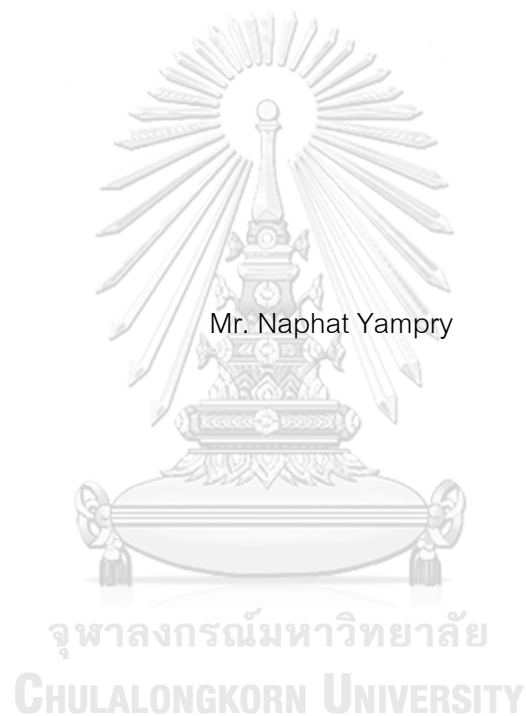Study of Thermal and Mechanical Properties of Tertiary Blend of Poly(lactic acid),

Poly(hydroxybutyrate-co-hydroxyvalerate) and Thermoplastic starch

Mr. Naphat Yampry

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

FACULTY OF ENGINEERING

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การศึกษาสมบัติเชิงความร้อนและเชิงกลของสารผสมระบบสามองค์ประกอบของพอลิแลคติคแอ
ซิด พอลิไฮดรอกซีบิวทิเรต-โค-ไฮดรอกซีวาเลอเรต และเทอร์โมพลาสติกสตาร์ช

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Thesis Title	Study of Thermal and Mechanical Properties of Tertiary Blend of Poly(lactic acid), Poly(hydroxybutyrate-co-hydroxyvalerate) and Thermoplastic starch
By	Mr. Naphat Yampry
Field of Study	Chemical Engineering
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Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

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ณภัทร แย้มพราย : การศึกษาสมบัติเชิงความร้อนและเชิงกลของสารผสมระบบสาม
องค์ประกอบของพอลิแลคติคแอซิด พอลิไฮดรอกซีบิวทิเรต-โค-ไฮดรอกซีวาเลอเรต และ
เทอร์โมพลาสติกสตาร์ซ. (Study of Thermal and Mechanical Properties of Tertiary
Blend of Poly(lactic acid), Poly(hydroxybutyrate-co-hydroxyvalerate) and
Thermoplastic starch) อ.ที่ปรึกษาหลัก : รศ. ดร.อนงค์นาฏ สมหวังธนโรจน์, อ.ที่ปรึกษา
ร่วม : ผศ. ดร.วันชัย เลิศวิจิตรจรัส

ปัจจุบันพลาสติกแบบใช้ครั้งเดียวเช่น หลอด ถุงพลาสติก เป็นสาเหตุให้เกิดปัญหาขยะ
พลาสติกเนื่องจากพลาสติกส่วนใหญ่ซึ่งเป็นพลาสติกที่ผลิตจากปิโตรเลียมนั้นไม่สามารถย่อยสลายได้
และยากที่จะนำไปรีไซเคิล ดังนั้นพลาสติกย่อยสลายได้ทางชีวภาพเป็นทางเลือกที่เหมาะสมที่จะมา
แทนที่พลาสติกแบบดั้งเดิม งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาสัณฐานวิทยา สมบัติเชิงความร้อนและ
เชิงกลของสารผสมระบบสามองค์ประกอบของพอลิแลคติคแอซิด (PLA) พอลิไฮดรอกซีบิวทิเรต-โค-
ไฮดรอกซีวาเลอเรต (PHBV) และเทอร์โมพลาสติกสตาร์ช (TPS) ขั้นตอนการเตรียมของผสม
PLA/PHBV และ PLA/PHBV/TPS มีดังนี้ เตรียมของผสม PLA/PHBV ที่อัตราส่วนน้ำหนัก 80/20,
70/30 และ 60/40 สำหรับของผสม PLA/PHBV/TPS เติม TPS ไปในสัดส่วน 1, 5 และ 10 phr ลงใน
ของผสม PLA/PHBV ที่อัตราส่วนน้ำหนัก 80/20 สารที่ถูกเตรียมไว้จะถูกผสมด้วยเครื่องอัดรีดแบบสก
รูคู่เพื่อเตรียมแผ่นฟิล์ม ผลที่ได้คือการเติม PHBV ใน PLA/PHBV ทำให้คุณสมบัติเชิงกลเพิ่มขึ้น
อย่างไรก็ตามการเติม TPS ลงไปในระบบพบว่าคุณสมบัติเชิงกลลดลง ภาพจากกล้องจุลทรรศน์
อิเล็กตรอนเผยว่าการผสมของ PLA/PHBV นั้นไม่เป็นเนื้อเดียวกัน และการเติม TPS ส่งผลต่อ
คุณสมบัติเชิงกล นอกจากนี้ผลการทดสอบด้วยเทคนิค DSC แสดงให้เห็นว่าการเติม PHBV และ TPS
ลงในพอลิเมอร์มีผลต่อคุณสมบัติทางความร้อนของแผ่นฟิล์มอย่างมีนัยสำคัญ

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต ....
ปีการศึกษา	2562	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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KEYWORD: Polylactic acid, Poly(hydroxybutyrate-co-hydroxyvalerate), Thermoplastic starch, Polymer blend

Naphat Yampry : Study of Thermal and Mechanical Properties of Tertiary Blend of Poly(lactic acid), Poly(hydroxybutyrate-co-hydroxyvalerate) and Thermoplastic starch. Advisor: Assoc. Prof. ANONGNAT SOMWANGTHANAROJ, Ph.D. Co-advisor: Asst. Prof. Wanchai Lerdwijitjarud, Ph.D.

Nowadays, single-use plastics such as straws, plastic bags cause plastic waste problems because the majority of these plastics which are petroleum-based plastics are not compostable and difficult to recycle. As a result, biodegradable plastic is a proper option to replace traditional plastic. The objective of this work was to study the morphology as well as the thermal and mechanical properties of tertiary blend of poly(lactic acid) (PLA), poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and thermoplastic starch (TPS). PLA/PHBV at weight ratios of 80/20, 70/30, and 60/40 were prepared to find the optimal ratio. Then the PLA/PHBV at weight ratio of 80/20 was added by TPS 1,5 and 10 phr. The cast-film extrusion was used to prepare film sheets. It was found that the addition of PHBV in PLA/PHBV blends led to an increase in tensile properties. However, the addition of TPS in PLA/PHBV/TPS blends brought about lower in tensile properties. SEM micrographs revealed that PLA/PHBV blends were not miscible and the addition of TPS in PLA/PHBV/TPS blends affected their mechanical properties. Moreover, DSC data indicated that the addition of PHBV and TPS had significantly affected the thermal properties of film sheets.

Field of Study:	Chemical Engineering	Student's Signature	....
Academic Year:	2019	Advisor's Signature	....
		Co-advisor's Signature	....

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

1.1 Introduction

Plastic pollution becomes a vast problem in the world. The plastic products have many types; one of them that mostly leads to plastic pollution is a single-use plastic. Single-use plastics are petroleum-based which cannot be biodegraded in a short time and difficult to recycle because this type of plastic is contaminated with food. These causes lead to the plastic waste problem not only in Thailand but also worldwide. Also, Thailand's Roadmap on Plastic Waste Management 2018-2030 (draft) [1] has considered passing the law by the Department of Pollution Control for major ban on single-use plastic bags, to be effective by 2021. Furthermore, the roadmap seeks to ban plastic bags, styrofoam, cups, and straws by 2022. Moreover, the roadmap defines 7 types of plastics that are within the scope of being reduced and discontinued by the year 2025 and has a combined goal of recycling 70% of single-use plastic products in the year 2037, with the use of renewable materials that are more environmental friendly.

To reduce plastic waste problems, biodegradable plastic is a good alternative to produce biodegradable single-use plastic. According to ISO 472:1998, biodegradable plastics are plastic designed to undergo a significant change in its chemical structure into natural compounds such as water, carbon dioxide, methane under specific environmental conditions resulting in a loss of some properties and change in chemical structure which is results from the action of naturally occurring microorganisms. As a result, biodegradable polymers were used in this study. Polylactic acid (PLA) is the most well-known biodegradable plastic because PLA has good mechanical properties, cheap and good biodegradability [2] but PLA is brittle due to low impact strength and elongation. Polyhydroxyalkanoates (PHAs) such as poly-3-hydroxybutyrate (PHB) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) are more promising due to their inherent biodegradability, sustainability and environmental friendly. In general, PHAs has better biodegradability than PLA because the degradation of PHAs are caused by

bacteria catalyzed erosion from the surface to the internal part, while PLA is hydrolytically degraded [3]. PHAs has high crystallinity and good biodegradability but PHAs are difficult in processing and expensive. *Zhang and Thomas* [4] studied the mechanical properties of PLA/PHB blends. The results showed that adding PHB in PLA/PHB blends led to a reduction in exponential decay of elongation at break and tensile strength. *Armentano et.al.* [5] also studied the mechanical properties of PLA/PHB blends. The PLA/PHB 85/15 blend showed an increase in elongation at break without significantly changed in tensile strength but Young's modulus had been decreased when compared with neat PLA. Apart from PLA and PHA bioplastic, there are many studies focusing on starch as a cheap and abundant renewable polymer. The development and production of biodegradable, thermoplastic starch (TPS) is considered important in reducing the total amount of plastic waste [6]. *Teixeira et.al.* [7] studied the PLA/TPS blends and found that adding TPS led to a reduction of Young's modulus and tensile strength without significantly changed in elongation at break due to the higher crystallization of TPS. In this study, the thermal and mechanical properties of binary blends between PLA and PHBV and tertiary blend between PLA, PHBV and TPS were examined to explore the possibility to use these tertiary blends in single use plastic in food packing application.

1.2 Objective of the research

To study of thermal and mechanical properties of binary and tertiary blend of PLA, PHBV and TPS.

1.3 Scopes of Work

- Study the binary system with PLA as the first component and PHBV as a second component.
- Vary PLA/PHBV weight ratios of 80/20, 70/30 and 60/40.
- Study the tertiary system with PLA as the first component, PHBV as a second component and TPS as the third component.
- Vary TPS in 1, 5 and 10 phr in PLA/PHBV 80/20 ratio.
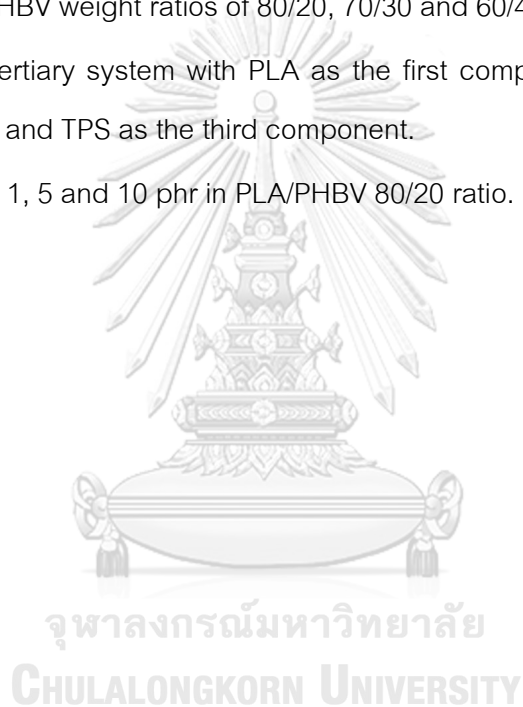
CHAPTER II
THEORY AND LITERATURE REVIEWS

2.1 Biodegradable plastics

Biodegradable plastics are plastics that can be decomposed by the action of living organisms usually microorganisms under the suitable conditions which are converted into water, carbon dioxide, and biomass [8]. Biodegradation is a process that can occur in many environments such as soils, compost sites, water treatment facilities, marine environments and even in the human body. The processes consist of two steps. Firstly, the degradation step in which the long-chain polymer is cut into the shorter-chain polymer. Secondly, the biodegradation step in which the short-chain polymer is converted to water, biomass, carbon dioxide or methane by microorganisms under suitable conditions. However, oxo-plastic is not a biodegradable material due to the process of degradation is only physical degradation into a microplastic following ASTM D6400.

Following ASTM D6400, compostable plastics are plastic that can be decomposed into natural minerals and compounds such as carbon dioxide, water and biomass. The biodegradation step is in a controlled condition suitable for industrial composting or composting organic fertilizer. Compostable plastics are always biodegradable but biodegradable plastics are unnecessary compostable.

2.2 Poly(lactic acid)

Poly(lactic acid) (PLA) is a thermoplastic that is a part of aliphatic polyester family. The chemical structure of PLA is shown in Figure 2.1. PLA is produced from the renewable resources in which the monomer is normally produced by fermentation of a renewable agricultural source such as corn, cassava, sugarcane or sugar beet pulp [9]. The reaction for PLA production is the reaction among α-hydroxy acids called ring-opening polymerization [10]. The most common pathway to produce PLA is in solution or suspension process by the ring-opening polymerization of lactide with several metal catalysts. PLA is a biobased polymer because it is the product that is obtained from the fermentation of sugar feedstocks. In addition, PLA is biocompatibility, while under optimal conditions, PLA is totally biodegradable. However, PLA is not compostable like PHAs; that is why the processes of decomposing PLA needs to be under optimal circumstances [11]. PLA is an industrial compostable material which means that PLA can be composted in industrial scale. In the industrial composting process of PLA-based materials, the abiotic hydrolysis occurred by the random scission of ester bonds and led to successive reduction in a molar mass and an increase in the dispersity index of the samples. After longer incubation time, the samples were disintegrated and then start to decompose into the acidic water-soluble degradation products [12].
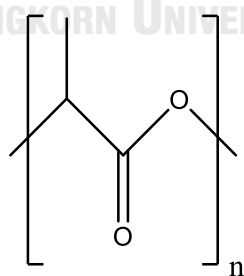
Figure 2.1 Structure of PLA [10].

PLA is the most well-known biodegradable plastic and used widely in many applications due to the low cost and good properties [2]. The advantages of PLA are good mechanical properties, biodegradable and renewable. Nevertheless, the disadvantages of PLA are its brittleness, low impact strength, low elongation and low heat resistance. This research wanted to improve the elongation and impact strength of PLA blends to the closer to a petroleum-based polymer such as polypropylene (PP) and low-density polyethylene (LDPE). To compare with a petroleum-based polymer, the properties of PLA, PP and LDPE were shown in Table 2.1.

Table 2.1 Properties of Poly(lactic acid), Polypropylene and Low-density polyethylene.

Properties	PLA [13]	PP [14]	LDPE [15]
Glass transition temperature (°C)	55 - 60	-10 to 0	-110
Melting temperature (°C)	145 - 160	160 - 165	100 - 110
Crystallinity (%)	N/A	70 - 80	60-80
Young's modulus (MPa)	3600	1100 - 1600	200
Tensile strength at yield (MPa)	53	33	8 - 15
Elongation at break (%)	6	150	90 - 800

2.3 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are a group of thermoplastic polymers classified as biodegradable and compostable. The chemical structure of PHAs is shown in Figure 2.2. PHAs derivatives consist of 3 main types, short-chain length (C_3-C_5), medium-chain length (C_6-C_{14}) and long-chain length (>C_{14}), which can be used for several applications such as PHAs were also used for biomedical applications. For example, suturing and controlled drug delivery, fishing lines and nets, pesticides, food packaging and daily products [16]. Therefore, PHAs were suitable to be used as a single-use plastic product [17, 18].
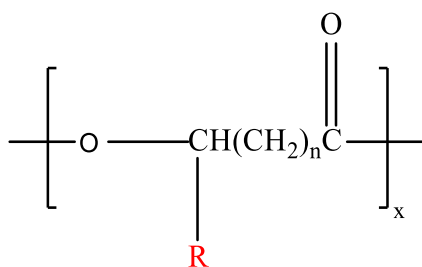
R = hydrogen	Poly-3-hydroxypropionate
R = methyl	Poly-3-hydroxybutyrate
R = ethyl	Poly-3-hydroxyvalerate
R = propyl	Poly-3-hydroxyhexanoate
R = pentyl	Poly-3-hydroxyoctanoate
R = nonyl	Poly-3-hydroxydodecanoate

Figure 2.2 Chemical structure of PHAs [17].

The decomposing of PHBV was studied under real soil conditions by the samples of PHBV that were buried in the soil and located at depths of 20 cm from the soil surface. The temperature of the soil was mainly at 20±3 °C in which it was suitable for the living and reproduction of bacteria. The results showed that the degradation of PHA was caused by erosion of bacteria from the surface to the center of the samples, while PLA was hydrolytically degraded [3]. For this reason, the degradation rates of PHAs is higher than that of PLA. There are many types of derivative PHAs in which the popular commercial types are poly-3-hydroxybutyrate (PHB), poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH). The properties of PHB, PHBV and PHBH are shown in Table 2.2. This study aimed to improve the mechanical properties of PLA because PLA has low impact strength and elongation at break, so PHBV is chosen due to several good qualities of PHBV which are in between those of PHB and PHBH. The length of the functional group

of PHBV was in between PHA and PHBH. Moreover, another important point was that the derivative PHAs have much higher impact strength than PLA.

Table 2.2 *Properties of Poly(lactic acid), Poly-3-hydroxybutyrate, Poly-3-hydroxybutyrate-co-3-hydroxyvalerate and Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).*

Properties	PLA [13]	PHB [19]	PHBV [20]	PHBH [21]
Glass transition temperature (°C)	55 - 60	6 - 7	4	2
Melting temperature (°C)	145 - 160	175 - 180	175 - 180	145
Young's modulus (MPa)	3600	1600 - 2100	1600 - 2100	1820
Tensile strength at yield (MPa)	53	38	39	36
Elongation at break (%)	6	3.2	3.8	4.0
Impact [J/m]	8.8	6-7	4	2

จุฬาลงกรณ์มหาวิทยาลัย

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2.4 Thermoplastic Starch

Thermoplastic starch (TPS) is a bio-based polymer which is available from a natural source directly and is non-toxic materials. TPS is a renewable material and can be incorporated into soil as an organic fertilizer in a landfill and/or microbial action [22]. Starch-based materials such as crops, rice, corn, cassava and beans are used as the main raw materials for TPS production. TPS consists of amylose and amylopectin in its structure. The chemical structure of amylose and amylopectin are shown in Figure 2.3. TPS is flexible material that can be easily used in different processes including injection molding, extrusion blow molding, compression molding, and extrusion. Table 2.3 shows the properties of TPS. In general, the native starch cannot be molded by heat treatment like normal plastic due to its crystalline structure of starch. Starch would be burnt and degraded before melting [23]. Therefore, it is necessary to convert the starch into thermoplastic materials so that it can be molded in the same process as conventional plastics.

Table 2.3 Properties of Thermoplastic Starch properties.

Properties	TPS [24]
Glass transition temperature (°C)	N/A
Melting temperature (°C)	N/A
Crystallinity (%)	N/A
Young's modulus (MPa)	77
Tensile strength at break (MPa)	5.4
Elongation at break (%)	51
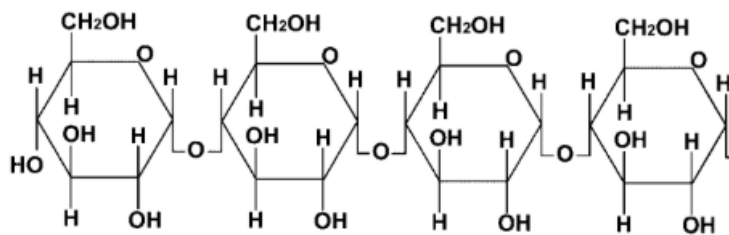
Amylose
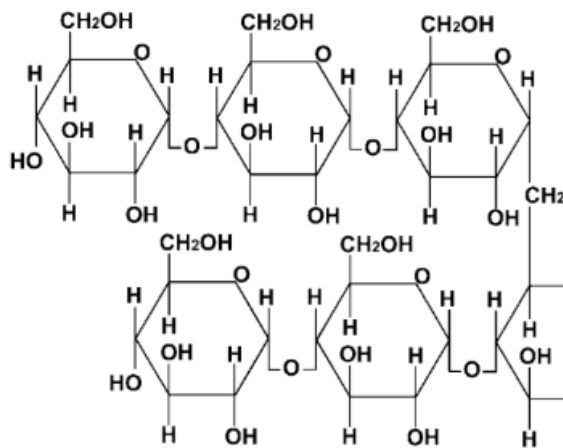
Amylopectin

Figure 2.3 *Chemical structure of amylose and amylopectin [25].*
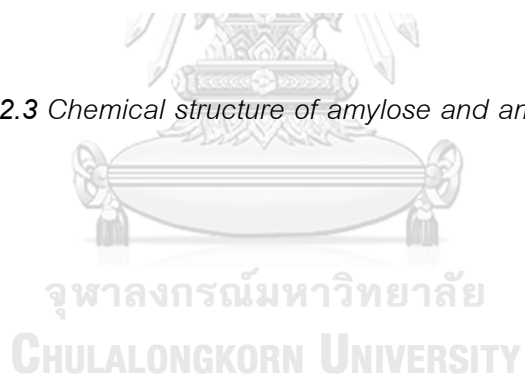
2.5 Polymer blend

The polymer blend is a member of a class of materials analogous to metal alloys, in which at least two polymers are blended together to create a new material with different physical properties [26]. There are many topics studied about the effect of mixing binary compounds of PLA and other biopolymers. *Zhang and Thomas* [4] studied the mechanical properties of PLA/PHB blends at several PLA/PHB weight ratios (100/0, 75/25, 50/50, 25/75, 0/100) which were prepared by melt compounding process. The mechanical properties of the blends were studied but the processability of pure PHB was very poor due to its low melt viscosity and brittleness, so the mechanical data for neat PHB was not obtained. Figure 2.4 showed the tensile properties of PLA and PLA/PHB blends as a function of PLA content. The 75/25 ratio of PLA/PHB blend showed better elongation at break and tensile stress than pure PLA which could be due to its relatively strong cold crystallization peak in the DSC profile at the first heating step and also in second heating step, which was due to the finely dispersed PHB crystals acting as nucleating agents in PLA. Figure 2.5 showed DSC thermograms of PLA/PHB blends in the first heating step, cooling step and second heating step with a heating rate of 10 °C/min.
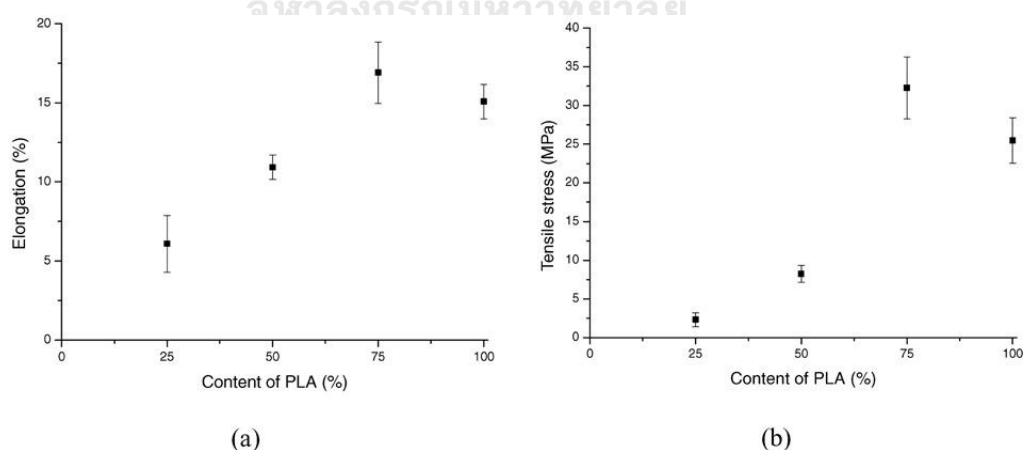
Figure 2.4 Mechanical properties: (a) elongation at break and (b) tensile stress of PLA and PLA/PHB blends as a function of PLA content [4].
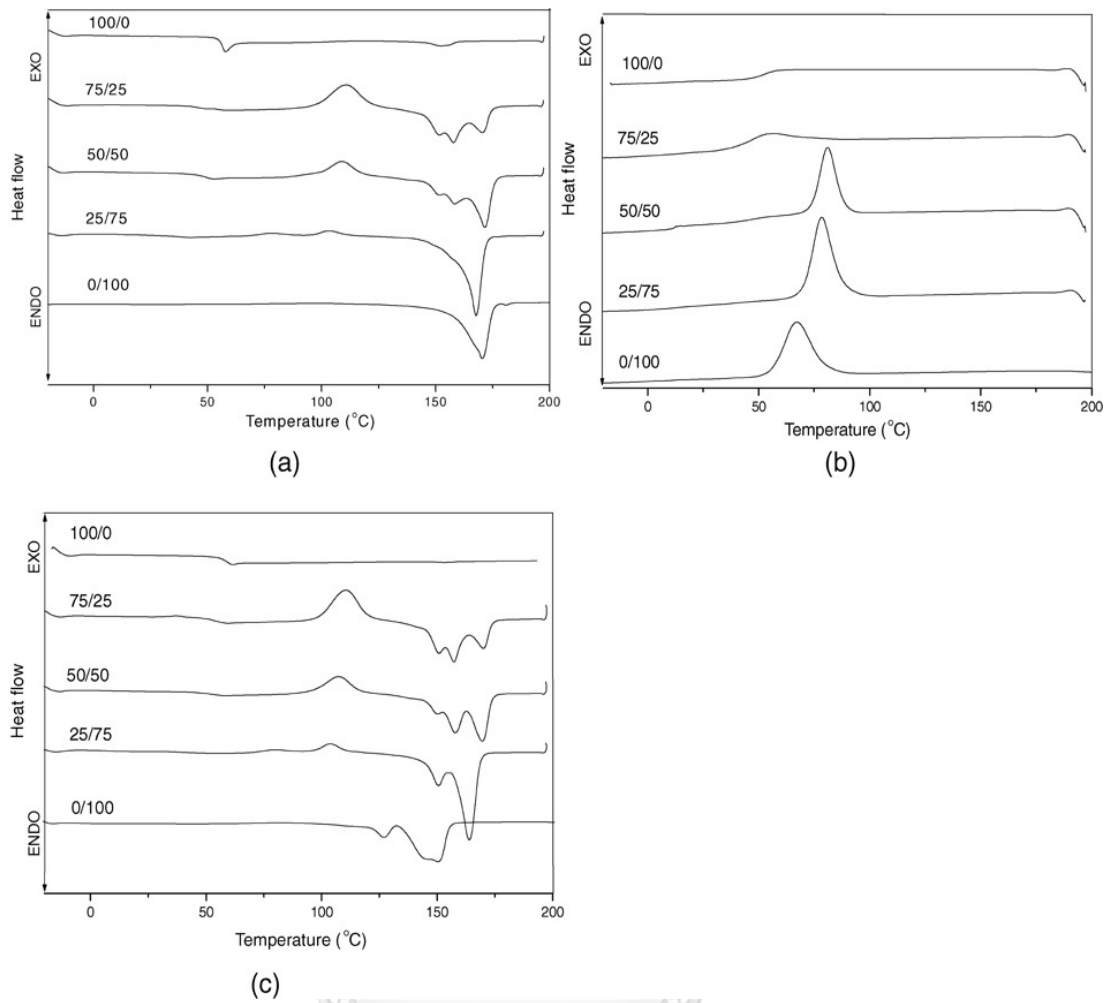
Figure 2.5 *DSC* thermograms *of ratio PLA/PHB blends* with a heating rate of 10 ˚C/min *(a) first heating* step*, (b) cooling* step*, and (c) second heating* step *[4]*.

Similarly, *Armentano et.al.* [5] studied the tensile properties of PLA/PHB blends using 85/15 weight ratio of PLA/PHB blend compared with neat PLA. The tensile properties of neat PLA and PLA/PHB weight ratio 85/15 are shown in Table 2.4. The mechanical properties of PLA/PHB blends in this study is consistent with those in the previous study [4], which showed that PLA/PHB weight ratios 85/15 compared with neat PLA had not significantly changed in tensile strength and Young's modulus compared with neat PLA. Figure 2.6 showed SEM micrographs in different magnifications of neat PLA and PLA/PHB 85/15 blend. While the SEM micrographs of neat PLA showed a uniform and smooth surface which was typical image for a semicrystalline polymer, the SEM micrographs of PLA/PHB 85/15 blend showed the PHB domains well dispersed in the continuous PLA polymer matrix.

Table 2.4 Mechanical properties of neat PLA and PLA/PHB blend [5].

Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
PLA	40 ± 7	3.4 ± 0.4	1300 ± 180
PLA/PHB 85/15	40 ± 5	3.8 ± 0.5	1220 ± 140

Figure 2.6 SEM micrographs in different magnification of (a) neat PLA and (b) PLA/PHB 85/15 [5].

Furthermore, *Amor et.al.* [27] studied the morphology and mechanical properties of PLA/PHBV blends with 90/10 weight ratio. Figure 2.7 showed an Atomic Force Microscopy (AFM) micrograph of PLA/PHBV 90/10. An AFM micrograph of PLA/PHBV films indicated that the dispersed PHBV phase had a relatively small average diameter with a typical morphology dispersed in the PLA polymer matrix. Table 2.5 showed the tensile properties of neat PLA, neat PHBV and PLA/PHBV blend. The mechanical properties of PLA and PHBV were studied but the processability of neat PHBV was very poor due to its low melt viscosity and brittleness, so this study used the data from the datasheet as the reference of the mechanical properties of PHBV. It can be seen that adding PHBV in PLA matrix slightly lowered the tensile strength and elongation at break of the blend but the Young's modulus of the blend increased by25% when compared with neat PLA.
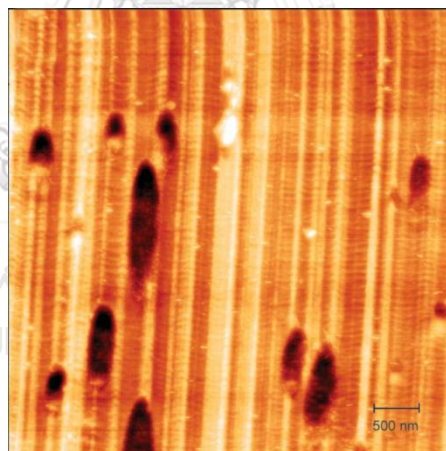
Figure 2.7 AFM micrographs of PLA/PHBV 90/10 [27].

Table 2.5 *Mechanical properties of neat PLA, neat PHBV and PLA/PHBV blend [27].*

Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
PLA	45 ± 4	3.1 ± 1.0	2050 ± 481
PHBV	39	2.0	2800 - 3500
PLA/PHBV 90/10	43 ± 5	3.0 ± 1.0	2507 ± 252

Moreover, *Karla et.al.* [28] studied the mechanical properties of PHB/TPS blend with weight ratio 65/35. TPS in that study was prepared by mixing starch, water, and glycerol in a composition of 60/15/25 weight ratio, respectively. Table 2.6 showed the tensile properties of neat PLA, neat TPS and PLA/TPS blend. The mechanical properties of PHB/TPS blend was decreased because the PHB/TPS blend consisted of a high percentage of TPS. Therefore, the tensile strength of the PHB/TPS blend was lower than that of neat PHB by half. The reduction of tensile strength related to the stiffness of TPS. As a result, all of the tensile properties of PHB/TPS blends with 65/35 weight ratio were decreased. The decrease was also related to the lack of compatibility between the polymers.

Table 2.6 *Mechanical properties of neat PHB, TPS and PHB/TPS blend [28].*

Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
PHB	24.2 ± 1.5	3.65 ± 0.21	1560 ± 283
TPS	3.37 ± 0.4	11.90 ± 3.00	109 ± 25
PHB/TPS 65/35	13.2 ± 2.8	1.50 ± 0.28	1175 ± 120

Armentano et.al. [5] studied the mechanical properties of PLA/PHB/OLA tertiary blends in which OLA was lactic acid oligomer (OLA) and the PLA/PHB blend with weight ratio 85/15 and OLA was added at 15, 20 and 30 phr. Table 2.7 showed the tensile properties of neat PLA and PLA/PHBV/OLA blends. As a result, the tensile strength was decreased with an increase in the OLA content because OLA as a plasticizer causing a substantial decrease in the strength of the polymer blend [29]. The reduction of Young's modulus was continuing with the increase of OLA content because the presence of OLA would decrease the rigidity of polymer blend. However, the elongation at break of PLA/PHB blend strongly increased with the addition of OLA whose structure would improve the ductility of the blends. Figure 2.8 showed the SEM micrographs with different magnifications of neat PLA, PLA/PHB blend and PLA/PHB/OLA blends. The SEM micrographs of PLA/PHB/OLA blend showed a better interfacial adhesion between polymer phases and the size of the PHB phases in polymer blend were reduced by the addition of OLA.

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Table 2.7 Mechanical properties of neat PLA and PLA/PHB/OLA blend [5].

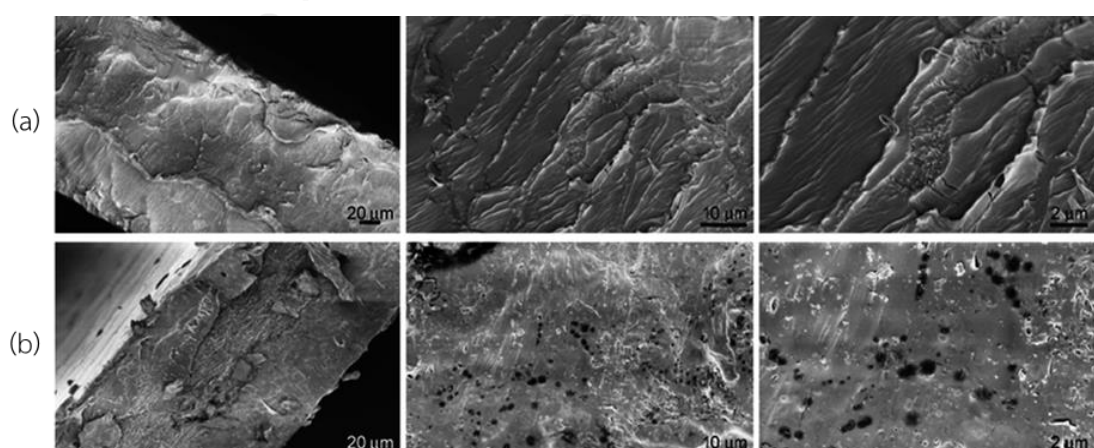| Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
PLA	40 ± 7	3.4 ± 0.4	1300 ± 180
PLA/PHB 85/15	40 ± 5	3.8 ± 0.5	1220 ± 140
PLA/PHB/15 OLA	32 ± 3	3.1 ± 0.3	1120 ± 60
PLA/PHB/20 OLA	23 ± 4	3.3 ± 0.9	950 ± 130
PLA/PHB/30 OLA	16 ± 3	3.8 ± 0.4	590 ± 50
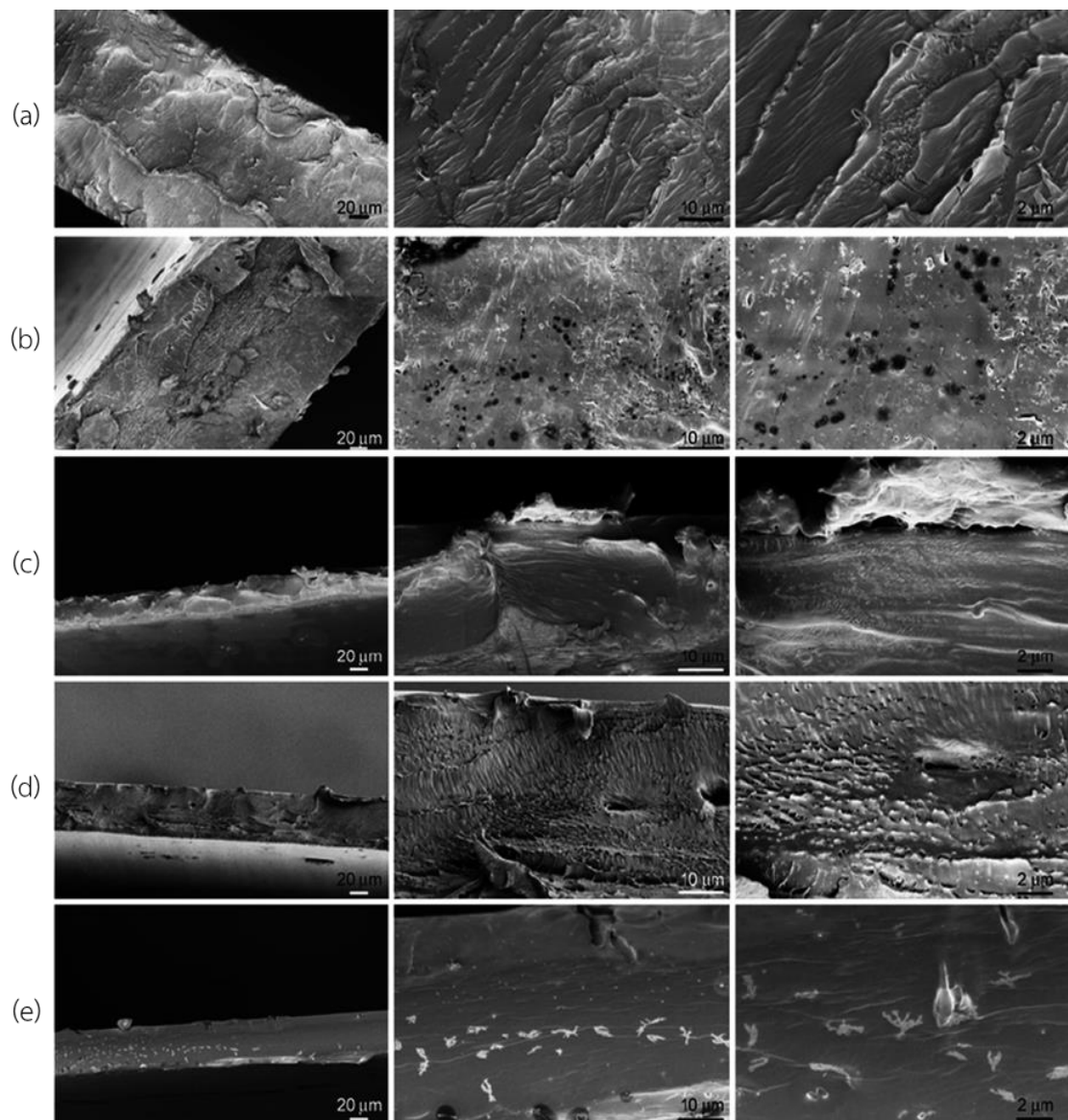
Figure 2.8 SEM micrographs of (a) neat PLA, (b) PLA/PHB 85/15, (c) PLA/PHB/15 OLA, (d) PLA/PHB/20 OLA and (e) PLA/PHB/30 OLA [5].

Amor et.al. [27] studied the mechanical properties of tertiary blending between PLA, PHBV and OLA. PLA, PHBV and OLA pellets were blended in proportions of (90 – x) % weight, 10 % weight and x % weight (with x = 0, 0.1, 0.5 or 1), respectively. The tensile properties of neat PLA, neat PHBV and PLA/PHBV/OLA blends were summarized in Table 2.8. The mechanical properties of polymers were tested except those of PHBV because data from the processability of neat PHBV was very poor due to its low melt viscosity and brittleness, so that study used the datasheet as the reference for mechanical properties. The addition of small amounts of OLA indicated a change in mechanical properties of PLA/PHBV/OLA blends, which led to a decrease in tensile strength and an increase in elongation at break of blends. In addition, the addition of OLA in PLA/PHBV/OLA blends did not significantly change the Young's modulus of the blends. Figure 2.9 showed the AFM micrographs of PLA/PHBV 90/10 and PLA/PHBV/1.0 OLA. AFM micrographs of PLA/PHBV 90/10 blend showed that the PHBV domains were quite small dispersed in PLA matrix and adding 1 % weight ratios of OLA in PLA/PHBV blend led to more reduction in the size of PHBV domains while the shape of PHBV did not change. The results showed that the effect of the presence of OLA led to the improvement of the mechanical properties for PLA/PHBV/OLA films.

Table 2.8 *Mechanical properties of neat PLA, neat PHBV and PLA/PHBV/OLA blend [27].*

Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
PLA	45 ± 4	3.1 ± 1.0	2050 ± 481
PHBV	39	2.0	2800 - 3500
PLA/PHBV 90/10	43 ± 5	3.0 ± 1.0	2507 ± 252
PLA/PHBV/0.1 OLA	47 ± 1	8.0 ± 2.0	2747 ± 452
PLA/PHBV/0.5 OLA	45 ± 4	6.0 ± 1.0	2709 ± 382
PLA/PHBV/1.0 OLA	44 ± 2	14.0 ± 3.0	2799 ± 133
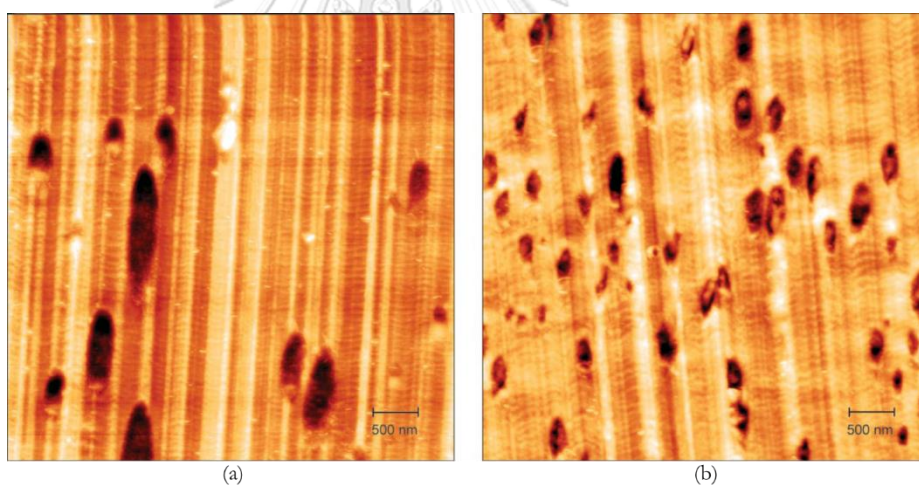
Figure 2.9 *AFM micrographs of (a) PLA/PHBV 90/10 and (b) PLA/PHBV/1.0 OLA [27].*

For the blown film extrusion process, *Diaz et.al.* [30] studied the mechanical properties of PLA/PHB blend with ratio of 90/10. The tensile properties of PLA/PHB blown films were similar to those from *Armentano et.al.* [5] study which means that processing condition did not significantly affect the mechanical properties of the blends. The tensile properties of neat PLA and PLA/PHB with weight ratio 90/10 were shown in Table 2.9.

Table 2.9 Mechanical properties of neat PLA and PLA/PHB blend [30].

Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
PLA	41.6 ± 5.0	2.5 ± 3.2	2280 ± 230
PLA/PHB 90/10	42.3 ± 3.7	3.1 ± 5.2	2170 ± 120

Nikushi et.al. [31], studied the mechanical properties of blends between PLA, PHB and PHBV with wood fiber (WF) and maleic anhydride (MA) in compression molding process. That study aimed to improve the mechanical properties of biodegradable biobased polymer composites by blending biobased polymers with other biodegradable natural fillers to create a composite polymer. For binary blend the 30 wt% WF was mixed with 70 wt% neat polymers. Also, for the tertiary blend, 65 wt% of neat PHB or PHBV 65 % weight polymer was mixed with 5 wt% of MA grafted polymer and 30 wt% of WF. The addition of WF into a polymer blend caused a significant decrease in the impact properties of PLA, PHB and PHBV [32]. Figure 2.10 showed the impact properties of neat polymers and composites. It can be seen that by adding the MA grafted polymer in PLA/WF and PHBV/WF composites, the impact properties of composites were improved because the adhesion between the filler and the polymer was improved [33]. The addition of WF caused a significant increase in Young's modulus of PLA and PHBV; however, the presence of MA grafted polymer did not

improve the Young's modulus of composites. Figure 2.11 showed Young's modulus of neat polymers and composites.
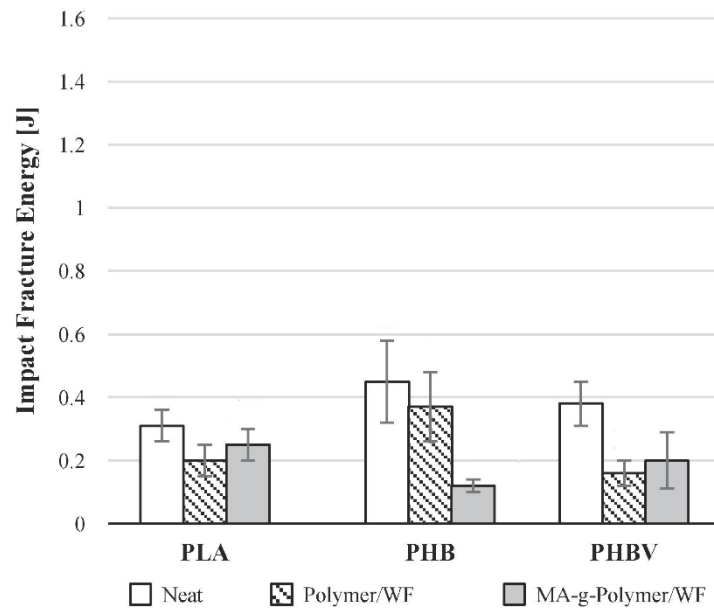
Figure 2.10 *Impact properties of neat polymers and composites [31].*
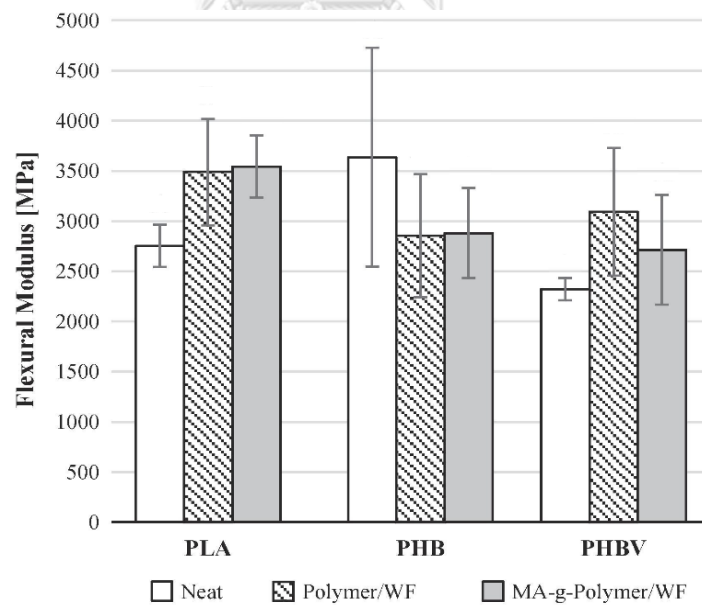
Figure 2.11 *Young's modulus of neat polymers and composites [31].*

Ecker et.al. [34] studied the mechanical properties of PLA/PHB blends from injection process using PLA/PHB weight ratios 80/20. Young's modulus and tensile strength at yield of neat PLA and PLA/PHB blend are shown in Figure 2.12 and Figure 2.13, respectively. The 3D_80C_45° and 3D_80C_0° were the samples from 3D printed at 80 $^{\circ}$C in different angle infill patterns which were 45° and 0°, respectively. Both Young's modulus and tensile strength were decreased, while added PHB into PLA/PHB blend system. These led to a reduction of tensile properties due to the rubber-like behavior of amorphous PHB and PHBV copolymer.
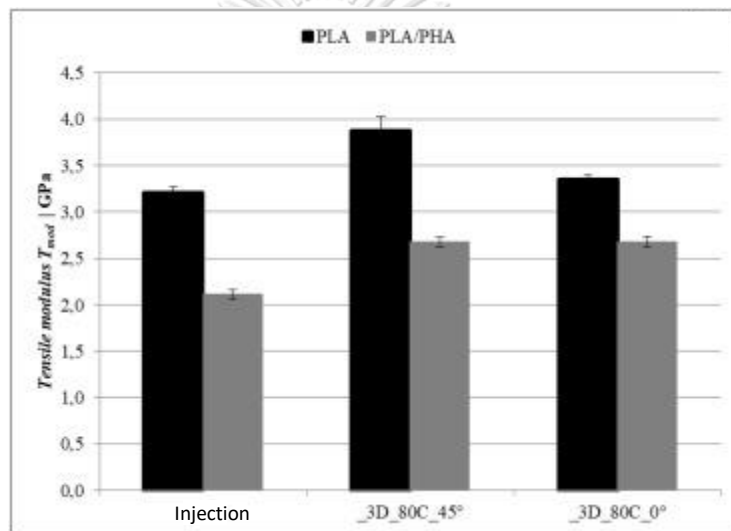
Figure 2.12 Young's modulus of neat PLA and PLA/PHB blend [34].
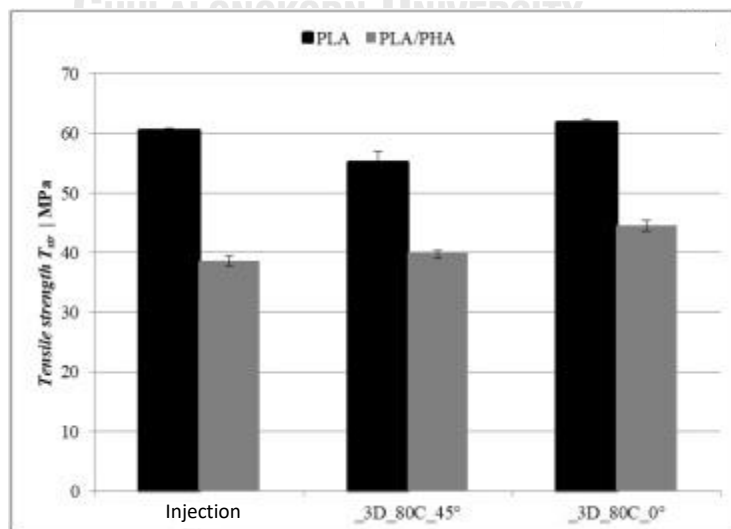
Figure 2.13 Tensile strength at yield of neat PLA and PLA/PHB blend [34].

CHAPTER III

METHODOLOGY

In this chapter, materials, mixing process, cast film process, characterization of films and summary of methodology were described as follows.

3.1 Materials

PLA used in this study was commercial type Ingeo 4043D from NatureWorks LLC, USA. which was available in pellet form. According to the manufacturer, PLA has tensile strength at yield at 53 MPa, elongation at break at 8.8% and Young's modulus at 3600 MPa. Meanwhile, the commercial pellet of PHBV in the name of ENMAT Y1000P was supplied by TianAn Biologic Materials Co. Ltd. (China). With reference to the supplier, PHBV has following properties: tensile strength at yield at 38 MPa, elongation at break at 3.2% and Young's modulus at 1600-2100 MPa. Lastly, TPS (TAIPIOPLAST) was supplied by SMS Corporation (Thailand) in pellet form. TPS has moisture content lower than 4% and density lower than 1.6 g/cm^3.

3.2 Material processing

At first, the drying process was required; PLA, PHBV and TPS were dried in an oven at 60 °C for 24 hours to remove moisture. The weight mixing ratios of PLA/PHBV/TPS were shown in Table 3.1. In the blending process, the twin screw extruder (LABTECH, LTE 20-40) was used to prepare the well-mixed pellets. The screw speed was around 26 rpm and the processing temperature in all zone of the extruder was 180°C. After that, the pellets were dried before the next processing in an oven at the same condition of the first drying process.

Table 3.1 The ratio of PLA/PHBV/TPS in this study.

Samples	Weight fraction (%)		phr
	PLA	PHBV	TPS
PLA	100.00	-	-
PLA/PHBV 80/20	80.00	20.00	-
PLA/PHBV 70/30	70.00	30.00	-
PLA/PHBV 60/40	60.00	40.00	-
PLA/PHBV/1 TPS	80.00	20.00	1
PLA/PHBV/5 TPS	80.00	20.00	5
PLA/PHBV/10 TPS	80.00	20.00	10

3.3 Cast film process

The twin-screw extruder (Hakke Rheomix PTW 16/25D) equipped with T-die was used to cast a film. The conditions were follows: feeder speed 60 rpm, screw speed 50 rpm and the processing temperature of the extruder at zone one, two, three and four were 170 °C, 165 °C, 180 °C and 195 °C, respectively and that for die zone was 180 °C. Afterward, the hot viscous polymer was cold drawn on the calendering machine by the rollers. The temperature of the rollers was set at 30 °C in which water was used as a heat transfer medium and speed of 120 rpm.

3.4 Characterization

     3.4.1 Thermal properties

       Thermal properties of films were investigated by differential scanning calorimeter (DSC) model Mettler Toledo DSC 1 STAR system. The measurements were carried out on film samples of about 5 – 10 mg, placed in sealed aluminum pans. Moreover, all the measurements were performed under nitrogen atmosphere (N_2 99.99 % flow rate of 50 mL/min). The samples were subjected to the cycle, in which the heating and cooling rates for all measurements were 10 °C/min. Firstly, the samples were heated from -50 °C to 200 °C to erase the thermal historical properties of the samples. After that, the cooldown step by decrease temperature from 200 °C to -50 °C. Finally, a heating step for the second scan by increase temperature from -50 °C to 200 °C. The glass transition temperature (T_g), melting temperature (T_m), and enthalpy of transition were determined from the DSC thermograms.

     3.4.2 SEM morphology analyses

       The surface morphology of the films were observed by using a scanning electron microscope (SEM) model S3400N Hitachi (serial number 340637-09) to investigate the fracture surface of the films. First of all, the samples of films were dipped into liquid nitrogen. Then, the samples were obtained through fracturing in liquid nitrogen. After that, the samples were coated with a thin platinum layer. The SEM micrograph which obtained from the SEM microphotographs software indicated the morphology of the polymer blends.

3.4.3 Mechanical properties

A universal testing machine model Instron 5567 was used to measure the tensile properties which consisted of tensile strength at yield, elongation at break and Young's modulus according to ASTM D882. The dimension of the sample was a rectangle with wide of 10 mm and length of 100 mm. The universal testing machine was set with 1 N load cell with a loading speed 12.5 mm/min.

An impact tester model Film Impact Tester Digital type, TOYOSEIKI; was used to measure the impact strength of films according to ASTM D3420. The pendulum had a maximum velocity of about 74 m/minute and maximum energy of about 5 J. The samples were cut into a square shape with wide and length 10 cm that could fit in the testing area of impact tester.

3.5 Summary of methodology

This research was divided into 2 parts. The Part I was about the preparation and development of the proper formulation of binary blending between PLA and PHBV. The Part II was about the development of tertiary blending between PLA, PHBV and TPS. The thermal properties, morphologies and mechanical properties of the samples were investigated in both Part I and Part II. The methodological scheme was shown in Figure 3.1.
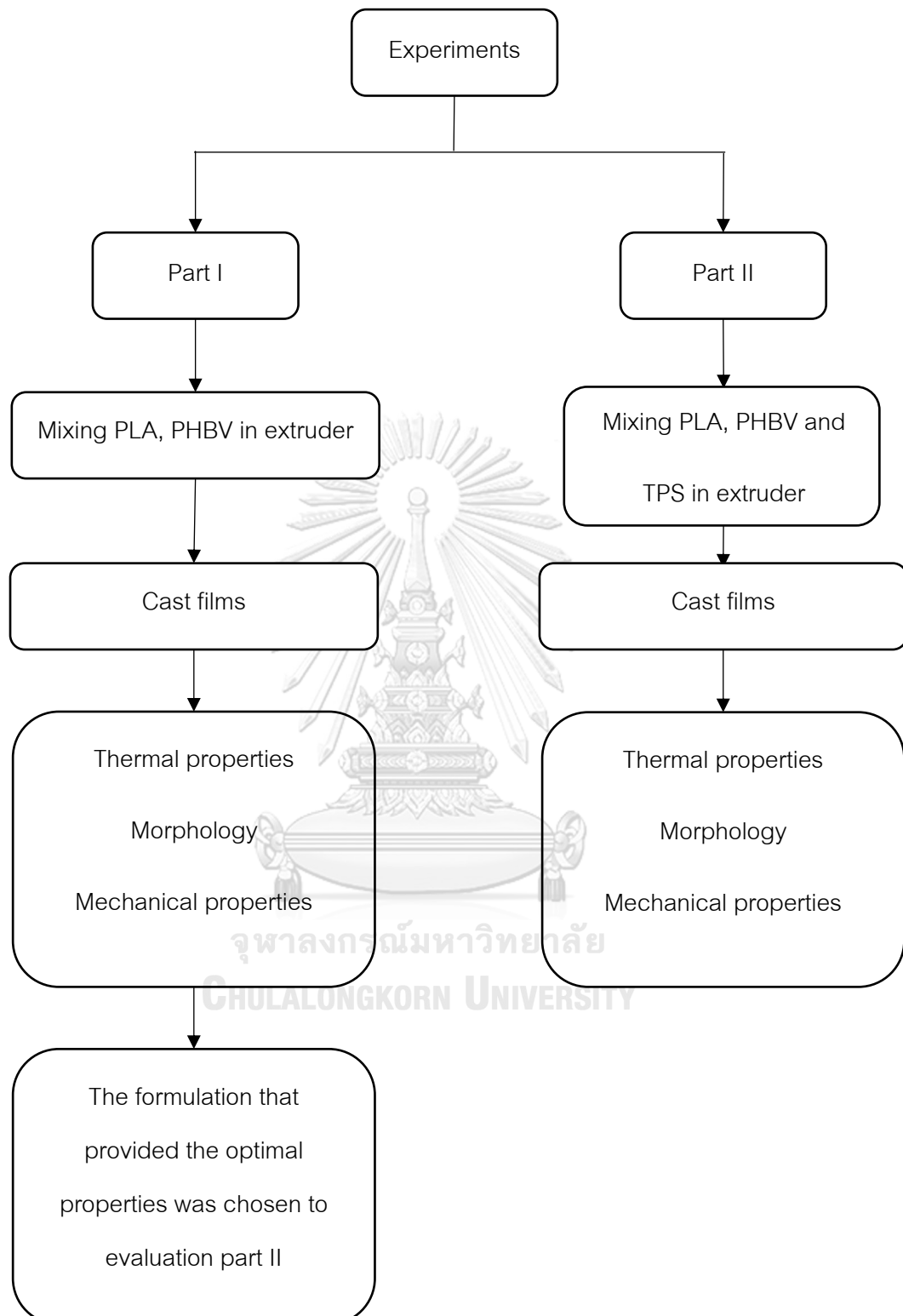
Figure 3.1 *Summary of methodology.*

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Thermal properties

The DSC thermograms of the second heating run of neat PLA, neat PHBV and PLA/PHBV blends with a heating rate of 10 °C/min were shown in Figure 4.1. Figure 4.2 showed DSC thermograms of the second heating run of PLA/PHBV/TPS blends with a heating rate of 10 °C/min. The DSC profiles revealed different thermal properties as follows: the glass transition temperature (T_g), the cold crystallization temperature (T_{cc}), the melting temperature (T_m). All these data were shown in Table 4.1. The evaluation of in T_g, T_{cc}, T_m, Enthalpy of cold crystallization, (ΔH_{cc}) and Enthalpy of crystallization (ΔH_m) were described in Appendix A. Table 4.1 and Figure A-2, neat PLA had a glass transition temperature at 58.21 °C and a melting temperature at 149.91 °C. The values of glass transition temperature and melting temperature of PLA conformed to the manufacturer's data sheet which were 55 - 60 °C and 145 - 160 °C, respectively [13]. The glass transition temperature value of PHBV was about 2.50 °C as shown in Figure A-2; also, a melting temperature was observed at 173.88 °C. The value of melting temperature conformed to the manufacturer's data sheet which was 175 - 180 °C but the glass transition temperature slightly decreased from the manufacturer's data sheet which was 4 °C [20]. Figure 4.1 indicated that the PLA/PHBV blends had a glass transition temperature of PLA in the rage of 57.55 – 57.94 °C. These implied the non-significant changes in the glass transition temperature when compared with the glass transition temperature of neat PLA [4]. Also, PLA/PHBV/TPS blends had a glass transition temperature of PLA in the rage of 55.27 – 55.94 °C. The results showed a slight decrease in glass transition temperature compared with neat PLA. Figure 4.2 represented the analogous trend of the glass transition temperature of PLA/PHBV 80/20

blend and PLA/PHBV/TPS blends. It could be concluded that the glass transition temperature of PLA and PHBV did not change significantly [4].

When polymer was cooled too fast, the polymer chains did not have enough time to arrange itself in order; therefore, polymer chains would rearrange while heating which is called cold crystallization process or recrystallization process.The small amount of PHBV had significantly affected the mechanical properties of film sheets due to the increment of the degree of crystallinities of PLA/PHBV blends [35]. The cold crystallization temperatures of PLA were about 120 - 127 °C in PLA/PHBV blends and PLA/PHBV/TPS blends which higher than neat PLA. These results indicated that the addition of PHBV could make PLA to cold crystallization while heating in all compositions [36]. The cold crystallization temperatures of PHBV were about 35 - 39 °C in all PLA/PHBV blends and PLA/PHBV/TPS blends. Moreover, the PLA/PHBV 80/20 blend showed the highest cold crystallization peak, which was due to the finely dispersed PHBV crystals acting as heterogeneous nucleation sites.
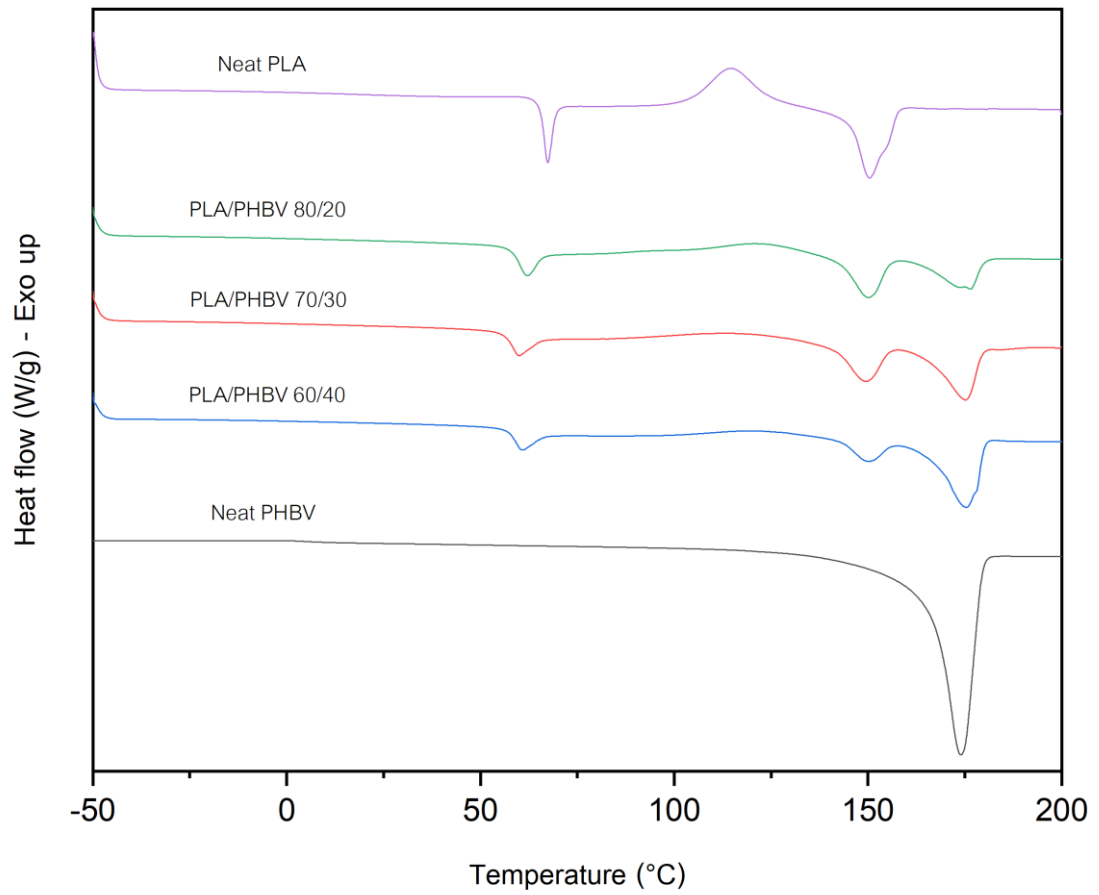
Figure 4.1 DSC thermograms with a heating rate of 10 °C/min of neat PLA, neat PHBV and PLA/PHBV blends.
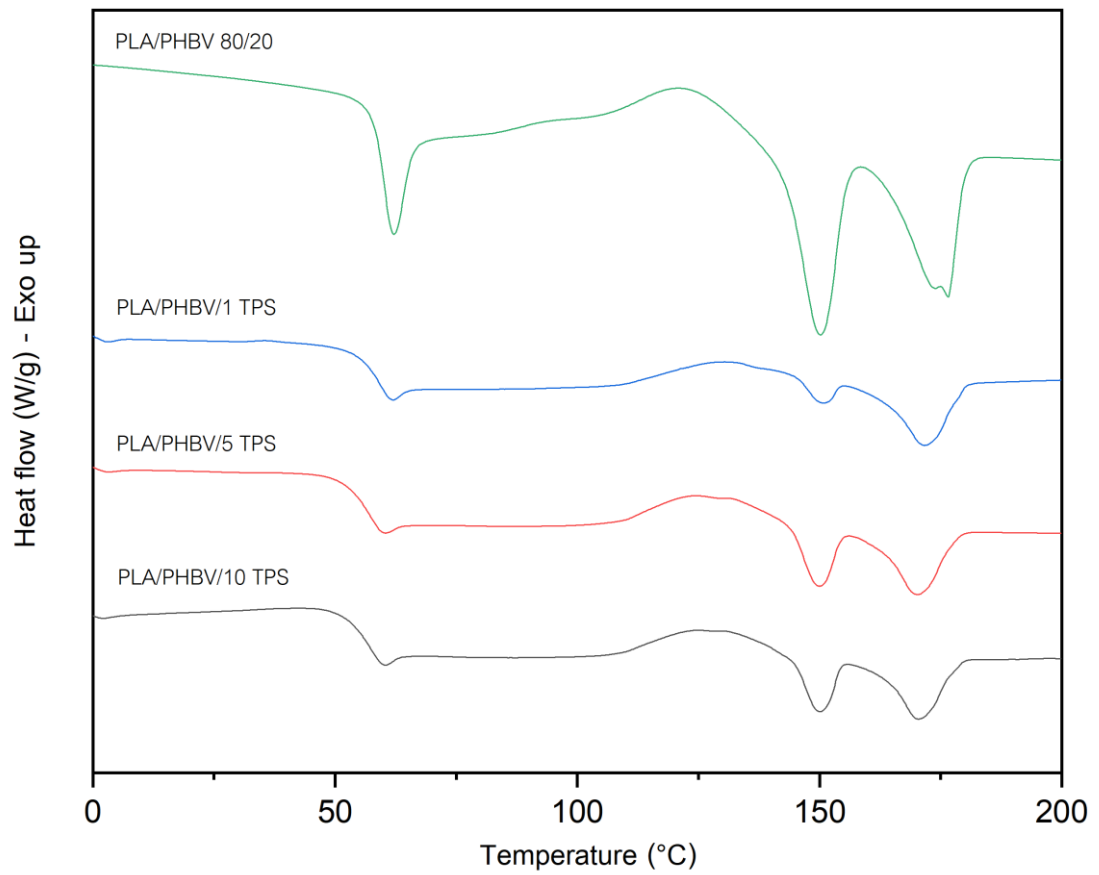
Figure 4.2 DSC thermograms with a heating rate of 10 °C/min of PLA/PHBV 80/20
blend and PLA/PHBV/TPS blends.

Table 4.1 Thermal analysis of neat PLA, neat PHBV, PLA/PHBV blends and
PLA/PHBV/TPS blends.

Samples	T_g(°C)		T_{cc} (°C)				T_m (°C)		
	PLA	PHBV	PLA	ΔH_{cc} (J/g)	PHBV	ΔH_{cc} (J/g)	PLA	PHBV	ΔH_m (J/g)
Neat PLA	58.21	-	114.86	25.87	-	-	149.91	-	26.85
PLA/PHBV 80/20	57.94	-1.51	123.88	4.63	36.60	0.26	151.39	171.95	11.50
PLA/PHBV 70/30	57.85	-1.62	122.06	6.16	35.18	0.23	151.52	171.22	25.00
PLA/PHBV 60/40	57.55	-0.04	120.57	6.55	34.36	0.06	150.16	175.04	39.77
Neat PHBV	-	2.50	-	-	-	-	-	173.88	92.78
PLA/PHBV/ 1 TPS	55.27	-1.03	126.31	4.87	35.49	0.12	150.96	171.61	6.54
PLA/PHBV/ 5 TPS	55.31	-1.23	124.60	5.42	36.79	0.01	149.87	170.30	5.94
PLA/PHBV/ 10 TPS	55.94	-1.66	125.47	5.24	38.91	0.01	150.10	170.43	5.56

Note T_g is Glass transition temperature (°C)

T_{cc} is Cold crystallization temperature (°C)

T_m is Melting temperature (°C)

ΔH_{cc} is Enthalpy of cold crystallization (J/g)

ΔH_m is Enthalpy of crystallization (J/g)

4.2 SEM morphology analyses

SEM micrographs were used to analyze the morphology of the PLA/PHBV and PLA/PHBV/TPS blends.

Figure 4.3 showed SEM micrographs of the samples in the cross-sectional area perpendicular to the machine direction of neat PLA, PLA/PHBV 80/20, PLA/PHBV 70/30 and PLA/PHBV 60/40 blends. Irregular PHBV particles, dispersed in the PLA matrix were observed in all samples.

The morphology of neat PLA and PLA/PHBV blends in machine direction and in transverse direction were similar as shown in Figure 4.4. The PLA and PHBV phases in PLA/PHBV blends were separated into two phases. Therefore, the presence of PHBV domains as shown in SEM micrographs were complementary to the unchanged of the glass transition temperature of neat PLA of PLA/PHBV blends which confirm that PLA and PHBV were immiscible. The PLA/PHBV 80/20 blend had a finely dispersed domain of PHBV which led to improvement of its mechanical properties. Also, SEM micrographs showed that when adding more PHBV in PLA/PHBV blends the mechanical properties of blends decreased because of too large of PHBV domains in PLA matrix.

Figure 4.5 showed SEM micrographs of the samples in the cross-sectional area perpendicular to the machine direction of PLA/PHBV 80/20, PLA/PHBV/1 TPS, PLA/PHBV/5 TPS and PLA/PHBV/10 TPS and Figure 4.6 represented SEM micrographs of those perpendicular to the transverse direction of PLA/PHBV 80/20 and PLA/PHBV/TPS in all ratios. The TPS particles had a white round shape dispersed in the samples. Also, TPS particles were not uniformly dispersed in the matrix of the polymer blend which was PLA and PHBV due to the difference of hydrophilic nature of PLA, PHBV and TPS phases [37, 38]. The addition of the TPS in polymer blends led to a rough surface of the sample sheet which affected their mechanical properties. Figures 4.5 and 4.6 showed cavities in the SEM micrographs of PLA/PHBV/TPS blend sheets that were caused by the friction from the TPS pellets on the cast film process. The

surface of PLA and PLA/PHBV blend sheet were smooth surface in which PLA has the smoothest surface when compared with those of PLA/PHBV 80/20, PLA/PHBV 70/30 and PLA/PHBV 60/40 sheets. However, the surface of PLA/PHBV/TPS was rough in which the surface of PLA/PHBV/10 TPS was rougher than that of PLA/PHBV/5 TPS and PLA/PHBV/1 TPS sheets, respectively.

Figure 4.3 SEM micrographs in machine direction of (a) neat PLA (b) PLA/PHBV 80/20
(c) PLA/PHBV 70/30 and (d) PLA/PHBV 60/40.

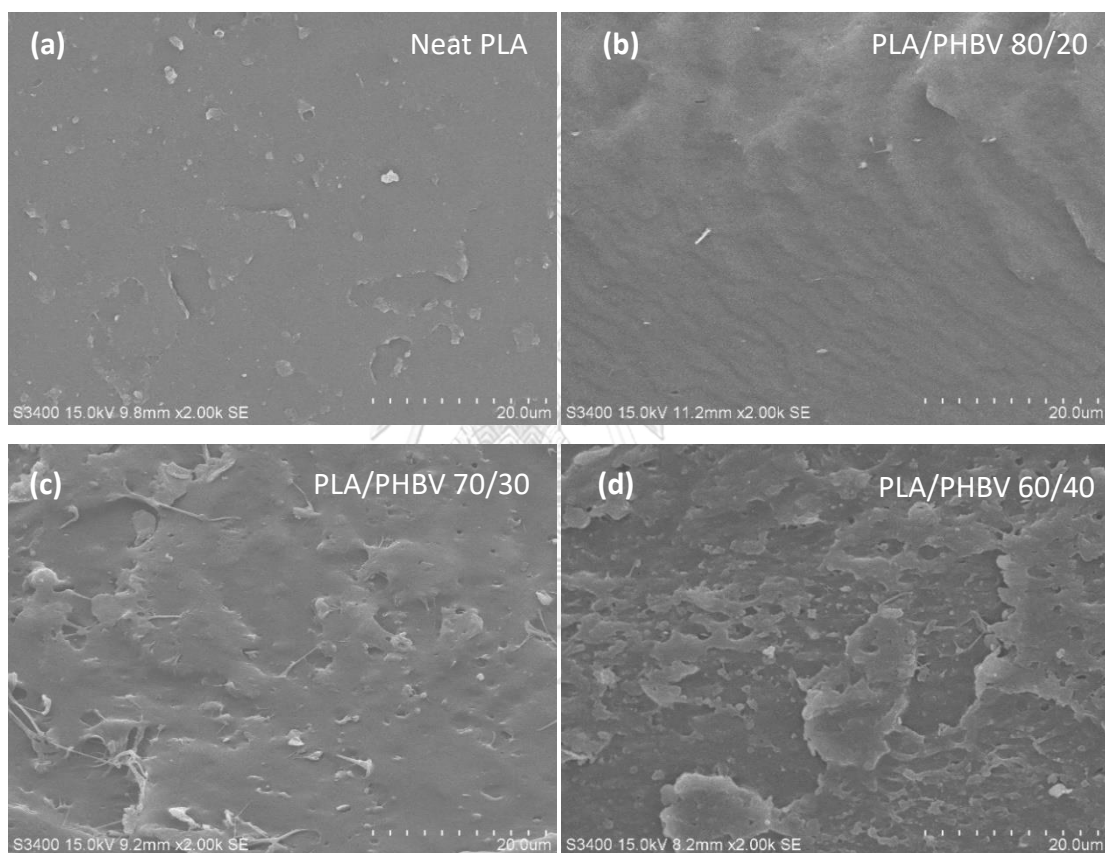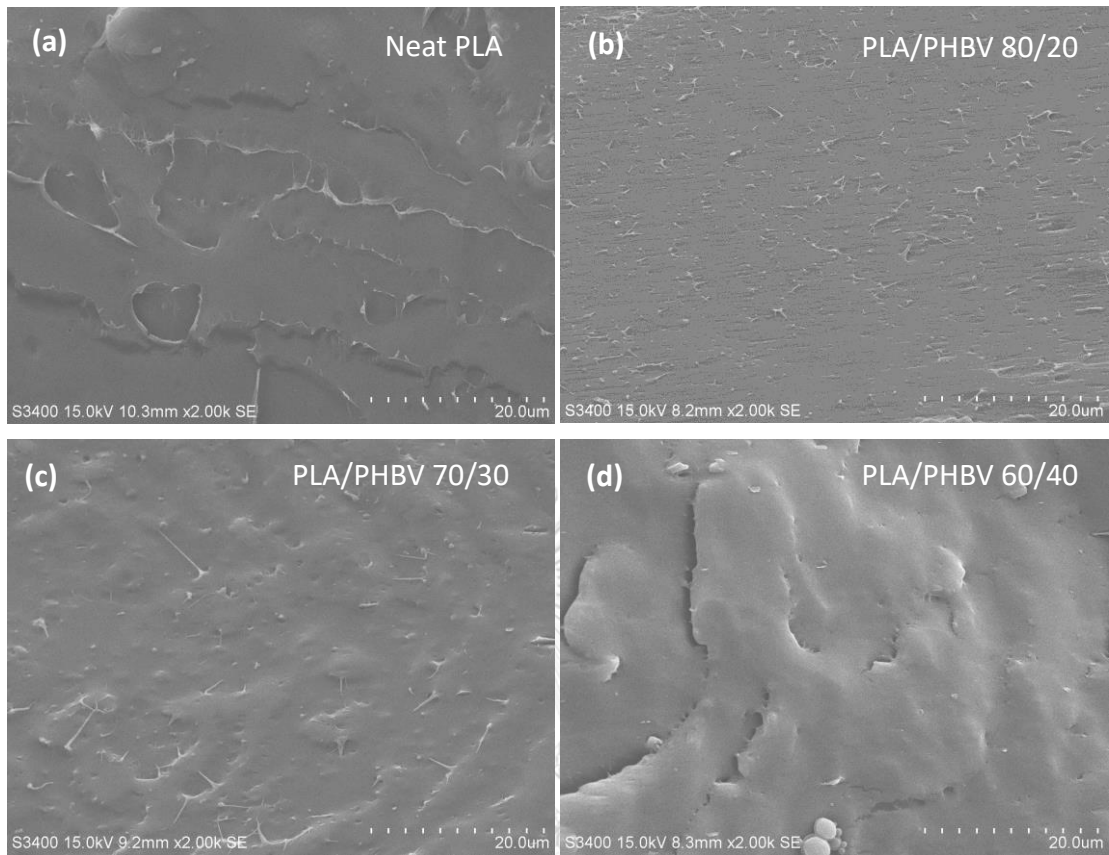*Figure 4.4* SEM micrographs in transverse direction of (a) neat PLA (b) PLA/PHBV
80/20 (c) PLA/PHBV 70/30 and (d) PLA/PHBV 60/40.
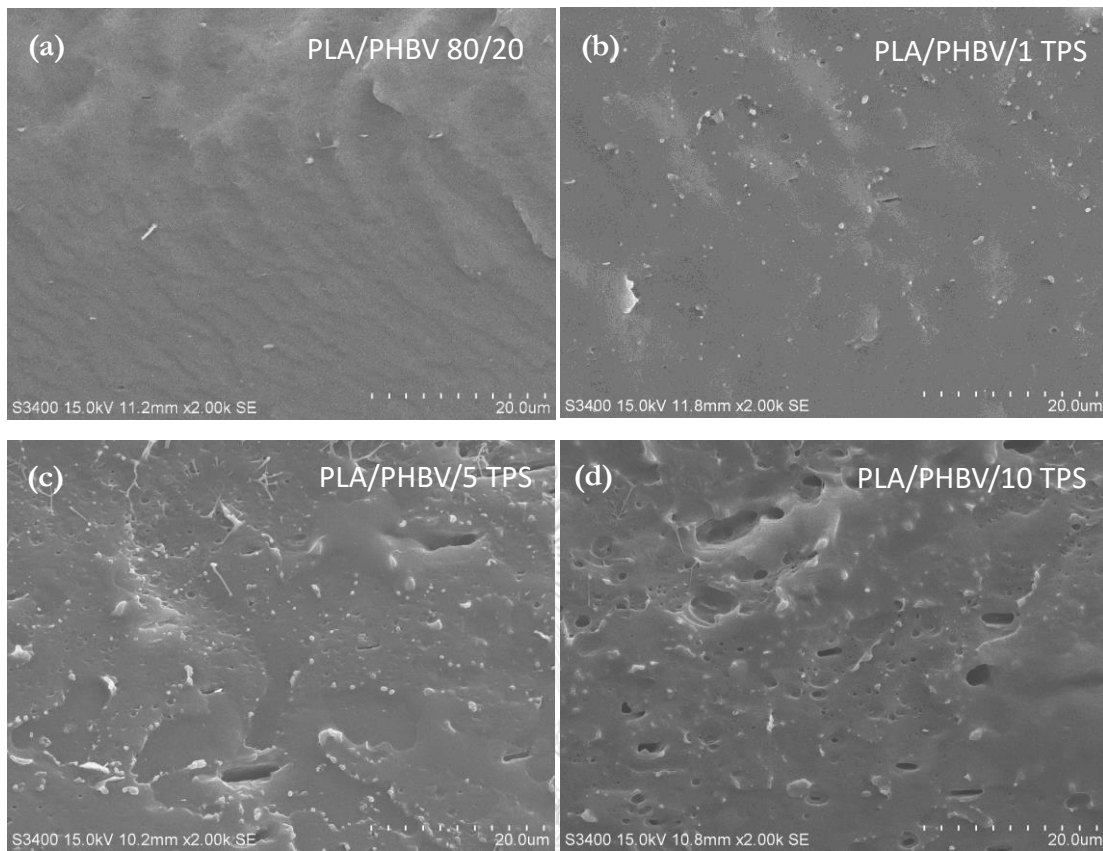
Figure 4.5 SEM micrographs in machine direction of (a) PLA/PHBV 80/20 (b)
PLA/PHBV/1 TPS (c) PLA/PHBV/5 TPS and (d) PLA/PHBV/10 TPS.
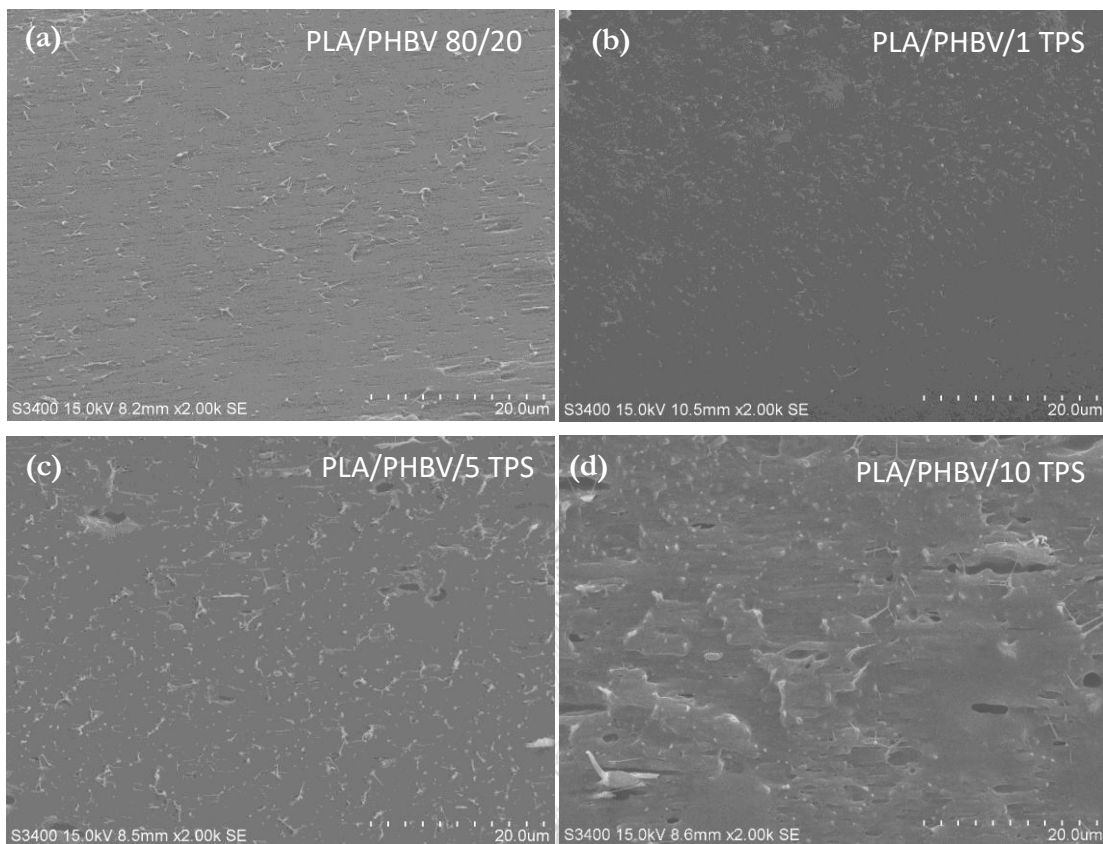
Figure 4.6 SEM micrographs in transverse direction of (a) PLA/PHBV 80/20 (b) PLA/PHBV/1 TPS (c) PLA/PHBV/5 TPS and (d) PLA/PHBV/10 TPS.

4.3 Mechanical properties

The neat PHBV and TPS were poor processability because PHBV and TPS were very brittle and had low melt viscosity. For this reason, in this study did not consist of mechanical properties of neat PHVB and TPS. In general, the addition of PLA in the binary polymer blend improved the processability of PHAs [34].

The tensile strength, Young's modulus and elongation at break in machine direction of neat PLA, PLA/PHBV blends and PLA/PHBV/TPS blends with different weight ratios were presented in Table 4.2. The stress–strain curve of the samples in machine direction were shown in Figure 4.7. Figure 4.7 showed the mechanical properties of PLA/PHBV blends and PLA/PHBV/TPS blends.

Table 4.2 The tensile properties in machine direction of neat PLA, PLA/PHBV blends and PLA/PHBV/TPS blends.

Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
Neat PLA	46.2 ±1.5	8.8 ± 2.0	2334.6 ± 29.2
PLA/PHBV 80/20	40.5 ± 1.6	34.9 ± 3.5	2593.9 ± 37.5
PLA/PHBV 70/30	39.2 ± 1.1	22.0 ± 5.1	2536.7 ± 35.6
PLA/PHBV 60/40	39.1 ± 1.1	11.7 ± 3.5	2512.7 ± 24.6
PLA/PHBV/1 TPS	38.7 ± 0.4	19.0 ± 3.2	2204.8 ± 30.4
PLA/PHBV/5 TPS	34.6 ± 0.7	8.4 ± 2.2	2131.5 ± 34.8
PLA/PHBV/10 TPS	31.3 ± 1.0	7.0 ± 1.5	2072.5 ± 48.1
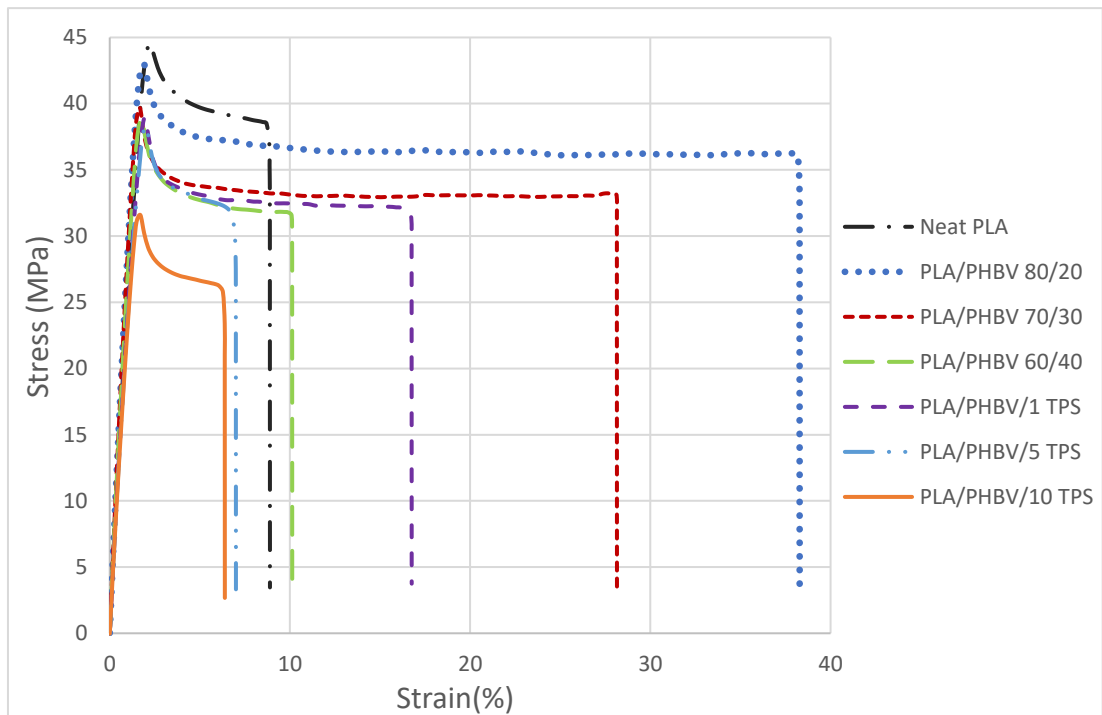
Figure 4.7 Stress–strain curves in machine direction of neat PLA, PLA/PHBV blends
and PLA/PHBV/TPS blends.

Figure 4.8 showed the tensile strength of neat PLA and PLA/PHBV blends as a function of PHBV content in machine direction. As a result, the PLA/PHBV 80/20 blend sheets had the highest tensile strength compared with other PLA/PHBV blends. For PLA/PHBV 60/40 and 70/30 blend sheets where PHBV was the continuous phase [36], the values of tensile strength did not change significantly. The addition of PHBV in PLA/PHBV blends brought about an increase of Young's modulus and elongation at break compared to neat PLA. Figure 4.9 showed the elongation at break of neat PLA and PLA/PHBV blends as a function of PHBV content in machine direction. Figure 4.9 showed that when the PHBV content increased in PLA/PHBV blends, elongation at break of blends decreased which could be due to the domain size of PHBV increased. However, all of PLA/PHBV blend sheet had higher elongation at break more than neat

PLA. Figure 4.10 showed Young's modulus of neat PLA and PLA/PHBV blends as a function of PHBV content in the machine direction. The trend of Young's modulus of PLA/PHBV blends in Figure 4.10 indicated that when the PHBV content in PLA/PHBV blend sheet increased, it led to a reduction in Young's modulus. Although the value of Young's modulus of PLA/PHBV blends were decreased while increased PHBV, Young's modulus of in all PLA/PHBV blends was higher than that of neat PLA.
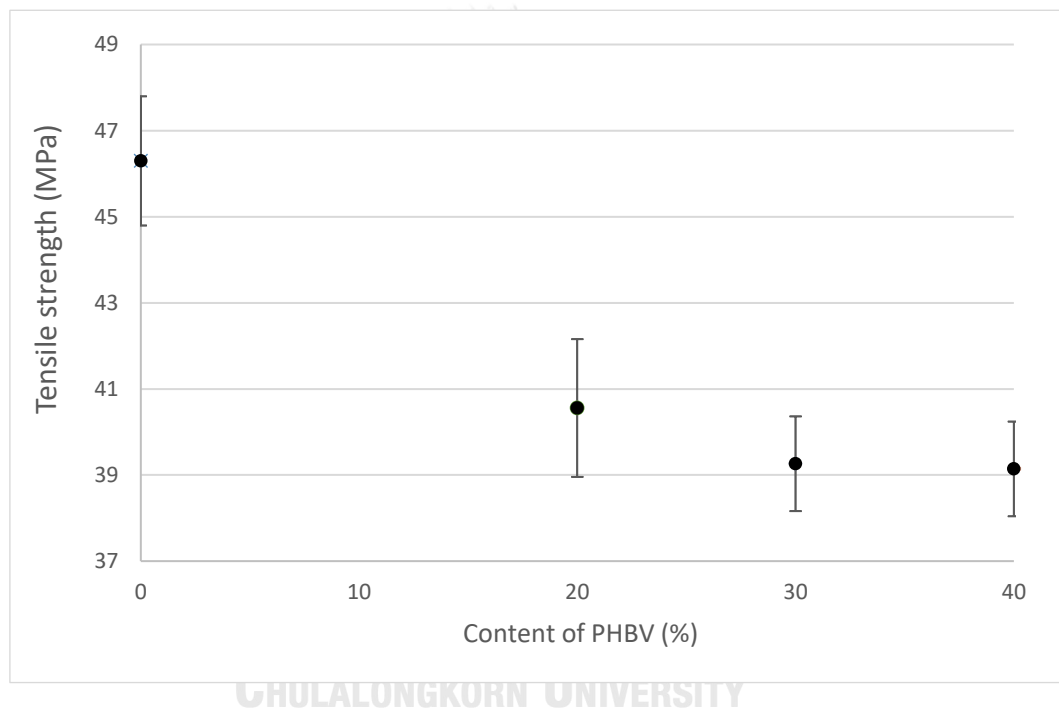
Figure 4.8 Tensile strength of neat PLA and PLA/PHBV blends in machine direction as a function of PHBV content.

Figure 4.9 Elongation at break of neat PLA and PLA/PHBV blends in machine direction
as a function of PHBV content.

Figure 4.10 Young's modulus of neat PLA and PLA/PHBV blends in machine direction
as a function of PHBV content.

The tensile strength, Young's modulus and elongation at break in transverse direction of neat PLA, PLA/PHBV blends and PLA/PHBV/TPS blends with different weight ratios were presented in Table 4.3. Figure 4.11 showed stress–strain curves in machine direction and transverse direction of PLA/PHBV in all ratios. The results showed that the mechanical properties of sheets in the machine direction were higher than those in transverse direction due to the processing condition of cast film process in which the sheets were subjected to stretching force in the machine direction more than in the transverse direction

Table 4.3 *The tensile properties in transverse direction of neat PLA, PLA/PHBV blends and PLA/PHBV/TPS blends.*

Samples	Mechanical properties		
	Tensile strength at yield (MPa)	Elongation at break (%)	Young's modulus (MPa)
Neat PLA	38.5 ±1.1	2.9 ± 0.3	2132.8 ± 29.2
PLA/PHBV 80/20	36.5 ± 2.7	19.2 ± 4.1	2492.7 ± 42.0
PLA/PHBV 70/30	36.0 ± 1.0	9.1 ± 0.6	2482.3 ± 42.1
PLA/PHBV 60/40	35.1 ± 1.7	6.5 ± 1.2	2452.4 ± 48.1
PLA/PHBV/1 TPS	34.8 ± 0.7	3.0 ± 0.2	2124.8 ± 19.9
PLA/PHBV/5 TPS	30.7 ± 0.5	3.5 ± 0.3	2006.8 ± 33.8
PLA/PHBV/10 TPS	26.7 ± 1.1	1.9 ± 0.2	2028.0 ± 49.7
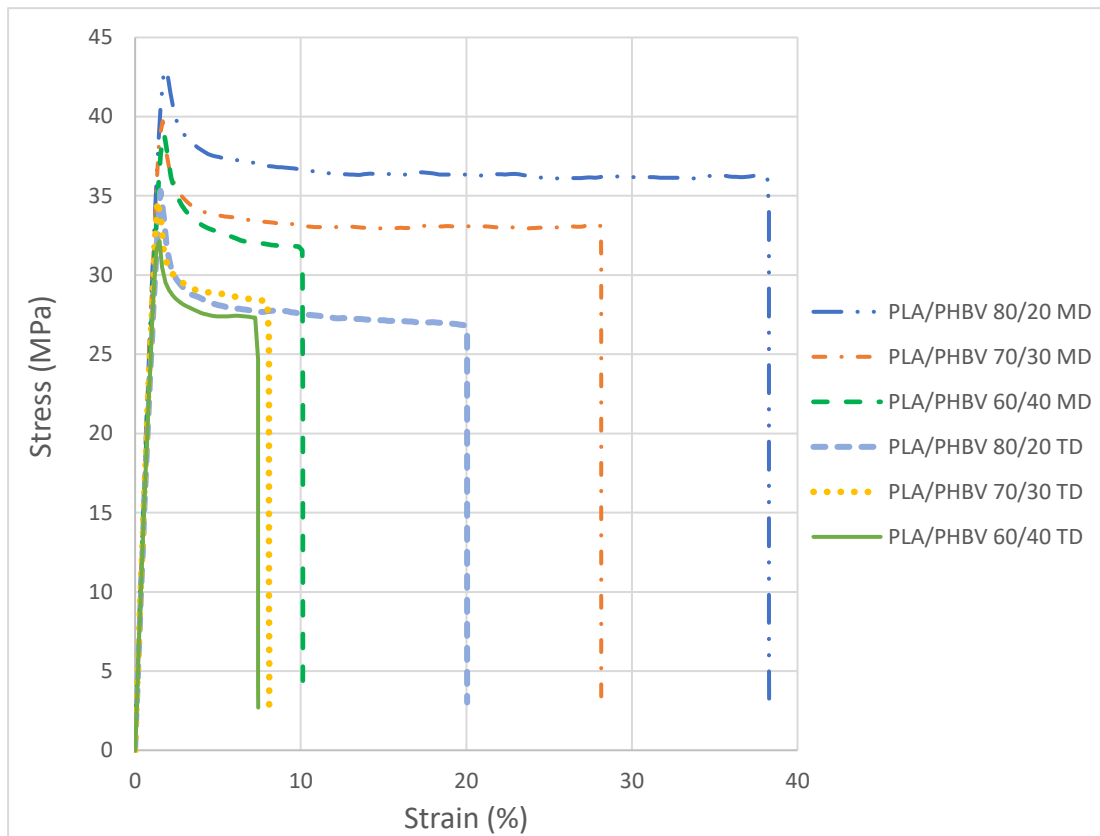
Figure 4.11 Stress–strain curves in machine direction and transverse direction of PLA/PHBV in all ratios.

The PLA/PHBV 80/20 blends were used to prepare PLA/PHBV/TPS blends in different content of the TPS in the unit of phr because PLA/PHBV 80/20 blend had the highest tensile strength, Young's modulus and elongation at break compared to other blends. Figure 4.12 showed tensile strength of PLA/PHBV 80/20 and PLA/PHBV/TPS blends in machine direction as a function of TPS content. As a result, adding more TPS in PLA/PHBV/TPS blends led to a reduction of tensile strength. Figure 4.13 showed the elongation at break of PLA/PHBV 80/20 and PLA/PHBV/TPS blends in machine direction as a function of TPS content. The elongation at break of PLA/PHBV/TPS blends was weaker when the TPS content increased. The reduction of the tensile strength and elongation at break of PLA/PHBV/TPS blends were associated with the lack of compatibility between the polymers, low interfacial interaction and weak adhesion between PLA, PHBV and TPS [39-41]. Figure 4.14 showed the Young's modulus of PLA/PHBV 80/20 and PLA/PHBV/TPS blends in machine direction as a function of TPS content. The results showed that Young's modulus of all the PLA/PHBV/TPS blends were decrease. The higher content of TPS in PLA/PHBV/TPS blends led to lower Young's modulus of polymer blend sheets. The decrease of Young's modulus associated with the presence of TPS that was much more flexible than PLA and PHBV [28].
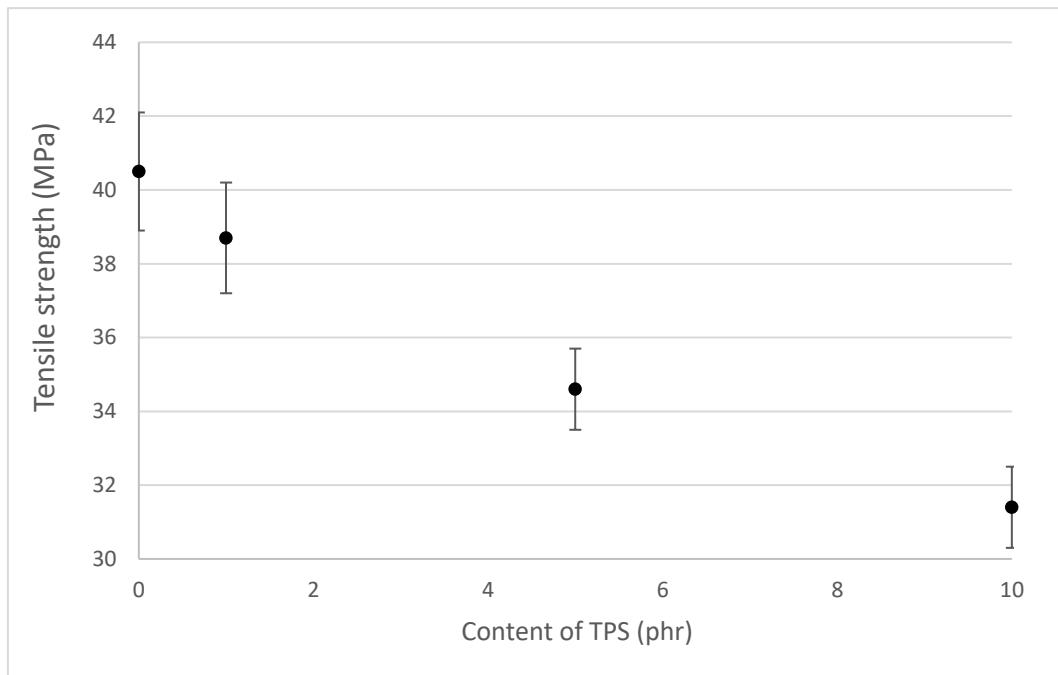
Figure 4.12 Tensile strength of PLA/PHBV 80/20 and PLA/PHBV/TPS blends in machine direction as a function of TPS content.
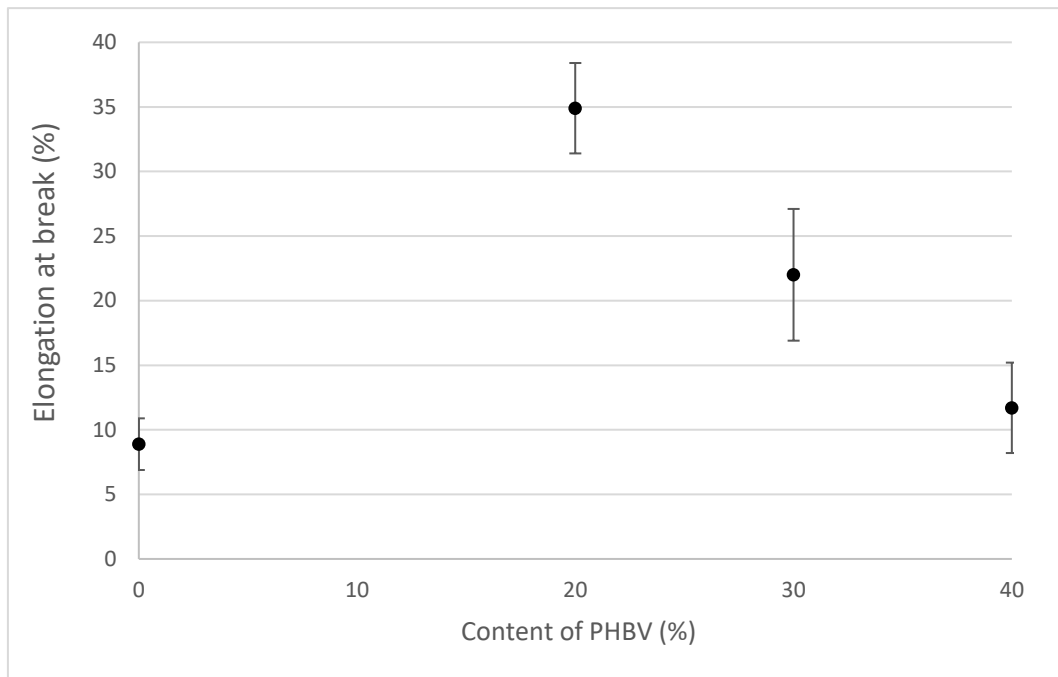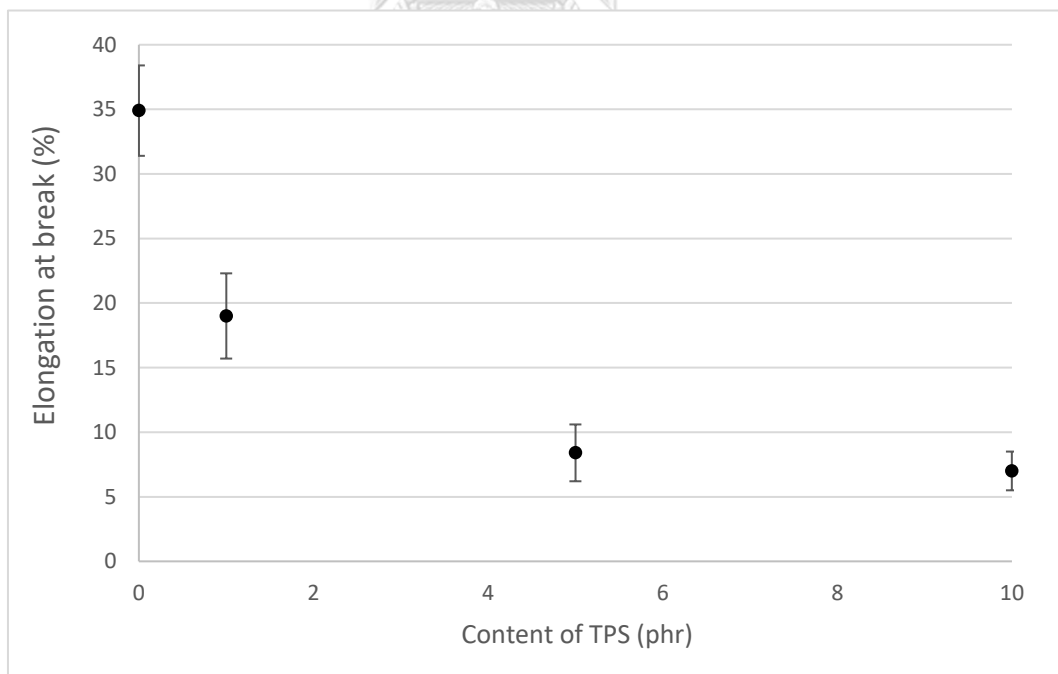

Figure 4.13 Elongation at break of PLA/PHBV 80/20 and PLA/PHBV/TPS blends in machine direction as a function of TPS content.
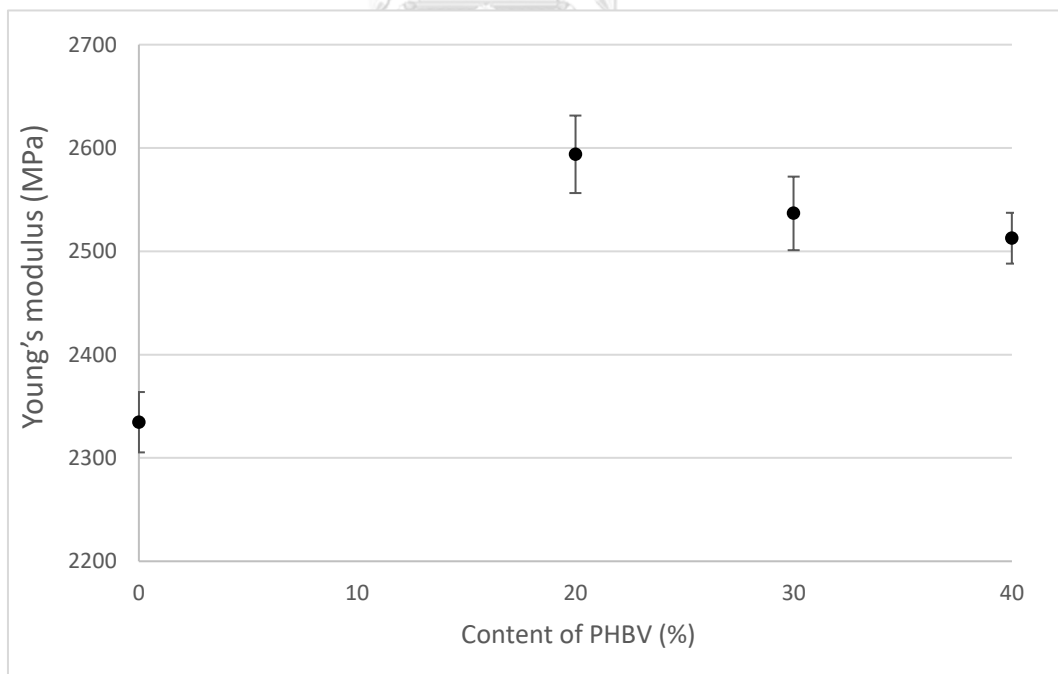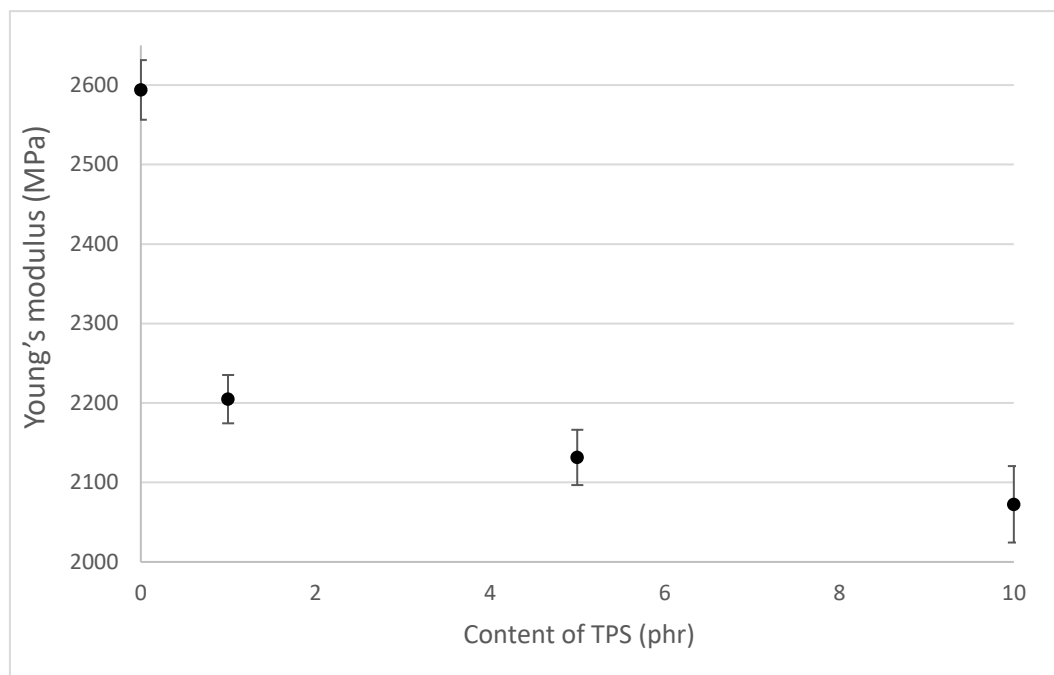
Figure 4.14 Young's modulus of PLA/PHBV 80/20 and PLA/PHBV/TPS blends in
machine direction as a function of TPS content.

The impact properties of neat PLA, PLA/PHBV blends and PLA/PHBV/TPS blends in different weight ratios were shown in Table 4.4. The addition of PHBV in PLA led to an increase of impact property in polymer blend sheet due to the rubber-like behavior of amorphous PHBV. PLA/PHBV 80/20 blend sheet showed better impact property than other sheets as well as neat PLA due to a finely dispersed of PHBV that improved the impact properties of 80/20 blend sheet. Figure 4.15 showed the impact strength of PLA and PLA/PHBV blends as a function of PHBV content. Consequently, the higher content of PHBV in PLA/PHBV blends led to a reduction of impact strength in PLA/PHBV blends compared with neat PLA.

Furthermore, the addition of TPS in PLA/PHBV 80/20 blends led to a decrease in impact property due to the reduction of rigidity of the sheets. Figure 4.16 showed the impact strength of PLA/PHBV 80/20 and PLA/PHBV/TPS blends as a function of TPS content. Figure 4.16 showed that when the amount of TPS in PLA/PHBV/TPS blend sheet increased, it led to an increase of impact strength. As a result, the PLA/PHBV/10 TPS blend sheets had better impact strength compared with other blend sheets.

Table 4.4 The impact properties of neat PLA and PLA/PHBV blends and PLA/PHBV/TPS blends.

Samples	Impact strength (J/cm)
Neat PLA	5.1 ± 0.3
PLA/PHBV 80/20	7.4 ± 0.2
PLA/PHBV 70/30	6.8 ± 0.4
PLA/PHBV 60/40	5.8 ± 0.6
PLA/PHBV/1 TPS	5.3 ± 0.2
PLA/PHBV/5 TPS	6.1 ± 0.2
PLA/PHBV/10 TPS	6.6 ± 0.2

Figure 4.15 Impact strength of neat PLA and PLA/PHBV blends as a function of PHBV content.
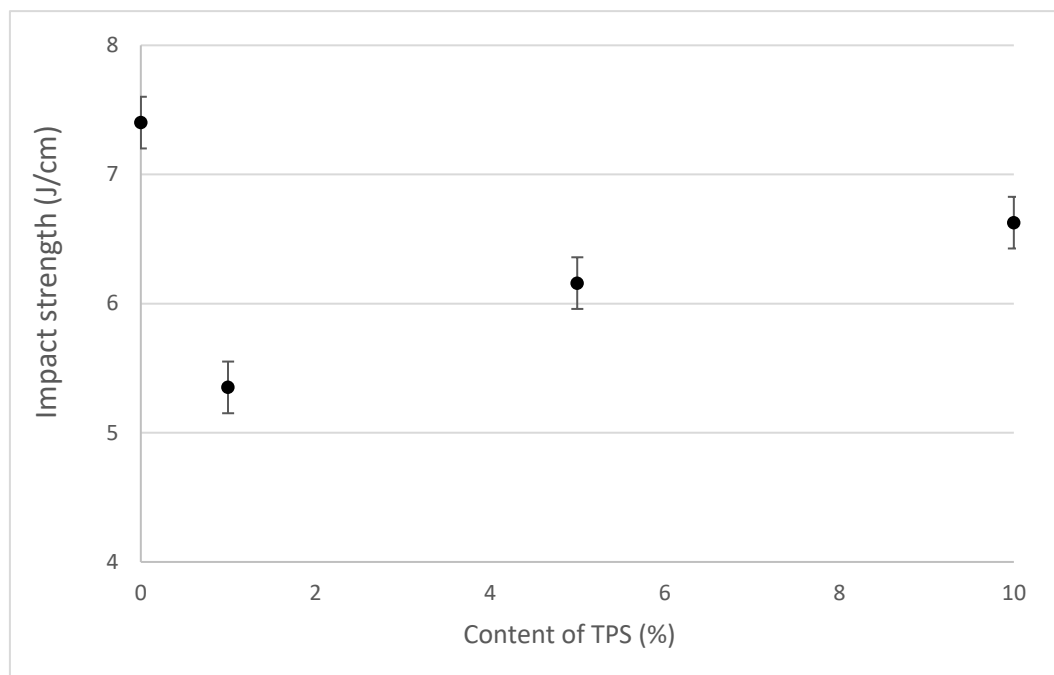
Figure 4.16 Impact strength of PLA/PHBV 80/20 and PLA/PHBV/TPS blends as a function of TPS content.

CHAPTER V
CONCLUSIONS
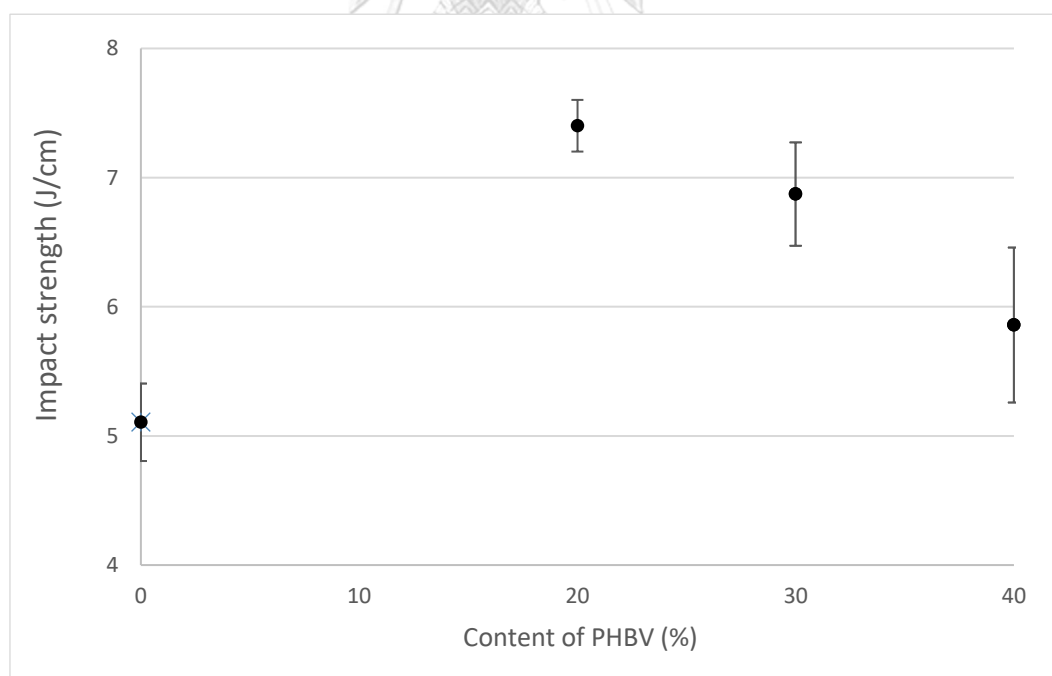
5.1 Conclusion

This research aimed to study of the thermal and mechanical properties of binary blends between PLA and PHBV and tertiary blend between PLA, PHBV and TPS. The binary blends of PLA and PHBV and tertiary blends of PLA, PHBV and TPS were mixed by twin-screw extruder. The thermal properties, morphology and mechanical properties of blends were investigated by differential scanning calorimeter (DSC), scanning electron microscope (SEM), universal testing machine and impact tester, respectively.

The DSC study revealed that the glass transition temperature of neat PLA and neat PHBV were 58.21 °C and 2.50 °C, respectively. Moreover, the adding more PHBV in PLA/PHBV blends did not significantly change the glass transition temperature, cold crystallization temperature and melting temperature of PLA and PHBV. Also, adding more TPS in PLA/PHBV/TPS blends did not significantly change the glass transition temperature, cold crystallization temperature and melting temperature of PLA and PHBV. The morphology study indicated that PLA/PHBV blends were separated into two phases. The PLA/PHBV 80/20 blend had a finely dispersed of PHBV domains in PLA matrix which affected the mechanical properties of sheets. Moreover, the SEM micrographs of PLA/PHBV/TPS blends indicated that TPS particles were not uniformly dispersed in the PLA and PHBV matrix. The study of tensile properties indicated that the addition of PHBV in PLA/PHBV blends led to an increase in Young's modulus, elongation at break and impact properties compared to a neat PLA. However, these also led to a decrease in tensile strength. Furthermore, the study of tensile properties indicated that the addition of TPS in PLA/PHBV/TPS blends led to lower in tensile strength, Young's modulus, elongation at break and impact properties.

5.2 Recommendations

From the results of this research, the following recommendations were suggested:

- The PLA/PHBV 80/20 blend had good mechanical properties to produce single-use dinnerware such as straw. Before using, the weight loss should be tested because the polymer may be dissolved in a cold drink.

- Study biodegradation behavior of PLA/PHBV/TPS blends system to confirm the biodegradability following ISO 17088, EN13432 or ASTM 6400.

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APPENDIX

APPENDIX A

EVALUATION OF THERMAL PROPERTIES

Differential scanning calorimeter (DSC) Mettler Toledo DSC 1 STAR system was used to obtain the DSC profiles of neat PLA, PLA/PHBV and PLA/PHBV/TPS. Then the software STAR Evaluation was used to evaluate all thermal properties. Figure A-1 showed the raw data of DSC thermogram of the second heating run of PLA/PHBV 80/20.
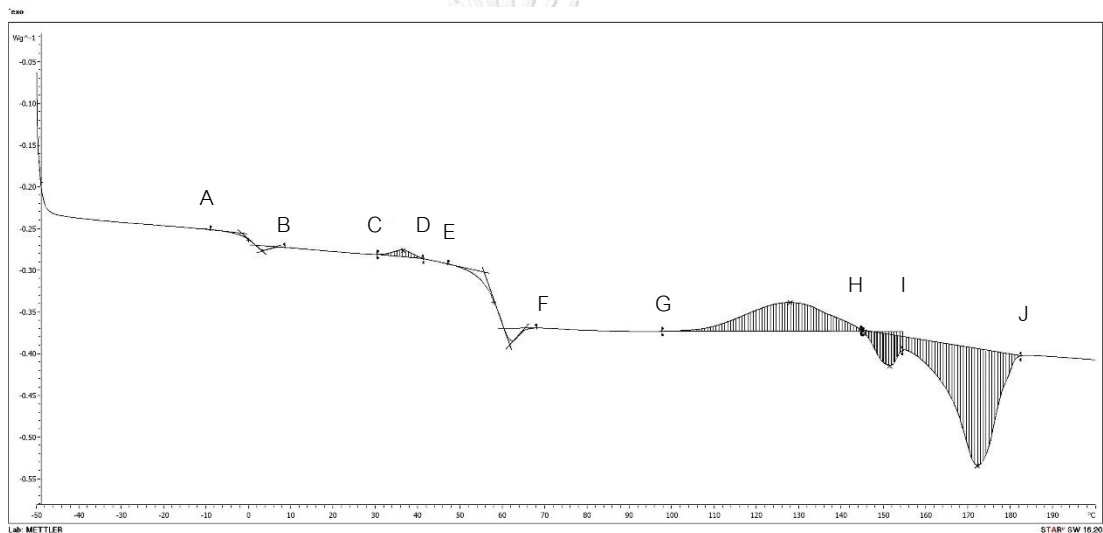

Figure A-1 *DSC thermogram of PLA/PHBV 80/20.*

1. Evaluation the T_g of PHBV

From Figure A-1, the range A to B was used to evaluate the glass transition temperature (T_g) of PHBV in the blend system by plotted the slope from A to B because the T_g value of neat PHBV (2.50 °C) from the experiment was in this region. The midpoint of the slope was defined as the T_g of PHBV.

2. Evaluation the T_g of PLA

From Figure A-1, the range E to F was used to evaluate the T_g of PLA in the blend system by plotted the slope from A to B because the T_g value of PLA (58.21 °C) from the experiment was in this region. The midpoint of the slope was the T_g defined as of PLA.

3. Evaluation the T_{cc} and ΔH_{cc} of PHBV

From Figure A-1, the range C to D was used to obtain the cold crystallization temperature (T_{cc}) and enthalpy of cold crystallization (ΔH_{cc}) of PHBV in the blend system because the cold crystallization peak was the exothermic peak occurring when the polymer releases heat while arranging the polymer chains to be crystalline part in polymer in the heating step. The cold crystallization temperature of PHBV was about 40 °C [42]. The area under the graph was ΔH_{cc} of PHBV and the value of peak point was defined as the T_{cc} of PHBV.

4. Evaluation the T_{cc} and ΔH_{cc} of PLA

From Figure A-1, the range G to H was used to obtain the T_{cc} and ΔH_{cc} of PLA in the blend system because the cold crystallization peak was the exothermic peak occurring when the polymer releases heat while arranging the polymer chains to be crystalline part in polymer in the heating step. The cold crystallization temperature of PLA was about 110 °C [43]. The area under the graph was ΔH_{cc} of PLA and the value of peak point was defined as the T_{cc} of PLA.

5.   Evaluation the T_m of PLA

From Figure A-1, range H to I was used to evaluate the melting temperature (T_m) of PLA in the blend system. The melting peak was the endothermic peak showing that polymer chains decrystallized to change from solid to liquid phase. The T_m of PLA from the experiment was about 150 °C. The value of the lowest peak point was the T_m of PLA.

6.   Evaluation the T_m of PHBV

From Figure A-1, the range I to J was used to evaluate the T_m of PHBV in the blending system. The melting peak was the endothermic peak showing that polymer chains decrystallized to change from solid to liquid phase. The T_m of PHBV from the experiment was about 173 °C. The value of the lowest peak point was the T_m of PHBV.

7.   Evaluation the ΔH_m of blending system

From Figure A-1, the range H to J was used to evaluate the ΔH_m of the blend system because its associated with the melting peak which was the endothermic peak of the DSC curve. The area under the graph was ΔH_m of the blend system.

APPENDIX B

THERMAL PROPERTIES OF PLA AND PHBV
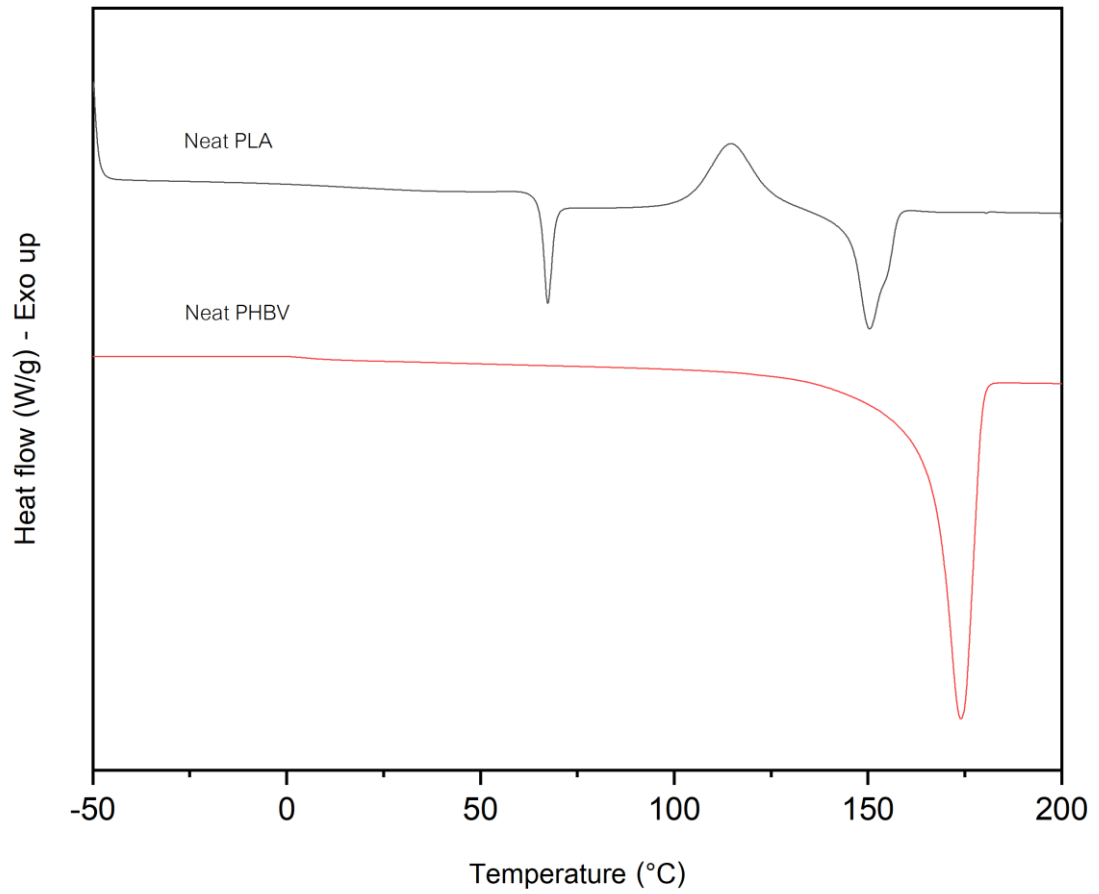
Figure A-2 DSC thermogram of PLA and PHBV.

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