CHAPTER V
POLY(LACTIC ACID)/THERMOPLASTIC STARCH MULTI-LAYERED FILMS

5.1 Abstract

Poly(lactic acid) (PLA) and thermoplastic starch (TPS) multi-layered films are formed by using blown-film co-extrusion process. In non-isothermal crystallization studies, it indicates that TPS can act as plasticization and nucleation for PLA as evidenced from an increasing of crystallinity. The mechanical properties, especially elongation at break improve by adding TPS content in PLA-based multi-layered films. The addition of TPS content shows an increasing of water absorption. Moreover, TPS effects on oxygen permeability by decreasing the O_2 molecules pass through the multi-layered films.

Keyword: multi-layered film, poly(lactic acid), thermoplastic starch (TPS)

5.2 Introduction

Multi-layered film is one of s potential approach to combine two or more polymers together with properties enhancement. In daily life, the well-known products made of multi-layered film are syringe, cheese, and rice packaging, etc.[1] At present, conventional multi-layered films, petroleum-based polymers, are satisfying the basic functions in term of transparency, high modulus, and high strength. And specific functions, for instance, Thellen et al. reported multi-layered film of polyamide incorporated with low-density polyethylene which provided good oxygen barrier.[2]

Currently, biodegradable polymers are recognized as the materials for environmental friendly. The use of them reduces disposal problem. However, biodegradable polymers have the main limitation because their cost is higher than conventional petroleum-based ones.[3] Based on this view point, in order to add value to biodegradable polymers, creating multi-layered film was proposed.

One of the most potential biodegradable polymers is poly(lactic acid) (PLA) and thermoplastic starch (TPS). PLA possess a tremendous market potential due to the properties of high strength and modulus, transparency, and moderate barrier properties.[4,5,6] For TPS, it is abundant and renewable polymer which provides completely biodegradability and inexpensive.[7,8] Thereby it often used to reduce cost of the products.

Here, we proposed value-added biodegradable multi-layered film between PLA and TPS by blown-film co-extrusion process. The effect of adding TPS was studied in terms of thermal, mechanical, water absorption, and oxygen barrier properties compared to neat PLA multi-layered film.

5.3 Experimental Section

5.3.1 Materials

Commercial PLA (2003D) was purchased from NatureWorks LLC, USA. Tapioca starch was purchased from ETC International Trading Co., Ltd., Thailand. Glycerol was bought from Siam Absolute Chemicals Co., Ltd., Thailand.

5.3.2 Instruments

5.3.2.1 Thermal Analysis

Thermal properties were carried out by a DSC 200 F3 Maia NETZCH differential scanning calorimetry (DSC). Dry nitrogen gas was allowed to flow. The samples were heated at 5 ^{o}C min^{-1}. The temperature ranged between 0 and +200 ^{o}C. The percent of crystallinity (X_c)[9] of the multi-layered films was calculated by the equation below:

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

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^o is the reference value of melting enthalpy which represents the perfect crystalline PLA homopolymer (93.01 J/g)[10]. All of the data was determined through first heating scan.

5.3.2.2 Mechanical Testing

Tensile strength, elongation at break, and Young's modulus were evaluated by a LRX LLOYD universal testing machine with a 500 N load cell. The testing was followed the ASTM Standard D 638M-91a. The five specimens were tested on each test.

5.3.2.3 Morphology Analysis

A TM3000 Hitachi scanning electron microscope (SEM) was used to observe morphology of samples. The samples were coated with a thin layer of platinum. The accelerating voltage of machine was 15 kV to produce SEM images.

5.3.2.4 Barrier Study

Oxygen transmission rate (OTR) was evaluated by an Ox-Tran 2/21 MOCON oxygen analyzer with an oxygen flow rate 20 cm^3/min at 23 °C at 0% RH. The testing was carried out according to ASTM Standards D3985-81.

5.3.3 Methodology

5.3.3.1 Preparation of Thermoplastic Starch (TPS)

Tapioca starch and glycerol were mixed together at a weight ratio of 70/30 and gelatinized by a Labtech Engineering LTE 20-40 counter-rotating twin screw extruder. The temperature and screw speed setting were in the range of 130-170 °C and 40-50 rpm, respectively. The TPS obtained was quenched to the room temperature before cutting into pellet form (2.5 mm).

5.3.3.2 TPS Blend Preparation

TPS pellet was dried in a vacuum oven at 60 °C for 1 day. The TPS blended with PLA resin (2003D) was extruded by a Labtech Engineering LTE 20-40 counter-rotating twin screw extruder in various weight ratios (TPS/PLA 90/10, 80/20, 70/30, 60/40, and 50/50 w/w). All of the extruded processes were the temperature in range of 130-170 °C with 20-50 rpm of screw speed settings.

5.3.3.3 PLA/TPS/PLA Multi-layered Films Procedure

The multi-layered films were formed as the same instrument as the PLA/PBS/PLA multi-layered films. Temperature profile was set at 170-180 °C.

Table 5.1 Structure of PLA/TPS/PLA multi-layered films

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

5.4 Results and Discussion

5.4.1 Thermal Properties

Thermal properties of the multi-layered film were studied by non-isothermal temperature profile using DSC technique (Table 5.2). The neat PLA multi-layered film shows the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) at 57 °C, 101 °C, and 154 °C, respectively. The percent of crystallinity ($X_{c,Tm-Tc}$) was around 0 %. In term of TPS, it does not show T_g, T_c, and T_m during non-isothermal study.[11]

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 ($X_{c,Tm-Tc}$). These results implied that TPS can act as plasticizer and nucleating agent.

Table 5.2 Thermal properties of PLA/TPS/PLA multi-layered films

Multi-layered film	$T_{g,PLA}$ (°C)	$T_{m,PLA}$ (°C)	$T_{c,PLA}$ (°C)	$X_{c,Tm-Tc}$ (%)
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

*All of the data obtained from the first scan.

5.4.2 Mechanical Properties

Table 5.3 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 5.1). However, the elongation at break slightly increased until the core layer is the blend between TPS 90 % and PLA10 %. 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 5.1(f)).

Table 5.3 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

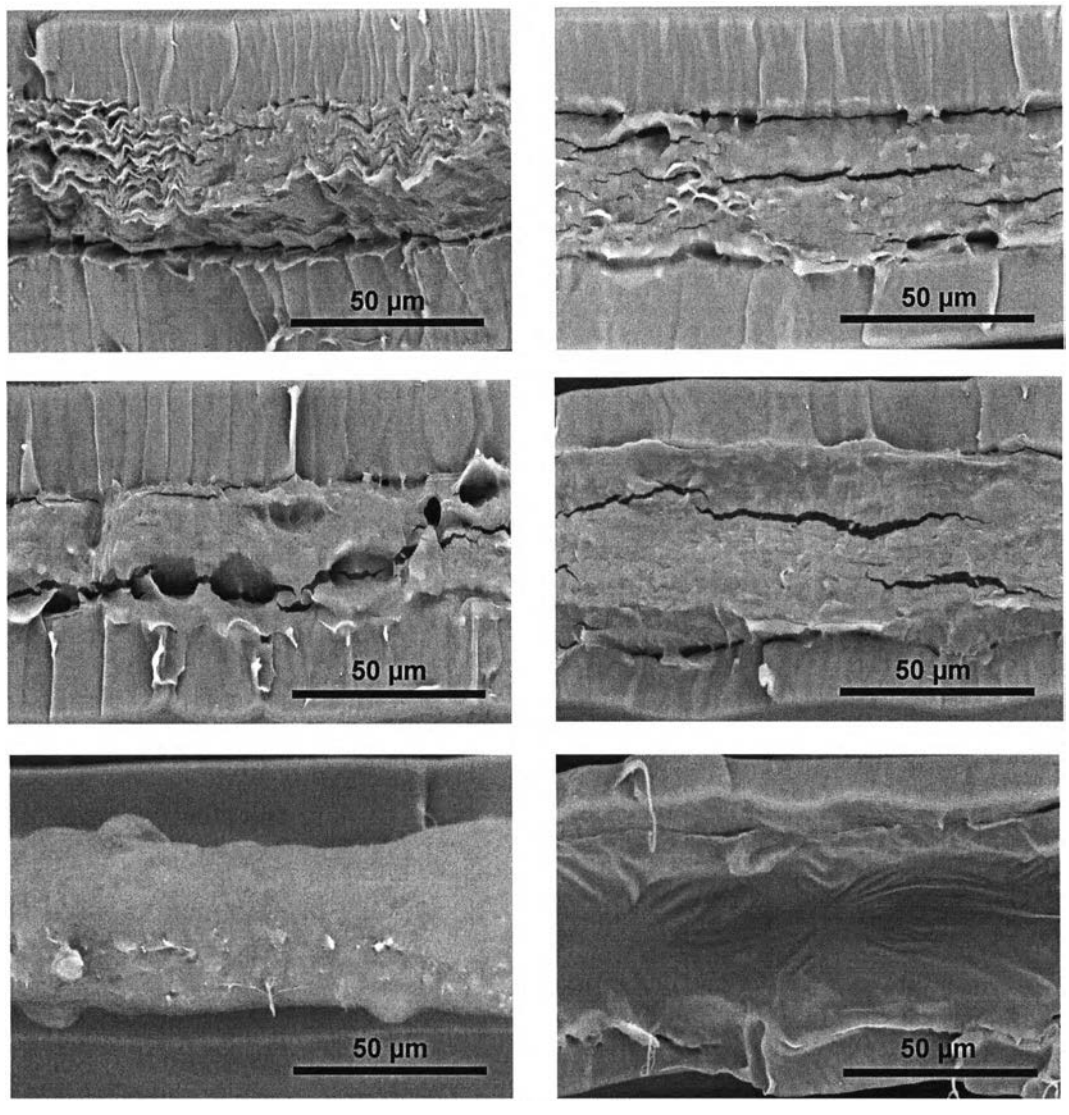

Figure 5.1 SEM images of multi-layered films: (a) PLA/TPS50/PLA, (b) PLA/TPS60/PLA, (c) PLA/TPS70/PLA, (d) PLA/TPS80/PLA, (e) PLA/TPS90/PLA, and (f) PLA/TPS100/PLA.

5.4.3 Water Absorption

In general, PLA is a hydrophobic polymer while starch is a hydrophilic polymer due to an abundance of hydroxyl groups. Figure 5.2 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.

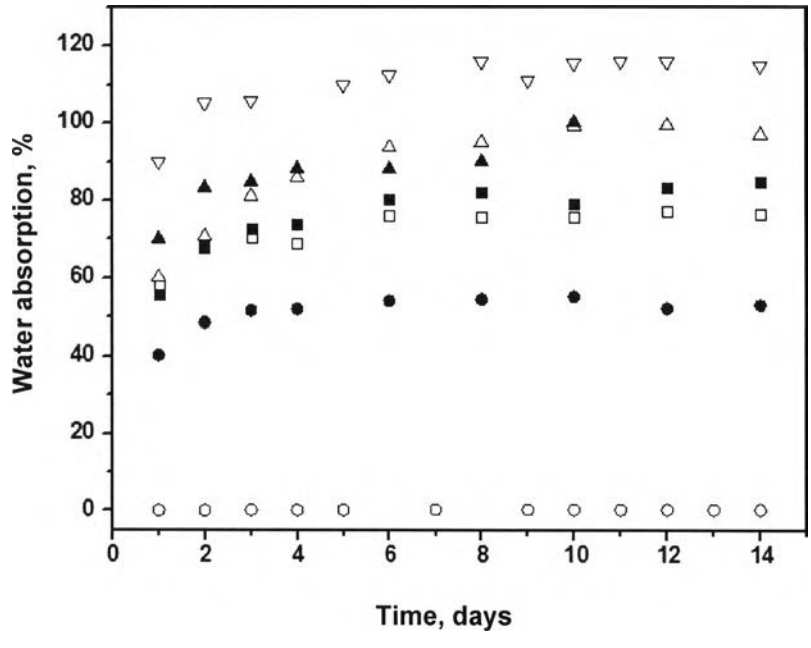

Figure 5.2 Effect of moisture content in the PLA/TPS/PLA multi-layered films on water absorption behavior: (○) PLA/PLA/PLA, (●) PLA/TPS50/PLA, (□) PLA/TPS60/PLA, (■) PLA/TPS70/PLA, (△) PLA/TPS80/PLA, (▲) PLA/TPS 90/PLA, and (▽) PLA/TPS100/PLA.

5.4.4 Oxygen Permeability

The oxygen permeability of multi-layered films was presented in Figure 5.3. 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 5.2, it was found that an increase in crystallinity was observed with increasing TPS content.

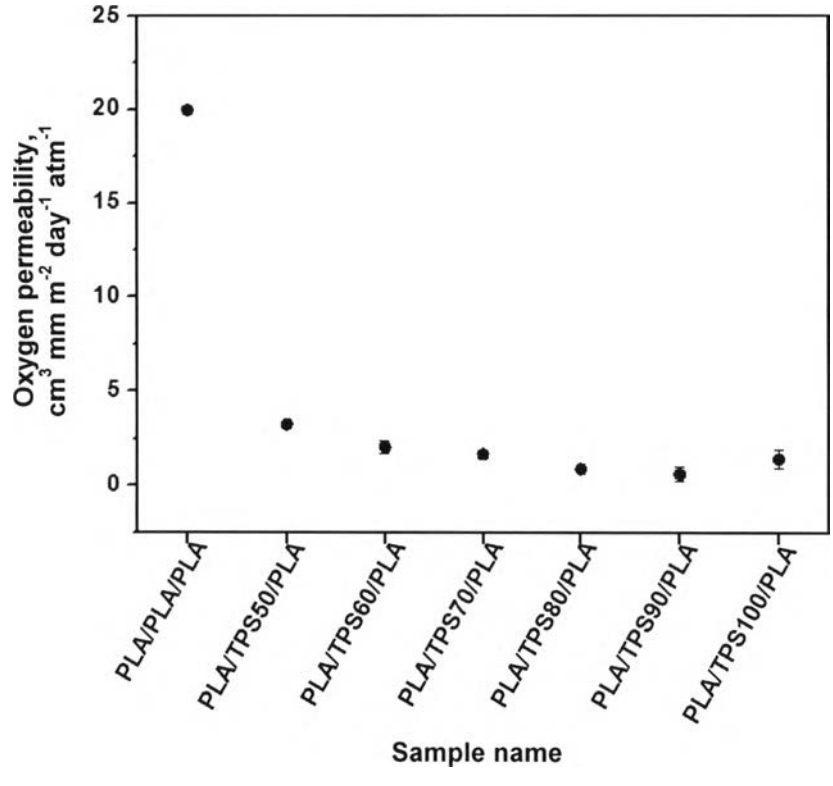

Figure 5.3 Oxygen permeability of PLA/TPS/PLA multi-layered films.

5.5 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.

5.6 Acknowledgements

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