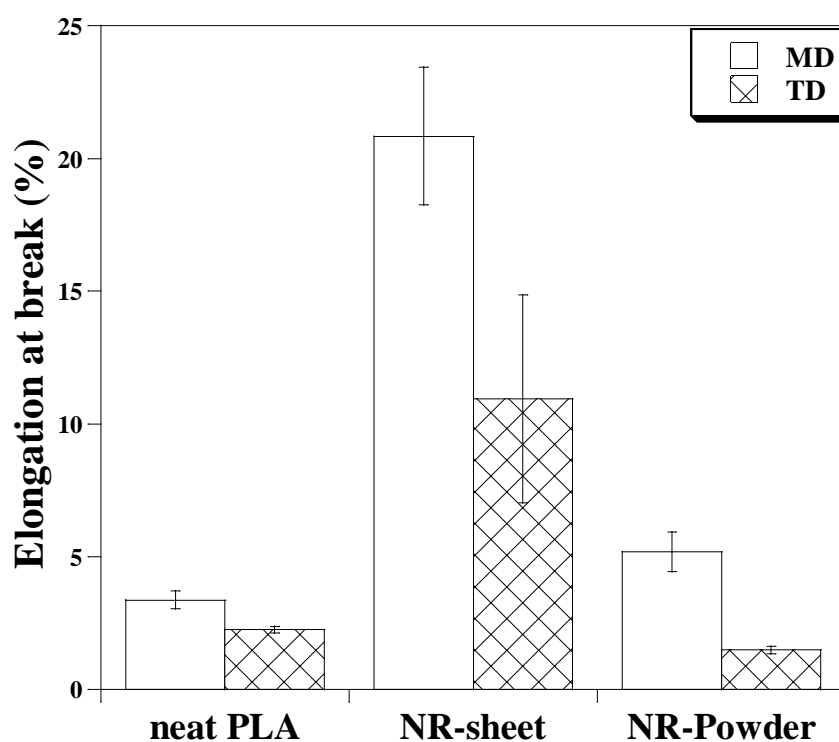


Figure 5.25 The elongation at break in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NRP at 3 wt%

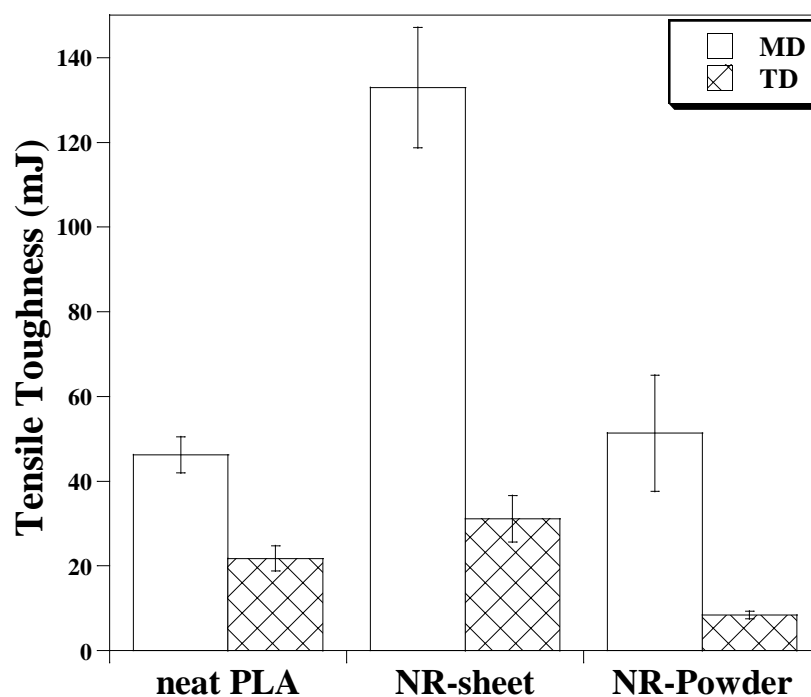


Figure 5.26 The tensile toughness in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NRP at 3 wt%

The elongation at break and the tensile toughness of neat PLA, PLA/NR and PLA/NRP blown films at 3 wt% are shown in Figure 5.25 and 5.26, respectively. These mechanical results showed the same trends in both MD and TD. The elongation at break of PLA/NR film in MD at 3 wt% was higher than that of neat PLA film and PLA/NRP film about 4 folds because interfacial adhesion between both polymers is low which can affect the crack around the rubber particles forming voids.

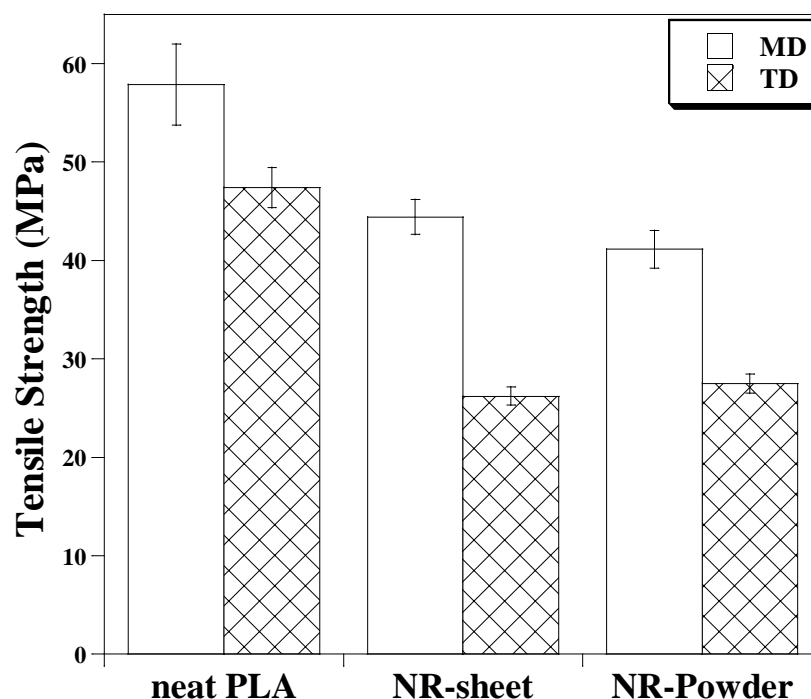


Figure 5.27 The tensile strength in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NRP at 3 wt%

Figure 5.27 and 5.28 exhibit the tensile strength and Young's modulus in MD and TD of neat PLA, PLA/NR and PLA/NRP blown film at 3 wt%. The tensile strength and Young's modulus of PLA/NR film in MD and TD showed the same trend with those of PLA/NRP films indicating that these properties of the blends did not significantly affect by the characteristic of natural rubber. However, the tensile strength and Young's modulus of both blends in MD decreased by about 15% and 20%, respectively, compared with those of neat PLA. In the same way, these properties of films in TD decreased about 1.5 times since NR has high elasticity and low strength.

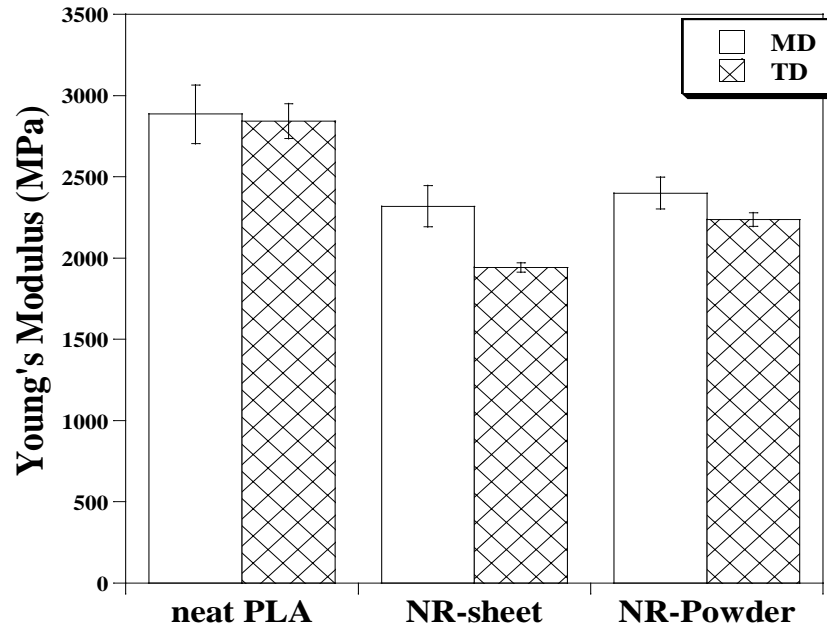


Figure 5.28 The Young's modulus in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NRP at 3 wt%

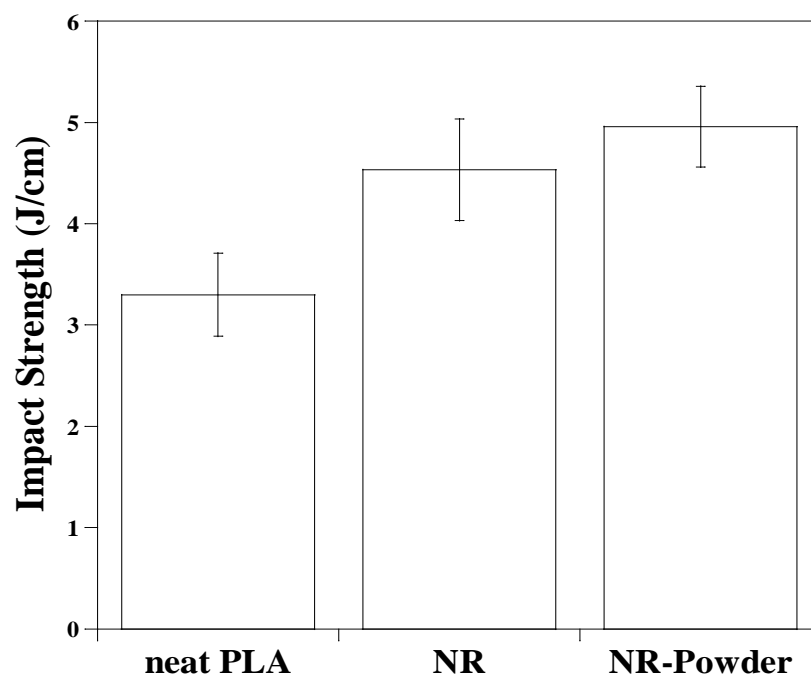


Figure 5.29 The impact strength of PLA/NR and PLA/NRP at 3 wt%

The impact strength of PLA/NR and PLA/NRP blown films is shown in Figure 5.29. High deformation speed (impact strength) was necessary in order to evaluate the mechanical properties of PLA films with the different of the prepared characteristic of natural rubber. From the obtained results, the impact strength of both blends slightly increased when compared with that of neat PLA film which might be due to the elasticity of NR and NRP and adsorption energy. The data is listed in Table D.21 (Appendix D).

5.4 Comparison between NR from HA-NR and NR-Commercial at various rubber content on physical properties of PLA/rubber blown films.

From %DRC and %TSC we found that NR from HA-NR has non-rubber component about 1% but NR-Commercial (ADS grade) is separated from non-rubber component by coagulation process.

5.4.1 Thermal properties

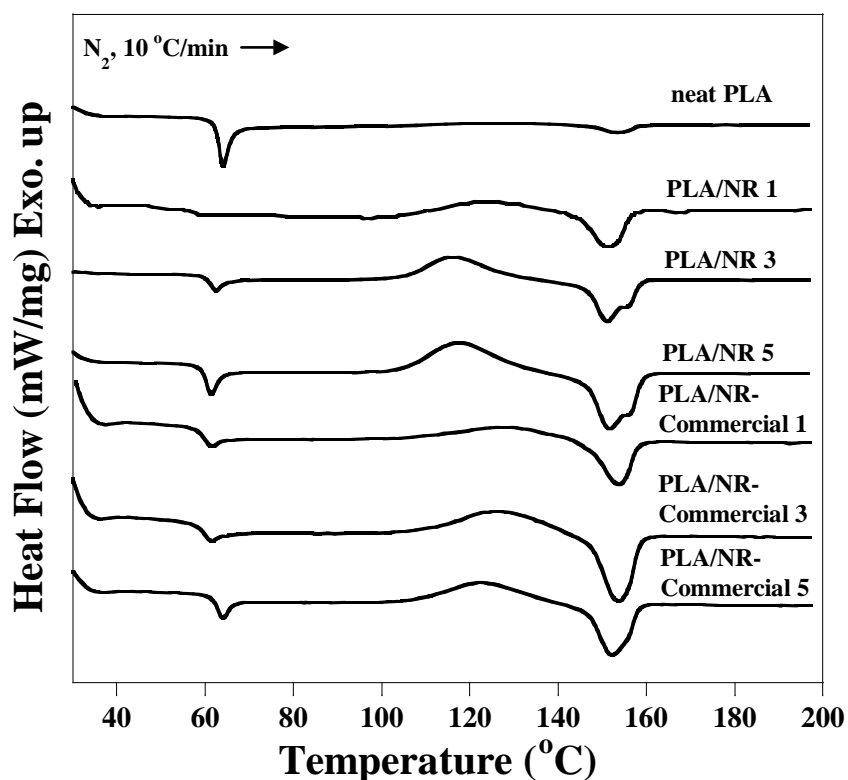


Figure 5.30 DSC first heating thermograms recorded at a heating rate of 10 °C/min under N₂ for neat PLA and PLA/rubber blown films containing NR and NR-Commercial at 1, 3, and 5 wt%

The DSC thermograms of PLA blown film was shown in Figure 5.30. The phase behaviors, T_g , T_{cc} , T_m and X_c , are listed in Table B.3 (Appendix B). Endothermic peaks corresponding to the T_g of PLA/NR-Commercial film at 1, 3 and 5 wt% were observed at 60, 60 and 63 °C which were closed to that of neat PLA (63 °C). It suggested that rubber did not affect the glass transition of PLA and PLA blend film which was immiscible blend.

The T_{cc} of PLA/NR and PLA/NR-Commercial film at 0, 1, 3, and 5 wt% was 124.48, 116.19, 116.97, 127.6, 126 and 122.78 °C, respectively. DSC showed that the T_{cc} of PLA/NR film was slightly lower than that of neat PLA film. On the contrary, incorporation of NR-Commercial into PLA matrix showed no effect on the T_{cc} . The X_c of PLA/NR-Commercial film at 1, 3, and 5% is 2.46, 3.23 and 2.31, respectively.

The T_m appeared around 153 °C for neat PLA film. In addition, Incorporation of rubber did not change T_m in comparison to that of neat PLA but gave double peaks of melting temperature for PLA/NR instead due to the decreased T_c because NR behaves like nucleating agent resulting in easy to crystallization.

5.4.2 Mechanical properties

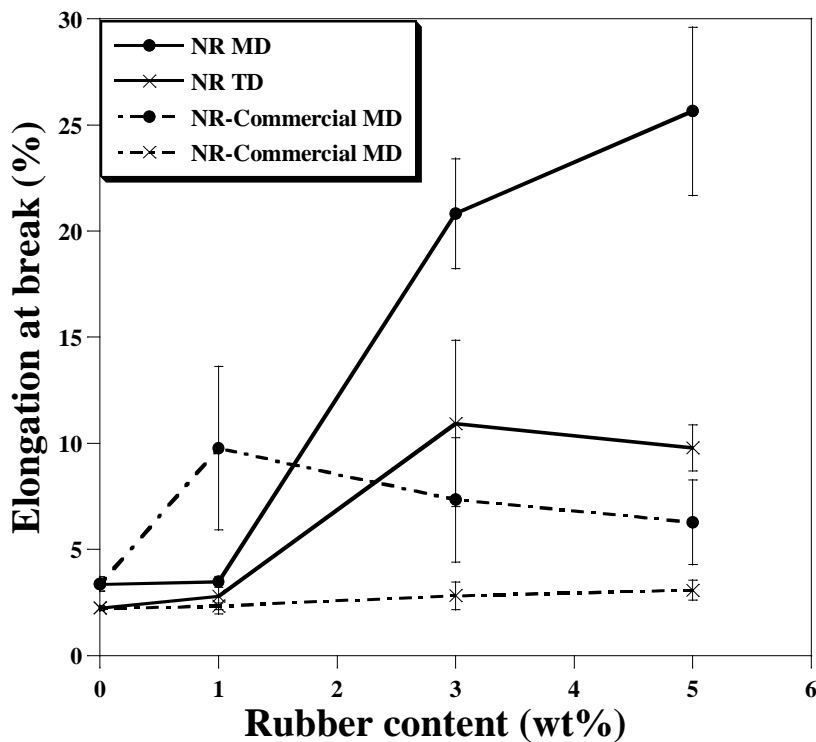


Figure 5.31 The elongation at break in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NR-Commercial film as a function of rubber contents

The elongation at break and tensile toughness in MD and TD of PLA/NR and PLA/NR-Commercial blown films at various rubber contents is shown in Figure 5.31 and 5.32, respectively. The elongation at break and tensile toughness of PLA/NR blown films in both directions increased with increasing rubber contents. However, PLA/NR-Commercial film in MD at rubber contents at 3 and 5 wt% tended to decrease because of stickiness of rubber that affect to coalescence of rubber. As the elongation at break and tensile toughness of PLA/NR film was higher than that of PLA/NR-Commercial film because NR is softer than NR-Commercial that affect

relaxation of rubber chain or may be cause low adhesive between surfaces of secondary polymer and PLA matrix due to non rubber component.

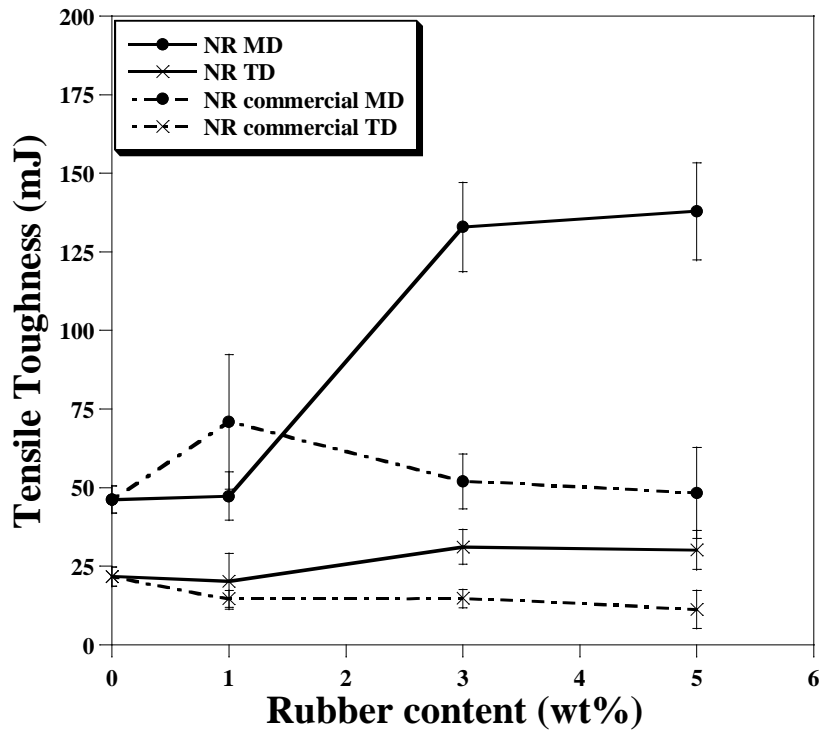


Figure 5.32 The tensile toughness in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NR-Commercial film as a function of NR and VNR contents

The tensile strength and Young's modulus of PLA films containing NR and NR-Commercial as shown in Figure 5.33 and 5.34 (summarize in Appendix D) exhibited the same trend as elongation at break mentioned above. The tensile strength of neat PLA was about 58 MPa. When increasing NR and NR-Commercial content, the tensile strength also decreased because the rubber has high elasticity and decrease the strength of polymer.

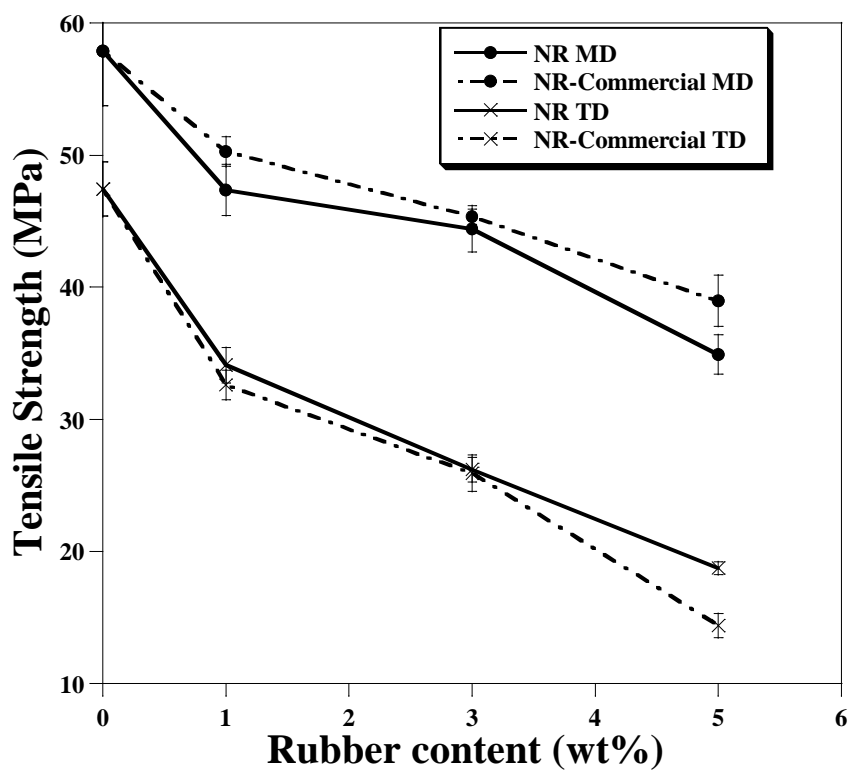


Figure 5.33 The tensile strength in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NR-Commercial film as a function of rubber contents

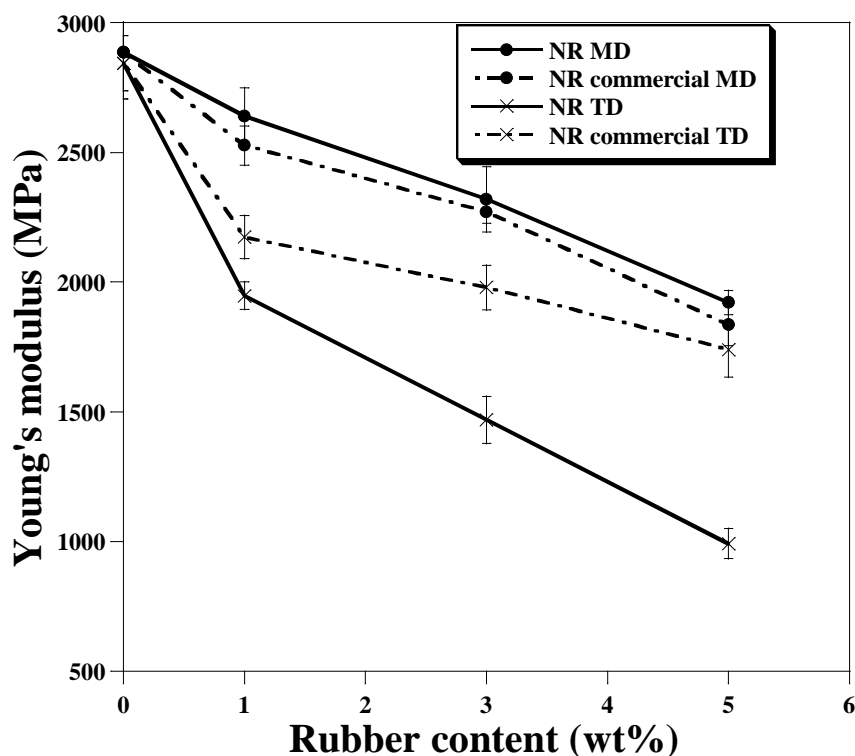


Figure 5.34 The Young's modulus in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/NR-Commercial film as a function of rubber contents

Figure 5.35 shows the impact strength of PLA blends. Impact strength of blends was higher than that of neat PLA. The impact strength was improved nearly 1.4 and 2 times for the presence of 3 wt% NR and NR-Commercial in PLA film, respectively which is attributed to smaller rubber particle size in the PLA matrix [51]. This might be due to elasticity of NR and NR-Commercial. In addition, the impact strength of PLA/NR-Commercial film is higher than PLA/NR film because degree of crystallization of PLA/NR-Commercial at 3 wt% ($X_c = 2.57\%$) is higher than PLA/NR ($X_c = 0.34\%$). The data of degree of crystallization is listed in Table B.3

(Appendix B). However, the impact strength of PLA/NR-Commercial film at 5 wt% slightly decreased due to NR-Commercial coalescence of rubber causing the increasing rubber domain size in the blends. In fact, a correlation between domain size of rubber and rubber content has been frequently observed for other rubber-modified polymer [51, 73]. Sundararaj et al. [74] reported that the particle size distribution broadens at higher concentrations because the breakup and coalescence are occurring concurrently during blending at higher concentrations. In fact, it also proves that the rubber domain size considerably affected the impact strength. Thus, the effect of polymer blends was slightly exhibited in the impact performance. The data of impact strength of all blends is listed in the Table D.21 (Appendix D).

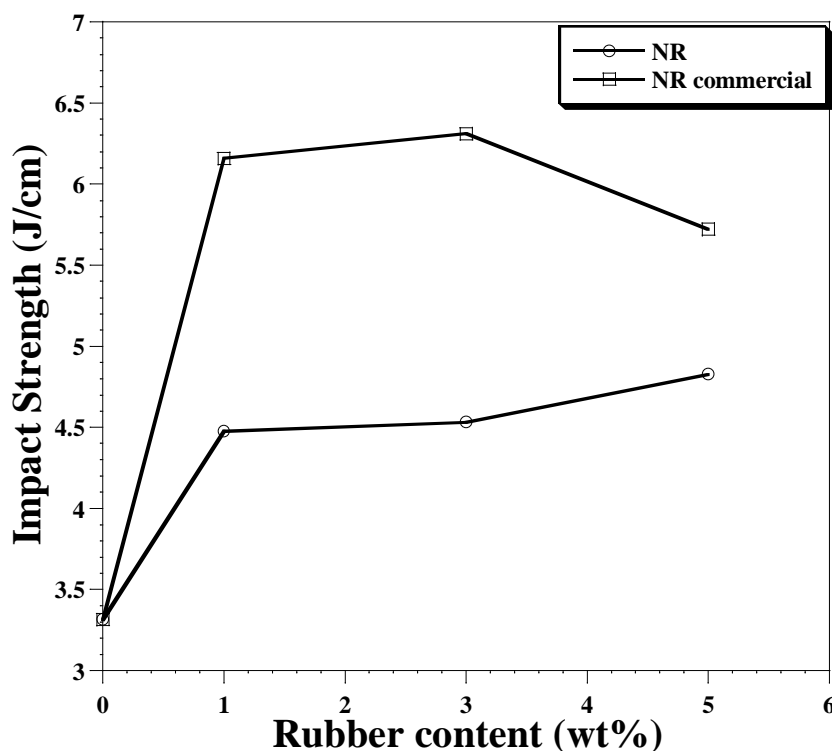
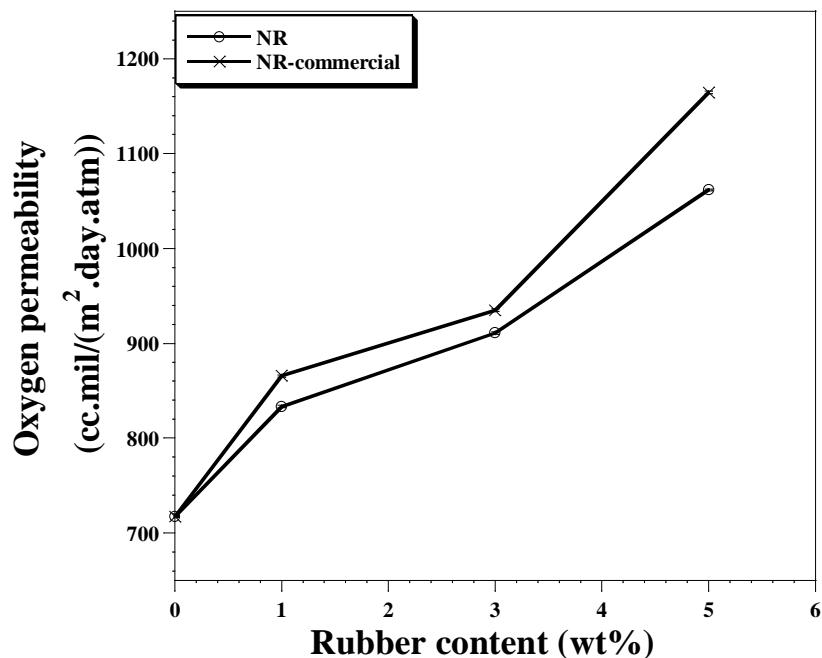


Figure 5.35 The impact strength of PLA/NR and PLA/NR-Commercial film as a function of rubber contents

5.4.3 Gas barrier properties

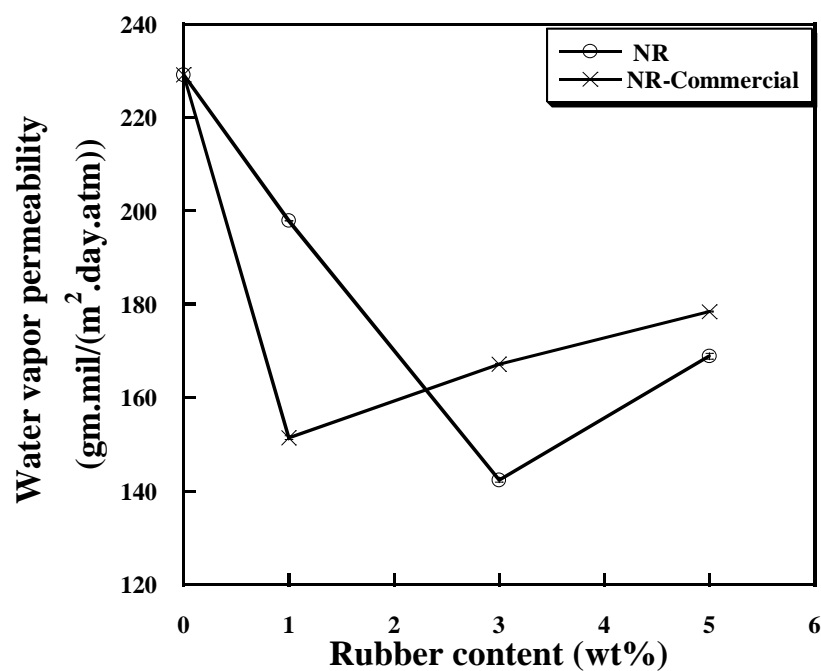


(a)

Figure 5.36 (a) Oxygen; and (b) water vapor permeability of PLA blown films containing 0, 1, 3 and 5 wt% of NR and NR-Commercial

Figure 5.36 is a plot between oxygen and water vapor permeability of PLA blown films as a function of NR and NR-Commercial content, respectively. The oxygen permeability of blended PLA films is demonstrated in Figure 5.36 (a). The oxygen permeability of neat PLA film was of 717 cc.mil/[m².day.atm] and increased with increasing rubber contents because diffusion rate, size of free volume. The oxygen permeability of PLA/NR and PLA/NR-Commercial blown films increased 48% and 62%, respectively. The results were similar with adding VNR in PLA matrix. It could be concluded that the NR, crosslinked natural rubber (VNR) and NR-

Commercial in latex is high oxygen permeability; however, it depends on diffusion rate, size of free volume of material. The data is listed in the Table E.2 (Appendix E).



(b)

Figure 5.36 *continue*

On the other hand, the results of water vapor permeability of blended PLA films which differs from oxygen permeability, is displayed in Figure 5.36 (b). The water vapor permeability of neat PLA film was 230 gm.mil/[m².day.atm]. Then, adding a hydrophobic polymer (NR and NR-Commercial) into PLA matrix decreased the water vapor permeability of blended PLA at 3wt% NR and 1wt% NR-commercial. It thus contributes strongly to increasing chain adhesive energy density after that the WVTR was increased with rubber contents because of coalescence of rubber which affects large size of gap. From Figure 5.36 (b), the water vapor permeability of

PLA/NR film decreased 14 – 38 % compared to that of neat PLA films until rubber concentration reaches 3 wt%. However, the water vapor permeability of PLA/NR-Commercial film decreased 34 % at 1 wt% of rubber content but increased at higher rubber content. This phenomenon can be explained with the same reason mentioned in section 5.2.4. The data is summarized in the Table E.2 and E.4 (Appendix E).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The biodegradable plastic, poly(lactic acid) (PLA), was blended with natural rubber (NR) as toughening agent, in order to improve the toughness of PLA blown film. NR, NR-Powder and NR-Commercial as secondary polymer were blended with PLA matrix with varying rubber contents. The properties of blended PLA film are investigated by DSC, DMA, SEM, OTR, WVTR and Universal testing machine which displays the thermal and physical properties of material. The overall results can be concluded as follows:

1. The effect of un-crosslinked and crosslinked natural rubber with rubber loading on physical properties was studied. The results indicated that the glass transition temperature of PLA slightly changed with the presence of rubber phase due to low rubber content implying that no interaction between polymer phase. In addition, the PLA/rubbers film showed the exothermic peak because the rubber helps to increase degree of crystallinity. Storage modulus from DMA did not significantly change with adding NR. In addition, tensile testing demonstrated that the elongation at break and tensile toughness of PLA films was improved by blending with NR.

While adding 5 wt% NR gave the highest properties, the percent elongation at break in machine direction (MD) and the impact strength of PLA/NR blown film was increased about 7-8 times and 2 times, respectively compared to those of neat PLA

film. However, VNR cannot significantly improve toughness of PLA matrix due to the stiffness of polymer network in rubber. Furthermore, the tensile strength and the Young's modulus in machine direction (MD) and transverse direction (TD) of PLA/NR and PLA/VNR film were decreased with rubber contents. OTR of both films increased with rubber contents but WVTR decreased at low rubber contents.

2. The properties of PLA/NR and PLA/NR-Commercial blown films were compared. We found that all blends were phase-separated from DSC. The elongation at break and tensile toughness in both directions of PLA/NR-Commercial film did not significantly improve compared with PLA/NR film by increasing rubber contents. In addition, the tensile strength and Young's modulus of two directions was increased approximate 2-3 folds which is the same trend with PLA/NR film. However, the impact strength PLA/NR-Commercial film is higher than PLA/NR film due to high flexibility of NR-Commercial film.

3. The effect of dispersion of NR in PLA matrix on physical properties of blown film was investigated. The NR-Powder did not enhance the toughness of PLA film because the particle size of NR is too large for blown films. Also, the elongation at break of PLA/NRP blown films was increased but the tensile strength, Young's modulus and impact strength was not change of compared with PLA/NR blown film.

4. This study can confirm the improvement of toughness of PLA blown films blended with NR which allows straightforward production of ductile PLA. The optimal NR content to improve toughness of PLA was found to be 5 wt% in this study. The elongation at break of PLA/NR film is higher than that of PLA/NRP and PLA/NR-Commercial blown films. The PLA/NR blown film is the completely

degradable material to overcome two main drawbacks of PLA for its use in the packaging sector. However, it is not improve in barrier properties.

6.2 Recommendations

1. The effect of temperature and rotor speed of mixing on domain rubber particle size with mechanical properties such as impact strength and elongation at break should be investigated.

2. Compatibilizer should be blended with PLA/NR. It is anticipated that the mechanical, thermal and thermomechanical properties would be improved.

3. Additionally, the extruder's screw should be longer to increase the mixing time between polymer matrix and additives resulting in mixing well.

4. The effect of other additives, including low glass transition temperature polymer such as polypropylene glycol (PPG) or antioxidant should help in decreasing the degradable and gel of NR by reducing temperature of mixing in extruder and protect oxidation in process.

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APPENDICES

Appendix A

Data of characterization of natural rubber latex

Table A.1 Particle size distributions of NR and VNR lattices

Sample	Average particle size (μm)	SD
NR	0.7830	± 0.11
VNR 1 h.	0.6908	± 0.15
VNR 3 h.	0.7930	± 0.17
VNR 5 h.	0.7465	± 0.19
VNR 7 h.	0.8570	± 0.21
VNR 8 h.	0.8570	± 0.21

Table A.2 Zeta-potential of NR and VNR lattices

pH	NR		VNR 8 h.	
	Zeta Potential (mV)	SD	Zeta Potential (mV)	SD
2	58.5	± 11.2	50	± 11.8
4	17.4	± 6.54	17.8	± 5.32
6	-59.7	± 8.53	-51.2	± 6.18
8	-66	± 5.75	-58.4	± 5.72
10	-71.9	± 8.82	-71.4	± 9.06
12	-83.7	± 7.86	-74.2	± 18.3

Table A.3 Swelling ratios of peroxide-prevulcanized natural rubber sheet

Prevulcanization time (h)	Natural rubber sheet	
	Swelling ratio (%)	SD
0	3283.35	± 93.7503
1	2395.95	± 55.8581
3	2131.71	± 29.1593
5	2058.04	± 39.8691
7	1950.40	± 20.1890
8	1906.51	± 26.0271

Appendix B

Data of thermal properties

Table B.1 Thermal properties and the degree of crystallinity of neat PLA and blended PLA with 3, and 5wt% of rubber

Natural rubber	Rubber content (wt %)	T_g (°C)	T_{cc} (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
None	0	63.03	124.48	2.01	153.44	3.09	1.16
NR	3	60.99	116.19	19.14	151.18	19.46	0.35
	5	60.11	116.97	19.31	151.91	21.78	2.80
VNR	3	59.20	114.99	18.52	159.96	20.86	2.60
	5	60.37	114.35	15.26	151.20	18.51	3.67

Table B.2 Thermal properties and the degree of crystallinity of neat PLA and PLA/rubber blended at 3 wt% of rubber

Natural rubber	Rubber content (wt %)	T_g (°C)	T_{cc} (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
None	0	63.03	124.48	2.01	153.44	3.09	1.16
NR	3	60.99	116.19	19.14	151.18	19.46	0.35
NR-Powder	3	56.69	126.67	16.43	153.87	15.95	0.54

Table B.3 Thermal properties and the degree of crystallinity of neat PLA and PLA/rubber blended with 1, 3 and 5 wt% of rubber content

Natural rubber	Rubber content (wt %)	T_g	T_{cc}	ΔH_c	T_m	ΔH_m	X_c
		(°C)	(°C)	(J/g)	(°C)	(J/g)	(%)
None	0	63.03	124.48	2.01	153.44	3.09	1.16
NR	1	57.02	122.29	14.17	151.31	14.24	0.08
	3	60.99	116.19	19.14	151.18	19.46	0.35
	5	60.11	116.97	19.31	151.91	21.78	2.80
NR-Commercial	1	59.77	127.6	8.11	153.81	10.39	2.48
	3	56.69	126.67	13.63	153.87	15.95	2.57
	5	62.65	122.74	17.08	152.23	19.23	2.43

Appendix C

Data of thermomechanical properties

Table C.1 Thermomechanical properties of neat PLA and blended PLA with 3, and 5wt% of rubber

Plasticizer type	Plasticizer content (wt %)	Storage modulus	T_g (<i>E'</i>) (°C)	T_g (<i>tan δ</i>) (°C)
None	0	2800.08	76.50	80.10
NR	3	2331.31	69.4	78.1
	5	2553.43	69.6	77
VNR	3	2378.41	69.3	77.8
	5	2065.41	68.7	75.9

Appendix D

Data of mechanical properties

Table D.1 Mechanical properties in MD of neat PLA

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	61.29	3023.93	3.31	48.37
2	53.34	2695.63	3.83	50.61
3	61.10	3047.55	3.25	47.33
4	61.30	3026.10	3.15	45.32
5	52.34	2637.03	3.18	39.44
Avg	57.87	2886.05	3.34	46.21
SD	4.12	180.54	0.25	4.24

Table D.2 Mechanical properties in TD of neat PLA

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	47.71	2803.19	2.26	23.2
2	49.58	2966.10	1.96	19.55
3	45.10	2698.69	2.22	21.71
4	44.98	2785.05	1.98	18.24
5	49.70	2966.03	2.32	25.69
Avg	47.41	2843.81	2.15	21.70
SD	2.06	105.88	0.15	2.96

Table D.3 Mechanical properties in MD of PLA/NR blend at 1 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	45.49	2506.64	3.20	58.38
2	46.59	2615.01	3.23	40.37
3	47.68	2663.53	3.50	40.83
4	47.50	2743.89	3.62	51.86
5	49.90	2775.77	3.78	44.92
Avg	47.40	2660.96	3.47	47.27
SD	1.61	107.23	0.24	7.73

Table D.4 Mechanical properties in TD of PLA/NR blend at 1 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	32.83	1895.00	2.15	13.58
2	33.30	1913.12	2.28	14.93
3	33.68	1941.00	2.83	17.96
4	35.26	2003.02	3.03	25.04
5	36.28	2012.08	3.66	32.89
Avg	34.27	1952.96	2.80	20.88
SD	1.45	52.50	0.61	8.04

Table D.5 Mechanical properties in MD of PLA/NR blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	41.83	2159.73	17.61	122.80
2	43.51	2237.99	19.93	125.96
3	44.43	2383.53	21.23	138.55
4	46.27	2423.18	22.5	148.38
5	46.30	2435.09	22.86	158.03
Avg	44.46	2327.90	20.83	138.74
SD	1.90	122.50	2.14	14.85

Table D.6 Mechanical properties in TD of PLA/NR blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	24.88	1334.06	7.03	23.66
2	25.14	1455.88	8.91	29.82
3	26.65	1516.68	9.88	30.23
4	26.78	1518.50	12.26	33.16
5	26.89	1571.37	16.86	38.73
Avg	26.07	1479.29	10.98	31.12
SD	0.97	90.90	3.78	5.48

Table D.7 Mechanical properties in MD of PLA/NR blend at 5 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	33.48	1862.82	20.47	124.16
2	33.84	1886.08	22.76	126.80
3	34.54	1913.22	24.17	130.09
4	36.12	1938.49	28.50	149.24
5	36.27	1999.50	33.50	159.02
Avg	34.85	1920.02	25.88	137.86
SD	1.28	52.74	5.16	15.39

Table D.8 Mechanical properties in TD of PLA/NR blend at 5 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	18.19	957.28	7.91	24.76
2	18.35	961.23	9.09	26.09
3	18.36	977.58	9.14	31.12
4	19.07	986.05	9.27	33.20
5	19.41	1070.32	9.99	39.48
Avg	18.67	990.49	9.08	30.93
SD	0.53	46.14	0.75	5.91

Table D.9 Mechanical properties in MD of PLA/VNR blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	43.97	2245.56	4.34	40.20
2	45.48	2285.56	4.48	41.18
3	45.79	2337.17	5.60	44.97
4	47.06	2367.18	6.91	51.68
5	47.52	2424.38	7.93	52.03
Avg	45.96	2331.97	5.85	46.01
SD	1.40	69.69	1.55	5.62

Table D.10 Mechanical properties in TD of PLA/VNR blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	31.43	1798.70	2.17	17.65
2	31.86	1799.06	2.32	18.99
3	32.81	1833.16	2.53	19.04
4	33.27	1849.23	2.72	21.44
5	33.28	1996.32	2.84	22.83
Avg	32.53	1855.29	2.51	19.99
SD	0.84	81.82	0.28	2.09

Table D.11 Mechanical properties in MD of PLA/VNR blend at 5 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	43.63	2257.56	3.98	32.89
2	44.15	2265.42	4.18	37.36
3	45.10	2363.27	4.62	39.04
4	47.82	2423.19	6.35	44.78
5	48.21	2558.52	7.64	55.51
Avg	45.78	2373.59	5.35	41.92
SD	2.10	124.42	1.58	8.71

Table D.12 Mechanical properties in TD of PLA/VNR blend at 5 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	25.13	1344.99	3.73	19.64
2	25.92	1356.59	3.93	22.61
3	26.04	1426.73	4.36	25.60
4	27.72	1454.32	4.63	29.28
5	28.00	1497.28	5.66	29.73
Avg	26.56	1415.98	4.46	25.37
SD	1.24	64.73	0.76	4.32

Table D.13 Mechanical properties in MD of PLA/NR-Powder blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	39.87	2334.19	4.44	38.11
2	39.90	2345.58	4.74	43.57
3	40.33	2383.89	5.25	50.48
4	42.17	2425.94	5.62	55.71
5	43.73	2568.54	5.70	69.53
Avg	41.20	2411.62	5.15	51.48
SD	1.69	94.80	0.54	12.10

Table D.14 Mechanical properties in TD of PLA/NR-Powder blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	25.74	2191.01	1.31	7.04
2	26.92	2193.05	1.43	7.89
3	27.39	2261.08	1.45	8.16
4	27.86	2269.01	1.53	8.87
5	28.41	2271.03	1.64	9.52
Avg	27.26	2237.04	1.47	8.29
SD	1.01	41.25	0.13	0.94

Table D.15 Mechanical properties in MD of PLA/NR-Commercial blend at 1 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	48.9	2450.22	5.78	53.85
2	49.78	2455.24	7.91	68.69
3	50.4	2498.98	9.16	79.43
4	50.48	2595.62	12.75	75.28
5	51.95	2603.66	13.95	77.52
Avg	50.30	2520.74	9.91	70.95
SD	1.12	74.53	3.39	21.37

Table D.16 Mechanical properties in TD of PLA/NR-Commercial blend at 1 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	31.51	2055.00	2.18	11.15
2	31.65	2136.00	2.22	13.34
3	32.56	2160.00	2.35	14.41
4	33.76	2194.00	2.49	17.17
5	34.17	2315.00	2.54	17.29
Avg	32.73	2172.00	2.35	14.67
SD	1.20	94.94	0.15	2.61

Table D.17 Mechanical properties in MD of PLA/NR-Commercial blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	44.33	2205.06	4.72	42.96
2	44.89	2221.88	5.59	47.88
3	45.41	2296.12	7.65	50.96
4	45.76	2314.06	9.81	56.13
5	45.98	2320.85	10.29	66.13
Avg	45.27	2271.59	7.61	52.81
SD	0.66	54.15	2.47	8.85

Table D.18 Mechanical properties in TD of PLA/NR-Commercial blend at 3 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	24.58	1910.00	2.42	11.10
2	24.67	1926.00	2.58	13.96
3	25.71	1973.00	2.66	14.34
4	26.95	2056.00	3.11	15.17
5	27.36	2084.00	3.71	17.89
Avg	25.85	1989.80	2.89	14.49
SD	1.27	77.42	0.52	2.44

Table D.19 Mechanical properties in MD of PLA/NR-Commercial blend at 5 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	37.09	1767.47	4.17	32.23
2	38.61	1770.99	5.28	36.29
3	39.01	1822.99	5.82	52.45
4	39.71	1832.58	7.12	52.60
5	40.25	1975.27	9.16	66.90
Avg	38.93	1833.86	6.31	48.09
SD	1.20	84.37	1.91	13.99

Table D.20 Mechanical properties in TD of PLA/NR-Commercial blends at 5 wt%

No.	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tensile toughness (mJ)
1	13.46	1615.00	2.65	6.63
2	14.09	1731.00	2.87	8.85
3	14.43	1762.00	2.98	10.58
4	14.50	1857.00	3.33	12.76
5	15.48	1869.00	3.63	14.48
Avg	14.39	1766.80	3.09	10.66
SD	0.73	103.59	0.40	3.10

Table D.21 Mechanical properties in TD of PLA/NR-Commercial blown films at 5 wt%

Natural rubber	Rubber content (wt %)	Impact strength (J/cm)
None	0	3.32 ± 0.405
NR	1	4.47 ± 0.001
	3	4.53 ± 0.519
	5	4.82 ± 0.656
VNR	3	4.09 ± 0.402
	5	4.67 ± 0.327
NRP	3	4.95 ± 0.400
NR-Commercial	1	6.16 ± 0.627
	3	6.13 ± 0.401
	5	5.72 ± 0.424

Appendix E

Data of gas barrier properties

Table E.1 Oxygen permeation (cc.mil/(m².day.atm)) of blended PLA films at different rubber loading

Sample	neat PLA	PLA/NR films		PLA/VNR films	
		3 wt%	5 wt%	3 wt%	5 wt%
1	718.42	909.68	1060.85	882.28	884.52
2	717.74	910.28	1061.18	884.12	884.67
3	716.58	911.60	1061.86	884.70	884.75
4	716.88	912.71	1062.74	885.01	885.51
Avg.	717.41	911.07	1061.66	884.03	884.86
SD	0.83	1.35	0.83	1.22	0.44

Table E.2 Oxygen permeation (cc.mil/(m².day.atm)) of blended PLA films at different rubber loading

Sample	neat PLA	PLA/NR films			PLA/NR-Commercial films		
		1 wt%	3 wt%	5 wt%	1 wt%	3 wt%	5 wt%
1	718.42	832.70	909.68	1060.85	864.40	933.46	1163.17
2	717.74	834.26	910.28	1061.18	864.57	934.29	1163.87
3	716.58	831.86	911.60	1061.86	866.31	935.24	1165.49
4	716.88	833.98	912.71	1062.74	867.05	936.48	1165.69
Avg.	717.41	833.20	911.07	1061.66	865.58	934.87	1164.55
SD	0.83	1.12	1.35	0.83	1.30	1.29	1.23

Table E.4 Water vapor permeation (gm.mil/(m².day.atm)) of blended PLA films at different rubber loading

Sample	neat PLA	PLA/NR films		PLA/VNR films	
		3 wt%	5 wt%	3 wt%	5 wt%
1	229.20	141.79	168.15	145.41	155.14
2	229.19	142.35	168.68	145.56	155.40
3	229.05	143.03	169.01	145.80	155.44
4	229.07	142.52	169.69	145.64	156.01
Avg.	229.10	142.42	168.88	145.60	155.50
SD	0.08	0.51	0.64	0.16	0.36

Table E.5 Water vapor permeation (gm.mil/(m².day.atm)) of blended PLA films at different rubber loading

Sample	neat PLA	PLA/NR films			PLA/NR-Commercial films		
		1 wt%	3 wt%	5 wt%	1 wt%	3 wt%	5 wt%
1	229.20	197.85	141.79	168.15	151.79	166.99	178.40
2	229.19	197.90	142.35	168.68	150.89	167.06	178.37
3	229.05	198.03	143.03	169.01	151.42	167.11	178.45
4	229.07	197.88	142.52	169.69	151.75	167.40	178.52
Avg.	229.10	197.92	142.42	168.88	151.46	167.14	178.44
SD	0.08	0.08	0.51	0.64	0.41	0.18	0.06

VITA

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