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.

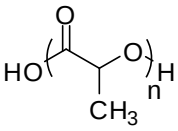
1.4.2 Biodegradable Polymers

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

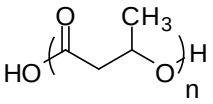
microorganisms such as bacteria, fungi, and algae, and the second one is non-enzymatic processes such as chemical hydrolysis (Gross *et al.*, 2002). By-products of degradation process are carbon dioxide (CO_2), water (H_2O), and biomass which can be converted to be a new renewable material as shows in Figure 1.1 (Siracusa *et al.*, 2008).

Scheme 1.1

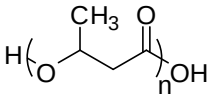
Renewable resources



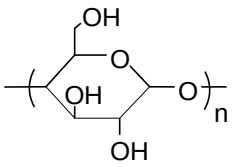
Poly(lactic acid), PLA



Poly(hydroxybutylene), PHB

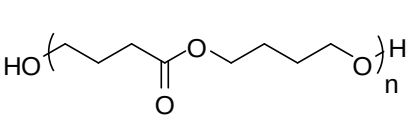


Poly(hydroxyvalerate), PHV

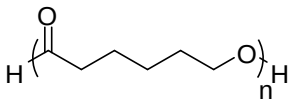


Starch

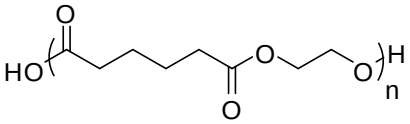
Petroleum resources



Poly(butylene succinate), PBS



Poly(caprolactone), PCL



Poly(ethylene adipate), PEA

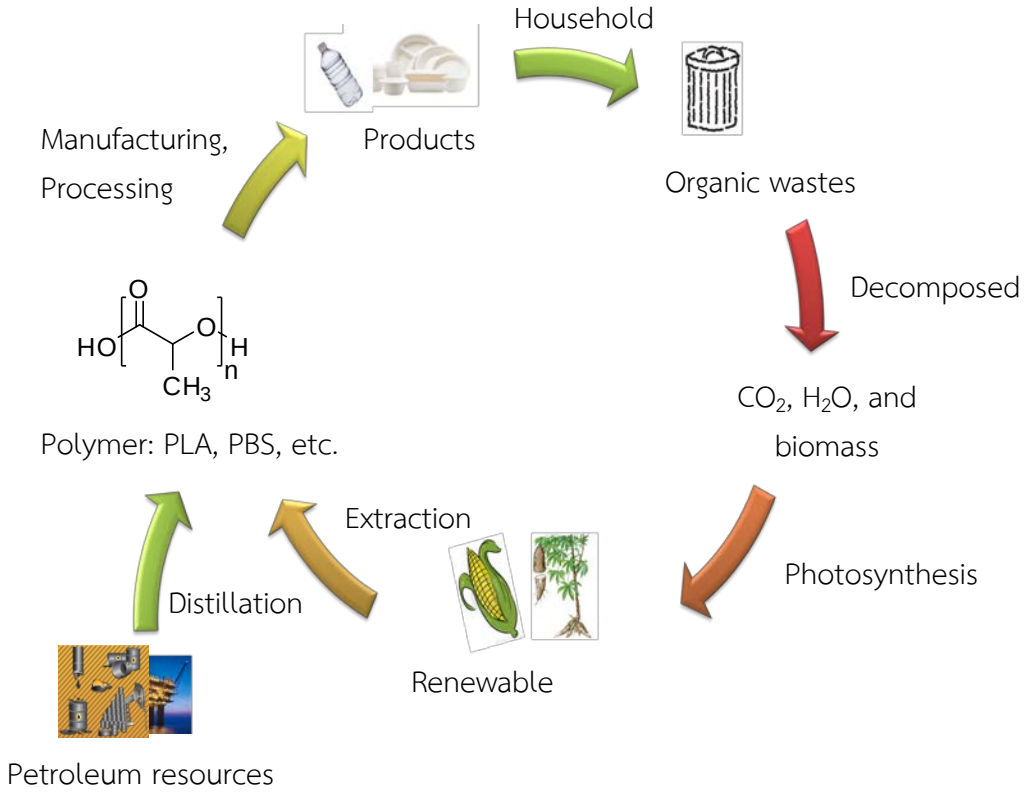


Figure 1.1 Cycle processes of biodegradable polymers.

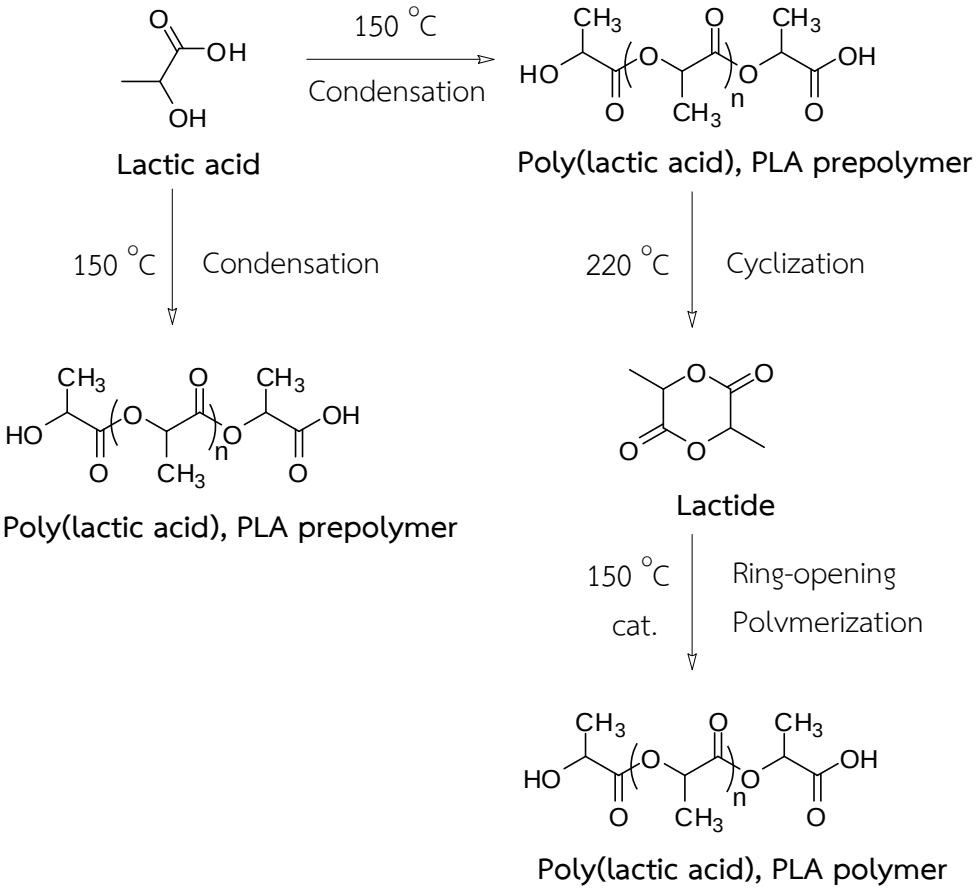
1.4.3 Poly(lactic acid) (PLA)

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).

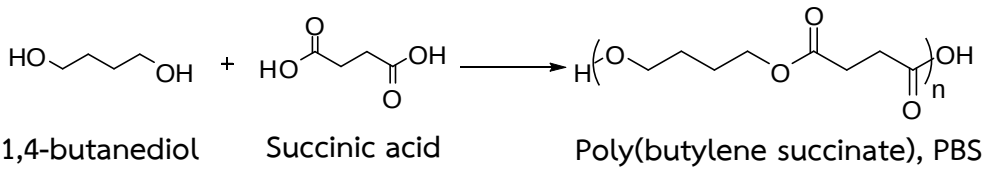
Scheme 1.2



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-butanediol **Succinic acid** **Poly(butylene succinate), PBS**

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.