DEVELOPMENT OF BIOPLASTIC BLOWN FILMS TO BE USED AS A PACKAGING FOR DRIED BANANA

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น.ส.อภิญญา วงศ์ธนโรจน์

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อภิญญา วงศ์ธนโรจน์ : การพัฒนาฟิล์มพลาสติกชีวภาพเพื่อใช้เป็นบรรจุภัณฑ์สำหรับกล้วยตาก. (DEVELOPMENT OF BIOPLASTIC BLOWN FILMS TO BE USED AS A PACKAGING FOR DRIED BANANA) อ.ที่ปรึกษาหลัก : รศ. ดร.อนงค์นาฏ สมหวังธนโรจน์, อ.ที่ปรึกษาร่วม : รศ. ดร.ขนิษฐา ธนานุวงศ์

งานวิจัยนี้ฉบับได้ทำการศึกษาผลของปริมาณ poly(butylene adipate-co-terephthalate) (PBAT) ต่อ คุณสมบัติของการผสมของ polylactic acid / poly(hydroxybutyrate-co-hydroxyvalerate) / poly (butylene adipate-co-terephthalate) (PLA/PHBV/PBAT) เพื่อใช้เป็นบรรจุภัณฑ์สำหรับเก็บกล้วยตาก ซึ่งทำการผสม PLA/PHBV ในอัตราส่วนร้อยละ 80/20 โดยน้ำหนัก โดยมีปริมาณของ PBAT อัตราส่วนร้อยละ 0-30 โดยน้ำหนัก แล้วทำการหลอมผสมและเป่าขึ้นรูปเป็นฟิล์ม ผลการศึกษาพบว่าการเติม PBAT ใน PLA/PHBV ลดสมบัติการกั้นผ่านแก๊สของ PLA/PHBV โดยสมบัติการกั้นผ่านแก๊สสามารถพิจารณาได้จากอัตราการซึมผ่านออกซิเจนและไอน้ำ ซึ่งมีค่าเพิ่มสูงขึ้นเมื่อมีปริมาณของ PBAT เพิ่มขึ้น สำหรับการผสมในทุกอัตราส่วนพบว่าให้ค่าสมบัติการกั้นผ่านที่ยอมรับได้เพื่อใช้ในการเก็บกล้วยตาก และยังพบว่าที่ปริมาณ PBAT ร้อยละ 20 โดยน้ำหนัก ให้คุณสมบัติความยืดหยุ่นสูง งานวิจัยเล่มนี้ยังศึกษาสัณฐานวิทยา และสมบัติเชิงความร้อนอีกด้วย ดังนั้นการผสม PLA/PHBV ด้วยปริมาณ PBAT ร้อยละ 20 โดยน้ำหนัก (PB2) ถูกเลือกเพื่อนำไปบรรจุกล้วยตากเป็นระยะเวลา 4 เดือนที่อุณหภูมิห้อง การเปลี่ยนแปลงสี, ปริมาณน้ำ, ค่ากิจกรรมของน้ำ และเนื้อสัมผัสของกล้วยตากถูกศึกษาในระหว่างการเก็บ โดยมีกล้วยตากที่บรรจุใสในบรรจุภัณฑ์ที่ใช้ทั่วไปถูกทดสอบเพื่อเป็นตัวควบคุม จากผลการศึกษาพบว่า การเปลี่ยนแปลงสีของกล้วยในทั้งสองบรรจุภัณฑ์แสดงผลที่คล้ายกัน อย่างไรก็ตาม ที่เวลาการเก็บรักษาเท่ากัน กล้วยตากที่บรรจุในบรรจุภัณฑ์ PB2 พบว่ามีปริมาณน้ำและค่ากิจกรรมของน้ำที่ต่ำกว่ากล้วยตากที่บรรจุในบรรจุภัณฑ์ที่ใช้ทั่วไป ส่งผลให้มีค่าความแข็งที่เนื้อสัมผัสสูงกว่า ยิ่งไปกว่านั้น ไม่พบการแตกหักของฟิล์ม PB2 เมื่อนำไปฝังดินเป็นระยะเวลา 6 เดือนเนื่องจากไม่มีการควบคุมอุณหภูมิ, ปริมาณน้ำ และค่า pH ของดินให้เหมาะสม

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อนิสิต .....

ปีการศึกษา 2562 ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

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Apinya Wongthanaroj : DEVELOPMENT OF BIOPLASTIC BLOWN FILMS TO BE USED AS A PACKAGING FOR DRIED BANANA . Advisor: Assoc. Prof. ANONGNAT SOMWANGTHANAROJ, Ph.D. Co-advisor: Assoc. Prof. KANITHA TANANUWONG, Ph.D.

This research aimed to study effects of poly(butylene adipate-co-terephthalate) (PBAT) contents on properties of polylactic acid / poly(hydroxybutyrate-co-hydroxyvalerate) / poly (butylene adipate-co-terephthalate) (PLA/PHBV/PBAT) blends to be used as a packaging for solar-dried bananas. The blend of PLA and PHBV (PLA/PHBV) was fixed at weight ratio of 80/20 while the PBAT content was varied from 0-30 wt%. The films were prepared by melt compounding and blown film extrusion. It was found that the addition of PBAT decreased barrier properties of PLA/PHBV film. Gas barrier which is oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) increased with increasing of PBAT content. The barrier properties of all blends were shown the acceptable values for dried banana storage. It was found that the blend with 20% of PBAT content show high flexibility. Meanwhile, morphology and thermal properties of films were also studied. Hence, PLA/PHBV with 20% PBAT (PB2) was selected to pack dried banana for 4 months at room temperature. Color change, moisture content, water activity and texture of dried banana during storage time were determined. The dried banana packed in commercial film was tested as control. The results show that the color change of dried banana in both commercial and bioplastic film show similar result. However, at the same storage time, the dried banana in PB2 film had lower moisture content and water activity than that in commercial film resulting in higher hardness value. Additionally, no fragmentation was visually observed in PB2 film during 6 months of soil burial test because the temperature, moisture content and pH of soil were not controlled in the suitable condition.

Field of Study:	Chemical Engineering	Student's Signature .....
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Apinya Wongthanaroj

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CHAPTER I

INTRODUCTION

1.1 General Introduction

In Thailand, solar-dried bananas have been famous since they are delicious and beneficial for health equal to fresh bananas. Solar-dried bananas are also more comfortable to be stored and transported than the fresh bananas which have the short shelf life. Fresh banana can be dried in order to extend the shelf life. Normally, dried banana's shelf-life is 6-12 months [1]. The technique which is used to extent shelf life of fresh banana is solar drying.

Solar drying technique is the interesting technique of fruits preservation especially dried banana because this technique is economical and safe methods. It is able to reduce contamination of insects, microbe and dirt. Solar drying is used to reduce water activity in fruit. Although moisture removing may help retard the growth of microorganisms, deterioration of dried banana quality such as change in color, moisture loss and texture hardening can occur during storage [2]. Therefore, solar-dried banana has to be stored in the good barrier packaging which can prevent contamination and maintain the quality of dried banana (e.g. color, moisture content, and texture). Moreover, the good mechanical properties of packaging are also very important to cover and protect product from the damage and it should withstand the deformation from external force.

Nowadays, the commercial plastic packaging (e.g. metalized film) is effective enough for keeping dried banana but most of them are made from non-biodegradable polymers and commonly use as single-use plastics. Thus, biodegradable polymers have obtained much attention because it is easy to degrade with food in composter. However, they still have some disadvantages such as low barrier properties and mechanical performance as well as high cost when compare with the non-biodegradable plastic. Polylactic acid (PLA) is an interesting alternative because of its transparence, good mechanical properties, processibility and

acceptable prices. However, barrier properties of PLA package need to be improved by blending PLA with poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) due to its high barrier properties. Nevertheless, the PLA/PHBV blends still have the main drawback which is its brittleness. Therefore, poly(butylene adipate-co-terephthalate) (PBAT) is blended to increase flexibility of packaging. In this research, packaging for dried banana was developed from ternary blends of PLA, PHBV and PBAT.

The objective of this work is to study the effect of PBAT content on gas permeability, mechanical properties, morphology and thermal properties of PLA/PHBV/PBAT blown films, PLA/PHBV weight ratio was fixed at weight ratio of 80/20 while PBAT was varied from 0 – 30 wt%. Moreover, the PLA/PHBV/PBAT blown film which has suitable gas permeability and mechanical properties was selected to make dried-banana package. Properties of dried banana which are color change, moisture content, water activity and hardness of dried banana during storage in bioplastic package were observed for 4 months. Moreover, the soil burial test for bioplastic packaging was also tested for 6 months.

1.2 Objectives of the research

1.2.1 To develop of bioplastic blown film for dried banana storage.

1.2.2 To study the quality of dried banana during storage.

1.2.3 To study biodegradable property of a bioplastic film.

1.3 Scopes of the research

1.3.1 Part I

1.3.1.1 Bioplastic blown film was prepared from the ternary blend of PLA/PHBV/PBAT.

1.3.1.2 The ratio of PLA/PHBV was fixed at 80/20 wt% whereas PBAT content was 0, 10, 20 and 30 wt%. Meanwhile, PLA/PBAT (80/20 wt%) was also studied.

1.3.1.3 Barrier and mechanical properties, morphology and thermal properties of bioplastic blown film were studied.

1.3.1.4 To select the optimal properties of bioplastic for dried banana storage.

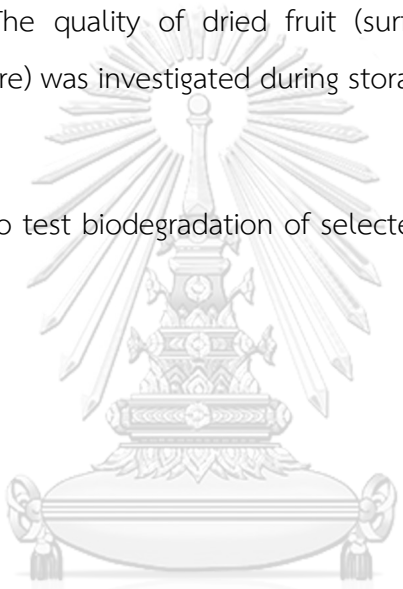
1.3.2 Part II

1.3.2.1 Dried banana was packed in bioplastic and commercial plastic for 4 months

1.3.2.2 The quality of dried fruit (surface color, moisture content, water activity and texture) was investigated during storage.

1.3.3 Part III

1.3.3.1 To test biodegradation of selected bioplastic film for observing the film appearance.



CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Solar-dried banana

Dried banana is a banana that has been dried, may be flavored before or after drying with other components such as honey. Its common characteristics are soft texture, good taste, and good smell. It has natural color and not contaminated from a foreign object such as hair, soil, sand, and dirt. Moreover, dried banana should be stored in clean, tightly closed packaging that can prevent contamination from the environment. [3]

Drying is one of the oldest methods for preservation of fruit. This method is used to remove the water in fruit to a level where it cannot be spoiled either naturally, through sun drying, or through the use of dryers or dehydrators without any apparent bad effect to the customers [4]. Sun drying is the most widespread method due to its economical and safe way, but it has a high level of contamination of insects, microbe and dirt because of spreading the fruit in thin layers on mats, trays or paved grounds and exposing to the sun. Then, solar drying has offered a promising alternative because it can reduce contamination and control fruit quality [5]. For these reasons, bananas were introduced to preserve with using solar drying and became solar-dried bananas.

2.2 Water in food

Moisture content is the total amount of water contained in food as lists in **Table 2.1**. It has a direct effect on the appearance and texture. Moisture in food is a solvent for sugars and salts, and electrolytes and thus in the translocation of food material and metabolism products. Moreover, it is also a part of the inmost structural portion of the cell.

Table 2.1 *The approximate moisture content of some typical food [6]*

Foods	**Moisture content (%)**
Apple	84
Banana	76
Broccoli	91
Cucumber	96
Peppers	92
Potato	79
Raw beef	73
Cooked beef	62
Raw chicken	69
Cooked chicken	62
Salami, beef	60
Bread, commercially prepared	36
Dried fruit	31
Wheat flour	11
Cookie biscuits	6
Peanut butter	2

Water can be classified into two portions of bound and free water [7]. The bound water is the portion which is held so tightly such as binding to polar groups, surfaces of large molecule or cell structures or ionic sites on molecules such as starch, pectin and protein. Bound water cannot be extracted easily, acted as a solvent, and cannot be available to support microbial growth, chemical or enzyme reactions and spoilage processes. Hence, the amount of bound water in fruit has no relation to fruit's stability. Simulated figure of free and bound water is shown in **Figure 2.1**. The free or available water is the portion of water which can be squeezed out and contains the dissolved solutes such as sugar, salt and other components. It promotes the growth of microorganisms as well as chemical or

enzyme reactions and spoilage processes. That means free water is very important for stability and safety of fruits [7].

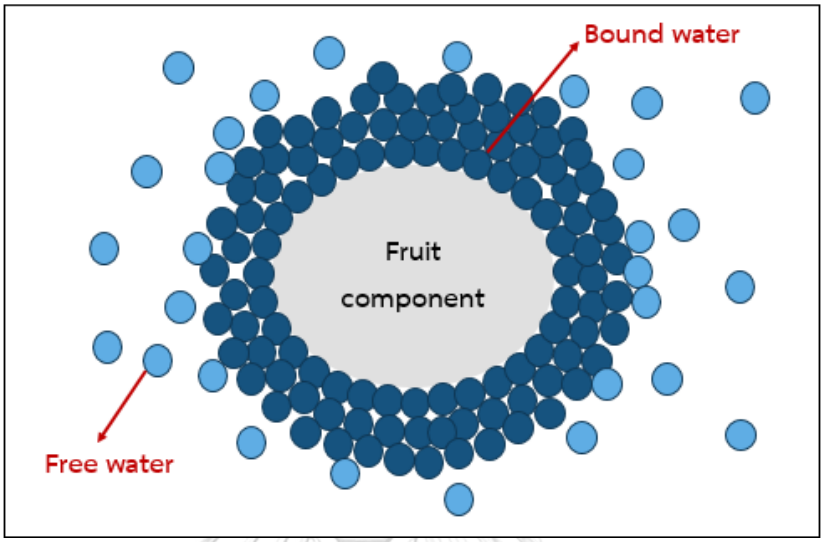


Figure 2.1 *Bound and free water in fruits*

2.3 Water activity

The most important property which can predict the fruit safety and stability is water activity (a_w) [7]. The water activity is the measurement of the energy status of water or availability of water to participate in chemical or biochemical reactions and microbial growth [8] By definition, the water activity is the measurement of water vapor pressure generated by the free or non-chemically bound water in fruit. The water activity is defined as the ratio of the partial vapor pressure of water in fruits (P) that is not bound to food molecules to the saturated vapor pressure of pure water (P_0) at the same temperature as shown in **Equation 2.1.** [9]

$$a_w = \frac{P}{P_0} \qquad \textbf{Equation 2.1}$$

Where a_w is the water activity.

P is the partial vapor pressure of water in fruits.

P_o is the saturated vapor pressure of pure water at the same temperature.

The water activity of fruit is measured from equilibrating between the liquid phase water in fruit and the vapor phase water in the headspace of the closed chamber. At equilibrium, the relative humidity of air in the headspace is equal to water activity of fruit. That means water activity of fruit is the same as the equilibrium relative humidity (ERH) of the headspace, expressed as a fraction, as described by following **Equation 2.2**. [9]

$$a_w = \frac{\text{ERH}\ (\%)}{100} \qquad \textbf{Equation 2.2}$$

Where ERH is the equilibrium relative humidity (%).

The food shelf life depends on a level of water activity [10]. **Table 2.2** shows water activity of food and **Figure 2.2** shows the relative of activity of micro-organisms, lipid and enzymes reactions as a function of water activity. When the food has very low water activity (0-0.2), the shelf life of food is limited primarily by a marked lipid oxidation whereas the non-enzymatic browning reactions (Maillard reaction) is dominant in the range of intermediate water activity (0.2-0.7). Maillard reaction is the chemical reaction between reducing sugar and amino acids. The final products of Maillard reaction are called melanoidins, pigments that provide brown colors in food products [11]. For foods with high water activity (0.7-1.0), the rate of enzyme reaction and oxidation increase since there is enough available water to transport the substrate to the enzyme. Moreover, the growth of microbial is also mainly cause in quality of food [12].

Table 2.2 *Water activity values of foods [6]*

Foods	Water activity
Fresh meat and fish	0.99
Raw vegetables (ex: carrots, cauliflower, peppers)	0.99
Raw fruits (ex: apples oranges, grapes)	0.98
Cooked meat, bread	0.91-0.98
Sausages, syrups	0.87-0.91
Flours, rice, beans, peas	0.80-0.87
Soy sauce	0.80
Peanut butter	0.70
Dried fruits	0.60-0.65
Dried spices, milk powder	0.20-0.60
Biscuits, chocolate	<0.60

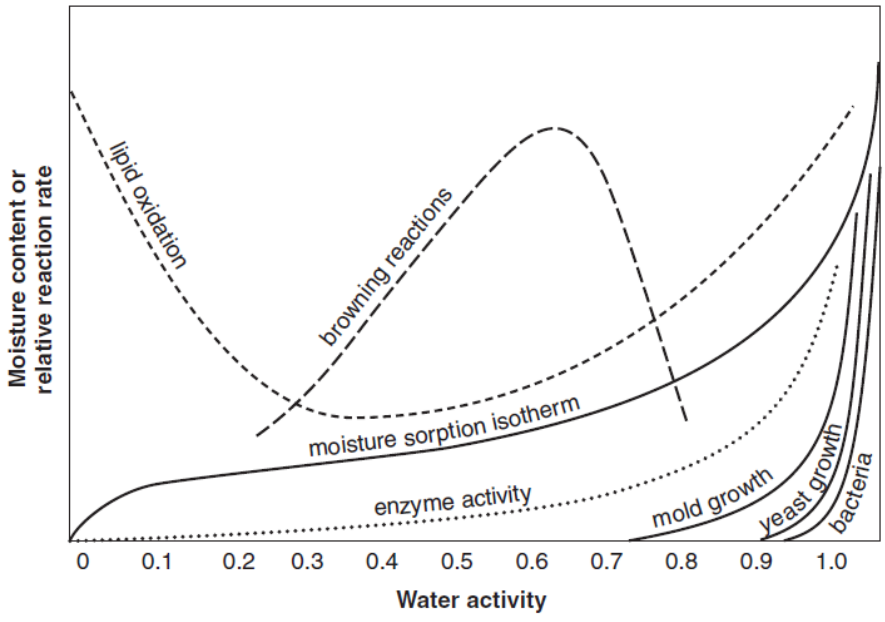


Figure 2.2 *Stability map of food as a function of water activity [8]*

Generally, the water in microbial is over 70%. The important function of water is to retain osmotic pressure within the cell of microbe and to transport

nutrients. This transport mechanism depends on osmotic forces between the inside of the cell and its surrounding or on water activity gradient. The high water activity of environment outside the cell move to a lower water activity within the cell. When water activity outside the cell becomes low enough, it causes osmotic stress: the cell cannot take up water and becomes dormant. Every microorganism has a minimum water activity for growth as shown in **Table 2.3**. The reduction in water activity affects the transport of nutrients into the cell interior. The result is retarded growth of the micro-organism, thus drying which remove the portion of available water can decrease water activity and then leads to extend shelf life of fruit. [10]

Table 2.3 *Minimum water activity values for growth of microorganism groups in food. [7]*

Organism group	**Water activity**
Most spoilage bacteria	0.90
Most spoilage yeasts	0.88
Most spoilage moulds	0.80
Halophilic bacteria	0.75
Xerophilic moulds	0.61
Osmophilic yeasts	0.61

2.4 Dried fruit storage

In general, storage times for most dried fruit is range in 6-12 months after that there are signs to be aware that dried fruit going bad as discoloration, hardness, loss of flavor and a rotten smell [13]. The shelf life of dried fruit depends on a variety of factors, such as the drying method and how the dried fruit was stored. Dried banana needs to be packed in a tightly closed packaging. Storage temperature and relative humidity of surrounding can affect the length of storage time because of the temperature dependence and the movement character of water [14]. Therefore, important factors that affect quality and shelf life of dried bananas are storage

conditions, including temperature and relative humidity, and gas transmission rate of packaging material.

2.4.1 Moisture migration and relative humidity of the environment

The water movement depends on the vapor pressure difference of dried fruit and air in the environment. The amount of vapor in the surrounding air is generally measured as relative humidity (RH) whereas vapor pressure is water activity or equilibrium relative humidity (ERH) in dried fruit. When the relative humidity in the air is below that of the dried fruit, moisture in vapor form of dried fruit is given off to the air in the environment. At the equilibrium point, water is neither given off nor absorbed and if dried fruit is exposed to high humidity environment, dried fruit's absorption of water occurs as shown in **Figure 2.3**. Change in water activity brings about undesirable changes in products, such as losing water to become crisp and hard, and shortens shelf life [15].

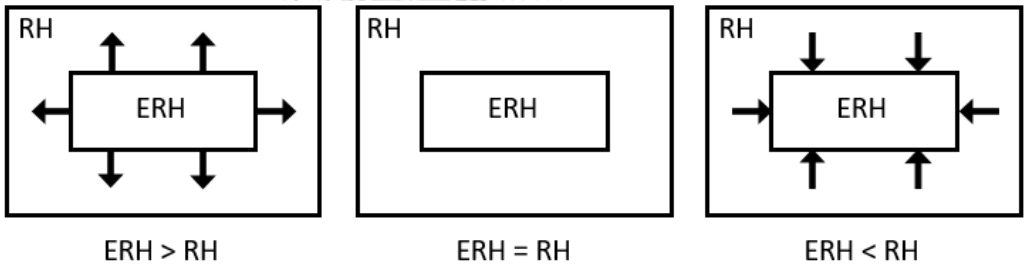


Figure 2.3 *Diagram represents the relation of relative humidity (RH) in the surrounding air and equilibrium relative humidity (ERH) in dried fruit [15]*

2.4.2 Packaging

Packaging for dried fruit storage has to maintain quality of dried fruits during storage. Phothapaeree [2] studied the effect of two types of packaging material (67 μm metalized film and 70 μm PLA-based film), three temperature for storage (30, 40 and 50 °C) and storage time (up to 6 months) on qualities (moisture content, water activity, color, texture and microbiological test) of solar-dried banana. Both packages had different water vapor transmission rate (WVTR) which are 0.8 g/m^2/day for metalized film and 120 g/m^2/day for PLA-based film. Oxygen transmission rate (OTR)

were 1.5 cm^3/m^2/day for metalized film and 365 cm^3/m^2/day for PLA-based film. The results showed that at low temperature, dried banana in both packages had the same qualities and can store up to 152 days (5 months). The changes of dried banana in PLA-based including lower moisture content and water activity as well as higher hardness was apparently observed at 40°C and had a faster rate at 50°C. While storage in metalized, these changes was obviously shown at 50°C and less than PLA-based as shown in **Figure 2.4** because PLA-based film had higher WVTR than metalized film, also WVTR is dependent on temperature. In case of color change (ΔE) which was calculated by following **Equation 2.3**.

$$\Delta E = [(L_0^* - L_t^*)^2 + (a_0^* - a_t^*)^2 + (b_0^* - b_t^*)^2]^{\frac{1}{2}} \qquad \textbf{Equation 2.3}$$

Where L_0^*, a_0^* and b_0^* were obtained from the samples at the beginning of storage time.

L_t^*, a_t^* and b_t^* were obtained from the samples at the specific storage time.

The color change results as shown in **Figure 2.5**, in which dried banana in PLA-based film was less than that in metalized one at the elevated storage temperature because water activity of dried banana during storage in metalized one (mostly higher than 0.6) was greater than that in PLA-based film (0.4-0.5) that leads to high free water remaining in sample and then occurred the non-enzymatic browning reaction, i.e. Maillard reaction. Maillard reaction could occur at higher rate in the food with water activity value of 0.6-0.8. While all dried bananas in both storages had total plate count less than 250 cfu/g, yeast and mold count less than 2,500 cfu/g and coliform count up to 9.2 MPN/g for 6 months that was an acceptable quality. Therefore, microbiological properties were not the most important factors for shelf life determination of dried banana, the critical parameters were physical properties (i.e. color and texture).

Therefore, the main requirement of packaging for dried fruit storage should be concerned in a good barrier characteristics. Meanwhile, mechanical performance is also important for packaging [16].

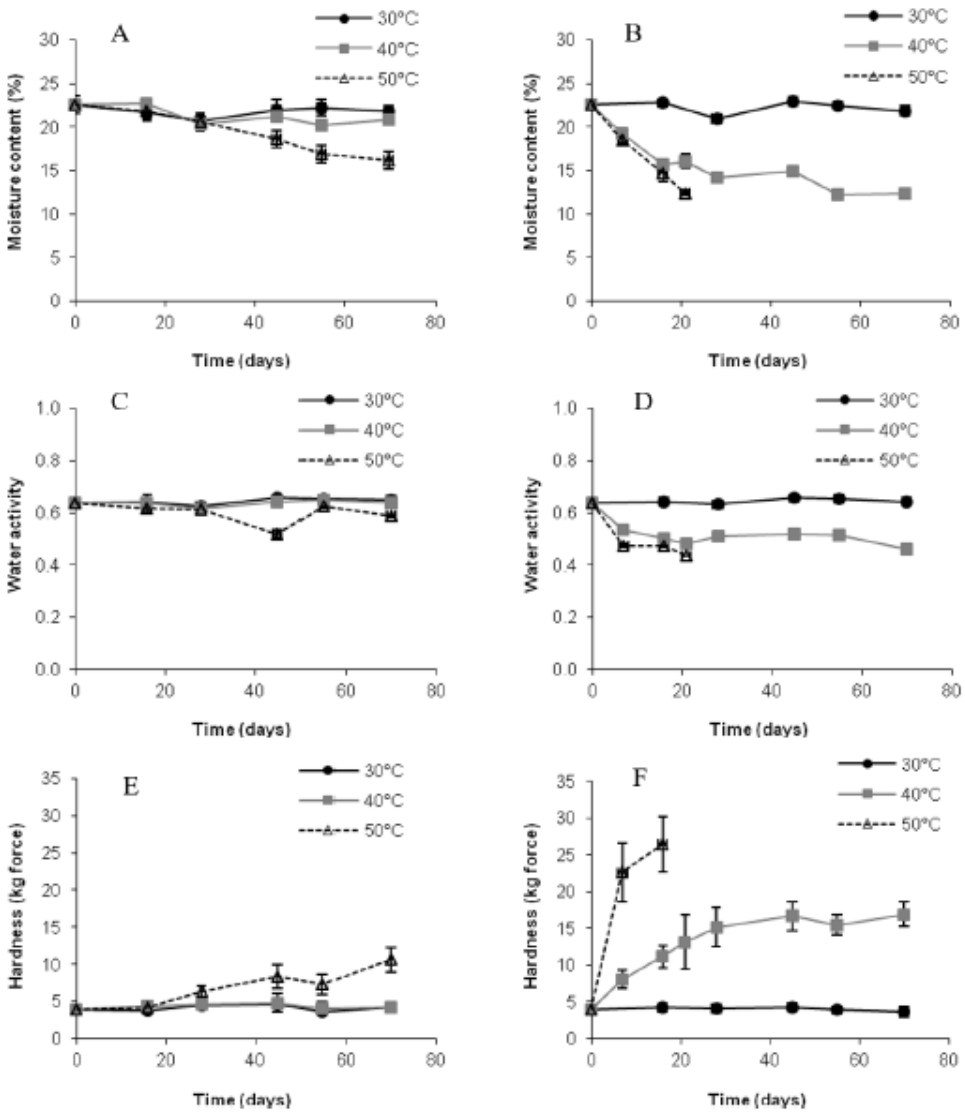


Figure 2.4 *Moisture content, water activity and hardness of the solar-dried banana packed in metalized plastic (A, C, E) and PLA-based films (B, D, F) at different storage temperatures [2]*

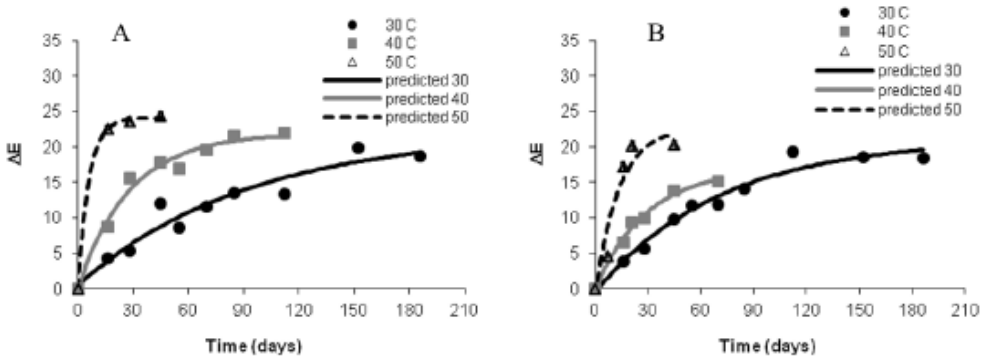


Figure 2.5 *Color change (ΔE) of the solar-dried banana packed in (A) metalized plastic and (B) PLA-based film at different storage temperatures. Connecting line represents the data fitted with fractional conversion model [2]*

The plastic packaging needs to have high gas barrier properties because it should protect dried fruits from excessive drying out and reabsorbing water or maintaining water activity values which affects both texture and taste. For dried fruits, the oxygen barrier property is less important than for other foods which have high fat content (i.e. nuts and meat) and then be susceptible to oxidation, while the water vapor barrier is more important to preserve moisture content and texture of dried fruit during storage [14, 17, 18]. Additionally, the mechanical properties are also significant for packaging. They should protect dried fruit from the damage of transportation through customers which are rigidity, resistance to mechanical damage, durability and ease of opening.

2.5 Bioplastic packaging

Nowadays, the commercial plastic packaging is effective enough for storing dried fruits away from contamination but most of them are made from non-biodegradable polymers and commonly use as single-use plastics. Furthermore, the concerns on the environmental impact of plastic waste are currently increased. This is the reason that biodegradable polymers have obtained much attention as an alternative to replace non-degradable materials.

2.5.1 Polylactic acid

Polylactic acid (PLA) or polylactide is one of the biodegradable thermoplastic that is widely used because it is synthesized from renewable agricultural crops such as corn, potato, cellulose and other polysaccharides and fermented to lactic acid [19, 20]. The advantages of PLA are transparency, good mechanical properties (high modulus and strength) and broad processing window. It is already commercialized mainly for short-life disposable packaging applications such as bottles, films, thermoformed trays and lids containers [21]. Even though PLA has many advantages for packaging purposes, it also shows some drawback that is low gas barrier properties and high rigidity at room temperature which limited its packaging applications. Many methods have been developed to improve gas barrier performance and flexibility such as the copolymerization and melt blending with other ductile polymers. Melt blending of polymer have been known to be the effective method that is a simple way to prepare and cost effective for obtaining new materials with improved properties and simple packaging formulations with desired performance by varying the blend composition [21-24]. It can be melted to mix all polymers without chemical reaction taking place. Thus, blending of PLA with other biodegradable polymer got attention from both industries and academia.

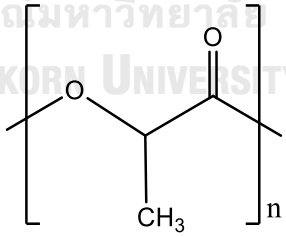


Figure 2.6 *Chemical structure of PLA*

2.5.2 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are a family of biodegradable polyesters that are naturally produced and accumulated as carbon and energy storage material by bacterial fermentation [20, 25]. They have been obtained considerable attention in

food packaging due to their prominent properties as barrier properties and good mechanical strength and they also have potential to be used in many applications, including packaging, moulded goods, paper coatings and performance additives [26]. The most common type of PHAs is polyhydroxybutyrate (PHB). Nevertheless, low resistance to thermal degradation, brittleness, and low strain at break of PHB make this polyester very difficult to be processed and not suitable for the food packaging. The random copolymer of PHB is synthesized with polyhydroxyvalarate (PHV) to improve toughness and flexibility that is poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). This copolymer has lower degree of the crystallinity, lower melting temperatures and more flexible than PHB which leads to a wider processing window. For these reasons, PHBV is chosen to be blended with PLA for enhancing the barrier character [25-27].

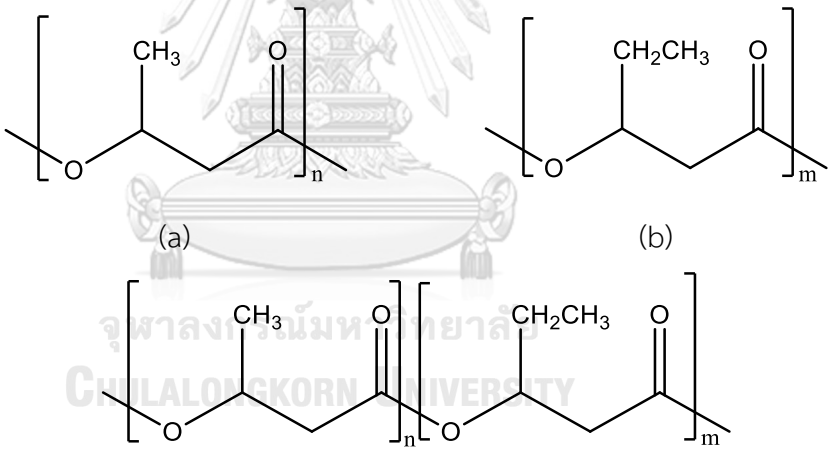
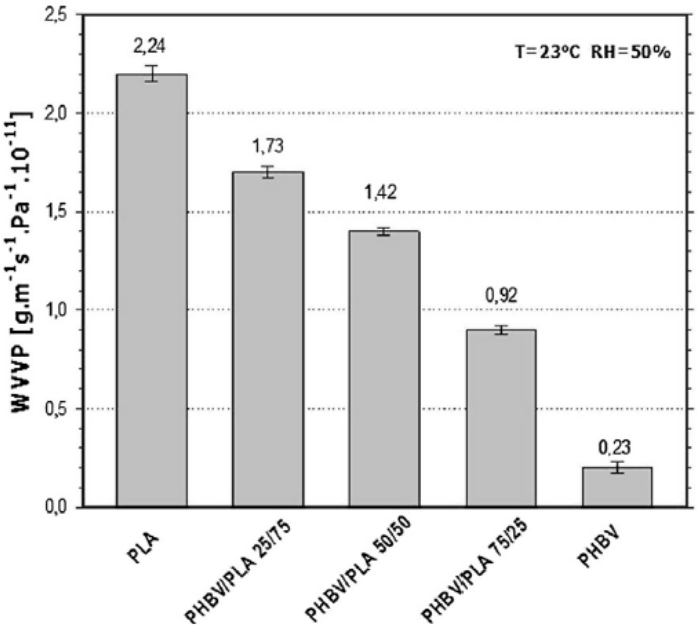


Figure 2.7 *Chemical structure of (a) PHB, (b) PHV and their copolymer (c) PHBV*

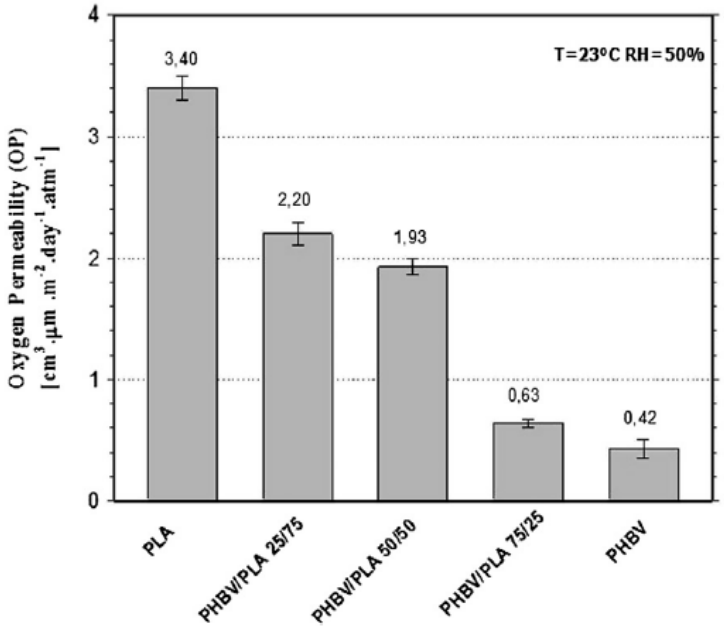
Zembouai [28] studied the properties of PHBV and PLA (PHBV/PLA) blends at various compositions including 100/0, 75/25, 50/50, 25/75 and 0/100 wt% with compression moulded technique. The results showed that increasing the PHBV content reduced the water vapor and oxygen permeability as shown in **Figure 2.8(a)** and **2.8(b)**, respectively due to the increase of degree of crystallinity in which PHBV

acts as a nucleating agents. The increase of degree of crystallinity will enhance the tortuosity of the transport path. In other word, the gas molecule can only permeate in the amorphous phase which is reduced by the inclusion of impermeable crystallites.

However, blending of PLA with PHBV materials is not appropriate to be used as packaging because they are still excessively rigid and brittle [27]. It is observed that elongation at break has no change when increasing PHBV content except at low weight ratio of PHBV between 10 and 30wt% because the finely dispersed PHBV particles act as a reinforcing filler to enhance the PLA properties [19, 25, 29]. It is known that mechanical property of large-size spherulitic material is more brittle than fine spherulite one [19]. This means that PHBV is more effective to improve the barrier properties of PLA material that is an important characteristic of packaging but the flexibility of PLA/PHBV blend still need to be improved.



(a)



(b)

Figure 2.8 *Effect of PHBV content on (a) water vapor and (b) oxygen permeability of PHBV/PLA blend [28]*

2.5.3 Poly(butylene adipate-co-terephthalate)

Poly(butylene adipate-co-terephthalate) (PBAT) is a biodegradable thermoplastic copolyester that is produced by random co-polymerization of 1,4-butanediol, adipic acid, and dimethyl terephthalate (DMT) monomers which has the excellent properties similar to polyethylene including flexibility and resilience as well as impact properties [30]. It can also be used for many similar applications (i.e. food packaging and plastic bag). Because of high flexibility, PBAT has been blended with other polymers to reduce their rigidity [27]. Thus, PBAT is a perfect candidate as blending composition to improve flexibility of PLA and PHBV.

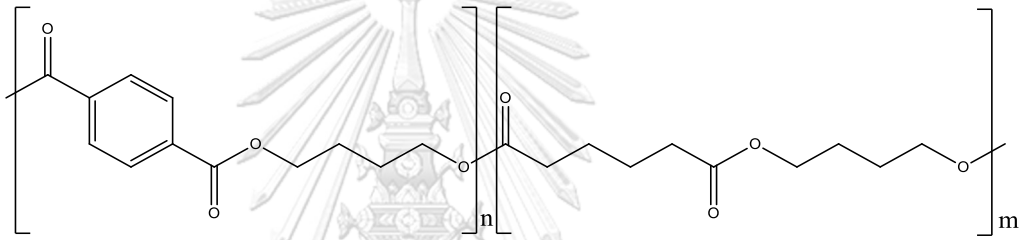
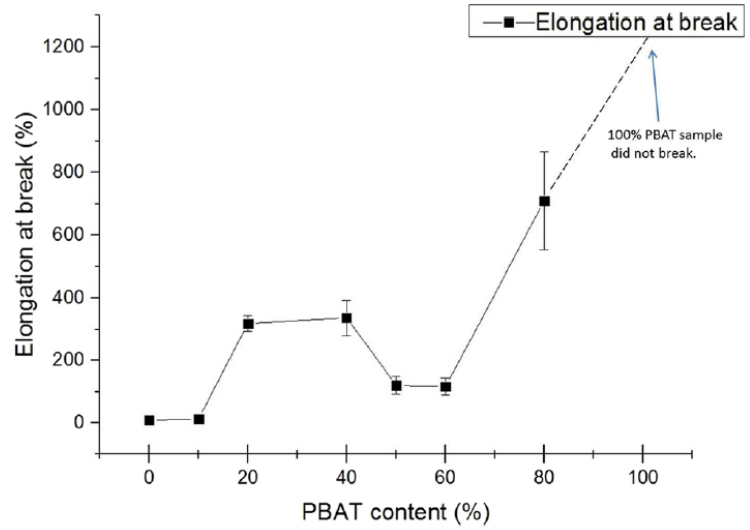


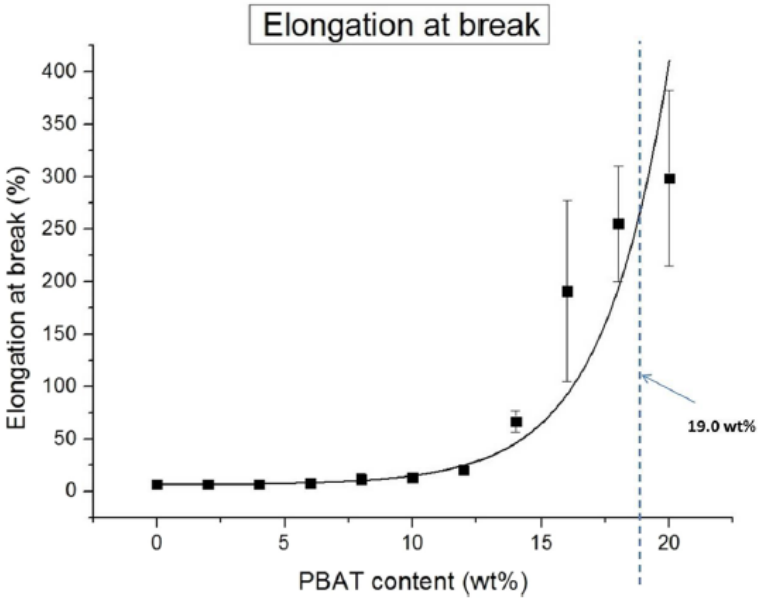
Figure 2.9 *Chemical structure of PBAT*

Deng [21] studied the morphology and mechanical properties of the PLA/PBAT blend with the various composition of PBAT (0-100 by weight) with compression moulded technique into sheets. The result shows that adding PBAT in the 10 and 20 wt% range can increase the elongation at break from around 10% up to 300% because the formation of co-continuous phase structure was occurred. When adding 20-40wt% PBAT, the elongation at break of specimens remains the same and then dropped to be around 100% at 50wt% of PBAT because it is limit of the co-continuous phase as shown in **Figure 2.10(a).** Moreover, the blend of PLA with 2% increment of PBAT between 0 and 20 wt% was further investigated as shown in **Figure 2.10(b).** It shows that the ductility of material is very poor at PBAT content below 14 wt% due to dispersion of PBAT particles in PLA matrix. However, the elongation at break of samples started to enhance at PBAT content between 16 and 19 wt% with large standard deviation, implying that some specimens have a

well-developed co-continuous phase structure whereas co-continuous structure of others is incomplete.



(a)



(b)

Figure 2.10 *Elongation at break of (a) various ratio of PLA/PBAT (b) PBAT content range from 0-20 wt% [21]*

In contrast, Young's modulus and tensile strength of blends decreased with increasing PBAT content due to the increasing of soft elastomeric phase of PBAT that reduced the crystallinity [21, 31, 32]. Meanwhile, the presence of PBAT can reduce brittleness of PLA which is evident from the enhancement of impact strength [31]. Nevertheless, adding of PBAT content in PLA would increase water vapor and oxygen permeability properties [32, 33]. As shown in **Table 2.4**, oxygen and water vapor permeability of the PLA/PBAT blown films at different PLA/PBAT concentrations (100/0, 80/20, 60/40, 40/60, 20/80 and 0/100 by weight), adding PBAT to PLA results in an increase of oxygen and water vapor permeability. This could be related to different glass transition temperatures of these polymers. PLA at 23℃ (the test temperature was set at 23℃) is in the glassy state, which means a low fraction of free volume between the polymer chains, and low chain mobility compared to PBAT that has a T_g below 23℃. These factors greatly influence the permeability of gas molecules, whose permeability is facilitated with high chain mobility and free volume fractions.

Table 2.4 *Oxygen and water vapor permeability coefficients of the films [32]*

Samples	**Oxygen permeability, PO_2 [cc.mil/m^2/day/atm]**	**Water vapor permeability, PH_2O [g.mil/m^2/day]**
PLA	1332.38	51.18
PLA PBAT 80 20	1631.57	55.12
PLA PBAT 60 40	2006.55	110.24
PLA PBAT 40 60	2469.30	114.17
PLA PBAT 20 80	2864.23	118.11
PBAT	3350.91	122.05

Likewise, blending of PHBV with PBAT, elongation at break of samples can be increased by enhancing the PBAT content because PBAT acts as plasticizer in PLA. On the other hand, increasing the PBAT content decreases water vapor barrier properties because PBAT materials have higher permeable properties and less crystallinity than PLA [34]. Therefore, the addition of PHBV in PLA improved barrier properties while PBAT offered higher ductility in PLA [27].

Therefore, in order to improve the barrier and mechanical properties of PLA/PHBV/PBAT films, to be used as dried bananas storage packaging, the films with different proportions of PLA/PHBV/PBAT were studied.

CHAPTER III

METHODOLOGY

In this chapter, materials, film preparation, characterization film properties and qualities of dried bananas after store inside packaging, are described as follows.

3.1 Materials

Polylactic acid (PLA) pellets with 4043D grade was supplied from NatureWorks Co., Ltd. The physical properties of PLA: density = 1.24 g/cm^3, glass transition = 55-60 °C and melting temperature = 145-160 °C. While poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), whose trade name was ENMAT Y 1000P, was manufactured by Tianan Biological Materials Co., Ltd. (China). According to the manufacturer, PHBV has the following properties: density = 1.25 g/cm^3, glass transition temperature = 8 °C and melting temperature = 165 °C. Lastly, Poly(butylene adipate-co-terephthalate) (PBAT) (Ecoflex F blend C1200 grade) was obtained by BASF Chemical Company, Germany. Its density is 1.26 g/cm^3 and melting temperature is 115 °C.

Solar-dried bananas (cv. Kluai Namwa) were obtained from Wang Kanai, Kanchanaburi province (Thailand) with the water activity values around 0.6-0.7.

3.2 Bioplastic blown films preparation

Prior to melt processing, all raw materials were dried at 60 °C for 24 hours to remove the absorbed water. The pellets of PLA, PHBV and PBAT were mixed together and place into a hopper of screw feeder in which the weight ratio of PLA/PHBV was fixed at 80/20 wt.-% while varying the PBAT content, i.e. 0, 10, 20 and 30 wt.-%. The PLA/PHBV/PBAT pellets were melt mixed by using twin screws extruder, Thermo Hakke Rheomex, Germany, and then blown into films with thickness of 30$\pm$5 μm via blown film extruder with the temperature profile was about 180-190 °C. The sample code of different PLA/PHBV/PBAT compositions film is shown in **Table 3.1**.

Table 3.1 *The code and composition of various PLA/PHBV/PBAT blends*

Sample	PLA (wt%)	PHBV (wt%)	PBAT (wt%)
PLA/PBAT	80	-	20
PLA/PHBV	80	20	-
PB1	72	18	10
PB2	64	16	20
PB3	56	14	30

3.3 Film characterizations

3.3.1 Morphology

The morphology of all bioplastic films was examined by a scanning electron microscope (SEM) with an accelerating voltage of 15.0 kV using a Hitachi S3400N. The cross-sectional fractured surface of films were observed in both machine and transverse direction. All bioplastic films were cryo-fractured by dropping it directly and fractured with blade in liquid nitrogen. Before observing, the surface of the sample films was coated with platinum to increase conductivity.

3.3.2 Thermal properties

Thermal properties of all blends were investigated by differential scanning calorimetry (DSC). The weight of the samples was approximately 5 - 8 mg. They were packed in an aluminum pan and first heated from 30°C to 200°C at a heating rate of 10°C/min and then kept isothermally for 2 minutes to remove the thermal history. After that the samples were cooled down with the same cooling rate of 10°C/min until their temperature approached 30°C, kept it there for 2 minutes and reheated to 200°C. In this process, all samples were analyzed under nitrogen atmosphere. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m) as well as enthalpy of cold crystallization (ΔH_{cc}) and enthalpy of melting (ΔH_m) were observed from the DSC profiles.

3.3.3 Water vapor permeability analysis

Water vapor permeability (WVP) of all bioplastic films was investigated by using water vapor permeation analyzer; PERMATRAN-W Model 398, Mocon, USA according to ASTM E-398. The bioplastic film was cut to be circular shape with area of 50 cm^2. The test film was attached between diffusion chambers, upper and lower chamber. Nitrogen gas was introduced into the upper of the chamber while a moisture-free carrier gas flows from the lower chamber which contain a pool of water through the sample film into the upper one. Molecules of water vapor diffusion through the film in the lower chamber were conveyed to the sensor by the carrier gas. The chamber temperature and relative humidity were fixed at 37.8 °C and 100%, respectively. Four films were repeated in order to obtain the accurate value.

3.3.4 Oxygen permeability analysis

Oxygen permeability (OP) of all bioplastic films was investigated by using oxygen permeation analyzer; OX-TRAN 2/21, Mocon, USA according to ASTM D3985. The bioplastic film was prepared into circular shape with tested area of 100 cm^2. The test film was clamped between diffusion chambers. One chamber is flowed with oxygen while a carrier gas flows into another chamber. The chambers were purged off the residual oxygen by using a carrier gas. Oxygen gas (99.8% purity) was introduced into the chamber and then permeate through the film into the chamber of a carrier gas. A coulometric sensor inside the carrier gas chamber can detect the amount of oxygen. The chamber temperature and relative humidity were fixed at 23 °C and 0%, respectively. Four films were repeated in order to obtain the accurate value.

3.3.5 Tensile measurement

Tensile test was performed by using Universal Testing Machine (Instron 5567, NY, USA), according to ASTM D882. It was used to determine the tensile properties include tensile strength at yield, Young's modulus and percentage of elongation at break of all bioplastic films. All the specimens were required in a rectangular shape with the width of 10 mm and the length of 130 mm. Ten tests were repeated for each sample set in order to reduce the deviation and approach the accurate value.

3.3.6 Impact test

Impact strength of bioplastic film is used to determine its capacity to resist a sudden applied load or force. In other word, impact strength is energy that required to break the sample. It was measured using impact tester (Film Impact Tester Digital type, TOYOSEIKI) according to ASTM D3420. All bioplastic films were cut into square shape with the area of 100 cm^2 and then, the pendulum head hits the sample films with a maximum velocity of about 74 m/min and a maximum energy of about 5 J. The test for each sample set was repeated ten times for reducing the deviation and increasing accuracy of experimental value.

3.4 Determination of Physical and chemical properties of dried banana

A solar-dried banana was packed under normal atmospheric pressure into the selected films. Packed sample was kept at 30±1°C for 4 months and characterized every 2 weeks of storage.

3.4.1 Color change

Color change of the dried banana was analyzed in the Commission International de l'Eclairage (CIE) L* (lightness), a* (redness and greenness), b* (yellowness and blueness) system using chroma meter (Minolta CR-400, Konica Minolta Sensing, Japan). Color measurement was made on surface of dried fruit and done in triplicate, using three pieces of dried banana. For each sample piece, color values at six positions were recorded.

3.4.2 Moisture content

The moisture content of dried banana was determined by hot air oven method, according to AOAC (2006). Dried banana was weighed until the weight remains constant. The moisture content (%) was done in triplicate, using three pieces of dried bananas, and calculated from the weight before and after drying by **Equation 3.1.**

$$\% \textbf{ Moisture content} = \frac{W_0 - W_t}{W_0} \textbf{ x } 100\% \qquad \textbf{Equation 3.1}$$

Where $\mathbf{W_0}$ is the weight of the samples before drying.

$\mathbf{W_t}$ is the weight of the samples after drying.

3.4.3 Water activity

Water activity (a_w) of the samples was determined by using water activity meter (AquaLab Series 3, Decagon, USA) with the chilled-mirror dew point technique. The sample was prepared to small pieces and put into the chamber containing a mirror and a photodetector cell for detecting condensation on the mirror. When the chamber was closed, the vapor pressure of sample was equilibrated within the headspace of the sealed chamber. At equilibrium, the relative humidity of the air in the chamber is equal to water activity of the sample. A beam of light is directed onto the mirror and reflected into a detector. The first condensation is detected from the change in reflectance. A thermocouple that attached to the mirror measured the dew-point temperature. Additionally, an infrared thermometer observed the temperature of sample. The ratio of the dew-point temperature saturation vapor pressure to saturation vapor pressure at the sample temperature are used to determine water activity [35, 36]. The measurement was done in triplicate, using three pieces of dried bananas.

3.4.4 Texture

Texture or hardness of dried banana was investigated by Texture Analyzer (TA-XT2i, Stable Micro Systems, Surrey, UK) with a 30 kg-load cell which the samples were cut with the test speed of 2 mm/s and 100% cutting distance with Warner-Bratzler blade. Hardness (maximum cutting force) was identified from the force distance curve using Texture Expert software. Each sample piece was cut at two positions. The measurement was performed on six pieces of the banana samples (six replicates).

3.5 Soil burial test

Biodegradation of film under real soil burial conditions was carried out in a laboratory scale in the department of chemical engineering at Chulalongkorn University. The film specimen was cut into size of 5 cm x 5 cm and was buried at a

depth of 10 cm from the soil surface. Every 30 days a sample was retrieved, and it was cleaned and dried at room temperature. The appearance of sample was observed.

3.6 Methodology

In this research, experiment was separated in 3 parts as shown in **Figure 3.1**. **Part I** is the preparation and characterization of bioplastic blown film packaging. Barrier and mechanical properties were investigated following topic 3.3. Then the bioplastic blown film packaging with optimal properties was chosen for dried fruit storage. **Part II** is to compare the efficiency of selected bioplastic film from part I and commercial packaging for storage of dried banana. The qualities of dried banana, which was packed in packaging, were assessed following topic 3.4. **Part III** is to test the biodegrability of selected bioplastic film from part I.

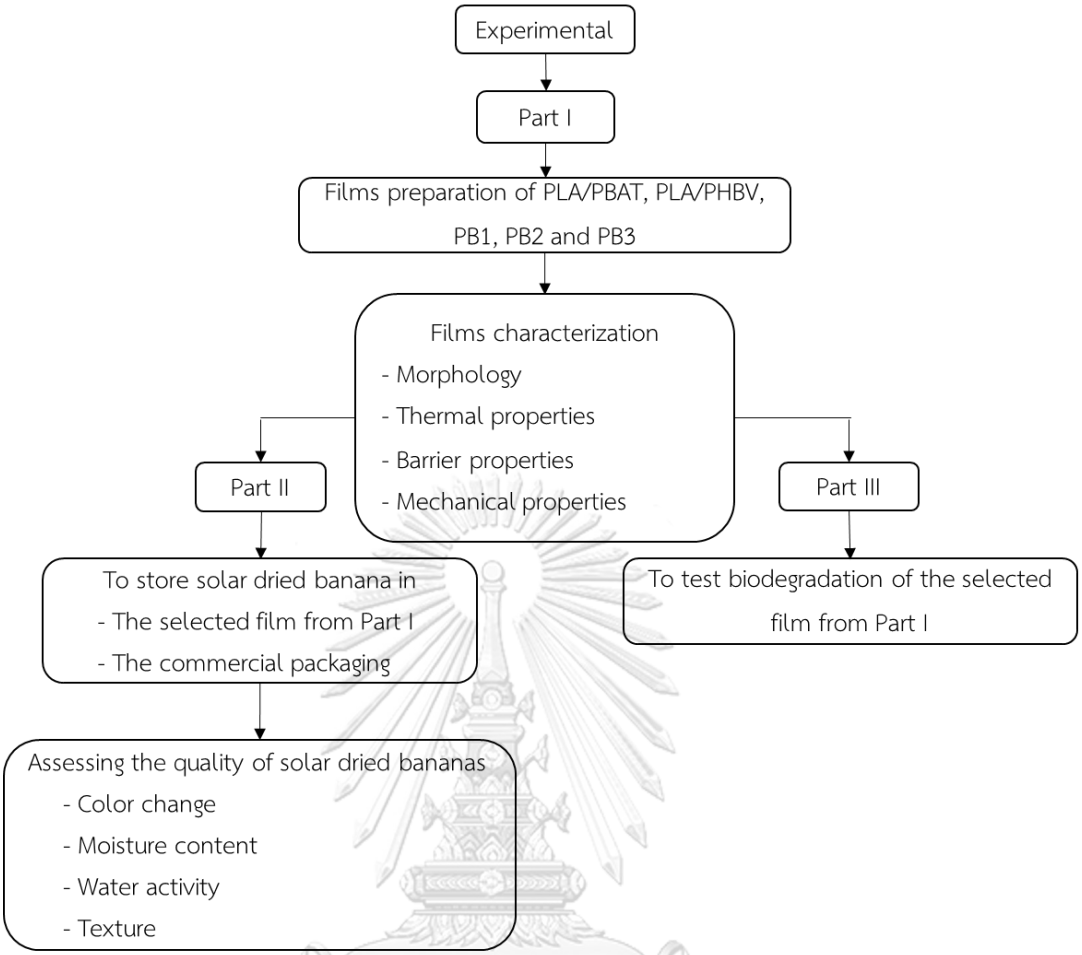


Figure 3.1 *Methodology of this research*

CHAPTER IV
RESULTS AND DISCUSSION

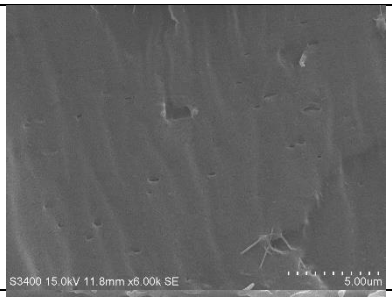
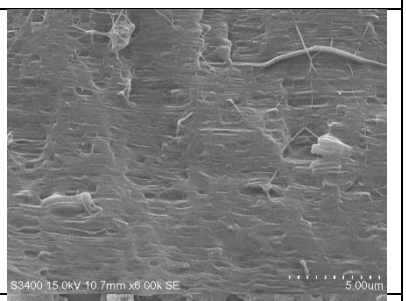
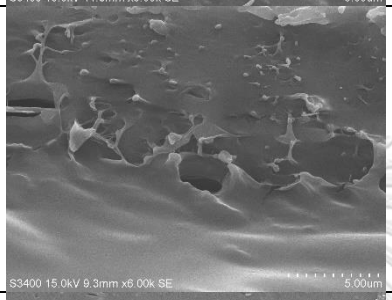
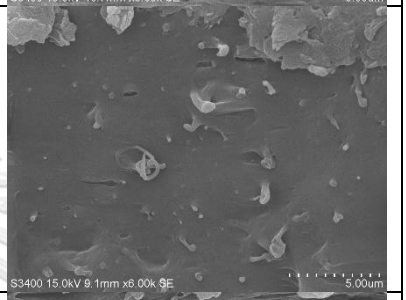
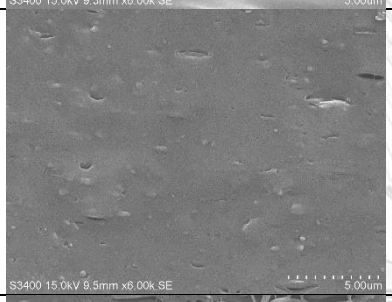
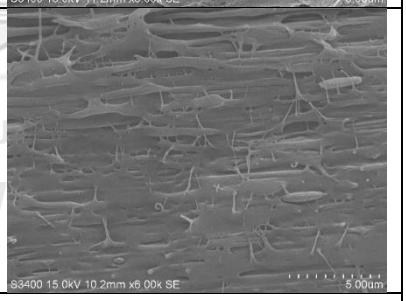
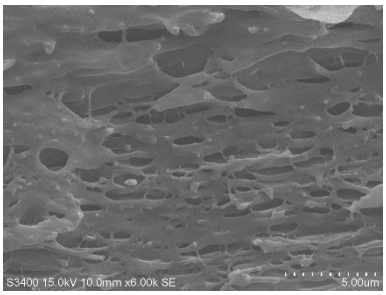
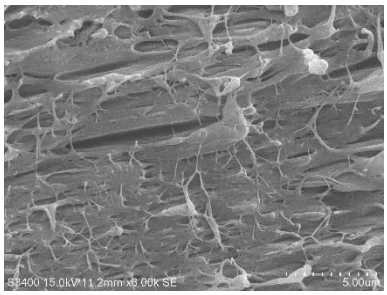
This chapter contains three parts which are the characterization of bioplastic blown films, physical and chemical properties of dried banana stored in packaging, and soil burial test of bioplastic package. The effect of PBAT content on the morphology as well as thermal, gas barrier, and mechanical properties was described. The suitable formulation of film was selected to use as the dried banana packaging compared with the commercial package. The physical and chemical properties of dried banana such as moisture content, water activity, and hardness were characterized and determined the shelf-life of dried banana. Moreover, the soil burial test for bioplastic film was also tested.

4.1 Characterization of plastic film packaging

4.1.1 Morphology

The micrographic images of the fractured surface of bioplastic films in machine direction (MD) and transverse direction (TD) were shown in **Table 4.1**. For PLA/PBAT and PLA/PHBV at the same weight ratio of 80/20 wt/wt, it was noticed that the PBAT and PHBV was dispersed in PLA matrix in the form of spherical particles. Furthermore, the SEM micrograph of PLA/PBAT film in TD clearly shows the elongated fibrous which is consistent with Farsetti et al. work on where the ductile fracture with several filaments was observed [37]. It indicated that PLA/PBAT film have high interaction in this composition. In case of ternary blend of PLA/PHBV/PBAT at PBAT weight content of 10%, 20% and 30%, the small oval cavities and the elongated fibrous can be observed in the fractured surface when PBAT was introduced. The cavitation in polymer blend was caused by interfacial debonding of PBAT from PLA. It was also found that the size of oval cavities increased with increasing of PBAT content in both MD and TD because of inclusions of PBAT. Meanwhile, the number of the elongated fibrous was also increased.

Table 4.1 *Micrographic images of fractured surface of all films in both MD and TD*

Sample	Machine Direction (MD)	Transverse Direction (TD)
PLA/PBAT		
PLA/PHBV		
PB1		
PB2		
PB3		

4.1.2 Thermal properties

Thermal properties such as glass transition temperature (T_g), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m), and enthalpy of fusion (ΔH_m) of all blends were investigated using differential scanning calorimeter (DSC). The second heating of DSC thermograms are shown in **Figure 4.1.**

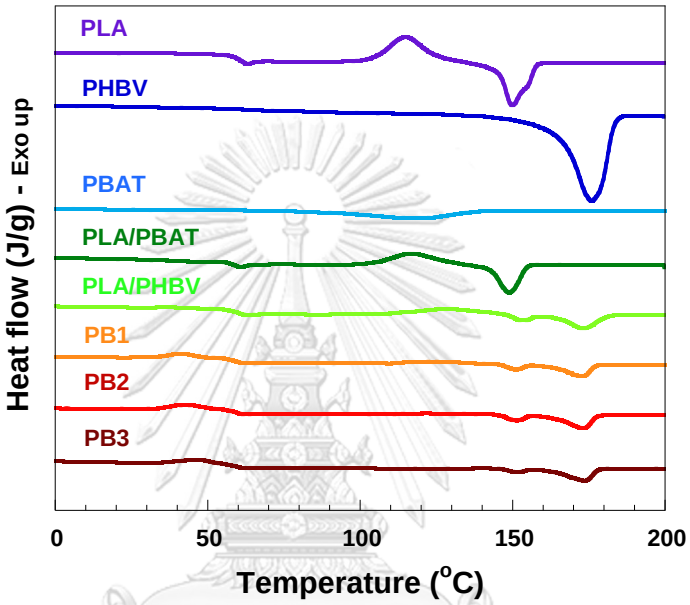


Figure 4.1 *DSC thermograms of neat PLA, PHBV, PBAT and all blends*

Table 4.2 tabulates the thermal properties of neat PLA, PHBV, PBAT as well as all blends from the DSC thermograms. The glass transition, cold crystallization and melting of neat PLA is 59.61℃, 114.86℃ and 149.91℃, respectively. While the glass transition temperature of PHBV and PBAT is about 2.80 ℃ and -29.22 ℃, respectively. DSC profiles show that the glass transition temperature is separated in both binary and ternary blends and barely changes regardless of the concentration of PBAT. These indicate that PHBV and PBAT are not miscible with PLA. The increase of $T_{cc,PLA}$ and the decrease of enthalpy of cold crystallization of PLA in both PLA/PBAT and PLA/PHBV indicated that the PBAT and PHBV disrupt the ordering of the blends by hindering chain diffusion and folding into the crystalline lattice, making the crystallization of the PLA phase slower in which this work is consistent with Yang et

al. [38]. In the case of ternary blend, $T_{cc,PLA}$ was slightly decreased at 10% and 20% PBAT. While $T_{cc,PLA}$ was increased at 30% PBAT since the chain of PBAT hinder chain diffusion of PLA. $T_{cc,PHBV}$ was observed when PHBV was blended with PLA as PLA/PHBV 80/20 wt/wt. It indicates that PHBV did not have ability to completely crystallized because of hindering chain diffusion of PHBV from PLA. Hence, the cold-crystallization of PHBV occurred. The presence of PBAT also causes increasing of $T_{cc,PHBV}$ and $\Delta H_{cc,PHBV}$. The T_m and ΔH_m of all blends were slightly changed. The melting behavior of the PBAT phase could not be observed because its broad melting peak is located within the cold crystallization temperature range of PLA [38].

Table 4.2 *Thermal characteristics of the PLA, PHBV, PBAT and all blends*

Sample	Glass transition temperature, T_g (°C)			Cold crystallization temperature, T_{cc} (°C)				Melting temperature, T_m (°C)			
	PLA	PHBV	PBAT	PLA	ΔH_{cc} (J/g)	PHBV	ΔH_{cc} (J/g)	PLA	PHBV	PBAT	ΔH_m (J/g)
PLA	59.61			114.86	19.51			149.91			23.23
PHBV		2.80							173.38		84.90
PBAT			-29.22							119.21	16.70
PLA/PBAT	57.55		N/A	116.65	13.01			149.00			16.12
PLA/PHBV	59.58	0.73		128.44	8.66	37.13	0.31	153.22	173.17		13.59
PB1	58.83	0.25	N/A	124.97	2.74	40.99	2.54	150.94	172.58		11.13
PB2	59.31	-0.64	-32.31	121.27	1.45	42.81	3.32	150.90	173.19		13.15
PB3	59.84	1.16	-30.10	139.60	0.52	46.48	3.10	151.10	173.06		10.37

4.1.3 Gas barrier properties

Gas barrier properties of all blends were investigated by using oxygen and water vapor permeation tester. The results of water vapor permeability (WVP) and oxygen permeability (OP) of a polymeric film are presented in **Figure 4.2.** PLA/PBAT film has higher WVP and OP than that of PLA/PHBV because of high value of OP and WVP of PBAT itself. In case of ternary blend between PLA, PHBV and PBAT, it is observed that the PBAT content enhances both WVP and OP due to the increase of the size of PBAT droplet which can be observed from SEM micrographs as the presence of oval cavities in the fractured surface of film. The oval cavities caused by interfacial debonding of PBAT from PLA. The size of oval cavities was increased with increasing of PBAT concentration because of inclusions of PBAT. Therefore, WVP and OP of ternary system film were enhanced.

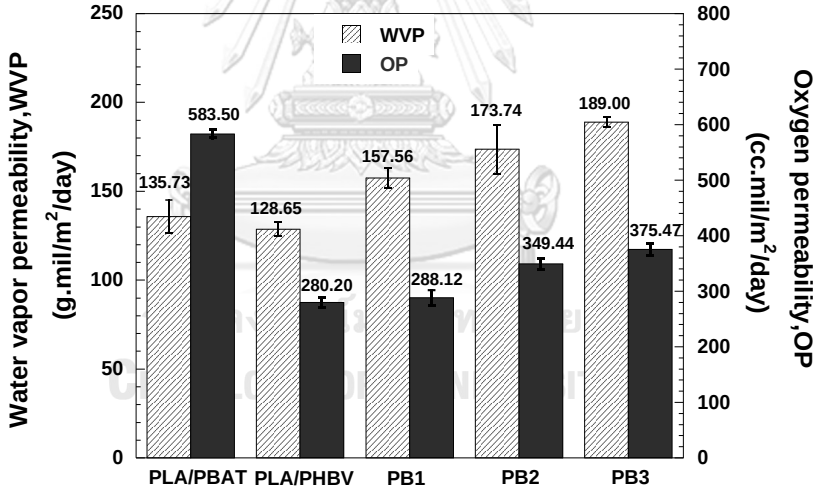
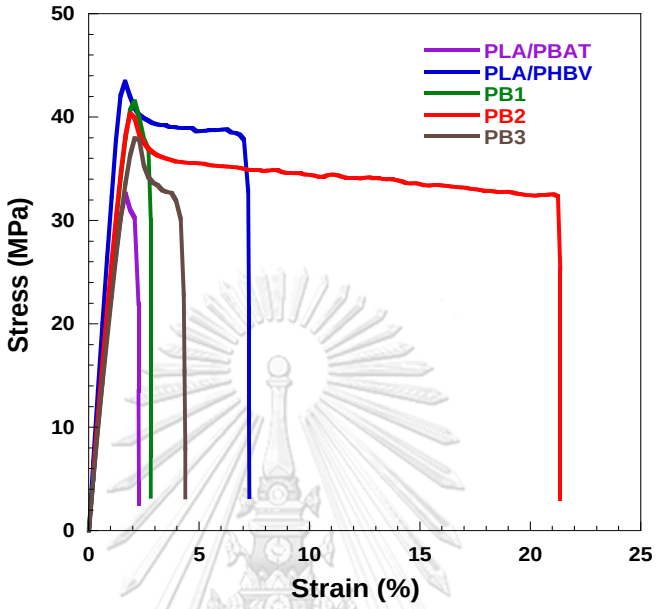


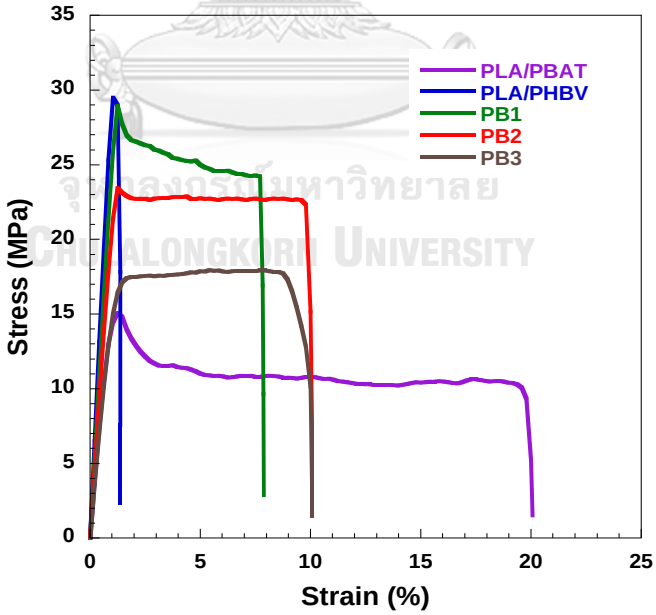
Figure 4.2 *Effect of PBAT content on water vapor and oxygen permeability of all blends*

4.1.4 Mechanical properties

Figure 4.3 demonstrated the stress-strain curves of all blends in both MD and TD.



(a)



(b)

Figure 4.3 Stress-strain curve of all blends in both (a) MD and (b) TD

PLA/PHBV film showed a maximum value in the stress with low strain, especially in TD of film. It indicated that PLA/PHBV film showed brittle deformation behavior. Meanwhile PLA/PBAT showed a minimum load. In case of ternary blend, the stress was shown in the range between PLA/PHBV and PLA/PBAT with ductile deformation behavior which could be obviously observed in TD of films.

The tensile strength at yield, Young's modulus, and elongation at break of all films was shown in **Figure 4.4**, **4.5** and **4.6**, respectively. The results showed that PLA/PHBV film is very brittle and stiff with low flexibility because it showed pretty high tensile strength at yield and Young's modulus. The tensile strength at yield of PLA/PHBV is about 43 MPa in MD and 29 MPa in TD while Young's modulus is 2947 MPa in MD and 3045 MPa in TD. However, elongation at break in MD and TD of PLA/PHBV is only 10% and 1%, respectively. PLA/PBAT film is more flexibility with 31 MPa in MD and 18 MPa in TD of tensile strength at yield, 2369 MPa in MD and 1925 MPa in TD of Young's modulus as well as 3% in MD and 20% in TD of elongation at break. In case of ternary blend, tensile strength at yield and Young's modulus was decreased with increasing PBAT content. The tensile strength at yield was reduced from 43 MPa (PLA/PHBV) to 37 MPa (PB3) in MD and from 29 MPa (PLA/PHBV) to 18 MPa (PB3) in TD as shown in **Figure 4.4** whereas Young's modulus of films was decreased from 2947 MPa (PLA/PHBV) to 1966.40 MPa (PB3) in MD and 3045 MPa (PLA/PHBV) to 1574 MPa (PB3) in TD, as shown in **Figure 4.5**. This was expected since PBAT has a lower tensile strength at yield and Young's modulus than PLA and PHBV [27]. On the contrary, the elongation at break of ternary blend films is shown in **Figure 4.6** that the flexibility has increased by blending with some amount of PBAT contents. In MD, the elongation at break increased to a maximum at 20 wt% PBAT whereas to be reduced at 10 wt% and 30 wt% corresponding to the fracture surface from morphological study. 10% PBAT showed brittle fracture surface whereas 20% and 30% PBAT showed more elongated fibrous structure in the fractured surface and more inclusion of PBAT particle, respectively. In case of TD, the elongation at break tended to enhance with increasing of PBAT content.

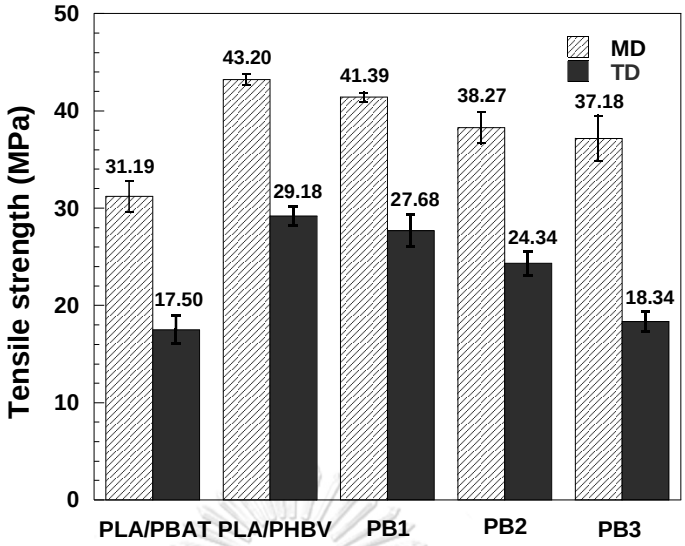


Figure 4.4 Tensile strength of all blends in both MD and TD

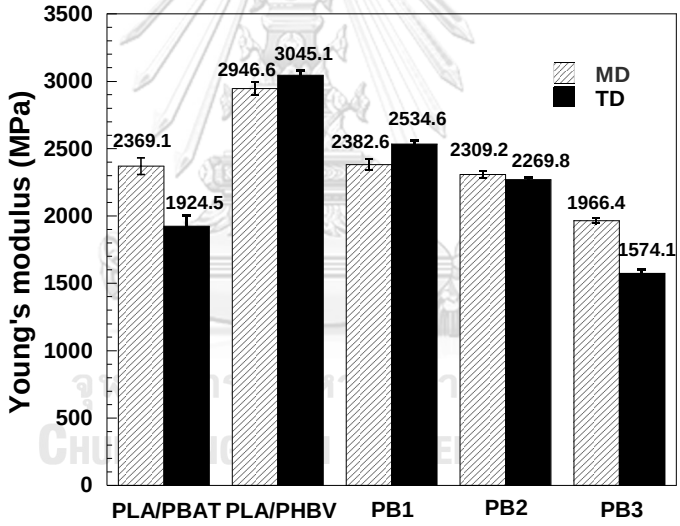


Figure 4.5 Young's modulus of all blends in both MD and TD

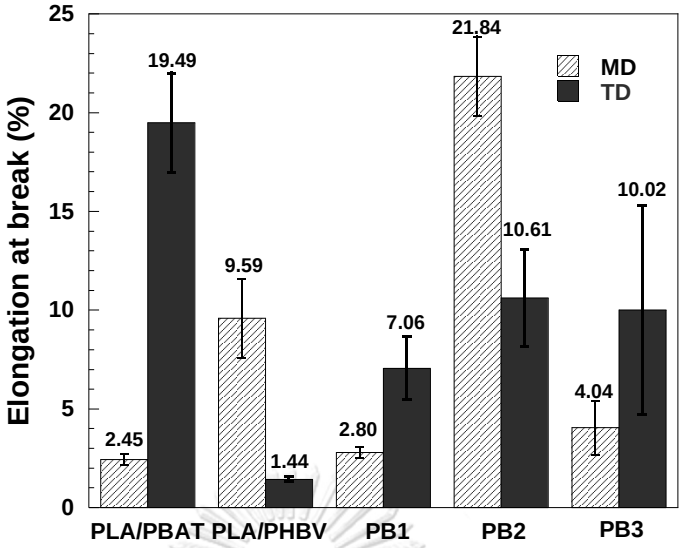


Figure 4.6 Elongation at break of all blends in both MD and TD

The impact strength of PLA/PBAT (19.22 J/cm) was more than PLA/PHBV (4.07 J/cm) at the same ratio 80/20 since PBAT could reduce its brittleness characteristics while PHBV was very brittle. In case of ternary blend, PLA/PHBV was slightly increased at 10wt% PBAT because of low PBAT content. While 20 and 30wt% PBAT, the impact strength was dramatically increased. The presence of PBAT reduces its brittleness characteristics which is evident from the increase of impact strength value from 4.07 J/cm in PLA/PHBV to 103.94 J/cm in case of PLA/PHBV/PBAT blend that is shown in **Figure 4.7**.

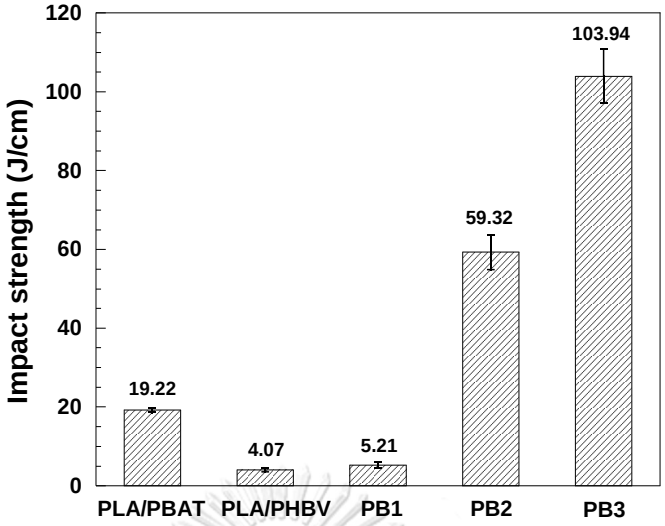


Figure 4.7 Impact strength of all blends

The packaging for dried banana should be good in gas barrier and mechanical properties. For gas barrier properties, all films have acceptable value for packing dried banana because of the range of WVP not over 331 g.mil/m^2/day [2]. In case of mechanical properties, PB2 film has the most optimal mechanical properties. Therefore, PB2 was chosen to pack the dried-banana and observed the physical and chemical properties of dried banana during storage in package for 4 months as well as study the biodegrability of PB2 film for 6 months.

4.2 Physical and chemical properties of dried banana

(a) (b)

Figure 4.8 Dried bananas packed in (a) PB2 film and (b) commercial film

The dried bananas were packed in both PB2 and commercial film as shown in **Figure 4.8**. The gas barrier properties of both films is shown in Table 4.3. Commercial film has lower water vapor transmission rate than PB2 film while oxygen transmission rate of commercial film is similar with that of PB2 film. The physical and chemical properties of dried banana such as color change, moisture content, water activity and texture were studied during storage.

Table 4.3 The comparison of gas barrier properties between PB2 and commercial films

Type of film		Thickness (μm)	Water vapor transmission rate (g/m^2/day)	Oxygen transmission rate (cc/m^2/day)
PB2 film		35	124.47	254.27
Commercial film	Metalized	70	4.91	283.25
	Transparent	70	16.85	237.09

4.2.1 Color change

Color parameters (L*, a* and b*) and progress of color change (ΔE) of the dried banana which was packed in both PB2 and commercial film for 4 month period of storage is depicted in **Figure 4.9**. The L* is for the lightness from black (0) to white (100) while a* is from green (–) to red (+) and b* is from blue (–) to yellow (+). The results show that the trend of color parameters and ΔE of dried banana is quite similar for both types of films. Moreover, it was observed that the L* decreased but a* and b* increased within the first 14 days of storage whereas the ΔE slightly increased. These changes in color parameters could be due to non-enzymatic browning reaction, i.e. Maillard reaction [39]. Maillard reaction could occur at higher rate in the food with a_w value of 0.6-0.8 [40]. At the 14^{th} day of storage, the variability of a* and b* which indicated by error bars was quite large, comparing to the values at other storage time. This could indicate greater variation of the sample color, which might relate to different sugar content of dried bananas. The ripeness degree of each banana before drying might be different, resulting in different sugar content in the dried samples. The unripe banana usually has lower sugar content than the ripe one [41]. After 14 days, the L* value tended to increase and seemed to be constant after 41 days of storage. This could be a result from sugar recrystallization, as shown in **Figure 4.10**. Sugar recrystallization is a major challenge for dried fruits with low moisture levels and high sugar contents or called supersaturation [42]. Once a critical supersaturation has been exceeded, nucleation occurs. Nucleation involves formation of a crystalline state of the solute from the supersaturated soluble state. Once nuclei form, they grow into product-sized crystals through incorporation of additional molecules into the crystal lattice, leading to the crystal growth. [43, 44]. In case of the a* and b* values, they tended to decrease, especially the b* value. However, these parameters remained constant after 41 days of storage. This could be due to extensive darkening indicated by high ΔE value after 41 days of storage. An increase in ΔE value during storage of dried banana at room temperature was previously reported [2]. This could confirm the surface darkening of dried banana during storage, regardless of packaging material used.

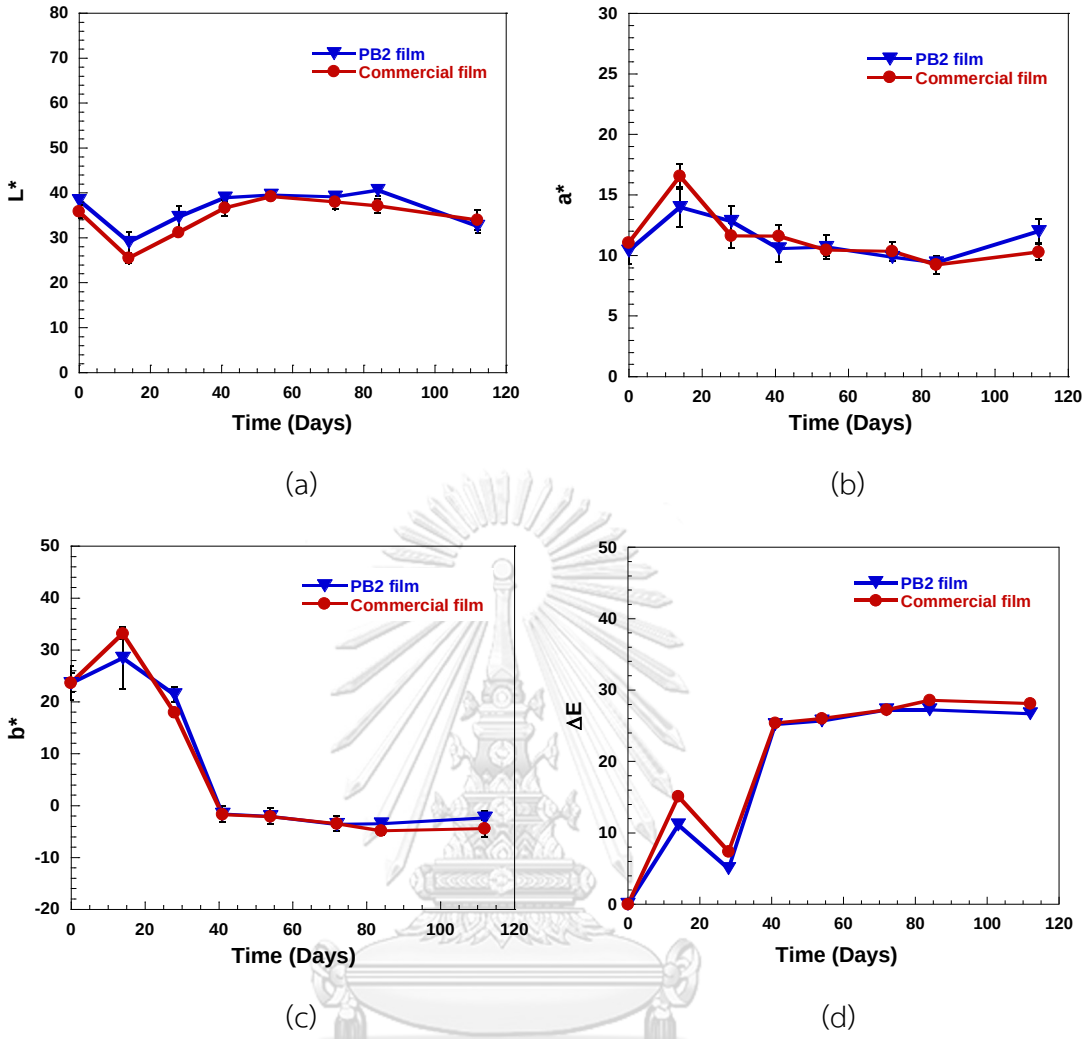


Figure 4.9 Color parameters in CIE L*, a*, b* system and Color change (ΔE) of the dried banana packed in PB2 and commercial films

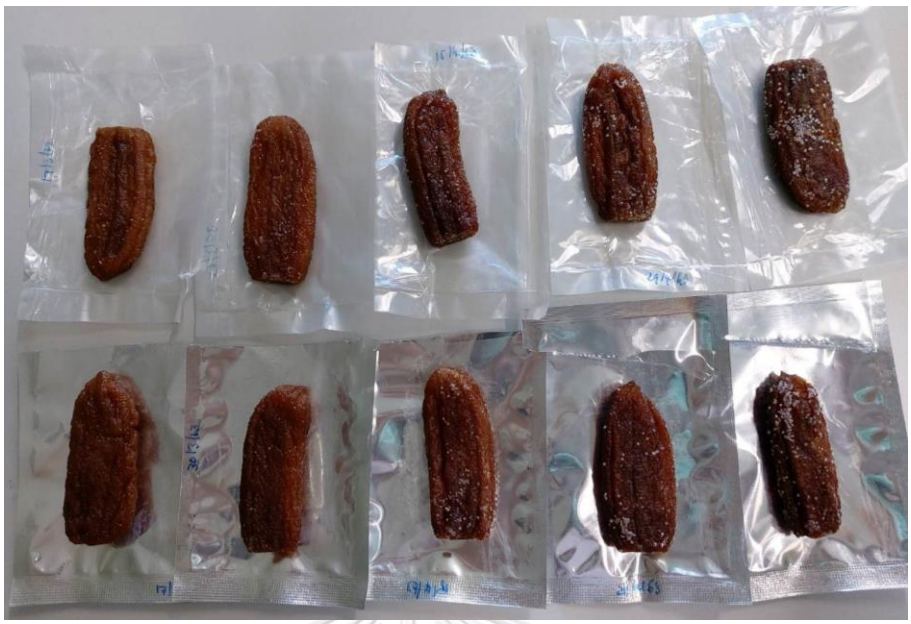


Figure 4.10 Sugar crystallization of dried banana which stored in both PB2 (above) and commercial (below) films at storage time 41, 54, 72, 84 and 112 days (from left to right)

4.2.2 Moisture content and water activity

Effect of packaging materials on moisture content of dried banana was shown in Figure 4.11. The initial moisture content of dried banana in PB2 and commercial film were 22.63% and 22.34%, respectively. After 112 days of storage at the room temperature, moisture content of dried banana in PB2 and commercial film were 19.43% and 22.49%, respectively. That means, for the samples packed in PB2 film, they tended to have greater moisture loss than the samples stored in commercial film. This might be due to the difference in water vapor transmission rate (WVTR) of film. PB2 film had higher WVTR, resulting in greater rate of changes in moisture loss than the commercial one at the same temperature.

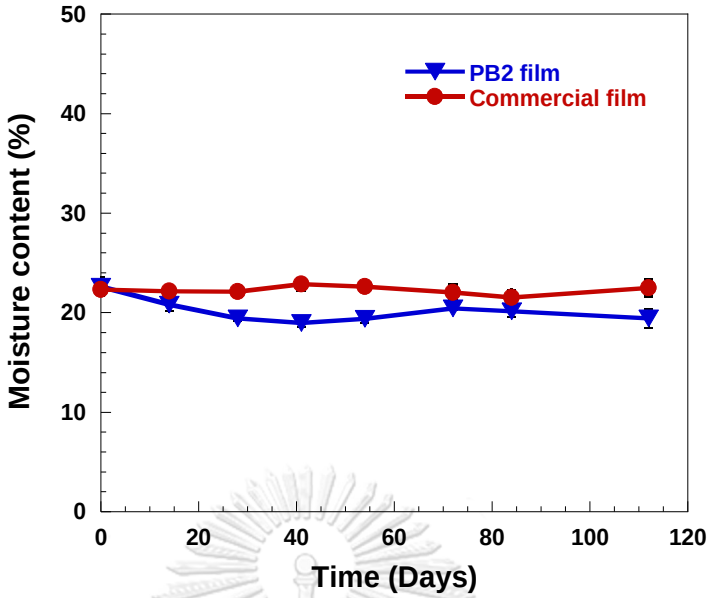


Figure 4.11 *Moisture content of the dried banana packed in PB2 and commercial films*

In case of water activity (a_w), as shown in **Figure 4.12**, the change in water activity of dried banana tended to be minimal during 112 days. Water activity of dried banana which was stored in PB2 and commercial films stayed within a narrow range 0.63-0.66 and 0.64-0.68, respectively. Moreover, it was observed that dried banana packed in PB2 film had little lower water activity than dried banana stored in commercial film during period of storage. It indicated that dried banana stored in PB2 film lose free water more than dried banana stored in commercial film during storage which was corresponding with the result of moisture content. Based on previous study, for the dried banana stored in the PLA-based film at room temperature for 186 days (corresponding to 6 months), moisture content and water activity were fluctuated within a range of 20-24% and 0.63-0.66, respectively [2]. Those data were in an agreement with the data reported in this study, especially for the dried banana samples stored in PB2 film.

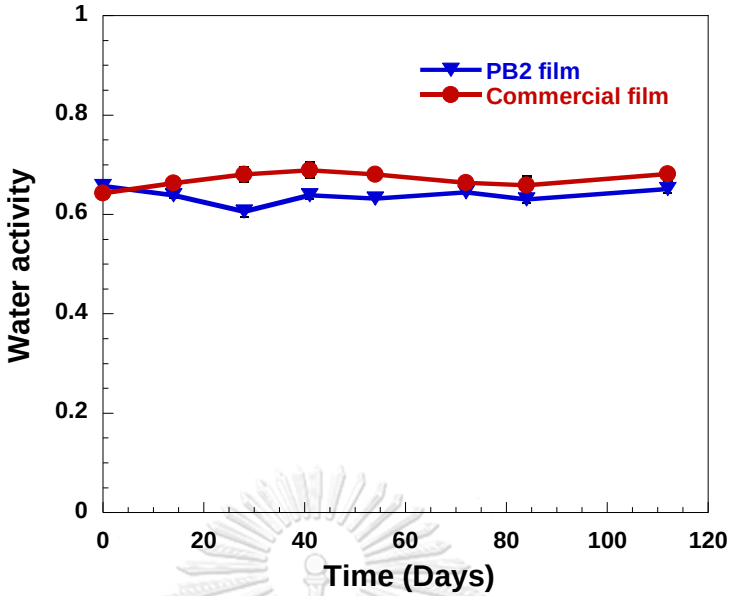


Figure 4.12 *Water activity of the dried banana packed in PB2 and commercial films*

4.2.3 Texture

Hardness of dried banana that was stored in both PB2 and commercial films tended to be slightly increased during storage time as shown in **Figure 4.13**. The hardness of dried banana packed in PB2 film was slightly greater than the sample in commercial film. It could be a result from having moisture loss and lower a_w value [45]. Sugar recrystallization might also cause an increase in hardness of dried fruits [42, 46]. However, previous study showed less extent of hardness increase during storage of dried banana at room temperature [2].

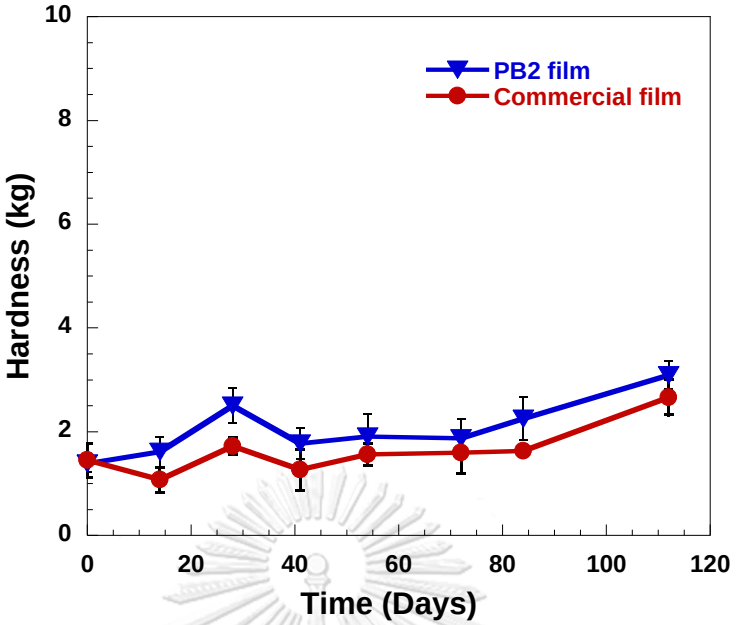


Figure 4.13 *Hardness of the dried banana packed in PB2 and commercial films*

In case of the appearance of dried banana during storage time, the dried banana which was stored in PB2 film showed dry and hard skin while the soft skin was shown for dried banana which was stored in commercial film corresponding to the results from moisture content, water activity and texture study. The color change of dried banana stored in both types of packages gave similar results. Nevertheless, dried banana stored in PB2 film was slightly harder because the gas permeability of PB2 film is greater. Since the hardness of dried banana packed in PB2 and in commercial films are not much different, it can be concluded that PB2 film can be used instead of commercial film for the samples stored at room temperature. For the higher temperature, it is found that the barrier properties of PB2 film should increase because the water vapor transmission rate will be higher. In case of sugar recrystallization during storage, it affects some quality attributes such as appearance, texture and shelf life in dried banana. Therefore, dried banana stored for a long time may not be accepted by consumers. However, further sensory evaluation, especially consumer acceptance test, should be performed to confirm the application of PB2 film as an alternative packaging material for storage of dried banana.

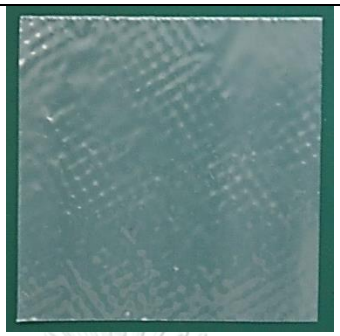
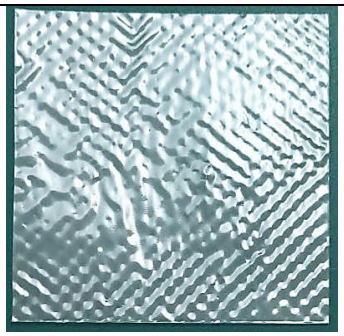
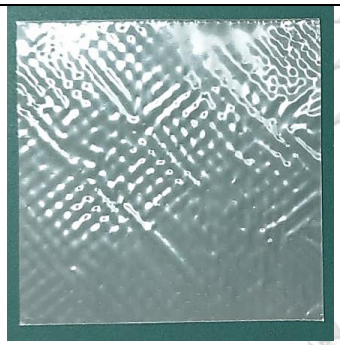
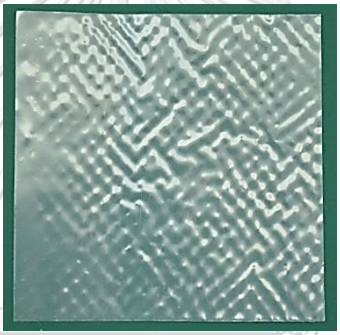
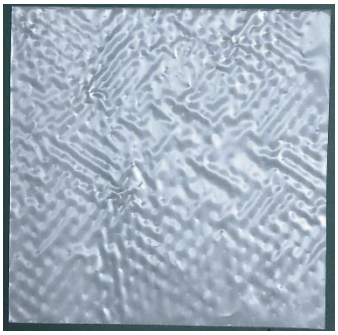
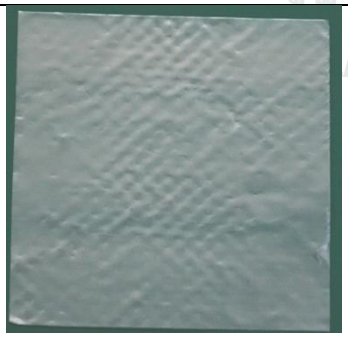
4.3 Soil burial test

The changes in appearance of PB2 films which was buried in soil from the top 10-cm depth during 6 months were observed by digital camera, and the photos are shown in **Table 4.4**.

The test location was set at outdoor and expose the sunlight. The temperature and relative humidity of surrounding was mainly at 30±2℃ and 66.5±4.0 % during 6 months. The temperature, moisture content and pH of soil was not controlled throughout the experiment. Moreover, the soil surface was observed to be dry as well as no watering and planting. These photos show that no fragmentation or disintegration was visually observed in sample during 6 months.

The result of the soil burial depends on the polymer type and the soil conditions [47]. The biodegradation of PLA under soil conditions is a complex process, and the degradation rate is relatively slow. The good biodegradation rates of PLA was found at or above glass transition temperature (T_g about 58-60℃) under compost or anaerobic biodegradation [48-50]. Moreover, other related works show the degradation of PLA could occur under the real soil at 20±3℃ which was suitable for the living and reproduction of bacteria, moisture content about 40-60% and pH of 7-8 [51-53]. Water content in soil is important for the microorganisms because it affects the intracellular metabolism, the movement of nutrients and adherence to clay particles. Another important factor in microbial growth is soil's pH, which can directly affect the metabolism, membrane permeability, and adsorption, or indirectly affect the physiology and solubility of toxic elements [47]. In case of PHBV and PBAT, they can be degraded under real soil conditions and composting conditions [50-52]. For binary blend system, PLA/PHBV blend and PLA/PBAT blend samples in the soil burial could degrade and had faster degradation rates than neat PLA but they were slower than neat PHBV and PBAT, respectively [51, 53]. Therefore, the improper tested condition caused no change in the samples.

Table 4.4 *The apparent variation of PB2 films during the burial in 10 cm depth soil*

		
9 December 2019 (0 month)	9 January 2020 (1 month)	9 February 2020 (2 months)
		
9 March 2020 (3 months)	9 April 2020 (4 months)	9 May 2020 (5 months)
		
9 June 2020 (6 months)		

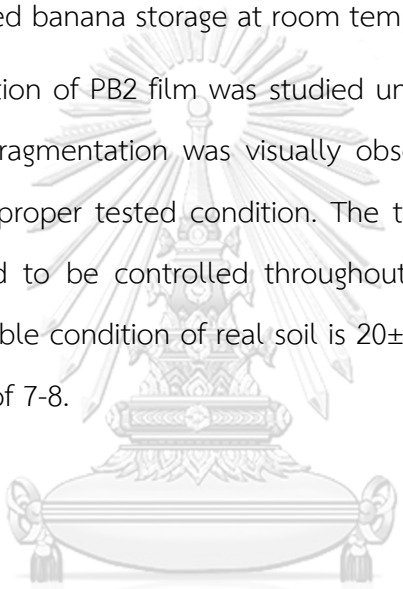
CHAPTER V
CONCLUSIONS

In this study, bioplastic packaging was developed from the ternary blend system of PLA/PHBV/PBAT. The ratio of PLA/PHBV was fixed at 80/20 (wt/wt) while the PBAT content was 0, 10, 20 and 30 wt%. Moreover, PLA/PBAT 80/20 film was also studied. The results show that the PBAT and PHBV were dispersed in PLA matrix in the form of spherical particles as can be observed by SEM micrograph of the fractured surface. Furthermore, PLA/PBAT film shows the elongated fibrous of PBAT as presented as ductile fracture behavior with several filaments. The addition of PBAT in PLA/PHBV film causes the small oval cavities and the elongated fibrous because of interfacial debonding between PLA and PBAT. The increase of PBAT content was also found that the size of oval cavities increased as a result of inclusion of PBAT whereas the number of the elongated fibrous was also increased. The immiscibility of blend system was confirmed by no change in the glass transition temperature which is separated in both binary and ternary blends regardless of the concentration of PBAT. In the case of barrier properties, PLA/PHBV film had higher barrier properties than PLA/PBAT one when PHBV was introduced in PLA matrix as a result of high permeability of PBAT. For the ternary blend, permeability of PLA/PHBV film was increased by adding PBAT concentration. However, PLA/PBAT film showed more flexible than PLA/PHBV one. Although the flexibility of film was increased when PBAT content was introduced in PLA/PHBV film, the addition of 20wt% PBAT content (PB2) showed the optimal mechanical properties.

The PB2 film was selected to store dried banana for 4 months at room temperature (30±2°C) to be compared with commercial film as the metallized film. The result shows that dried banana which was stored in PB2 and commercial films showed the similar results in color change. They tended to be darkened due to the non-enzymatic browning reaction, i.e. Maillard reaction. Moreover, sugar crystallization was appeared in dried banana in both types of packaging after 28 days

storage because of the low moisture levels and high sugar contents of the samples. In case of moisture content and water activity, dried banana in PB2 film had lower moisture content and water activity than the sample in commercial film because of higher water vapor transmission rate of PB2 film. Likewise, the texture of dried banana which was packed in PB2 film was harder than that packed in commercial package as a result of low moisture content and water activity. The color change, moisture content, water activity and hardness of dried banana packed in PB2 and commercial films are not much different, so PB2 film may be used instead of commercial film for dried banana storage at room temperature.

The biodegradation of PB2 film was studied under soil burial conditions. The result shows that no fragmentation was visually observed in the sample during 6 months due to the improper tested condition. The temperature, moisture content and pH of soil needed to be controlled throughout the experiment. From other related works, the suitable condition of real soil is 20±3°C of temperature, 40-60% of water content and pH of 7-8.



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