รายงานการวิจัย

ชื่อโครงการ

นวัตกรรมฟิล์มพลาสติกชีวภาพแบบหลายชั้นพร้อมหลายกลไกพิเศษ

Innovative Multi-layered Bioplastic Film with Multi-functions

โดย

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ปีงบประมาณ พ.ศ. ๒๕๕๗

ABSTRACT

Poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and thermoplastic starch (TPS) are good models for biodegradable multi-layered films. In the first part, PLA and PBS are formed as multi-layered film. The phase separation between PLA and PBS is observed. This is the reason why poly(lactic acid-*b*-butylene succinate) (PLA-*b*-PBS) copolymer is prepared via conjugating reaction to be a compatibilizer. The addition of PLA-*b*-PBS copolymer for 0.5 phr can improve compatibility between PLA and PBS phases resulting in improvement of oxygen barrier properties and mechanical properties, especially elongation at break. In the second part, PLA and TPS are blown as multi-layered film. The elongation at break of multi-layered films increases when the amount of TPS increases as well as the percent of water absorption.

บทคัดย่อ

ชื่อโครงการ: นวัตกรรมฟิล์มพลาสติกชีวภาพแบบหลายชั้นพร้อมหลายกลไกพิเศษ (Innovative Multi-layered Bioplastic Film with Multi-functions)

ชื่อผู้วิจัย: ศาสตราจารย์ ดร. สุวบุญ จิรชาญชัย

พอลิแลคติกแอซิด (PLA), พอลิบิวทีลีนซัคซิเนต (PBS), และเทอร์โมพลาสติกสตาร์ช (TPS) คือตัวอย่างที่ดีในการทำฟิล์มพลาสติกชีวภาพแบบหลายชั้น ในส่วนแรกของงาน ฟิล์มพลาสติกชีวภาพแบบหลายชั้นระหว่างพอลิแลคติกแอซิดกับพอลิบิวทีลีนซัคซิเนตแสดงให้เห็นถึงการแยกเฟส (phase separation) ระหว่างชั้นของพอลิแลคติกแอซิดและพอลิบิวทีลีนซัคซิเนต พอลิเมอร์ร่วมแบบกลุ่มระหว่างพอลิแลคติกแอซิดกับพอลิบิวทีลีนซัคซิเนต (PLA-*b*-PBS copolymer) ได้ถูกเตรียมขึ้นโดยปฏิกิริยาคอนจูเกชัน (Conjugating reaction) เพื่อใช้เป็นสารเสริมสภาพเข้ากันได้ (Compatibilizer) จากการศึกษาพบว่า การเติมพอลิเมอร์ร่วมแบบกลุ่มระหว่างพอลิแลคติกแอซิด

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CHAPTER I

INTRODUCTION

1.1 Introduction

In the present days, mono-layered films cannot desire the specific properties of films, for example, vacuum and high barrier properties (Fereydoon *et al.*, 2013), since the properties are limited with the material in use. Therefore, multi-layered films are alternative choice to use in specific applications and reach to the commercialized films. Multi-layered films comprise of two or more polymer layers in a single film. It can produce in many machines such as lamination and blown-film co-extrusion. At present, conventional multi-layered films which are made of petroleum-based polymers, are satisfying the basic functions (transparency, high modulus, and high strength (Goulas *et al.*, 2003)) and specific functions. For instance, Thellen *et al.* (2009) reported multi-layered film of polyamide incorporated with clay and low-density polyethylene which provided good oxygen barrier.

Nowadays, biodegradable polymers are recognized as the materials for environmental friendly. However, it has limitation due to the high cost. Therefore, creating value-added product, for example multi-layered film, it is accepted as an answer for solving this problem. In this present work, considering the combined properties of each biodegradable polymer, poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and thermoplastic starch (TPS) are good models for biodegradable multi-layered films. The combination of PLA and PBS might lead to the high strength and high toughness films regarding to the high tensile strength of PLA and high toughness of PBS. In term of TPS, it has efficiency which reduces cost of multi-layered film. The work also concerns the problem of phase separation between PLA and PBS polymers by proposing the use of PLA/PBS block copolymers. The systematic variations in processing condition are expected to the models of PLA-based multilayer films.

1.2 Objective

The objective of this work is to develop PLA-based multilayer films in terms of compatibility, mechanical and barrier properties.

1.3 Scope of Research

In this work, we prepare PLA-based multilayer films by using co-extrusion and study phase separation between layers. The alternative layers of multilayer films are composed of PLA/PBS/PLA and PLA/TPS/PLA bio-based plastics. Mechanical and barrier properties also will be investigated.

1.4 Theoretical Background and Literature Reviews

1.4.1 Multi-layered Films

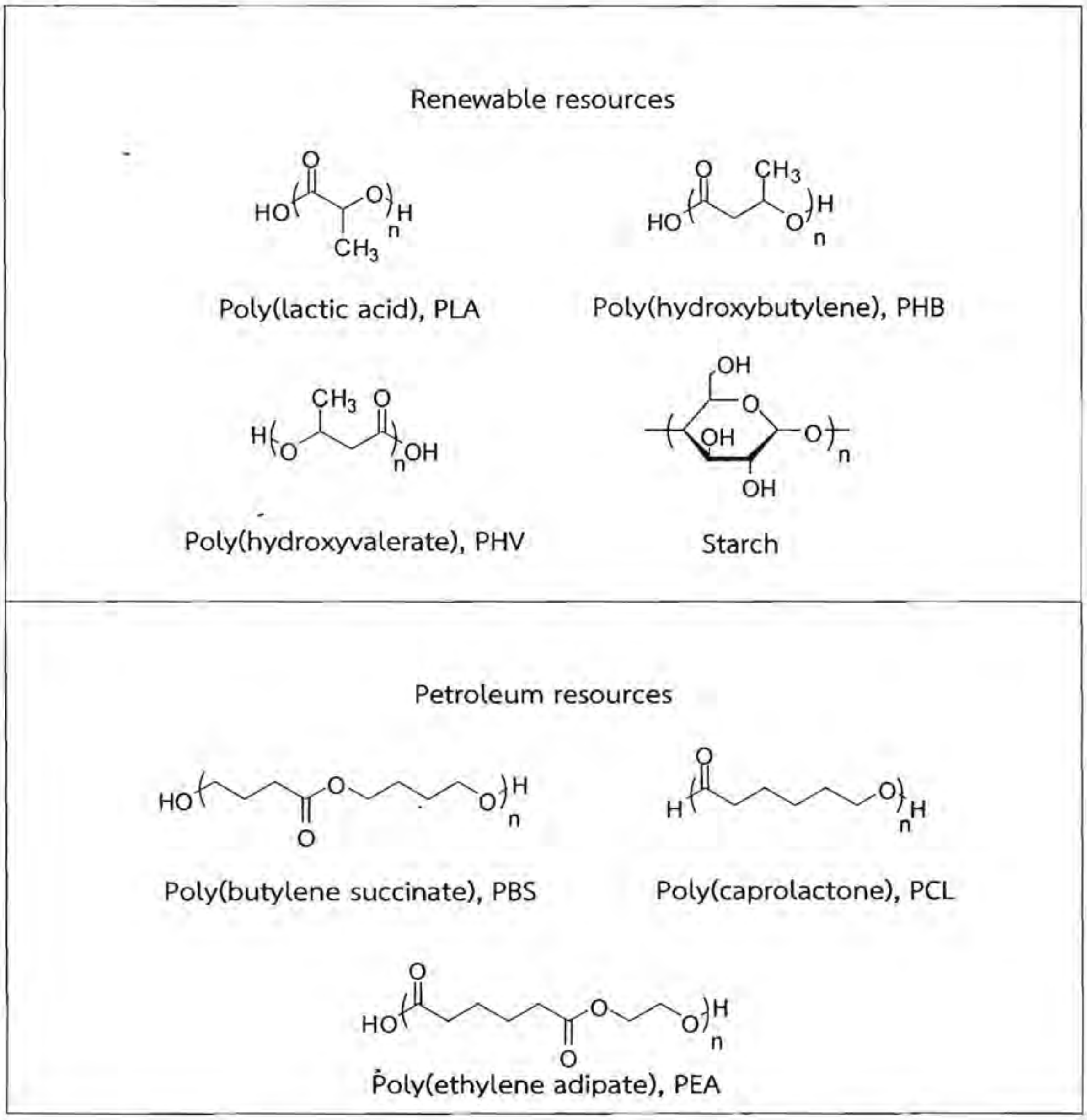
Mono-layered films are a film which comprises of one layer in a single film. The layer can be a single polymer or polymer blends. However, the mono-layered films are carried out only basic required properties of a film, for examples, flexibility, high modulus and impact strength. For specific properties, especially in packaging films, for instance, vacuum and high barrier properties, multi-layered films play an important role to replace mono-layered films (Fereydoon *et al.*, 2013). Multi-layered films are a film which consists of two or more polymer layers in a single film. Each layer has individual properties depended on type of polymers and additives in use. Multi-layered films can be produced by lamination, co-extrusion and blown-film co-extrusion (Fereydoon *et al.*, 2013).

At present, conventional multi-layered films are made from petroleum-based polymers such as polyethylene (PE) (Chytiri *et al.*, 2008), poly(ethylene terephthalate) (PET) (Boufarguine *et al.*, 2012), and polyamide (PA) (Thellen *et al.*, 2009). For example, multilayer packaging films incorporated montmorillonite layered silicate (MLS)/poly(m-xylylene adipimide (MXD6) nanocomposites as the oxygen barrier layer and low density polyethylene (LDPE) as the moisture resistant layer were produced through co-extrusion process (Thellen *et al.*, 2009). However, multi-layered films based on petroleum-based polymers cannot be degraded. It makes environmental problem. Therefore, the attractive polymers are biodegradable polymers.

1.4.2 Biodegradable Polymers

In the present days, biodegradable polymers become essential in many fields due to its environmental friendly, for example, packaging, agriculture, and medicine (Vroman *et al.*, 2009). It can be produced from 2 resources which are renewable and petroleum resources. The examples of biodegradable polymers are poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and thermoplastic starch (TPS) which can be classified as shown in Scheme 1.1. It can be degraded by broken down in polymer chain. The reaction which uses to degraded is divided into 2 types; the first one is enzymatic action of microorganisms such as bacteria, fungi, and algae, and the second one is non-enzymatic processes such as chemical hydrolysis (Gross *et al.*, 2002). By-products of degradation process are carbon dioxide (CO_2), water (H_2O), and biomass which can be converted to be a new renewable material as shows in Figure 1.1 (Siracusa *et al.*, 2008).

Scheme 1.1


Renewable resources

Poly(lactic acid), PLA

Poly(hydroxybutylene), PHB

Poly(hydroxyvalerate), PHV

Starch

Petroleum resources

Poly(butylene succinate), PBS

Poly(caprolactone), PCL

Poly(ethylene adipate), PEA

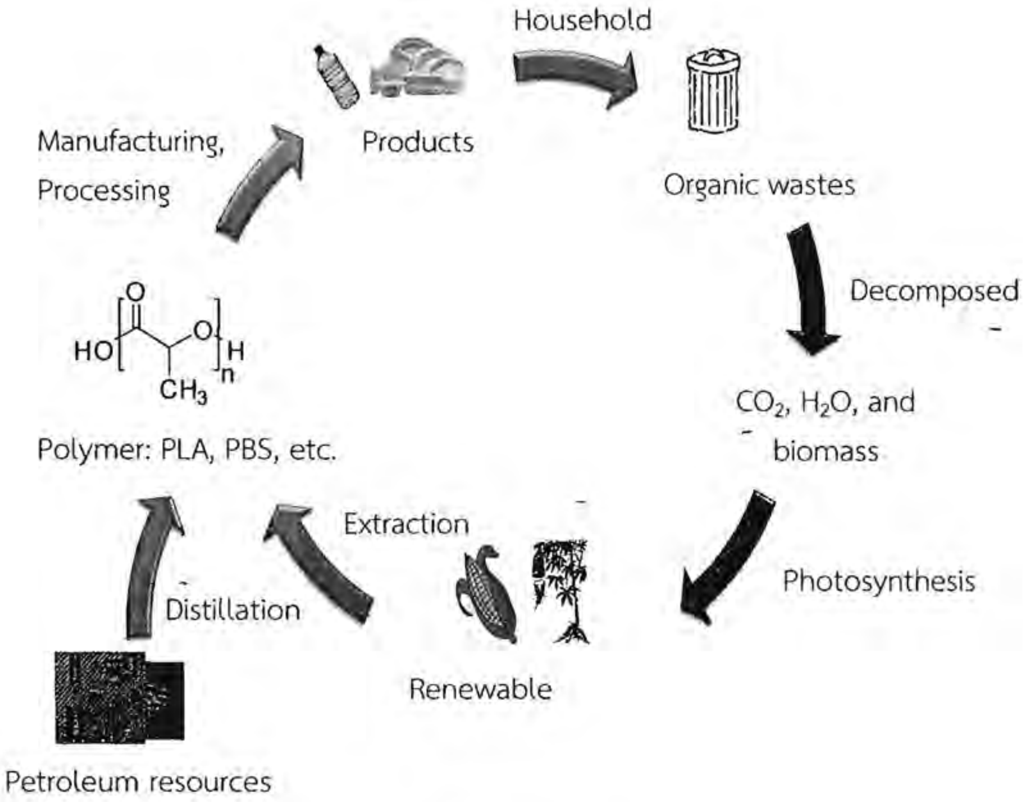


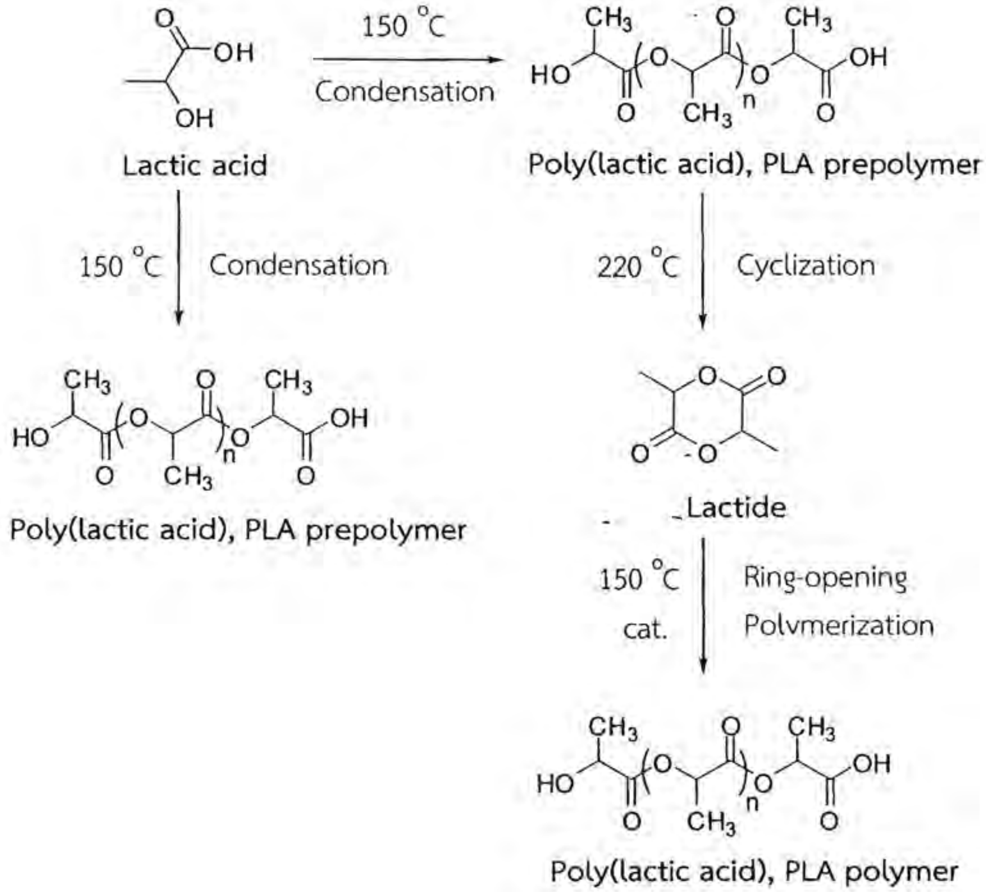
Figure 1.1 Cycle processes of biodegradable polymers.

1.4.3 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) is a biodegradable polymer and produced from renewable resources. The synthesis of PLA starts from the production of lactic acid and ends with its polymerization (Avérous, 2013). Scheme 1.2 shows the step of PLA synthesis (Sriputtirat *et al.*, 2012). It shows good transparency and good mechanical properties such as high strength and modulus (Boufarguine *et al.*, 2012). Moreover, PLA is commercially available and less price compared with other biodegradable polymers. Therefore, it has performance to use as polymer-based in biodegradable multi-layered films. For instance, Gu *et al.* (2013) studied barrier multilayer films in food packaging which were alternative layers of sodium alginate (ALG)/polyethyleneimine (PEI) on biaxially oriented poly(lactic acid) (BOPLA) films in order to produce bio-based all-polymer thin films with low gas permeability.

However, PLA is still limited with brittle properties. Generally, biodegradable polymers which show good flexibility are used to improve PLA properties such as poly(caprolactone) (PCL) (Harada *et al.*, 2007) and poly(butylene succinate) (PBS) (Bhatia *et al.*, 2007).

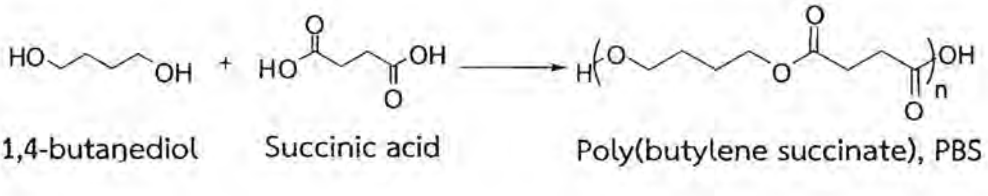
Scheme 1.2



1.4.4 Poly(butylene succinate) (PBS)

Poly(butylene succinate) (PBS), one of the aliphatic polyesters, was produced by polycondensation reaction between 1,4-butanediol and succinic acid. It has high flexibility, excellent impact strength, and thermal and chemical resistance (Ba *et al.*, 2003). PBS can be processed easily and is the best choice to blend or modify with PLA to improve flexibility (Bhatia *et al.*, 2007). The synthesis of PBS can follow in the Scheme 1.3 (Ba *et al.*, 2003).

Scheme 1.3



1.4.5 Thermoplastic Starch (TPS)

The main limitation of PLA is high cost. Therefore, low cost polymers play an important role as filler for PLA (Jun, 2000). Starch is biodegradable and renewable inexpensive polymer (Zeng *et al.*, 2011). It is made by cereals, tubers, and roots (Mishra *et al.*, 2006). The structure of starch has very strong inter- and intra-molecular hydrogen bonds resulting in the thermal degradation temperature of starch is lower than its melting point. Therefore, it cannot be processed without plasticizer. In case of thermoplastic starch (TPS), it can be produced by mixing starch with plasticizer such as glycerol (Fishman *et al.*, 2000), glycol (Yu *et al.*, 1996), and sugars (Barrett *et al.*, 1995), under heat and high shear force (Zeng *et al.*, 2011).

1.4.6 Bioplastic Multi-layered Films

Bioplastic multi-layered films are the attractive way to solve environmental problem. Therefore, in present day, there are many researches about bio-based multi-layered films. For examples, PLA-based multi-layered films laminated with PCL, PBS, and PBAT show good flexibility, transparency, and biodegradability (Patent WO 2012/053820), PLA/ethylene vinyl acetate multi-layered film via extrusion coated process is suitable as sealable or peelable for closing foodstuff containers (Patent US 2013/0068769).

1.4.7 Points of the work

Creating value-added biodegradable multi-layered films are proposed. By using PLA-based polymer, the multi-layered films of three layers of PLA/PBS/PLA and PLA/TPS/PLA were formed via blown-film co-extrusion process. This work extends to overcome the phase separation between PLA and PBS by using copolymer as a compatibilizer and the properties of films, for example mechanical properties and oxygen barrier properties. The systematic variations also study for suitable condition.

CHEPTER II

EXPERIMENTAL

2.1 Materials

2.1.1 Polymers

Commercial PLA (trade name 2003D) was purchased from NatureWorks LLC, the United State (M_w = 287,900, M_n =163,500). Commercial PBS was purchased from the Mitsubishi Chemicals Co., Ltd, Japan (M_w = 47,000, M_n =37,000). Tapioca starch was purchased from ETC International Trading Co., Ltd., Thailand.

2.1.2 Chemical Reagents

L-lactic acid (L-LA) was a gift from PURAC, Thailand, with 88 wt% aqueous solution. Analytical-grade 1,4-butanediol (with 99% purity) and tin(II)-2-ethylhexanoate ($SnOCt_2$) (with 95% purity) was purchased from Sigma-Aldrich, the United state. Analytical-grade succinic acid (with 99% purity) was bought from Ajax, Australia. *N-N'*-dicyclohexylcarbodiimide (DCC) was purchased from Fluka, Germany. 4-Dimethylaminopyridine (DMAP) was bought from MERCK, Germany.

2.1.3 Solvents

Analytical-grade methanol (CH_3OH), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and HPLC-grade chloroform was purchased from RCI Labscan. Deuterated chloroform ($CDCl_3$) was purchased from Sigma-Aldrich, the United State.

2.2 Instruments and Equipment

2.2.1 Structural Characterization

2.2.1.1 Fourier-transform Infrared Spectroscopy (FTIR)

Architecture polymer was characterized by using an ALPHA Tensor series Bruker Fourier-transform infrared spectrometer. All FTIR spectra were measured under the room temperature over a scanning range of 4000-550 cm^{-1} with 32 scans and a resolution 4 cm^{-1}.

2.2.1.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H, ^{13}C, and HMBC 2D NMR analysis were obtained from an Ultrashield 500 Plus Bruker (500 MHz) at room temperature. $CDCl_3$ were used to dissolve the samples. The chemical shifts were calibrated by using the residual resonance of the solvent peak (7.26 ppm).

2.2.2 Thermal Analysis

Thermal properties were determined by using a DSC 200 F3 Maia NETZCH differential scanning calorimetry under a nitrogen atmosphere. The sample was weighed approximately 5 mg and sealed in an aluminum pan. The temperature ranged between -50 and +200 °C (PLA-based multi-layered films with PBS) and 0 and +200 °C (PLA-based multi-layered films with TPS).

The percent of crystallinity (X_c) is then calculated using the following equation 1 (Mathew *et al.*, 2006):

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0 \times f} \times 100\% \qquad \text{eq. (1)}$$

where ΔH_m and ΔH_c are the enthalpy of melting and crystallization determined by integrating the areas (J/g) under the peaks. ΔH_m° is the reference value of melting enthalpy which represents the perfect crystalline PLA homopolymer (93.01 J/g) (Fischer *et al.*, 1973).

2.2.3 Mechanical Testing

Tensile strength, Young's modulus, and elongation at break of multi-layered films were carried out according to ASTM D 638M-91a on a LRX LLOYD universal testing machine with a 500 N load cell.

2.2.4 Compatibility Study

Compatibility of multi-layered films was investigated by a TM3000 Hitachi scanning electron microscope (SEM). The samples were coated with a thin layer of platinum. The accelerating voltage of machine was 15 kV.

2.2.5 Water Absorption

Multi-layered films were immersed in a water chamber at room temperature. After careful blotting of the surface liquid with paper, the samples were weighed as quickly as possible, almost every day until the weight is constant. Water absorption values were calculated as a percentage of initial weight by the following equation 2 (Amalvy *et al.*, 2002):

$$\%\text{Water absorption} = \frac{W_a - W_i}{W_i} \times 100\% \qquad \text{eq. (2)}$$

where W_a and W_i are the after weight and initial weight of samples, respectively.

2.2.6 Barrier Properties

Oxygen barrier testing was carried out in accordance with ASTM D3985-81. Oxygen permeation was measured by using an Ox-Tran 2/21 MOCON oxygen analyzer with an oxygen flow rate 20 cm^3/min at 23 °C at 0% RH.

2.2.7 X-ray Diffraction

A Rigaku X-ray diffractometer was applied to determine crystalline pattern of the samples. X-ray diffraction (XRD) experiments were run using Cu K_α radiation and operated at 40 kV/30 mA.

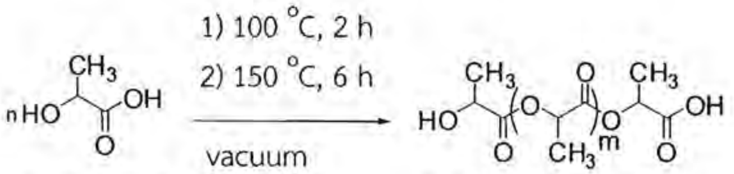
2.3 Methodology

2.3.1 PLA-based Multi-layered Films with PBS

2.3.1.1 Poly(Lactic Acid) Prepolymer

L-lactic acid (L-LA) (25.59 mL, 1 mol) in a three-necked round-bottom flask was heated at 100 °C for 2 h under high vacuum to eliminate initial water. After that the polymerization was occurred by adding $SnOCt_2$ (0.1 mol% of L-LA) at 150 °C for 6 h to obtain a viscous product. The viscous product was dissolved in chloroform, precipitated in cold methanol and washed with methanol several times. The precipitate was dried under vacuum at 50 °C for 24 h.

Scheme 2.1



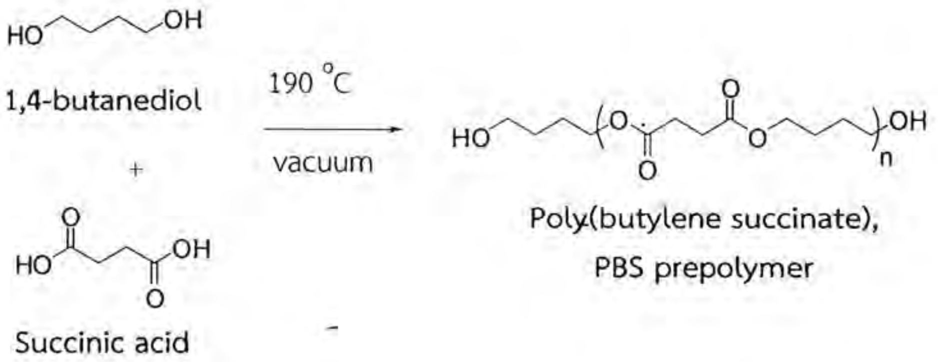
Lactic acid

Poly(lactic acid), PLA prepolymer

2.3.1.2 Poly(Butylene Succinate) (PBS) Prepolymer

1,4-butane diol (9.75 mL, 0.11 mol) and succinic acid (11.81 g, 0.1 mol) were mixed into a three-necked round-bottom flask with a magnetic stirrer. The reaction was at 190 °C for 6 h under vacuum to obtain a viscous product. The product was collected in the same way as PLA prepolymer to obtain PBS prepolymer.

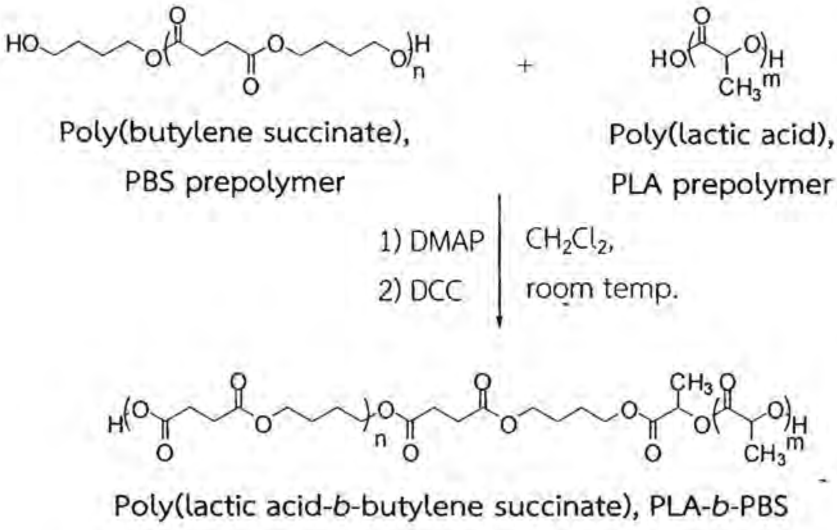
Scheme 2.2



2.3.1.3 Poly(Lactic Acid-b-Butylene Succinate) (PLA-b-PBS)

PLA prepolymer (MW = 1200-2200) (12 g, 6 mmol) and 10 mol% DMAP (73.3 mg) was dissolved in 120 mL of CH_2Cl_2 by stirring for 10 min at room temperature. The solution of DCC (1.24 g, 6 mmol) which dissolved in 13 mL of CH_2Cl_2 was mixed into the reaction for 10 min. PBS prepolymer (MW = 2000-3000) (21.5 g, 10 mmol) was dissolved in 215 mL of CH_2Cl_2 and added into the reaction. The mixture solution was continued for 36 h at room temperature. The precipitates were then filtered. The residual solution was heated to obtain viscous product. The viscous product was precipitated and washed in cold methanol several time. The product obtained was dried under vacuum at 50 °C for 24 h.

Scheme 2.3



2.3.1.4 PLA/PBS/PLA Multi-layered Film

Three-layered films were formed as films with ~0.05 mm thickness by using a LBE12.5-30 Labtech Engineering multi-layered film blowing line. Temperature and screw speed settings were in range of 140-180 and 40-50 rpm, respectively. The structure of multi-layered films and composition of compatibilizer which was added into core (PBS) layer were shown in Table 2.1, including the sample name that will be used throughout this work.

Table 2.1 Structure of multi-layered films with various PLA-*b*-PBS in PBS phase

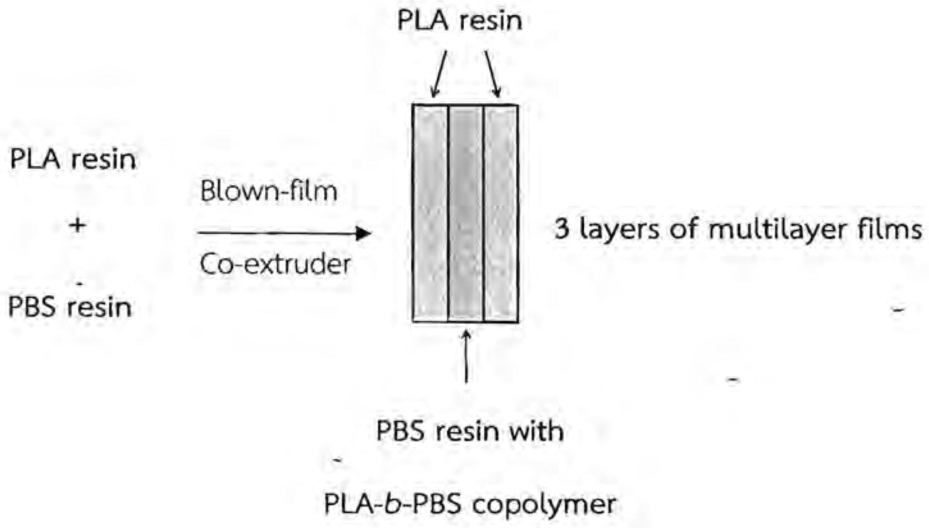
Multi-layered films	Content of PLA-*b*-PBS, phr
PLA/PLA/PLA	0
PLA/PBS/PLA	0
PLA/PBS+PLA-*b*-PBS0.5/PLA	0.5
PLA/PBS+PLA-*b*-PBS1/PLA	1.0
PLA/PBS+PLA-*b*-PBS3/PLA	3.0
PLA/PBS+PLA-*b*-PBS5/PLA	5.0

2.3.2 PLA-based Multi-layered Films with TPS

2.3.2.1 TPS Preparation

Tapioca starch (70 %) and glycerol (30 %) was mixed and then extruded by using a LTE-20-40 Labtech Engineering counter-rotating twin screw extruder. Temperature and screw speed setting were in range of 130-170 °C and 40-50 rpm, respectively.

Scheme 2.4



2.3.2.2 TPS Blend Preparation

TPS and PLA resin (2003D) were blended to obtain TPS blend resin in various weight ratios (TPS/PLA 90/10, 80/20, 70/30, 60/40, and 50/50 w/w) by a LTE-20-40 Labtech Engineering counter-rotating twin screw extruder. Temperature and screw speed were set at 140-170 °C and 20-30 rpm, respectively.

2.3.2.3 PLA/TPS/PLA Multi-layered Films

In the same way, PLA/TPS/PLA multi-layered films were blown by changing the layer of PBS to TPS blend. The procedure temperature and screw speed settings were 170-180 °C and 50-60 rpm, respectively. Table 2.2 shows the sample name, composition, and structure of multi-layered films.

Table 2.2 Structure of PLA-based multi-layered films with TPS

Multi-layered film	TPS/PLA blend ratio in core layer
PLA/PLA/PLA	-
PLA/TPS50/PLA	50/50
PLA/TPS60/PLA	60/40
PLA/TPS70/PLA	70/30
PLA/TPS80/PLA	80/20
PLA/TPS90/PLA	90/10
PLA/TPS100/PLA	100/0

CHEPTER III

RESULTS AND DISCUSSION

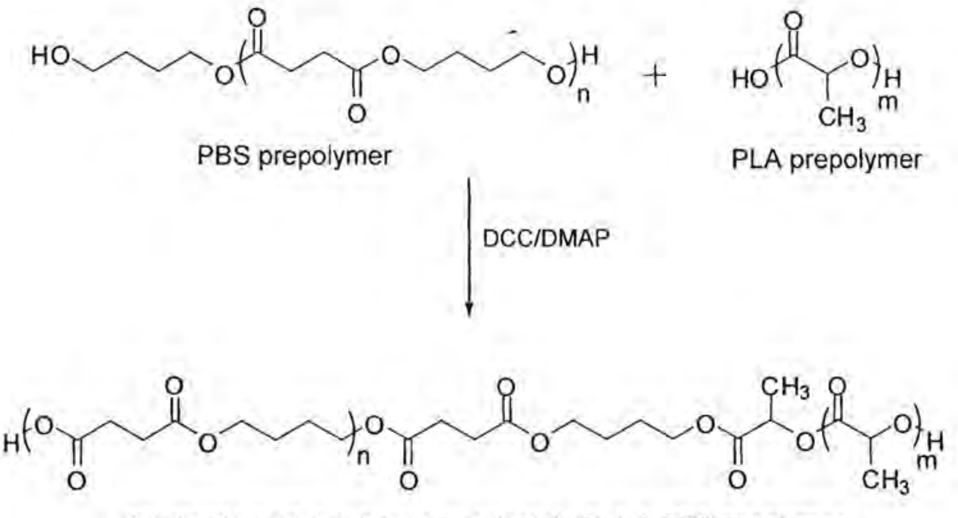
3.1 PLA-based Multi-layered Films with PBS

3.1.1 PLA-*b*-PBS Copolymer Characterization

3.1.1.1 Structural Analysis

PLA and PBS prepolymers were prepared via the Steglich esterification as shown in Scheme 3.1. The successful product was traced with FTIR spectra (Figure 3.1). The characteristic peaks at 1754 cm^{-1} and 1713 cm^{-1} refer to carbonyl group of PLA and PBS prepolymer, respectively (Figure 3.1). In case of PLA-*b*-PBS copolymer, it shows both carbonyl groups of PLA at 1757 cm^{-1} and PBS at 1713 cm^{-1} (Figure 3.1). This indicates that PLA-*b*-PBS copolymer was successfully prepared.

Scheme 3.1



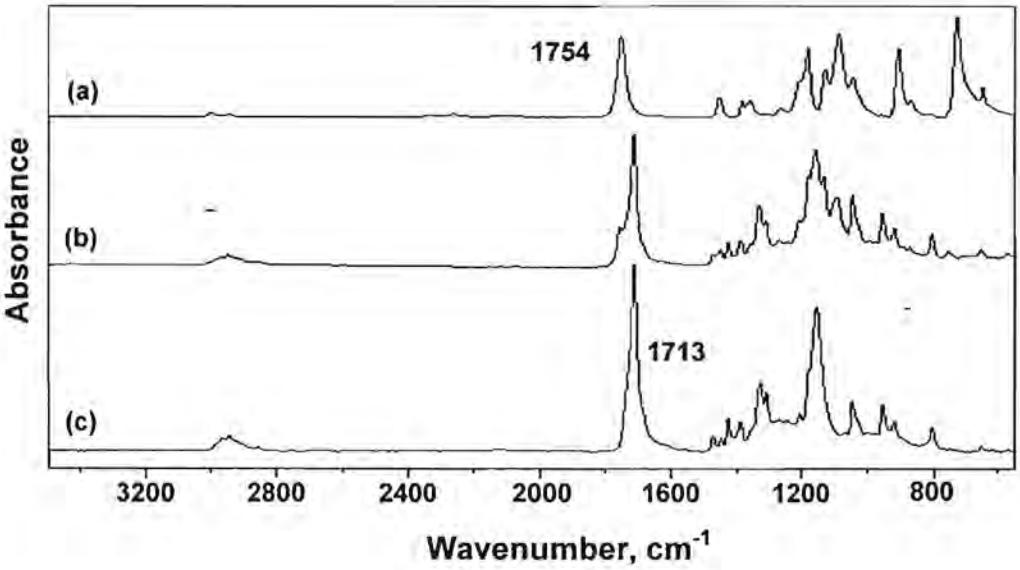


Figure 3.1 FTIR spectra of (a) PLA prepolymer, (b) PLA-*b*-PBS copolymer, and (c) PBS prepolymer.

^{1}H and ^{13}C NMR of PLA-*b*-PBS copolymer are shown in Figure 3.2. In order to clarify the structure of PLA-*b*-PBS copolymer, heteronuclear multiple bond correlation (HMBC) 2D NMR was used. This mode of NMR indicates the correlation between the carbon and proton via multiple bonds. The result shows one correlation between PLA and PBS units as indicated in the structure in Figure 3.3. The correlation was found between methyl group of PLA unit (at 1.57, 16.75 ppm) and methylene group of PBS unit (at 1.69, 25.34 ppm).

In addition, the number-average molecular weight ($M_{n\text{-NMR}}$) of PLA-*b*-PBS copolymer (3904 g/mole) was calculated according to equation 1 by using quantitative ^{1}H-NMR analysis (You *et al.*, 2004).

$$M_{n\text{-NMR}} = \left(\frac{I_{1.57}/3}{I_{3.67}/2} \times 72\right) + \left(\frac{I_{2.61}/4}{I_{3.67}/2} \times 172\right) \qquad \text{(Eq. 1)}$$

where $I_{1.57}$ is the integral value of the peak at δ_H = 1.57 (3H, d, -O-CH(CH$_3$)-) in PLA. $I_{2.61}$ and $I_{3.67}$ are the integral value of the peaks at δ_H = 2.61 (4H, s, -(C=O)-CH$_2$-) and 3.67 (2H, s, HO-CH$_2$-CH$_2$-) in PBS. 72 and 172 are the molecular weight (g/mole) of PLA and PBS unit, respectively.

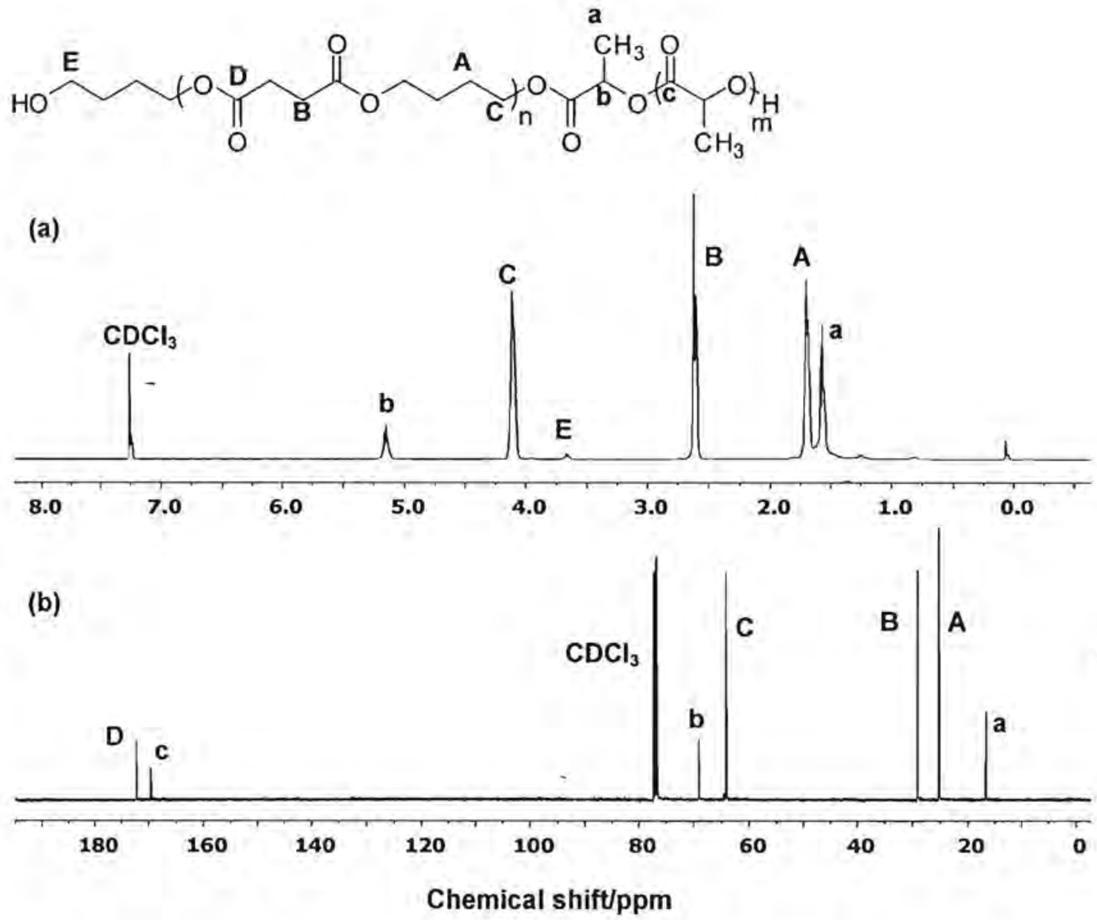


Figure 3.2 (a) ^{1}H and (b) ^{13}C NMR of PLA-*b*-PBS copolymer.

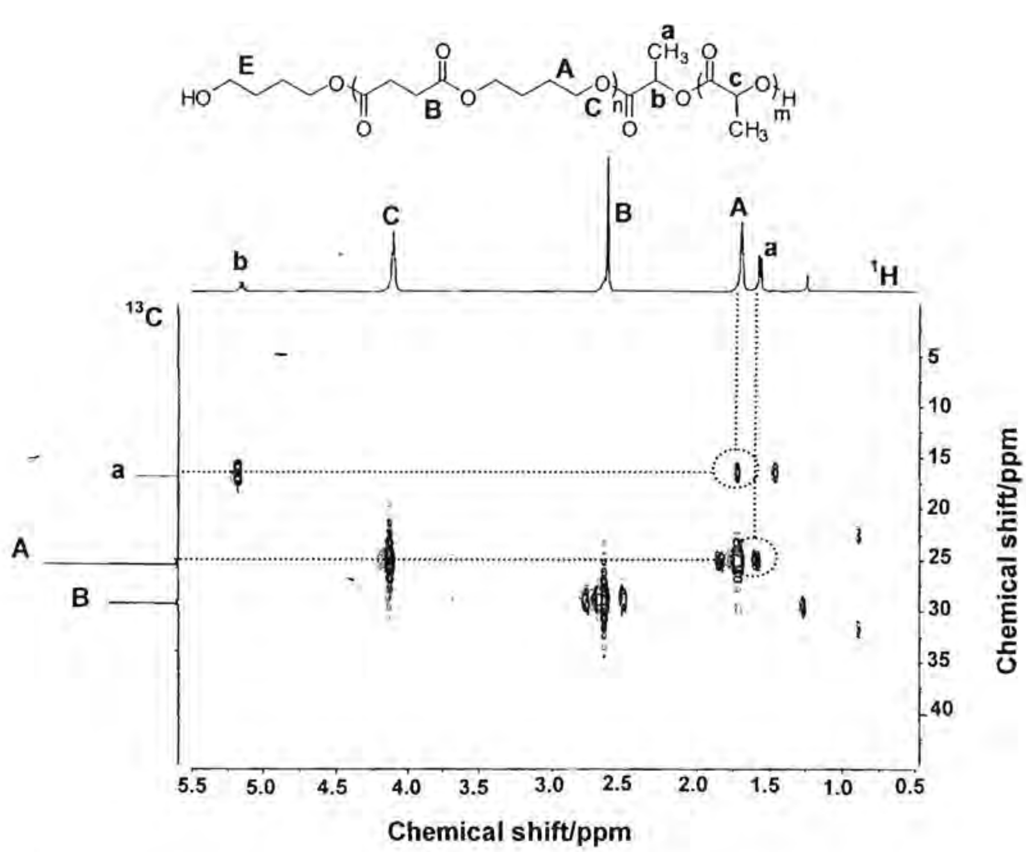


Figure 3.3. ^{1}H-^{13}C HMBC 2D NMR spectrum of PLA-*b*-PBS copolymer.

3.1.1.2 Thermal Analysis

As shown in Figure 3.4, PLA-*b*-PBS block copolymer shows the melting points of PBS and PLA chains around 110.7 °C and 151.4 °C, respectively. The intensity of endothermic peak of PLA block is relatively low, compared to that of PBS block. This might be the effect of slow crystallization of PLA although it covalently bonds with high crystalline PBS block.

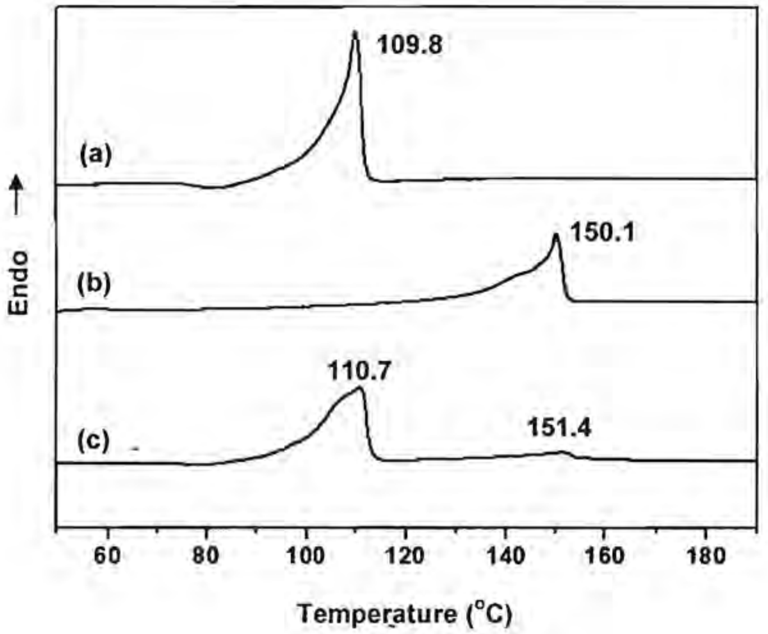


Figure 3.4 DSC curves of (a) PBS prepolymer, (b) PLA prepolymer, and (c) PLA-*b*-PBS copolymer.

3.1.1.3 Spherulite Study

The crystallization in macroscopic scale of PLA-*b*-PBS copolymer can be observed by using an optical microscope. In general, the highly crystalline polymer melt shows spherulite formation during cooling down temperature from the crystallization temperature to the glass transition temperature. Here, the crystallization behavior of PLA-*b*-PBS copolymer was observed at isothermal thermal temperature of 70 °C which is close to the onset of the crystallization temperature of PBS. Figure 3.5 presents the spherulite morphologies of PLA-*b*-PBS copolymer. At 135 s, it shows that the average radius of the spherulites is about 54 μm with the growth spherulites rate about 0.8 μm/s.

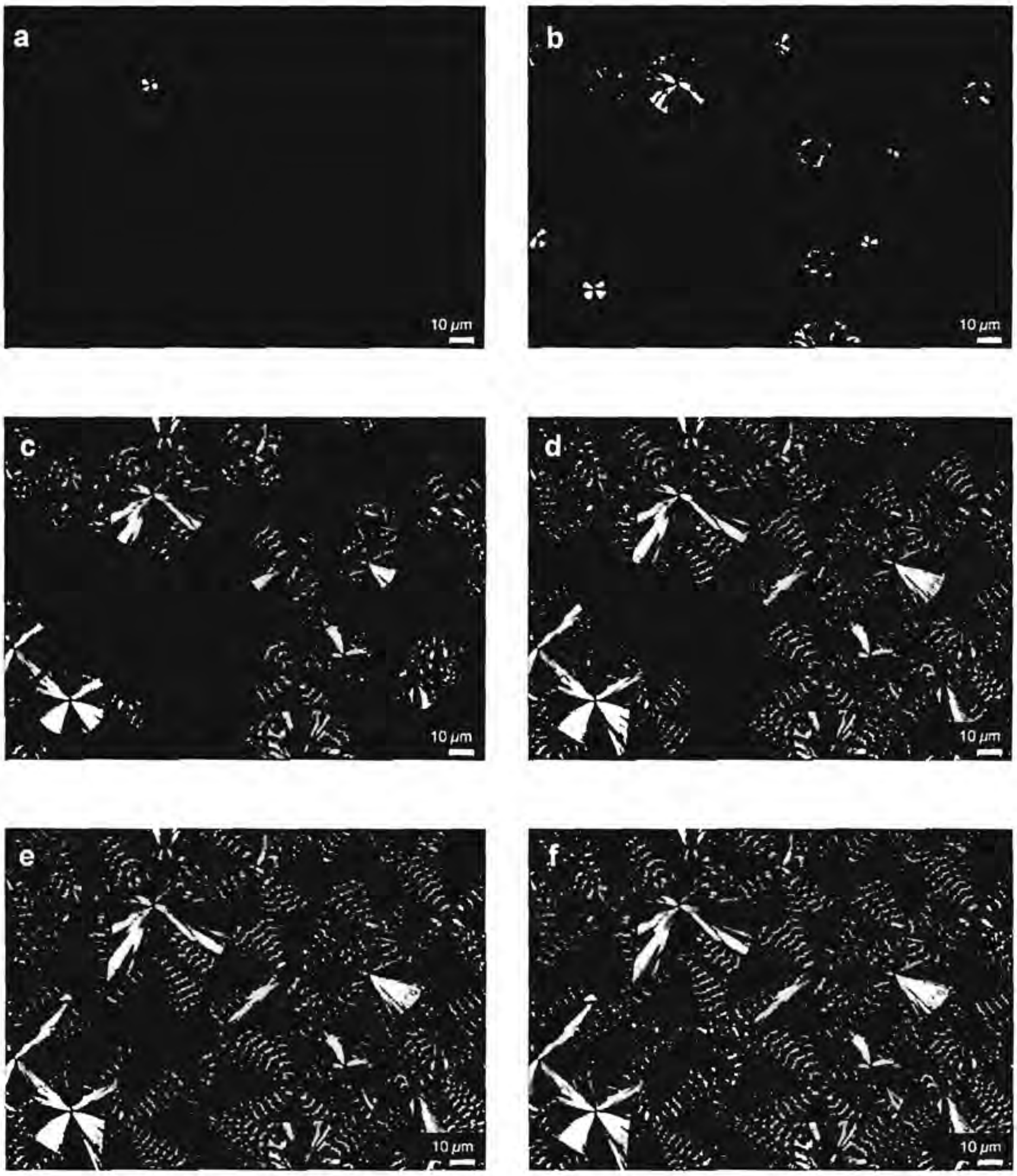


Figure 3.5 Polarizing optical micrographs for PLA-*b*-PBS at isothermal temperature (70 °C): (a) 10 sec, (b) 35 sec, (c) 60 s, (d) 85 sec, (e) 110 sec, and (f) 135 sec.

3.1.2 Characterizations of PLA/PBS/PLA Multi-layered Films

3.1.2.1 Compatibility Study

The efficiency of PLA-*b*-PBS copolymer can evaluate from the compatibility of PLA/PBS/PLA multi-layered films containing PLA-*b*-PBS copolymer as a compatibilizer. Figure 3.6 ((A), (B), (C), (D), (E)) represents morphology of the multi-layered film with 0, 0.5, 1, 3, 5 phr of copolymer, respectively. It is clear that the addition of copolymer shows the improvement of compatibility between PLA and PBS phases as identified by decreasing of the white line between two-phase polymers. This white line refers to interphase which is the boundary between two-phase polymers. In other words, the PLA-*b*-PBS copolymer can increase interfacial adhesion between PLA and PBS polymers.

In order to investigate whether PLA-*b*-PBS copolymer interact with PLA and PBS, total correlation spectroscopy (TOCSY) 2D NMR technique was applied. This technique determines the correlation between the proton and proton via multiple bonds. Figure 3.7B represents the PLA/PBS/PLA multi-layered film containing PLA-*b*-PBS copolymer. The correlation at 1.70 ppm (CH_2-A of PBS) and at 5.17 ppm (CH-b of PLA) indicates the interaction of PLA, PBS, and PLA-b-PBS copolymer. It should be noted that the result of PLA/PBS/PLA multi-layered film without PLA-*b*-PBS copolymer was not found any correlation in that region (Figure 3.7A).

GPC technique was also used to confirm the number of component in multi-layered film containing copolymer. It should be mentioned that Figure 3.8c is the mixture of PLA/PBS/PLA multi-layered film and PLA-*b*-PBS copolymer in the solvent of HPLC-grade chloroform ($CHCl_3$), which 2 peaks at 25.762 min (PLA-PBS phases) and 31.876 min (PLA-*b*-PBS) were observed, while Figure 3.8b is the PLA/PBS containing PLA-*b*-PBS/PLA multi-layered film passed extruder. The observation of one peak at 25.807 min in Figure 3.8b implied that PLA-PBS phases and PLA-*b*-PBS copolymer after processing have one component in the system. In other word, some chemical bonds between them were occurred.

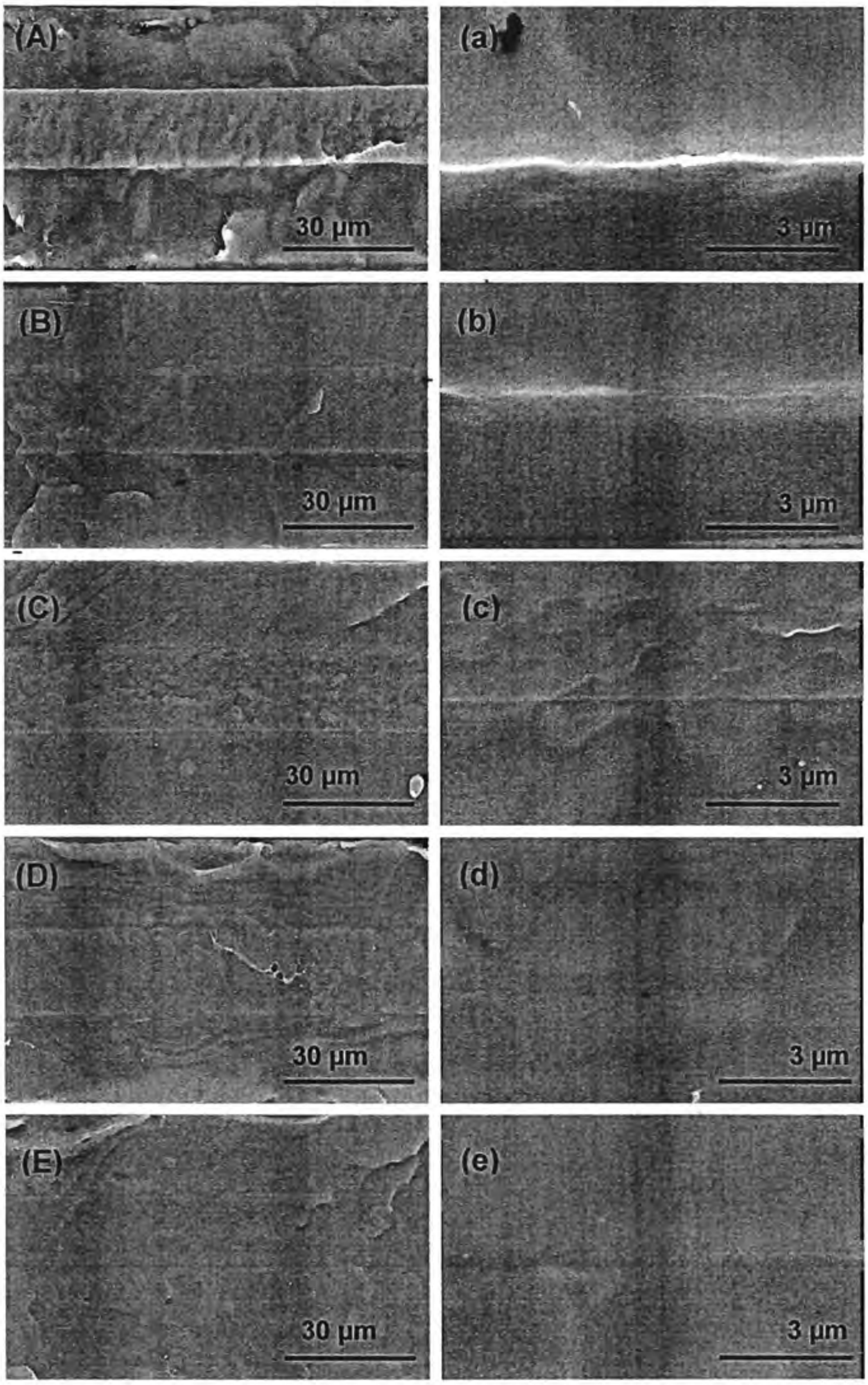


Figure 3.6 SEM images of PLA/PBS/PLA multi-layered films with PLA-*b*-PBS copolymer (A,a) 0 phr, (B,b) 0.5 phr, (C,c) 1.0 phr, (D,d) 3.0 phr, and (E,e) 5.0 phr.

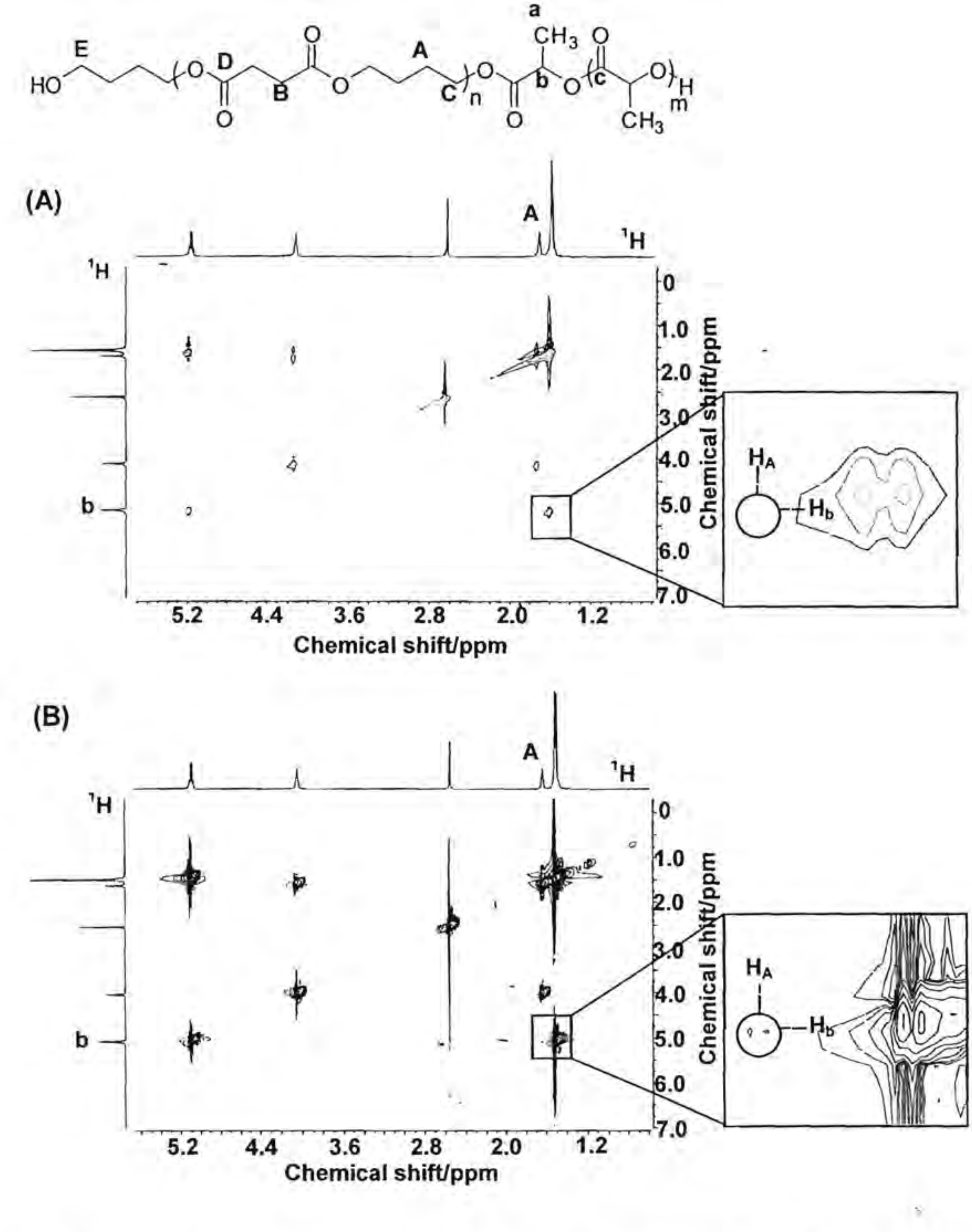


Figure 3.7 ^{1}H-^{1}H TOCSY 2D NMR spectra of (A) PLA/PBS/PLA and (B) PLA/PBS+PLA-*b*-PBS5/PLA multi-layered films.

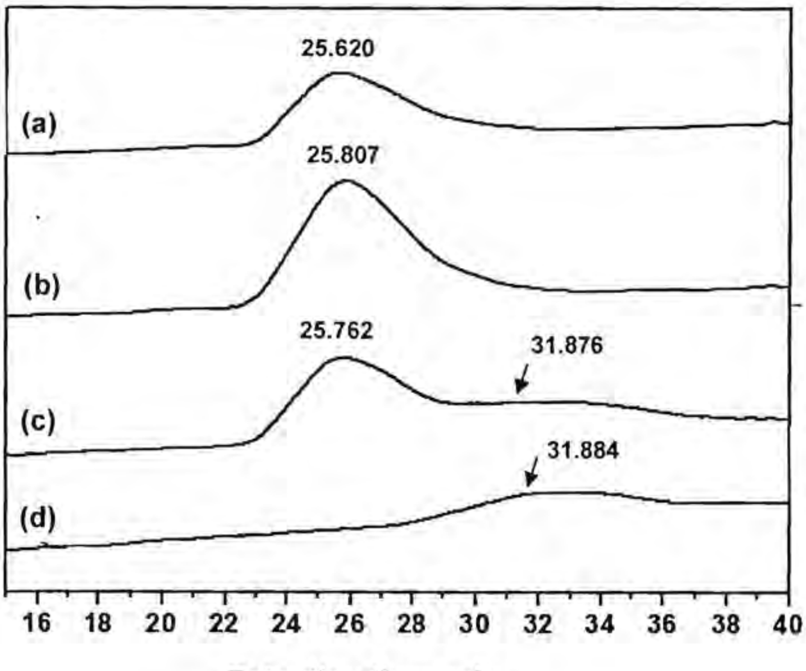


Figure 3.8 GPC chromatogram of (a) PLA/PBS/PLA film, (b) PLA/PBS+PLA-*b*-PBS5/PLA film, (c) PLA/PBS/PLA mixing with PLA-*b*-PBS copolymer 5 phr, and (d) PLA-*b*-PBS copolymer.

3.1.2.2 Thermal Properties and Crystallization Behavior

Thermal properties and crystallization behavior of the multi-layered films were evaluated using DSC (Table 3.1). The PLA/PBS/PLA and PLA/PBS+PLA-*b*-PBS/PLA multi-layered films show the decrease in T_g with an increase of PLA-*b*-PBS. In other words, the ease of chain mobility occurs when PBS phase contained PLA-*b*-PBS. This leads to an understanding that PLA-*b*-PBS plays the role as compatibilizer for PLA and PBS. The compatibility of PBS and PLA in the multi-layered films also leads to the decrease of T_c as well as the increase of degree of the crystallinity (X_c).

Table 3.1 Thermal properties and crystallinity of PLA/PBS/PLA multi-layered films

Multi-layered film	$T_{g,PLA}$ (^{o}C)	$T_{m,PBS}$ (^{o}C)	$T_{m,PLA}$ (^{o}C)	$T_{c,PLA}$ (^{o}C)	X_c (%)
PLA/PLA/PLA	57.7	-	154.3	101.4	~0
PLA/PBS/PLA	55.3	109.0	152.7	85.8	8.07
PLA/PBS+PLA-b-PBS0.5/PLA	54.0	109.2	153.1	85.5	8.52
PLA/PBS+PLA-b-PBS1/PLA	53.5	109.0	152.0	85.1	9.11
PLA/PBS+PLA-b-PBS3/PLA	52.6	108.6	152.6	84.4	10.72
PLA/PBS+PLA-b-PBS5/PLA	52.1	109.1	152.3	84.2	12.01

3.1.2.3 Mechanical Properties

Figure 3.9 illustrates the mechanical properties of the multi-layered films. The result shows that PLA/PBS/PLA multi-layered film is decreased in tensile strength compared with the PLA/PLA/PLA film. This might be due to the phase separation between the two phases of the different polymers. However, the tensile strength of film is increased when containing PLA-*b*-PBS copolymer for 0.5 phr. In addition, it is clear from this table that the elongation at break is obviously increased for the multi-layered films containing PLA-*b*-PBS copolymer. This might be due to the role of PLA-*b*-PBS copolymer.

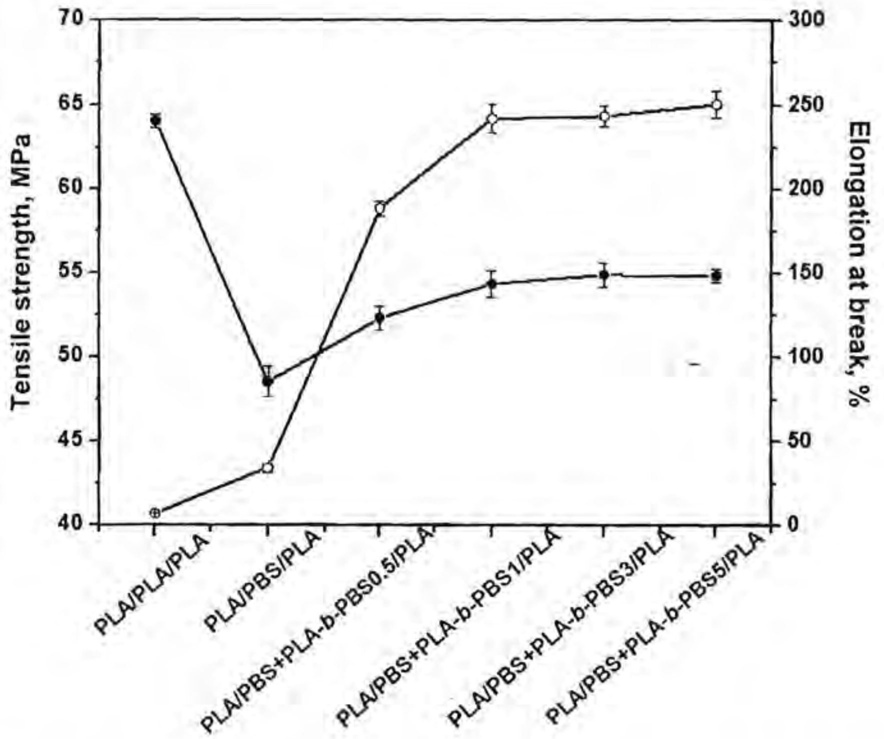


Figure 3.9 Tensile strength and elongation at break of PLA/PBS/PLA multi-layered films containing PLA-*b*-PBS copolymer.

3.1.2.4 Oxygen Permeability

As seen in Figure 3.10, the oxygen permeability of PLA/PLA/ PLA and PBS/PBS/PBS multi-layered films is about 20.0 and 28.5 cm^3 mm m^{-2} day^{-1} atm^{-1}, respectively. Unexpectedly, when PLA and PBS were formed together (PLA/PBS/PLA multi-layered film), the oxygen permeability is decreased (18.4 cm^3 mm m^{-2} day^{-1} atm^{-1}) less than their individual values. This suggests that PLA and PBS are synergistic property in term of oxygen permeability.

The fact that crystallinity can be affected on oxygen permeability.[11] As shown in Table 3.1 PLA/PBS/PLA multi-layered film shows an increase in crystallinity (X_c)

from ~0 % to 8.07 % compared with the PLA/PLA/PLA film. It should be noted that this reflects the packing structure of polymer chain resulting in obstructing O_2 molecules. In case of PLA/PBS+PLA-*b*-PBS/PLA multi-layered films, it slightly increases in crystallinity resulting in slightly decrease of oxygen permeability.

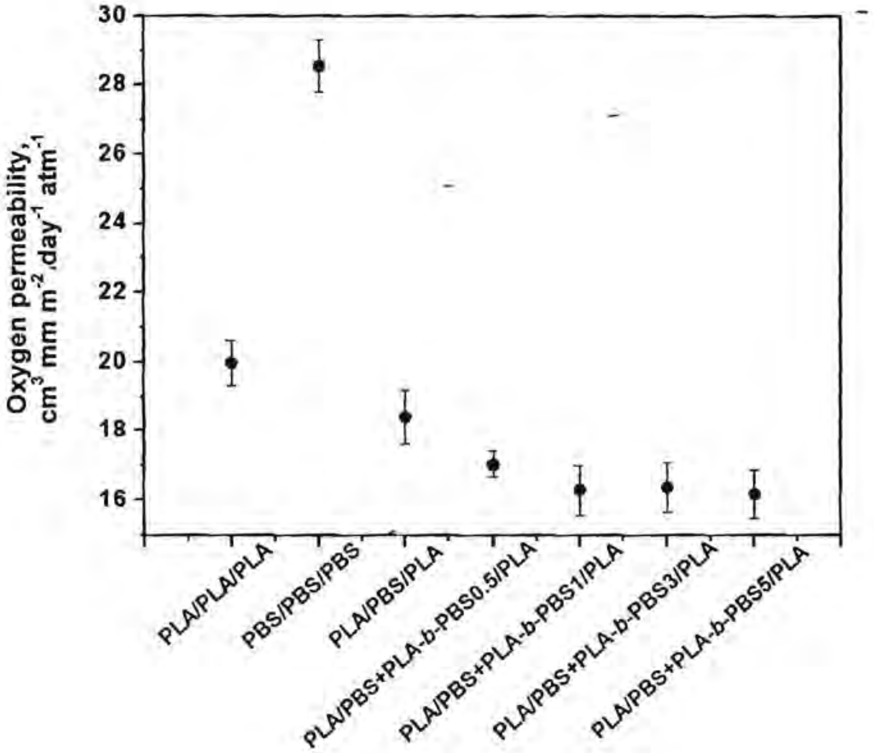


Figure 3.10 Oxygen permeability of PLA/PBS/PLA multi-layered films.

Moreover, XRD analysis was used to characterize the crystallinity pattern of the multi-layered films. The result shows that PBS can induce the crystallization of PLA ($2\Theta = 15.8^{\circ}$) as seen in Figure 3.11c.

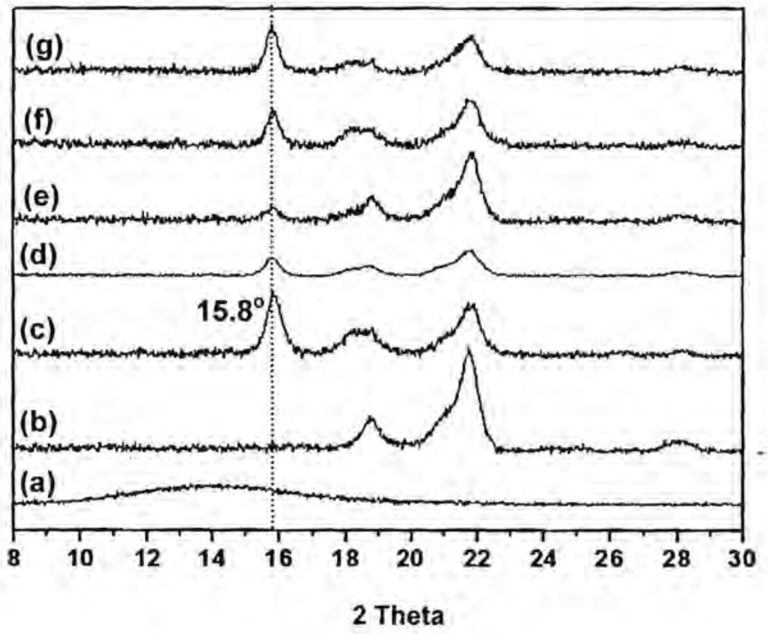


Figure 3.11 XRD pattern of (a) PLA/PLA/PLA, (b) PBS/PBS/PBS, (c) PLA/PBS/PLA, (d) PLA/PBS+PLA-*b*-PBS0.5/PLA, (e) PLA/PBS+PLA-*b*-PBS1/ PLA, (f) PLA/PBS+PLA-*b*-PBS3/PLA, (g) PLA/PBS+PLA-*b*-PBS5/PLA.

3.1.3 Vacuum Applications

Figure 3.12 illustrates PLA/PBS+PLA-*b*-PBS1/PLA multi-layered film in vacuum applications.

Figure 3.12 Vacuum packaging of PLA/PBS/PLA multi-layered film.

3.1.4 Conclusions

The present work demonstrated the PLA/PBS/PLA multi-layered films. By simply copolymerization PLA and PBS with conjugating reaction, PLA-*b*-PBS can be obtained. The addition of PLA-*b*-PBS in PLA/PBS/PLA multi-layered films clarified to us that PLA-*b*-PBS played an important role as compatibility for PLA and PBS. An increased of PLA-*b*-PBS content, in the range of 3-5 phr, led to an increase of film elongation at break for 5-8 times. The compatibility of PLA and PBS also initiated the change in packing structure of PLA as confirmed by the decrease in T_g and T_c as well as the increase in degree of crystallinity. Moreover, oxygen permeability of PLA/PBS/PLA and PLA/PBS+PLA-*b*-PBS/PLA multi-layered films was improved due to the crystallinity factor.

3.2 PLA-based Multi-layered Films with TPS

3.2.1 TPS Characterizations

3.2.1.1 Structural Analysis

The FT-IR spectrum of TPS is represented in Figure 3.13b. The board peak referred to hydroxyl group of pyranose ring in starch molecules shifts to lower wavenumber from at 3395 cm^{-1} to at 3299 cm^{-1}. It indicates that the strong hydrogen bonds in starch molecules become weaker which might be an impact of glycerol penetration in polysaccharide chains obstructing the packing structure. Additionally, the intensity of characteristic peaks in the range of 1200-1100 cm^{-1}, assigned to C-O-C stretching, decrease obviously which points out that chain scission of polysaccharide could occur under extrusion process, and consequently, destroy glycosidic linkage.

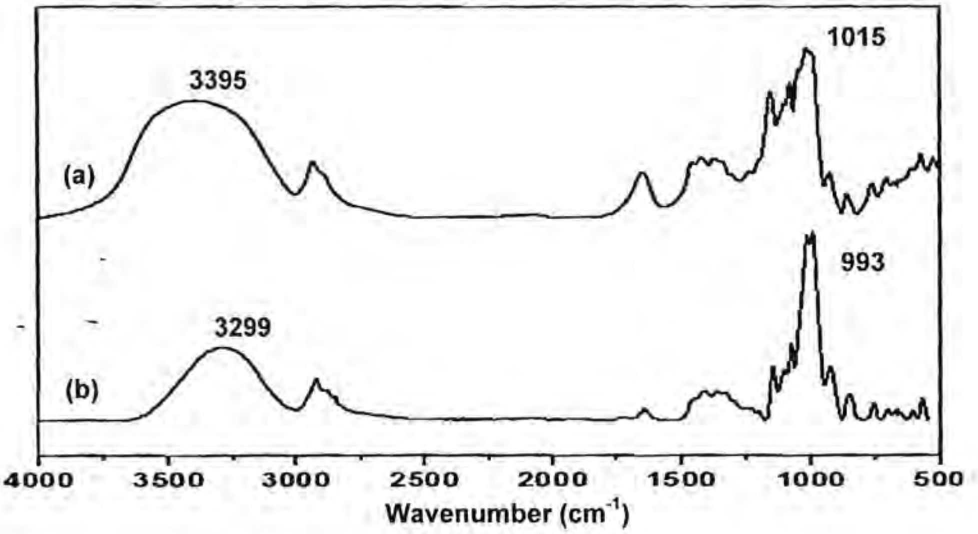


Figure 3.13 FT-IR spectra of (a) dry starch, and (b) TPS.

3.2.1.2 Thermal Analysis

The non-isothermal analysis by DSC technique was applied to study the thermal properties of TPS obtained. Normally, dry starch has high melting temperature (T_m) due to its degradation temperature (T_d) around ~220-230 °C, resulting in degradation before melting. Although TPS was formed, there was no any endothermic peak observed (Figure 3.14).

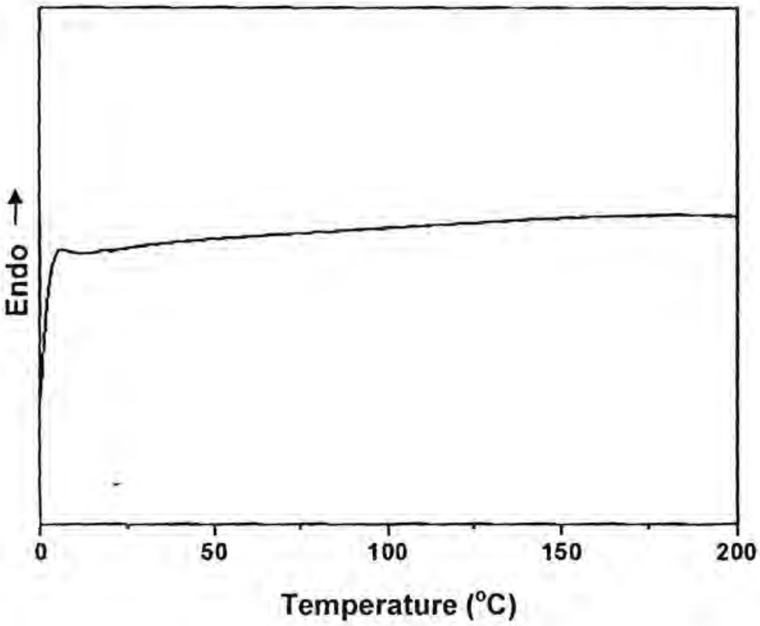


Figure 3.14 DSC curve of TPS.

3.2.1.3 Spherulite Study

In order to follow crystalline morphology change of TPS, the polarizing optical microscope was applied. In general, starch is highly crystalline material with high melting point (~230 °C) and it always shows a characteristic "maltese cross" under polarized light as shown in Figure 3.15a. After extrusion process (Figure 3.15b), the maltese crosses are mostly disappeared in TPS due to the extremely shear force and heat during process which breaks the highly packing structure of starch molecules. Moreover, the glycerol addition also limits the stacking of shorten polysaccharide chains to reform ordered packing.

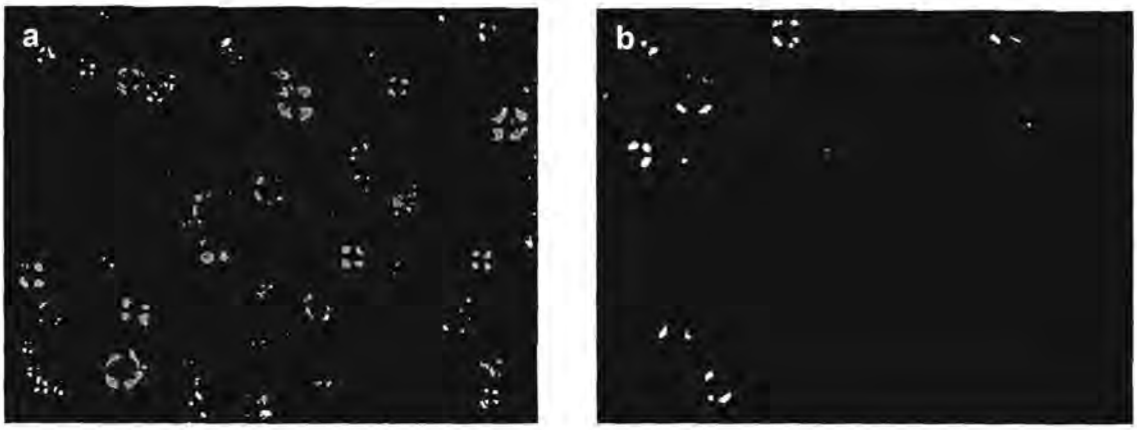


Figure 3.15 Polarizing optical micrographs of (a) tapioca starch and (b) TPS.

3.2.2 Characterizations of PLA/TPS/PLA Multi-layered Films

3.2.2.1 Thermal Properties

Thermal properties of the multi-layered film were studied by non-isothermal temperature profile using DSC technique (Table 3.2). The neat PLA multi-layered film shows the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) at 57 $^{\circ}$C, 101 $^{\circ}$C, and 154 $^{\circ}$C, respectively. The percent of crystallinity (X_c) was around 0 %. In term of TPS, it does not show T_g, T_c, and T_m during non-isothermal study (Guinault *et al.*, 2010).

After the addition of TPS into the PLA-based multi-layered films, it was found that T_g, T_c, and T_m decreased. As T_g represents the mobility of the polymer chains, the lower T_g means the polymer chain can be moved easier, in other word, chain mobility increases when TPS was added into the system. This might be due to the glycerol in TPS can cause plasticization. The shift of the T_c to the lower temperature means that the system allows crystallization easier as evidenced from increasing of crystallinity (X_c). These results implied that TPS can act as plasticizer and nucleating agent.

Table 3.2 Thermal properties of PLA/TPS/PLA multi-layered films

Multi-layered film	$T_{g,PLA}$ (°C)	$T_{m,PLA}$ (°C)	$T_{c,PLA}$ (°C)	X_c (%)
PLA/PLA/PLA	57.7	154.3	101.4	~0
PLA/TPS50/PLA	54.0	147.9	94.6	1.32
PLA/TPS60/PLA	54.6	147.3	95.8	3.45
PLA/TPS70/PLA	54.0	148.8	95.4	4.13
PLA/TPS80/PLA	54.8	148.4	96.2	4.29
PLA/TPS90/PLA	54.2	147.8	95.4	5.50
PLA/TPS100/PLA	53.2	148.1	94.7	6.53

3.2.2.2 Mechanical Properties

Table 3.3 illustrates the mechanical properties of the multi-layered films. The tensile strength and young's modulus of PLA/TPS/PLA multi-layered films decreased compared with the PLA/PLA/PLA multi-layered film. This might be due to the phase separation between PLA and TPS as seen from SEM images (Figure 3.16). However, the elongation at break slightly increased until the core layer is the blend between TPS 90 % and PLA 10 %. For PLA/TPS100/PLA multi-layered film, it is obviously increased in elongation at break because it is more homogeneous in core layer (TPS) (Figure 3.16(f)).

Table 3.3 Mechanical properties of PLA/TPS/PLA multi-layered films

Multi-layered film	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
PLA/PLA/PLA	64.03±0.4	3.47±0.1	7.24±0.2
PLA/TPS50/PLA	44.91±0.3	2.15±0.1	10.28±0.9
PLA/TPS60/PLA	40.05±0.6	2.13±0.04	14.16±0.5
PLA/TPS70/PLA	37.56±0.9	1.91±0.05	14.19±0.3
PLA/TPS80/PLA	35.57±0.8	1.77±0.04	14.95±0.7
PLA/TPS90/PLA	33.83±0.9	2.07±0.03	16.60±1.0
PLA/TPS100/PLA	32.58±0.9	2.04±0.03	26.66±0.6

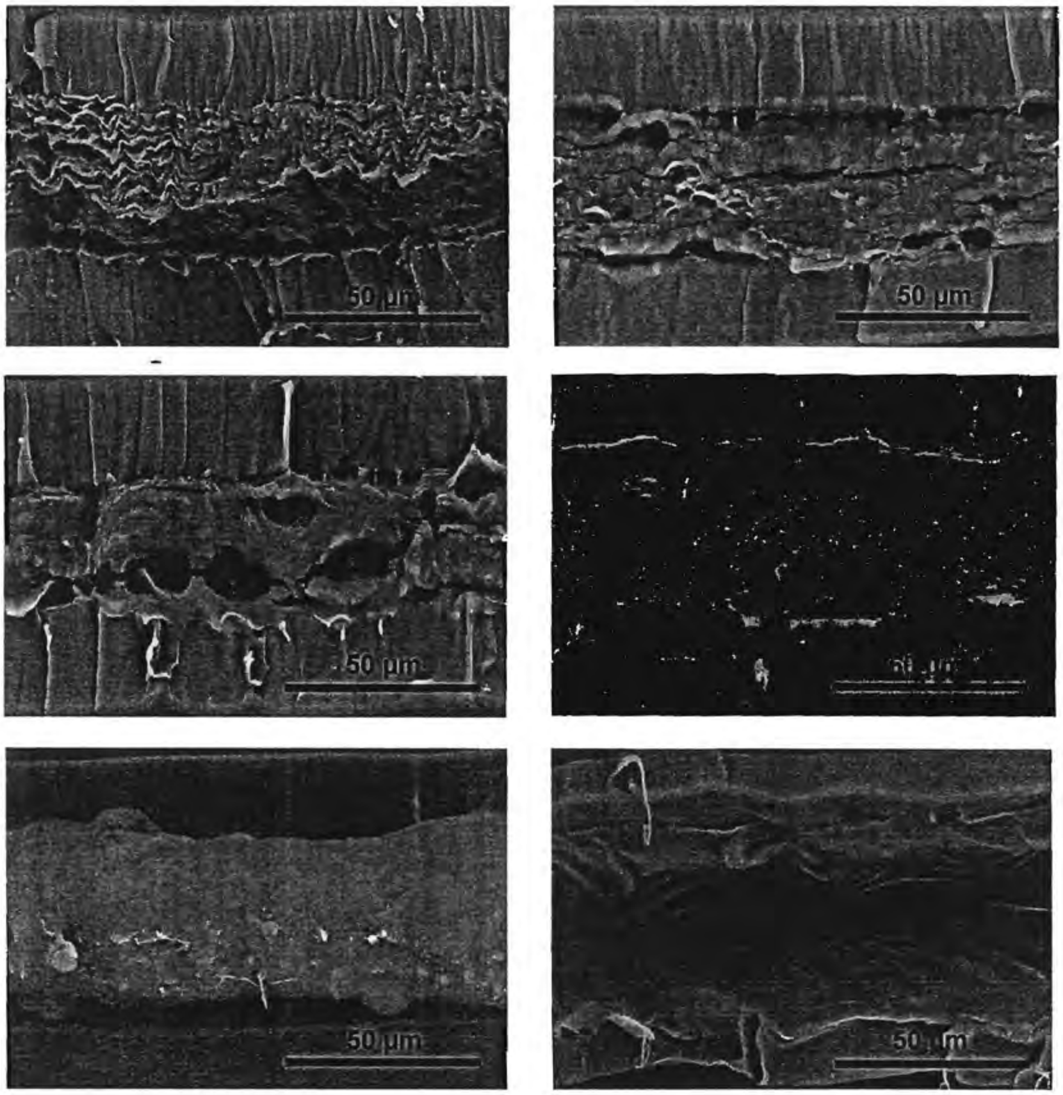


Figure 3.16. SEM images of multi-layered films: (a) PLA/TPS50/PLA, (b) PLA/TPS60/PLA, (c) PLA/TPS70/PLA, (d) PLA/TPS80/PLA, (e) PLA/TPS90/PLA, and (f) PLA/TPS100/PLA.

3.2.2.3 Water Absorption

In general, PLA is a hydrophobic polymer while starch is a hydrophilic polymer due to an abundance of hydroxyl groups. Figure 3.17 illustrates the percent of water absorption of the multi-layered films submerged in water chamber at 25 °C. The result shows that an increase of TPS content in PLA-based multi-layered films led to an increase of amount of water containing in the films. For 100 % TPS in the multi-layered film (PLA/TPS100/PLA), it can take up the water inside the films from 0.3 % to 115 % compared with neat PLA film (PLA/PLA/PLA). It indicated that the TPS was the major effect on the water absorption of the multi-layered films. All of the multi-layered films containing TPS were constant when the time passed for 6 days.

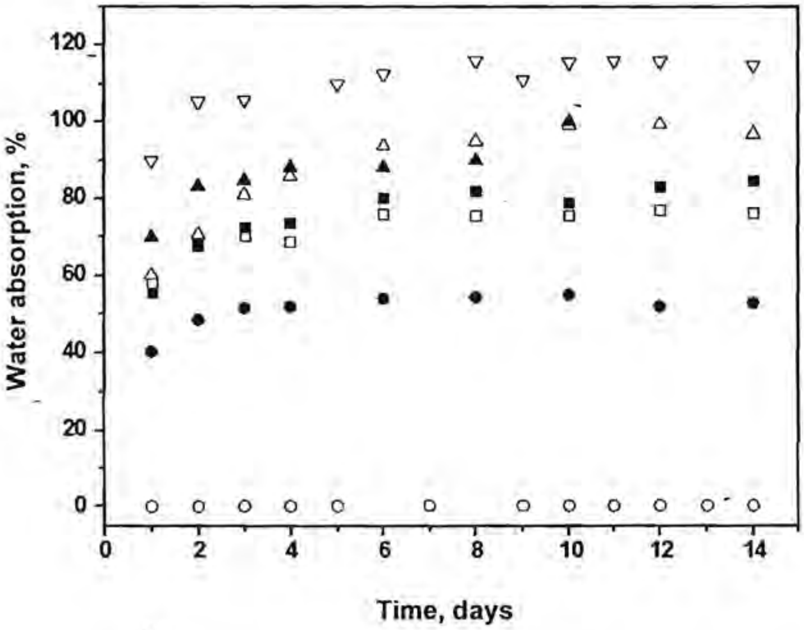


Figure 3.17 Effect of moisture content in the PLA/TPS/PLA multi-layered films on water absorption behavior: (○) PLA/PLA/PLA, (●) PLA/TPS50/PLA, (□) PLA/TPS60/PLA, (■) PLA/TPS70/PLA, (△) PLA/TPS80/PLA, (▲) PLA/TPS 90/PLA, and (▽) PLA/TPS100/PLA.

3.2.2.4 Oxygen Permeability

The oxygen permeability of multi-layered films was presented in Figure 3.18. Oxygen permeability of neat PLA film is about 20 cm^3 mm m^{-2} day^{-1} atm^{-1}. When TPS was combined into multi-layered films, the oxygen permeability decreased. As TPS can form H-bonding between polymer chains, this might result in tight packing structure obstructed O_2 molecules passing through the films. Another factor affected on oxygen permeability is crystallinity.[11] As shown in Table 3.2, it was found that an increase in crystallinity was observed with increasing TPS content.

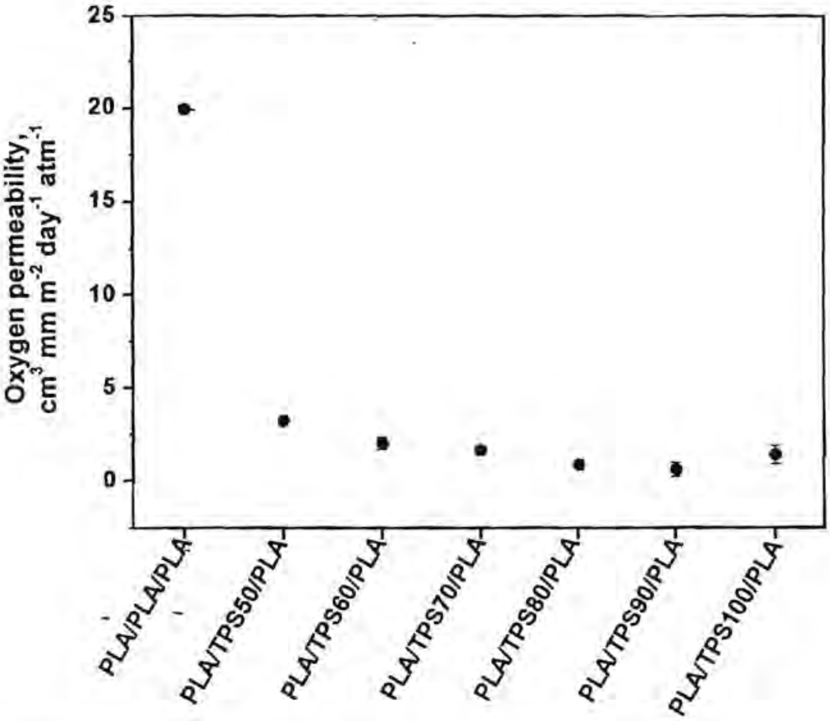


Figure 3.18 Oxygen permeability of PLA/TPS/PLA multi-layered films.

3.2.3 Conclusions

The present work proposed the biodegradable multi-layered films between PLA and TPS. The TPS and TPS blended with PLA were added in the core layer of PLA-based multi-layered films. The elongation at break was improved when the 100 % TPS content in core layer (PLA/TPS100/PLA) was performed. However, the water absorption obviously increased as the content of TPS increased. Furthermore, the addition of TPS into PLA-based multi-layered film resulted in a decrease of oxygen permeability.

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CONCLUSIONS

This work aims to create the value-added biodegradable multi-layered films of PLA, PBS, and TPS. The research consists of two parts. In the first part, PLA and PBS were formed as the multi-layered film. The phase separation between PLA and PBS was studied by adding PLA-*b*-PBS copolymer as a compatibilizer. The PLA-*b*-PBS was simply prepared through conjugating reaction. The addition of PLA-*b*-PBS resulted in an improvement in oxygen barrier and mechanical properties of multi-layered films.

In the second part, biodegradable multi-layered film is the combination between PLA and TPS. The addition of TPS into multi-layered films not only led to cost saving but also resulted in an improvement in mechanical and oxygen barrier properties. However, the more of TPS content increases the percent of water absorption which might impact to the quality of the films.

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Professional Experience:

July 2012 - Present	President of Polymer Society of Thailand
Oct. 2009 - Present	Professor in Polymer Science and Engineering, The Petroleum and Petrochemical College, Chulalongkorn University
Oct. 2007- Sep. 2008	Associate Dean of Research Affairs, The Petroleum and Petrochemical College, Chulalongkorn University

Oct. 2004 - Oct. 2007 Deputy Director of Research Affairs, The Petroleum and Petrochemical College, Chulalongkorn University

Jun. 2002 - Present Vice Center-Head, Center for Chitin-Chitosan Biomaterials, Chulalongkorn University

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Honors and Awards:

1. รางวัลอาจารย์ดีเด่นแห่งชาติ (ปอมท.), 2013
2. PTIT Innovation Award, 2011.
3. Best National Researcher: Chemical and Pharmaceutical Science, National Research Council of Thailand, 2009
4. Innovation Ambassador: Bio-based Materials/ National Innovation Agency, 2009.
5. Thailand Innovation Awards/ PTT Chem. and Ministry of Science and Technology, 2007.
6. Innovation Ambassador/ National Innovation Agency, 2006.
7. Micrograph Award (3rd prize), Microscopy Society of Thailand, 2006.
8. Hitachi Fellowship Scholar from Hitachi Scholarship Foundation, 1995-Present.

Research Activities:

A) Publications (lastet 5 years): (*: Corresponding Author)

1. Jarumaneeroj, C., Tashiro, K., Chirachanchai, S., "Shifting from Hydrogen Bond Network to $\pi - \pi$ Stacking: A Key Mechanism for Reversible Thermochromic Sulfonated Poly

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2. Jirawutthiwongchai, J.; Draeger, G.; Chirachanchai, S., "Rapid Hybridization of Chitosan-Gold-Antibody via Metal-free Click in Water basedSystem: a Model Approach for Naked-eye Detectable Antigen Sensor", Macromolecular Rapid Communications, *in press*, 2014. (Impact Factor 2013 : 4.608)
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5. Patomporn Chantarasataporna, Preenapha Tepkasikuld, Yuthana Kingchad, Rangrong Yoksane, Rath Pichyangkuraf, Wonnop Visessanguand, Suwabun Chirachanchai, "Water-based Oligochitosan and Nanowhisker Chitosan as Potential Food Preservatives for Shelf-life Extension of Minced Pork", Food Chemistry, 159, 463-470,2014 (Impact factor 2013 : 3.259)

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8. Phuphuak, Y.; Miao Y.;Zinck, P.; Chirachanchai S.* "Balancing Crytalline and Amorphous Domains in PLA through Star-structured Polylactide with Dual Plasticizer Nucleating Agent Functionality", Polymer, 54, 16, 7058-7070, 2013 (Impact Factor 2012 : 3.379)
9. Suchao-in, K. and S. Chirachanchai ""Grafting to" as a Novel and Simple Approach for Triple-Shape Memory Polymers", ACS Applied Materials & Interfaces, 5, 15, 6850-6853, 2013 (Impact Factor 2012 : 5.008)
10. Chatrabhuti, S. and S. Chirachanchai "Chitosan Core-corona Nanospheres: A Convenient Material to Tailor pH and Solvent Responsive Magnetic Nanoparticles." Polymer, 54, 16, 4318-4324, 2013 (Impact Factor 2012 : 3.438)
11. Chatrabhuti, S.; Chirachanchai, S.* "Single Step Coupling for Multi-responsive Water-based Chitin/Chitosan Magnetic Nanoparticles", Carbohydrate Polymers, 97, 2, 441-450, 2013. (Impact factor 2012 : 3.628)
12. Jirawutthiwongchai, J.; Krause, A.; Draeger, G.; Chirachanchai, S.* "Chitosan-Oxanorbornadiene: A Convenient Chitosan Derivative for Click Chemistry without

Metal Catalyst Problem", ACS Macro Letters, 2, 177–180, 2013. (Impact Factor 2012 : None)

13. Chantarasataporn, P.; Yoksan, R.; Visessanguan, W.; Chirachanchai, S.* "Water-based Nano-sized Chitin and Chitosan as Seafood Additive through a Case Study of Pacific White Shrimp (Litopenaeus vannamei)", Food Hydrocolloids, 32, 2, 341-348, 2013. (Impact Factor 2012 : 3.460)
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15. Pangon, A.; Chirachanchai, S.* "Poly(acrylic acid) containing multi-benzimidazole units: A simple approach to obtain polymer with proton donor-acceptor system", Polymer, 53, 3878-3884, 2012. (Impact Factor 2011 : 3.573)
16. Rungswang, W.; Kato, K.; Kotaki, M.; Chirachanchai, S.* "Size-controllable nanospheres prepared by blending a thermoset monomer in confined morphology with thermoplastic elastomer", Polymer, 53, 1167-1171, 2012. (Impact Factor 2011 : 3.573)
17. Rungswang, W.; Chirachanchai, S.*; Kotaki, M.; Sakurai, S.; Kimura, G.; Shimojima, T. "Directing Thermoplastic Elastomer Micredomain Parallel to Fiber Axis: A Model Case of SEBS with Benzoxazine through π-π Stacking", Macromolecules, 44, 9276–9285, 2011. (Impact Factor : 4.837)
18. Pangon, A., Tashiro, K., Chirachanchai, S. * "Polyethylenimine Containing Benzimidazole Branching: A Model System Providing a Balance of Hydrogen Bond

Network or Chain Mobility Enhances Proton Conductivity", Journal of Physical Chemistry Part B, 115, 11359–1367, 2011. (Impact Factor : 3.603)

19. Pangon, A., Totsatitpaisan, P., Eiamlamai, P., Hasegawa, K., Yamasaki, M., Tashiro, K., Chirachanchai, S.* "Systematic studies on benzimidazole derivatives: Molecular structures and their hydrogen bond networks formation toward proton transfer efficiency", Journal of Power Sources, 196, 6144–6152, 2011. (Impact Factor : 3.792)
20. Jithunsa, M., Tashiro, K., Nunes, S. P., Chirachanchai, S.* "Poly(acrylic acid-co-4-vinylimidazole)/ Sulfonated poly(ether ether ketone) blend membranes: A role of polymer chain with proton acceptor and donor for enhancing proton transfer in anhydrous system" International of Journal of Hydrogen Energy, 36, 10384-10391, 2011. (Impact Factor 2010 : 3.945)
21. Rungswang, W., Kotaki, M., Shimojima, T., Kimura, G., Sakurai, S., Chirachanchai, S.*, "Existence of microdomain orientation in thermoplastic elastomer through a case study of SEBS electrospun fibers" Polymer, 52, 844-853, 2011. (Impact Factor : 3.573)
22. Rungswang, W. , Chirachanchai, S.*, "Formation of Thermosets via Molecular Pockets in Thermoplastic Chains: A Simple and Direct Way to Nanospherical Thermosets" Macromolecular materials and Engineering, 296, 428-433, 2010 (Impact factor : 1.742)
23. Yoksan, R. *, Chirachanchai, S., "Silver nanoparticle-loaded chitosan-starch based film: Fabrication and evaluation of tensile, barrier and antimicrobial properties" Material Science and Engineering C, 30, 891-897, 2010. (Impact Factor 2008: 1.842)

B) Books

1. Chirachanchai, S.; Pangon, A.; Jarumaneeroj, C. "High Temperature Performance PolymerElectrolyte Membranes" In "Membrane ProcessesFor Sustainable Growth" ; Basile, A.; Cassano, A.; Nova Publisher, London, UK, 2013; pp. 247-288
2. Chirachanchai S.; Phongtamrug S.; and Tashiro K. "Supramolecular Chemistry of Benzoxazines: From Simple, Selective, Effective, and Efficient Macrocyclization Pathways to Host-Guest Properties" In Handbook of Benzoxazine Resins; Ishida, H.; Agag, T.; Eds.; Elsevier's Science & Technology: Oxford, London, UK, 2011; pp 332-355.
3. Chirachanchai S.; Phongtamrug S.; Laobuthee A.; and Tashiro K. "Mono-Substituted Phenol-Based Benzoxazines: Inevitable Dimerization via Self-Termination and Its Metal Complexation" In Handbook of Benzoxazine Resins; Ishida, H.; Agag, T.; Eds.; Elsevier's Science & Technology: Oxford, London, UK, 2011; pp 112-127.

C) Patents:

1. Chirachanchai, S.; บริษัท อุตสาหกรรมถุงพลาสติกไทย จำกัด (Thai Plastic Bags Industries Co.,Ltd) ; บริษัท วัลย์ดีพาณิชย์อุตสาหกรรม จำกัด (Wandee Panich Industry Co.,Ltd.) "แป้งปรับสภาพผิวเพื่อการผสมเนื้อเดียวกับพอลิเอสเทอร์แตกสลายได้ (Surface modified starch for homogeneous blend with polyester biodegradable plastics)", สถาบันทรัพย์สินทางปัญญาแห่งจุฬาลงกรณ์มหาวิทยาลัย, Patent pending.
2. Ichikawa, N.; Chirachanchai, S. (2007) "Chitosan Derivative and Polymer Coagulant", Japanese Patent (JP2007119533).

3. Phongying, S.; Lertwattanaseri, T.; Chirachanchai, S.* (2006) "Chitosan Nanoscaffold", Thai Patent Application, patent pending.
4. Chirachanchai, S.; Fungkangwanwong, J. (2006), "Chitosan Superabsorbent Gel", Thai Patent Application, patent pending.
5. Fungkangwanwong, J.; Yoksan, R.; Chirachanchai, S. (2006), "Preparation of Chitosan Aqueous Solution", Thai Patent Application, patent pending.
6. Pasanphan, W.; Chirachanchai, S. (2006), "Material for the Breeding Prevention of Apple Snails". Thai Patent Application, patent pending.