การเตรียมและสมบัติของของผสมพอลิแลกติกแอซิดกับแป้งมันสำปะหลังโดยใช้ซิเทรตและฟอร์มาไมด์

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PREPARATION AND PROPERTIES OF POLYLACTIC ACID AND CASSAVA STARCH BLENDS USING CITRATES AND FORMAMIDE

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	PREPARATION AND PROPERTIES OF POLYLACTIC ACID AND CASSAVA STARCH BLENDS USING CITRATES AND FORMAMIDE
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Field of Study	Petrochemistry and Polymer Science
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ขวัญจิตร รักชาติ: การเตรียมและสมบัติของของผสมพอลิแลกติกแอซิดกับแป้งมันสำปะหลังโดยใช้ซิเทรตและฟอร์มาไมด์ (PREPARATION AND PROPERTIES OF POLYLACTIC ACID AND CASSAVA STARCH BLENDS USING CITRATES AND FORMAMIDE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. มงคล สุขวัฒนสินิทธิ์, 74 หน้า.

งานวิจัยนี้ศึกษาการเตรียมพลาสติกย่อยสลายได้ทางชีวภาพพอลิแลกติกแอซิดกับแป้งมันสำปะหลังโดยผสมแป้งในปริมาณไม่ต่ำกว่า 50% ด้วยเครื่องเอกทรูดซ์ชนิดสกรูเดี่ยว โดยใช้ฟอร์มาไมด์และน้ำเป็นพลาสติไซเซอร์สำหรับแป้งเพื่อเตรียมเทอร์โมพลาสติกสทาร์ชที่มีความเป็นผลึกต่ำ ขณะที่ไทรเอทิลซิเทรต และ ไทรบิวทิลแอซิทิลซิเทรตนำมาใช้เป็นคอมแพตทิบิไลเซอร์ในการปรับปรุงความเข้ากันได้ระหว่างเทอร์โมพลาสติกสทาร์ชกับพอลิแลกติกแอซิด ผลจากการศึกษาสมบัติเชิงกลและสมบัติทางความร้อนพบว่าฟอร์มาไมด์เป็นพลาสติไซเซอร์ที่มีประสิทธิภาพมากกว่าสารละลายฟอร์มาไมด์ในน้ำในการเตรียมเทอร์โมพลาสติกสทาร์ช โดยทั่วไปของผสมระหว่างเทอร์โมพลาสติกสทาร์ชกับพอลิแลกติกแอซิดจะมีสมบัติเชิงกลและอุณหภูมิการเสียรูปที่ต่ำกว่าพอลิแลกติกแอซิดบริสุทธิ์ ซึ่งผลจากการศึกษาลักษณะทางสัณฐานวิทยาชี้ให้เห็นว่ามีการแยกเฟสในบางส่วนของของผสมที่ได้โดยเฉพาะเมื่อปริมาณแป้งเพิ่มขึ้น แต่จากการปรับปรุงความเข้ากันได้ระหว่างเทอร์โมพลาสติกสทาร์ชกับพอลิแลกติกแอซิดโดยใช้ไทรบิวทิลแอซิทิลซิเทรตและไทรเอทิลซิเทรตเป็นคอมแพตทิบิไลเซอร์นั้นพบว่าของผสมที่ได้เป็นเนื้อเดียวกันมากขึ้นและส่งผลให้สมบัติเชิงกลของของผสมดีขึ้นอยู่ในระดับที่น่าพึงพอใจ อย่างไรก็ตามการใช้ปริมาณของคอมแพตทิบิไลเซอร์ที่เพิ่มขึ้นส่งผลให้อุณหภูมิการเสียรูปลดต่ำลง

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
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KHWANJIT RUGCHAD: PREPARATION AND PROPERTIES OF POLYLACTIC ACID AND CASSAVA STARCH BLENDS USING CITRATES AND FORMAMIDE. THESIS ADVISOR: ASSOC.PROF. MONGKOL SUKWATTANASINITT, Ph.D., 74 pp.

Formulation and method for preparation of biodegradable plastics by blending of poly (lactic acid) (PLA) with at least 50% of low cost cassava starch are investigated using a single screw extruder. Formamide and water are tested as a plasticizer for cassava starch to form low crystallinity thermoplastic starch (TPS) while triethyl citrate and tributylacetyl citrate are used as a compatibilizer for the PLA/TPS blends. The tensile strength and DSC thermograms suggest that pure formamide is better than aqueous formamide solution for the preparation of amorphous TPS. The TPS/PLA blends generally have poorer mechanical properties and lower deformation temperature comparing to virgin PLA. The SEM images reveal that there is some phase separation between PLA and starch in the blends, especially at higher starch contents. The interfacial modification of PLA/TPS blends by using tributylacetyl citrate is better than triethyl citrate in promoting the miscibility between the starch and PLA that is important for improving the mechanical properties of the blends to acceptable level. However, increases the used amount of the citrate compatibilizers significantly decrease the deformation temperature of the blends.

Field of Study : Petrochemistry and Polymer Science Student's Signature : ....
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CHAPTER I

INTRODUCTION

1.1 Statement of problem

Plastics are extremely important to the job market as well as products and packaging throughout the world. Because of their advantages on physical properties such as durability, flexibility, toughness, light weight as compared with glass, metal or other materials and low cost, plastics have been used in a very wide range of products. As a result, the growth of their applications is so rapid that their disposal has make up about 20% by volume waste per year and has recently been a serious environmental trepidation because of their enduring degradation. Bio-based plastics have recently received increasing attention as a more environmentally compatible alternative than the petroleum-based plastics in terms of both biodegradability and global carbon recycling (Piya, 2005).

Polylactide (PLA) is one of the most promising bio-based polymers currently available on the market. The expected rise in the cost of petroleum based commodities in the next decades opens bright perspective for this material. The biodegradability and renewability are its main assets in the applications of which materials are difficult to recycle. PLA is derived from renewable starch or sugar resources and has therefore gained attention as an alternative to conventional synthetic polymers. Its properties are in many ways similar to poly (ethylene terephthalate) (PET). It is a highly transparent and rigid material with a relatively low crystallization rate that makes it a promising candidate for the fabrication of biaxially oriented films, thermoformed containers and stretch-blown bottles. Comparing to the controlling of crystalline content in PET with co-monomer content, the PLA crystalline content is controlled by either the monomeric ratio of D- and L-lactides used in the polymerization or the mixing ratio between the L-PLA and D-PLA. The crystalline content in PLA is typically smaller than in PET that its melting point and glass transition temperature are generally lower. Many of PLA’s properties are well suited for high-volume packaging applications. It exhibits good barrier properties to aromas and carbon dioxide permeability. The permeability of oxygen and water vapor is only slightly higher than that of PET. In terms of food contact, PLA has the advantage that the residual monomers are naturally occurring and non-toxic chemicals. PLA is thus safe to be used for food-contacting articles.

Starch is one of the most widely consumable naturally occurring polymers. It consists of amylose and amylopectin of which monomeric units are α-D-glucose. The ratio between amylose and amylopectin is dependent on the starch sources but amylose is typically the minor component of natural starch. It is a linear polymer with a molar mass in the range 10^5-10^6 g/mol. Amylopectin is a branched polysaccharide with a larger degree of polymerization and a molecular mass about 10^8 g/mol. The crystalline starch structure disappears when it is subjected to temperatures greater than 70 - 90°C in the presence of plasticizers such as water or glycerol. This transformation is named gelatinization and leads to the so-called thermoplastic starch (TPS). Because of its high molecular weight, relatively high plasticization levels are necessary for the gelatinization. Gelatinization of starch along with some molecular weight reduction can be readily achieved using extrusion technology, which provides a closed pressurized environment with sufficient heat and shear stress to break down the crystalline structure of the semi-crystalline starch and render completely amorphous. Once the starch is gelatinized and properly plasticized, the TPS can flow just as any synthetic polymer and is therefore suited for conventional molding and extrusion technologies.

Early work in starch/PLA blends have focused on the incorporation of dry starch into PLA to reduce the cost of the material while maintaining biodegradability. In this case, the starch acts as filler increasing the rigidity of the material but, at the same time, it also increases the intrinsic brittleness of PLA. The starch concentration at which useful materials can be prepared is therefore limited to a low range prior to which the properties of the composite suffer dramatically. This has prompted investigations on PLA plasticization with glycerol as a means to decrease the brittleness of the composites. This approach decreases the glass transition of PLA and increase the crystallinity level that occurs over time in the PLA crystallization temperature range (Jitendra, 2005).

1.2 Research Question and Hypotheses

The blending of the TPS and PLA can result in a wide variety of morphologies ranging from a dispersed starch/PLA matrix to a co-continuous starch/PLA structure or to phase inverted morphologies in which the starch is the matrix material (Michel, 2007). In this context, the interfacial modification plays a very important role controlling both the segregation scale and the solid-state adhesion between the components. As a high level of incorporation of low cost starch into the more expensive PLA can benefit the cost reduction of PLA-based biodegradable plastics, it is thus interesting to find out if the properties of the TPS/PLA blends with high TPS loading can be improved to an acceptable level through the choices and contents of plasticizers and interfacial modifying agents. Ideally, an appropriate interfacial modifying agent used for blending of TPS and PLA may be contemplated on the balance of hydrophobic parts and hydrogen bond forming groups in the molecular structure of the plasticizer and/or compatibilizer. The results obtained from this study should enable the tailoring the mechanical properties and biodegradability of the bio-based plastics according to application needs.

1.3 Statement of purpose

The major goal of this research is to prepare a bio-based plastic with acceptable mechanical properties from PLA containing at least 50% incorporation of cassava starch. In order to obtain a modified starch with low crystallinity and T_g that consequently allow a high level of starch incorporation in PLA, formamide and water have been selected as plasticizers for the preparation of TPS. To improve uniformity of the blends, tributylacetyl citrate and triethyl citrate are tested as compatibilizers. Morphology, impact strength, tensile strength and thermal properties of TPS/PLA blends are used to justify the optimum blending formula.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Biodegradable Polymers

Biodegradable polymers is a growing field as a vast numbers of biodegradable polymers found to be synthesized or destroyed in nature during the growth cycles of all life forms. Many microorganisms and enzymes capable of degrading them have been identified. Depending on the synthesis process, the biodegradable polymers have been classified into 4 categories of which 3 categories (categories a-c) are obtained from renewable resources (Figure 2.1): (a) polymers obtained from biomass such as agro-resources (*e.g.*, starch, cellulose), (b) Polymers obtained from microbial production (*e.g.*, the polyhydroxy-alkanoates), (c) Polymers obtained from synthetic monomers derived from agro-resources (*e.g.*, polylactide). (d) Polymers obtained from petroleum products through chemical synthesis

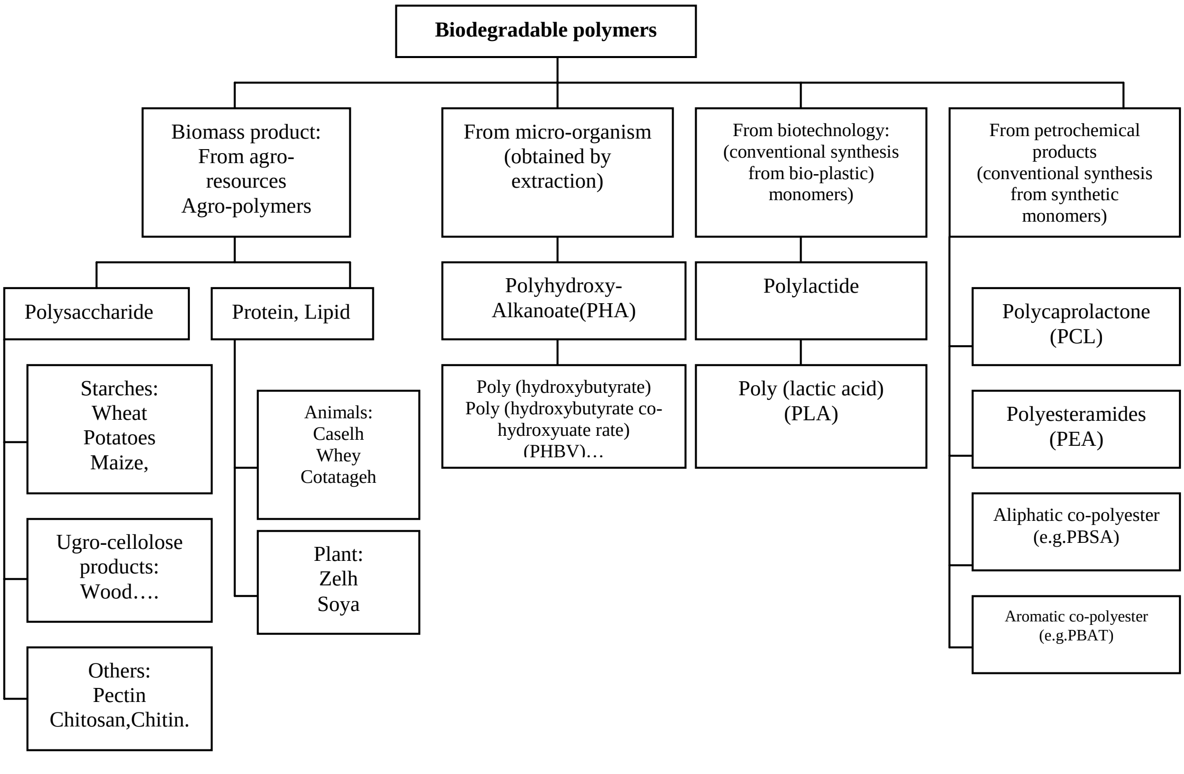


Figure 2.1. Classification of the biodegradable polymers (John, 1998).

The biodegradable polymers are also often classified into two main families: the agro-polymers (category a) and the biodegradable polyesters (categories b to d). PLA is degradable polyester produced from renewable raw materials such as corn, beets, and other biomass. It is fully degradable under composting conditions (temperature ~ 60°C), breaking down into water and carbon dioxide. Characteristics of PLA in comparison to conventional petroleum-based plastics from a life cycle perspective are shown in Table 2.1. Advantageous properties of PLA include its excellent transparency, strong mechanical properties and good processability, making it suitable for a wide range of plastic applications.

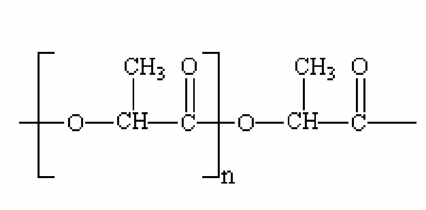
Table 2.1Life cycle perspective of PLA and conventional oil-based plastics

	PLA	Conventional plastics
Raw material	Renewable resources Grains, plants and biomass	Limited resources Fossil resources/ petroleum
Production process	Can be produced anywhere Chemical polymerization	Uneven distribution Chemical polymerization
Degradable After use	Degradable in compost	Not degradable
Recycling	Bio/eco, material and chemical and thermal	Material, chemical and thermal
Incineration	Release of CO_2 fixed in 1 year at a low heat of combustion	Release of CO_2 fixed in ancient time at a high heat of combustion

PLA is also claimed by its manufacturers as being recyclable in all senses. Its thermal energy can be recycled through combustion; it can be recycled biologically through composting; and it can be degraded to its chemical components to be made into new materials. The first commercial PLA product was the joint venture between Cargill Company and Dow Chemical Company. The most widely known product is probably a thermoformed yoghurt cup being utilized by the German "Dannon" brand. The life-cycle analysis of Cargill Dow's PLA shows that PLA has the potential to reduce the consumption of fossil resources by 20–50% when compared with some of the petroleum-based polymers. Currently, PLA also appears to be the only plant-based plastic with a chance of competing with petroleum-based polymers in terms of greenhouse emissions. PLA is certified to the German Standard, DIN 54900. At current status, the main disadvantage of PLA is that it is expensive (John, 1998).

2.2 Poly(lactic acid) or Polylactide (PLA)

Poly(lactic acid) or polylactide (PLA) is a biodegradable, thermoplastic, aliphatic polyester derived from renewable resources, such as corn starch (in the U.S.) or sugarcanes (rest of world) having a chemical structure as shown in Figure 2.2.



$$\left[-O-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-\right]_n-O-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-$$

Figure 2.2.Chemical structure of poly (lactic acid) (PLA) (Nolan-ITU, 2002).

PLA is generally produced by a catalytic ring opening polymerization of lactide. Lactide is the cyclic dimer of lactic acid produced from thermal cracking of oligomers of lactic acid. Lactic acid exists as two optical isomers, D and L which L-lactic acid is a natural isomer produced via starch fermentation. The L-PLA is derived from the natural L-lactide while DL-PLA is the synthetic blend of D-lactide and L-lactide. The homopolymer of L-lactide (L-PLA) is a semicrystalline polymer. These types of materials exhibit high tensile strength, low elongation, and consequently high modulus that make them more suitable for load-bearing applications such as in orthopedic fixation and DL-PLA is amorphous polymer, exhibiting a random distribution of both isomeric forms of lactic acid, and accordingly are unable to arrange into an organized crystalline structure. This material has low tensile strength, high elongation, and a much more rapid degradation time, making it more attractive as a drug delivery system. L-PLA has 37% crystalline, with a melting point of 175-178°C and a glass transition temperature of 60-65°C. Characteristic of PLA is contains ester linkages which are sensitive to both chemical hydrolysis and enzymatic chain cleavage. PLA is fully degradable when composted in a large scale operation with temperature of 60°C and above associated with its glass transition temperature around 60°C (Nolan, 2002). The first stage of degradation of PLA (two weeks) is via hydrolysis to water soluble compounds and lactic acid. Rapid metabolism of these products into CO_2, water and biomass by a variety of microorganism occurs after the hydrolysis. PLA dose not biodegrade readily at temperature less than 60°C.

2.3 Starch

Starch presents different industrial applications in fields such as food, paper, textile and adhesive. Among natural polymers, it is also the most economically feasible for biodegradable plastic because it is naturally abundant and can be processed with some plasticizers like a thermoplastic although it is not thermoplastic in dry form. Starch granules can be isolated from plants such as wheat, potato, maize, rice, cassava, pea, waxy maizes, and amylomaizes. Native starch granules have dimensions ranging from 0.5 to 175 microns and appear in a variety of shape. For instance, Figure 2.3 shows micrographs of the shape of different starch granules from wheat and pea (Whistler et al, 1980).

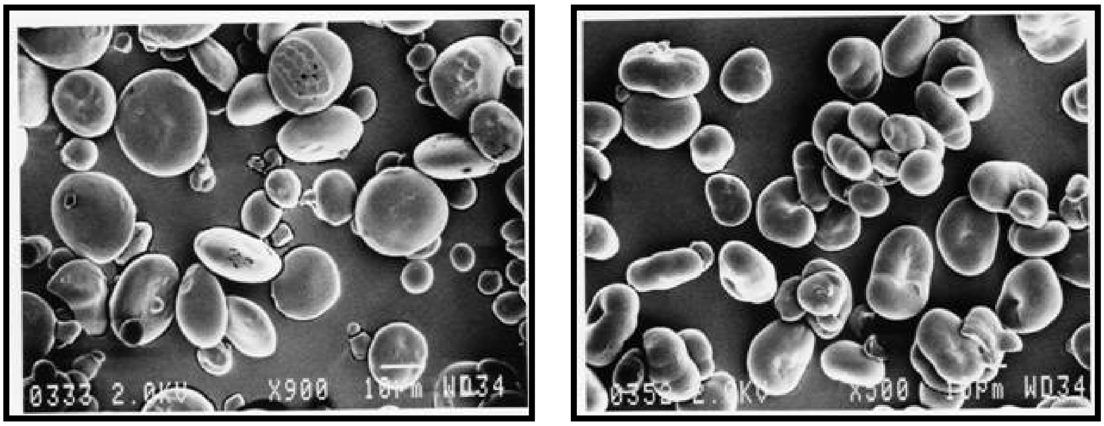


Figure 2.3. Micrographs of native starch (SEM observations): wheat starch (left) and pea starch (right).

Starch is generally described by the formula $(C_6H_{10}O_5)_n$ that consists of two types of polysaccharides: amylose and amylopectin. Usually, amylose and amylopectin are found in a ratio of 30:70 or 20:80. Amylose is a linear polysaccharide consisting of 1, 4-linked-D-glucose units (Figure 2.4) while amylopectin is a branched polysaccharide consisting of both 1,4 - and 1,6-linked-D-glucose units (Figure 2.5).

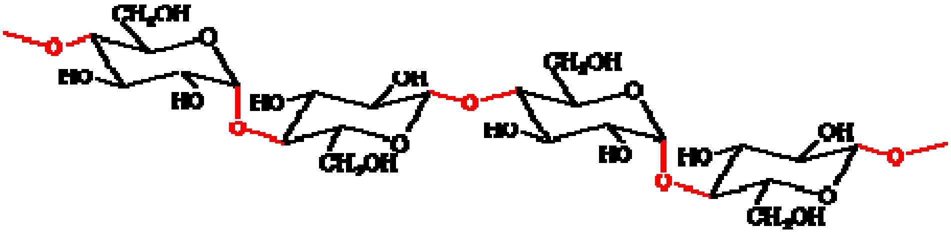


Figure 2.4. Amylose structure

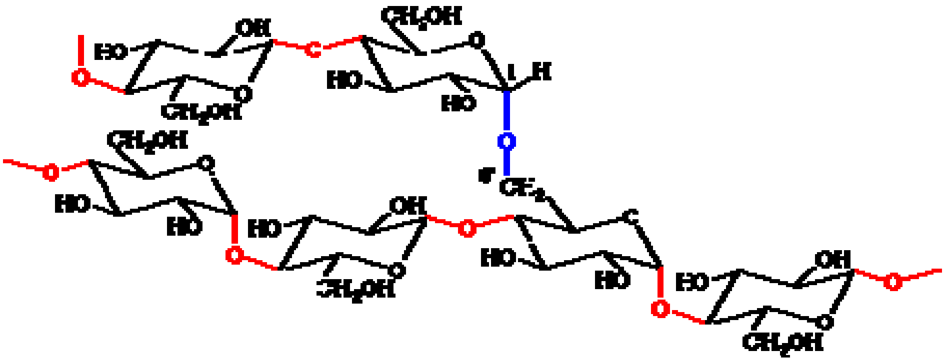


Figure 2.5. Amylopectin structure

Amylose and amylopectin possess two important functional groups, the hydroxyl (-OH) and ether groups (-O-C-O-) which is susceptible to chain breakage. The glucose units are linked to one another through C1, known as glycosidic bond. The glycoside linkage is stable under alkaline condition and hydrolyzed under acid condition.

The most abundant starch available in Thailand is cassava starch. It is very cheap and its supply is over domestic demand that it is usually exported in the forms of low price products like animal feed pellets, dry sheets and powder. It is thus worthwhile to explore the alternative utilization of cassava starch especially in more valuable products such as biodegradable plastics. Accordingly, this research has focused on the use of plasticizer and compatibilizer for incorporation of cassava starch into PLA at high starch content to attain thermoplastic with acceptable processability and mechanical strength.

Various types of starch have different compositions of amylase and amylopectin as revealed in Table 2.2 (Whistler et al, 1980). Cassava starch generally contains 17% amylose and 87% amylopectin that is similar rice starch but its amylopectin content is slightly higher than potato starch and significantly higher than corn starch.

Table 2.2 Amylose and amylopectin contents and degree of polymerization of various starch types (Whistler et al, 1980)

Starch	Amylose	Amylopectin	Average DP	
			amylose	amylopectin
Corn	28	72	80	2,000,000
Potato	21	79	3000	2,000,000
Wheat	28	72	800	2,000,000
Cassava	17	83	-	2,000,000
Waxy maize	0	100	-	2,000,000
Sorghum	28	72	-	-
Rice	17	83	-	-
Arrowroot	20	80	-	-
Amylomaize	50-80	20-50	-	-

DP = Degree of polymerization

2.4 Thermoplastic Starch (TPS)

Pure dry starch has melting temperature (T_m= 220-240°C) above its decomposition temperature (220°C). In most starch applications, except for the purpose as filler, the intermolecular structure of native starch must be destroyed before blending into the products. The most common destructuring agent is water. Starch granules can be gelatinized when being heated with water. Microscopically, gelatinization involves the disruption of the polysaccharide chain packing within the starch granules. Heat and water cause swelling of the starch granules, forming a viscous paste with destruction of most of inter-macromolecule hydrogen bonds. The gelatinized starch is solidified into amorphous starch with reduction of both melting temperature (T_m) and glass transition temperature (T_g). Figure 2.6 shows the relationship between the level of destructuration and the water content that provide different starch products and applications. Usually, the expanded structures of starch require rather high water contents (Whistler et al, 1980).

The gelatinization by water usually requires high content of water. Decreasing of the water content to less than 20 wt%, the melting temperature tends to close to the degradation temperature. To overcome this issue, a non-volatile (at the process temperature) plasticizer such as glycerol or others polyols has been employed. Other compounds such as those containing nitrogen (urea and amines) have also been used. Figure 2.6 shows that plasticized starches with high level of destructuration can be obtained at low water content. The first patents and articles on these processable materials were published at the end of the eighties. TPS is usually transformed under thermomechanical treatment as a thermoplastic, using conventional machines for plastic processing (e.g., by extrusion) (John, 1998). These plasticized starches are thus commonly called "thermoplastic starches" or TPS.

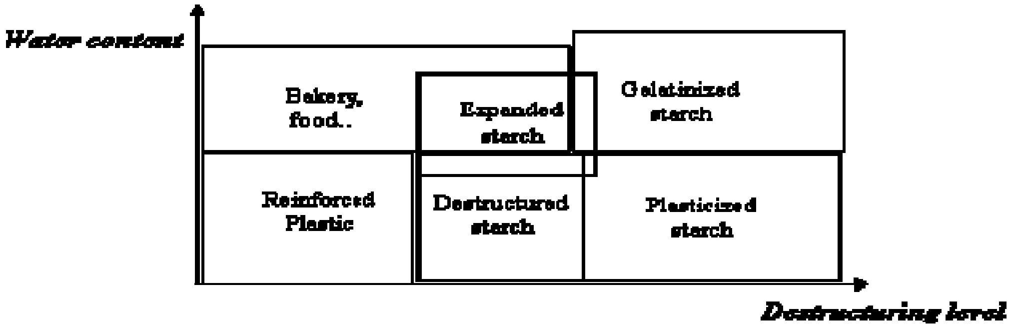


Figure 2.6. Illustration of starch products based on water content and destructuring level (Hatarirat, 1997).

The disruption of granular starch is the transformation of the semicrystalline granule into a homogeneous, rather amorphous material with the destruction of hydrogen bonds between the macromolecules. Disruption can be accomplished by casting (e.g., with dry drums) or by applying thermomechanical energy in a continuous process. The combination of thermal and mechanical inputs can be obtained by extrusion, a common plastic processing technique. Process can be in one or two stages. In a one-stage process, the extruder, usually a twin-screw extruder is fed with native starch along the barrel; water and liquid plasticizer are successively introduced. In a two-stage process, the first stage is a dry blend preparation. Into a turbo-mixer, under high speed, the plasticizer is added slowly into the native starch until a homogeneous dispersion is obtained. Then, the mixture is placed in a vent oven allowing the diffusion of the plasticizer into the granules. After cooling, the right amount of water is added to the mixture using a turbo-mixer. This dry blend is then introduced into an extruder. Figure 2.7 shows the different stages of the extrusion. First, the starch granules are fragmented mechanically. Second, under heating and shearing, starch is destructured, plasticized, melted but also partially depolymerized. After the processing, a homogeneous molten phase of starch is formed (Hatarirat, 1997).

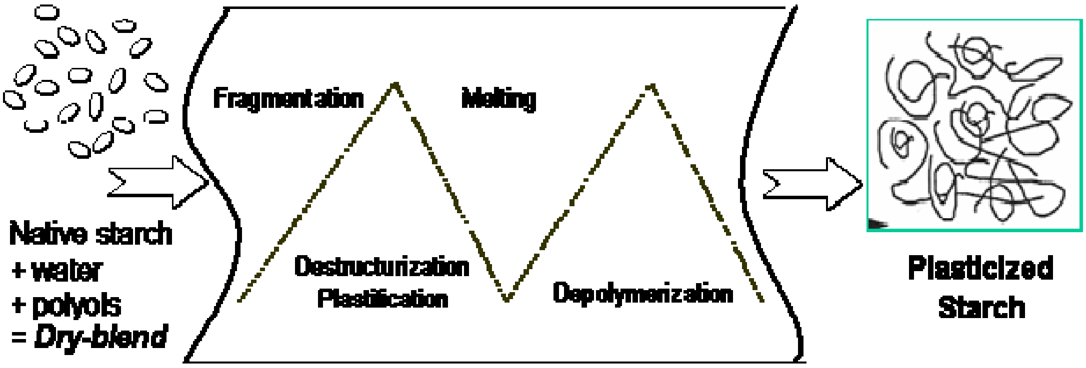


Figure 2.7. Schematic of starch process by extrusion (Hatarirat, 1997).

2.5 Polymer Blend

By definition, any physical mixture of two or more different polymers that are not linked by covalent bonds is a polymer blend. Development of a new polymer to meet a specific need is a lengthy and costly enterprise. If the desired properties can be realized simply by mixing two or more existing polymers, there is an obvious pecuniary advantage.

A number of technologies have devised to prepare polymer blend. It is so seldom that the choices of polymers are compatible enough to give miscible blend. Rather, they usually separate into discrete phases on being mixed, although an increasing number of completely miscible blends are being developed. Differences between the two types are manifested in appearances, miscible blends are usually clear, immiscible blends are opaque and in such properties as glass transition temperature, miscible blends exhibit a single T_g intermediate between those of the individual components, whereas immiscible blends exhibit the separation of T_g characteristic of each component. Miscibility is by no means prerequisite to commercial utility although it is desirable as the properties and processing characteristics of the homogeneous polymer blends are more convenient to predict. Physical or mechanical properties usually reflect to the weight average of the properties of each component. In general, the properties of blends are considerably affected by the miscibility of the polymeric constituents. The most difficult polymer blend category to clearly describe is that of the partially miscible system. The most common example of this blend category is one in which two completely immiscible polymer are made compatible with a third organic agent, called a compatibilizer. The compatibilizer usually increases the interfacial adhesion between the blended components.

Thermodynamically, the miscibility of the polymer mixture is associated with the negative value of the free energy of mixing (ΔG_m). For polymeric system, ΔG_m is approximately equal to the enthalpy of mixing (ΔH_m) as the change in entropy (ΔS_m) is relatively small. Miscible polymer blend has a single phase, in contrast, immiscible blend polymer is a polymer mixture in which constituents form separate phases. Thermodynamically, immiscible blend is associated with the positive value of the Gibb's free energy of mixing ($\Delta G_m = \Delta H_m > 0$) (Nuchanan, 1999).

The compatibilizers can in principle interact in complex ways to influence final blend properties. One effect of compatibilizers is to reduce the interfacial tension in the melt, causing an emulsifying effect and leading to extremely fine dispersion of one phase in another. Another effect is to increase the adhesion at phase boundaries, giving improve stress transfer. A third effect is to stabilize the dispersed phase against crystal growth during annealing, again by modifying the phase-boundary interface (Nuchanan, 1999).

Technological definition of compatibilization is a modification of blend to produce a desirable set of properties. A number of different lines of approach can be used which may assist the material developer to achieve thermodynamic miscibility. Broadly, these are: (a) addition of block and graft copolymer, (b) addition of functional/reactive polymer and (c) in situ grafting/polymerization (reactive blending).

The addition of block or graft copolymer represent the most extensively researched approach to compatibilization of blend. Block copolymers have been more frequently investigated than the graft copolymer, and in particular block copolymer containing blocks chemically identical to the blend component polymers. It is perhaps not surprising that blocks and graft copolymer containing segments chemically identical to the blend component are obvious choices of compatibilizers, given that the miscibility between the copolymer segments and the corresponding blend components is assured.

Many workers have described the addition of functional polymers as compatibilizer. Usually a polymer chemically identical to one of the blend component is modified to contain functional (or reactive) units, which have some affinity for the second blend component; this affinity is usually the ability to chemically react with the second blend component, but other types of interaction are possible. The functional modification may be achieved in a reactor or via an extrusion modification process. Example includes the grafting of maleic anhydride similar component to polyolefins, the resulting pendent carboxyl group having the ability to form a chemical linkage with polyamides via their terminal amino group (Akkapeddi, 1999).

A comparatively new method of producing compatible thermoplastic blends is via reactive blending, which relies on the in situ formation of copolymers or interacting polymers. This differ from other compatibilization routes in that the blend component themselves are either chosen or modified so that reaction occurs during melt blending, with no need for addition of a compatibilizer. This route has found commercial application, for example in blends of polyamides with graft functional polyolefin elastomer. Graft-functionalized elastomers, produced by melt modification, are commercially available for toughening nylons (Akkapeddi, 1999).

2.6 Literature Reviews

Piyarat (1997) studied the mechanical properties *i.e.* tensile strength and elongation at break, of LDPE/tapioca starch blends at various compositions. In order to improve the mechanical properties of the blends, several compatibilizers such as glycerol monosterate, zinc stearate and epolene, were added at 1% by weight of total blend. The mechanical properties of each blend were compared with blend with and without the compatibilizers. The results showed that the presence of glycerol monostearate or zinc stearate in the blends enhanced the mechanical strength better than the presence of epolene and that without the compatibilizers. Particularly, the addition of epolene decreased both tensile strength and elongation at break of the blends. In comparison of LDPE/corn starch blends and LDPE/tapioca starch blends at every composition, LDPE/tapioca starch blends had higher tensile strength and elongation at break in the presence of either glycerol monostearate or zinc stearate than LDPE/corn starch blends. SEM micrograph also showed that starch granules dispersed evenly in polyethylene matrix with either glycerol monostearate or zinc stearate.

Chang et al*.* (2000) studied PLA/starch blends with diisocyanates such as 4, 4'-methylenebis(phenylisocyanate) (MDI), Toluene diisocyanate (TDI), and diethylene triamine,1,6-Diisocyanatohexane (DIH) as cross-linked agents using the extrusion process. The effects of the reactive blending were investigated and significant improvements were confirmed by measuring the tensile strength, IR spectra and DSC. All three agents provided improvement of tensile strength. The PLA blended with 25% starch showed almost 90% strength increase compared with the original PLA. The blends with 50% starch showed the different effects of the three reacting agents on tensile strength, in the order MDI < TDI < DIH, respectively. It was found that the strength of the blend is more effectively increased when more flexible long chain DIH is used. The elongation did not show significant increases, even with reacting agents. These results show that cross-linking reactions can not provide plasticizing improvement, although they increased the compatibility.

Martin and Averous (2001) studied the plasticizing effects of various plasticizers on plasticized PLA. Plasticizing efficiency was evaluated in term of glass transition temperature (T_g) shift and mechanical properties improvement. Significant decrease in T_g and rise in the elongation at break was obtained with polyethylene glycol and oligomeric lactic acid. Furthermore, PLA was melt-blended with thermoplastic starch (TPS). The properties of subsequent TPS/PLA blends were investigated through tensile and impact testing, thermal analysis (DSC), dynamic mechanical analysis and microscopy (SEM). From the mechanical results, low level of compatibility was found. The blends showed two distinct T_g. However, the T_g of PLA phase shifted toward the T_g of TPS, indicating some degree of interaction. Microscopic observation revealed non-uniformly dispersed PLA inclusions in the TPS matrix, conforming that phase separation has occurred.

Ke and Sun (2001) characterized the blends of starch and PLA in the presence of various water contents. The initial moisture content of the starch showed no significant effect on its mechanical properties, but had a significant effect on the water absorption of the blends. The thermal and crystallization properties of PLA in the blend were not affected by moisture content. The blends prepared by compression molding had higher crystallinity than those prepared by injection molding. However, the blends prepared by injection molding had lower water absorption values, higher tensile strengths and elongations than those obtained from the compression molding. The crystallinity of the blends increased greatly with annealing treatment at the PLA second crystallization temperature (155°C).

Park and Im (2002) reported blends of PLA with gelatinized starch. Starch was initially gelatinized with various ratios of water/glycerol using a twin-screw mixer. Gelatinization of starch was found to lead to the destruction or diminution of hydrogen bonding in granules and a decrease in crystallinity of starch. DSC data showed that starch acted as a nucleating agent and glycerol acted as a plasticizer, contributing to an improvement in the crystallinity in the PLA blends. When the content of starch increased, the size of spherulites in PLA blends was smaller and less regular. These voids were not observed in the PLA/gelatinized starch. The mechanical properties gave a strong indication that a low level of compatibility existed in these blends. The blends showed two distinct T_g values. However, the T_g due to the PLA phase shifted toward the T_g of TPS with the blend composition, indicating certain degree of interaction.

Willett and Shogren (2002) studied the blends of starch and various thermoplastic resins to produce foams using a twin-screw extruder. Foams of cornstarch with poly(lactic acid) (PLA), poly(hydroxyester ether) (PHEE) or poly (3-hydroxybutyrate-co-3-hydroxyvalerate)(PHBV) had significantly lower densities and greater radial expansion ratios than the control starch. Most of the polymer occupied spherical to elongated domains 1–10 mm long, although PLA domains were much smaller. Surface polymer concentrations were larger than the bulk, and correlated with foam expansion and resistance to fragmentation. Foams were also extruded using blends of PLA or PHEE with high amylose starch (70% amylose), wheat starch and potato starch. The addition of either polymer resin significantly reduced the foam density and increased expansion. At constant relative humidity, compressive strength was a function of foam density only and not the type of resin or starch in the blends. Addition of the resins reduced the water sensitivity of the foams and increased the time needed for complete dissolution. Blends with PLA, PHEE or PHBV produced foams with densities comparable to commercial starch-based loose-fill foams.

Ke et al. (2003) studied the effect of amylose content in starches on the mechanical properties. Four dry corn starches with different amylose contents were blended at 185°C with PLA at various starches: PLA ratios using a lab-scale twin-screw extruder. Starch with 30% moisture content was also blended with PLA at a 1:1 ratio. Each extrudate was ground and dried. The powder was mixed with about 7.5% plasticizer, and injection molded into test tensile bars. These were characterized for morphology, mechanical properties and water absorption. Starch performed as filler in the PLA continuous matrix phase, but the PLA phase became discontinuous as starch content increased beyond 60%. Tensile strength and elongation of the blends decreased as starch content increased, but no significant difference was observed among the four starches at the same ratio of starch: PLA. The rate and extent of water absorption of starch/PLA blends increased with increasing starch. Blends made with high-amylose starches had lower water absorption than the blends with normal and waxy cornstarches.

Xiaofei and Jiugao (2004) studied the effects of water contents on mechanical properties of TPS plasticized by urea, formamide, acetamide or glycerol. The results showed that formamide-plasticized TPS (FPTPS) had a good flexibility at a wide scope of water contents, and the strain of urea-plasticized TPS (UPTPS) increased up to 65% at high water content (42%). Fourier Transform infrared (FT-IR) spectroscopy showed that a small percent of urea could react with starch at the given TPS processing conditions. The other plasticizers could not react with starch. The order of the hydrogen bond-forming abilities with starch was urea>formamide>acetamide>polyols, confirmed by B3LYP chemical computation. The hydrogen-bonding interaction in 1:1 complexes formed between starch and urea, formamide, acetamide or glycerol were 14.167, 13.795, 13.698 and 12.939 kcal/mol, respectively. Glycerol-plasticized TPS, FPTPS, acetamamide-plasticized TPS and urea-plasticized TPS were tested at three typical humidity levels using X-ray diffractometry. Urea and formamide could effectively restrain the retrogradation of TPS. The properties of TPS mainly relied on the hydrogen bond-forming abilities between plasticizers and starch molecules.

Wang et al. (2005) studied LLDPE/starch blend as prepared by one-step reactive extrusion in a single-screw extruder and characterized by means of mechanical tests, thermogravimetry (TG), scanning electron microscopy (SEM), rheological properties and Fourier transform infrared spectroscopy (FTIR). The thermal plasticization of starch and its modification with polyethylene were accomplished simultaneously in a single-screw extruder. The FTIR analysis showed that maleic anhydride (MAH) could graft onto the polyethylene chain using the same operational conditions as the preparation of the blends. The blends with MAH had better mechanical properties than the blends without MAH. From TG analysis, the thermal stability of the compatible blends was higher than the incompatible blends. The FTIR results also indicated that the compatibility between thermoplastic starch and polyethylene in the blends was truly improved with the addition of MAH.

Michel and Hongbo (2007) investigated the properties and interfacial modification of blends of polylactide (PLA) and glycerol-plasticized TPS. A twin-screw extrusion process was used to gelatinize the starch, evaporate the water to obtain a water-free TPS and then to blend into the PLA matrix. The concentration of TPS investigated ranged from 27 to 60% by weight of the blend. In the absence of interfacial modification, the TPS/PLA blend morphology observed through scanning electron microscopy was very coarse with TPS particles sizes ranging between 5 and 30 mm. Interfacial modification was achieved by free-radical grafting of maleic anhydride (MA) onto PLA and then by reacting the modified PLA with the starch macromolecules. Blends comprising MA-grafted PLA showed much finer dispersed phase size, in the 1-3 μm range and exhibited a dramatic improvement in ductility.

On-anong (2007) investigated LDPE/PLA blends with two molecular weight of LDPEs (125 kg/mol and 240 kg/mol) prepared by twin screw extruder with PLA content ranging from 5-20% with LLDPE-g-MA compatibilizer. The blend morphology was investigated by SEM which better distribution of the PLA dispersed phase was found in LDPE (240 kg/mol) blend. The effect of LLDPE-g-MA compatibilizer was observed for both types of LDPE as that the size distributions of dispersed PLA were reduced. DSC thermograms cannot detect a significant effect of the compatibilizer, LLDPE-g-MA. Tensile and Yong's modulus of the compatibilized blend were improved but Izod impact and elongation at break were dropped.

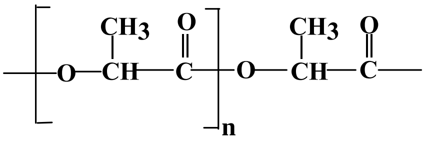
Ning et al. (2007) studied the compatibility between hydrophilic starch granules and hydrophobic poly(lactic acid) (PLA), using glycerol, formamide, and water as plasticizers for starch to enhance the dispersion and the interfacial affinity in thermoplastic starch (TPS)/PLA blend. The properties of TPS/PLA blends are investigated through microscopy (SEM), rheological, thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), tensile testing, and Dynamic mechanical thermal analysis (DMTA). In the presence of water and formamide, the plasticization of starch can be improved dramatically. At the same time, SEM can detect a homogeneous TPS/PLA blends. With increasing the dispersion between TPS and PLA, the blend becomes more thermal stability. It also proves that PLA degrades in the presence of water during melt processing. In addition, FT-IR spectroscopy proves that formamide and water can improve the interaction between TPS and PLA. The tensile testing and DMTA suggest that the compatibility between TPS and PLA is improved in this research.

CHAPTER III

EXPERIMENTS

3.1 Materials

3.1.1 Poly(lactic acid) (PLA)



$$-\left[O-\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}\right]_n-O-\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-$$

Figure 3.1. Poly(lactic acid)

PLA resin was obtained from Nature Work Company Limited, USA. It consists of 92/8 L/D-lactide with the weight average molecular weight of 74 kD and polydispersity index of 2. The polymer has density of 1.25 g/cm^3, glass transition temperature of 58°C and melting temperature of 149.9°C.

3.1.2 Cassava starch

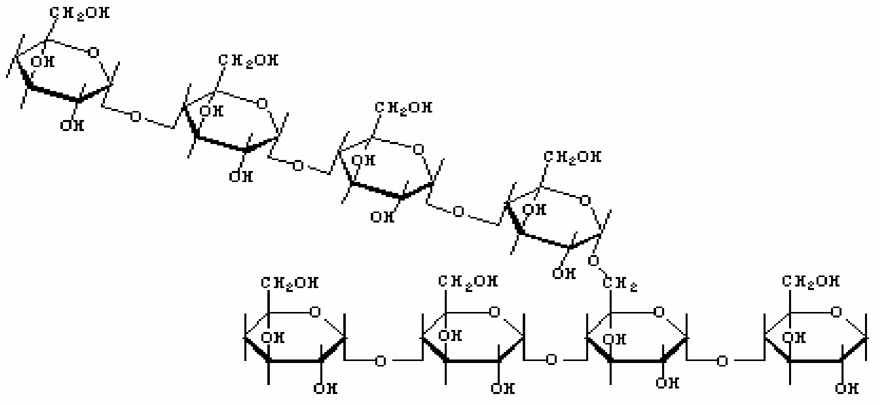


Figure 3.2. Cassava starch

Cassava starch used is a product of Siam Modified Starch, having moisture content 13% and sieve analysis 1.5% max on 250 micron.

3.1.3 Formamide ($HCONH_2$)

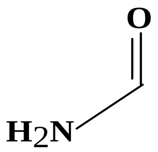


Figure 3.3. Formamide

Formamide is a product of Merck Company Limited, having molar mass 45.04 g/mol. Density (d 20°C / 4°C) and Boiling point about 103°C.

3.1.4 Triethyl citrate ($C_{12}H_{20}O_7$)

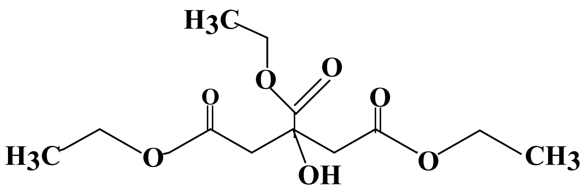


Figure 3.4. Triethyl citrate

Triethyl citrate is a product of Merck Company Limited, having Density 1.135 - 1.139 and Boiling point 294 °C.

3.1.5 Tributylacetyl citrate ($C_{20}H_{34}O_8$)

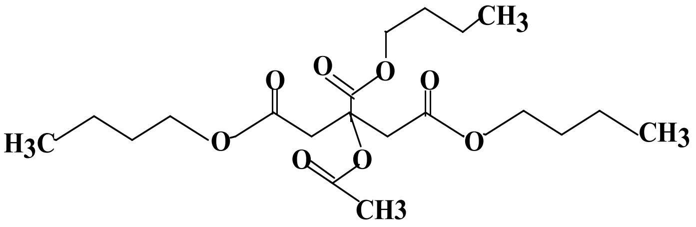


Figure 3.5. Tributylacetyl citrate

Tributylacetyl citrate is a product of Merck Company Limited, having Density 1.049 - 1.052 and Boiling point 170 – 173 °C.

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3.2 Instruments and apparatus

Instruments and apparatus used for this research are as follows:

1. Single screw extruder (SJ-25, made in China)
2. Injection machine (Model CLF-80T, Chuan Lih Fa, China)
3. Universal testing machine (Model 5565, Instron, USA)
4. Scanning electron microscopy (Model JSM-6480LV, JEOL, Japan)
5. Pendulum impact testing machine (Model BPI, Atlas, England)
6. Vacuum oven (Model J-DV01, JISIO, Japan)
7. Differential scanning calorimeter (Model DSC -7, Perkin Elmer,USA)
8. X-ray diffraction spectroscopy(JDX3530, JEOL, Japan)

3.3 Blend Preparation

3.3.1 Preparation of thermoplastic starch (TPS)

Cassava starch was dried in an oven at 100°C for 12 hours. Formamide and water were blended with cassava starch at various compositions in a high speed mixer at 3000 rpm for 2 minutes, and then stored overnight. The weight ratios of formamide and water were 35/0, 25/10 and 10/25 as specified in Table 3.1. The mixtures were manually fed into a single screw extruder with a die having 3 mm holes. The screw speed was 15 rpm and the temperatures set along the extruder barrel from feed zone to die were 140, 140, 140 and 115°C.

Table 3.1 Formulation of thermoplastic starch (TPS) and sample codes

Code	% Weight		
	Starch	Formamide	Water
SF35	65	35	0
SF25	65	25	10
SF10	65	10	25

3.3.2 Preparation of plasticized poly(lactic acid)

Poly(lactic acid) was dried in an oven at 60°C for 4 hours. A compatibilizer, triethyl citrate or tributylacetyl citrate, was mixed with PLA at various weight ratios in a high speed mixer at 3000 rpm for 15 minutes. The mixture was then extruded through a single screw extruder using the mixing speed of 15 rpm and the temperatures program from feed zone to die being 130, 140, 150 and 150°C. It was then allowed to cool to room temperature and crushed into small pieces. The weight ratios of PLA and compatibilizer prepared are given in table 3.2.

Table 3.2 Formulation of plasticized PLA and sample codes

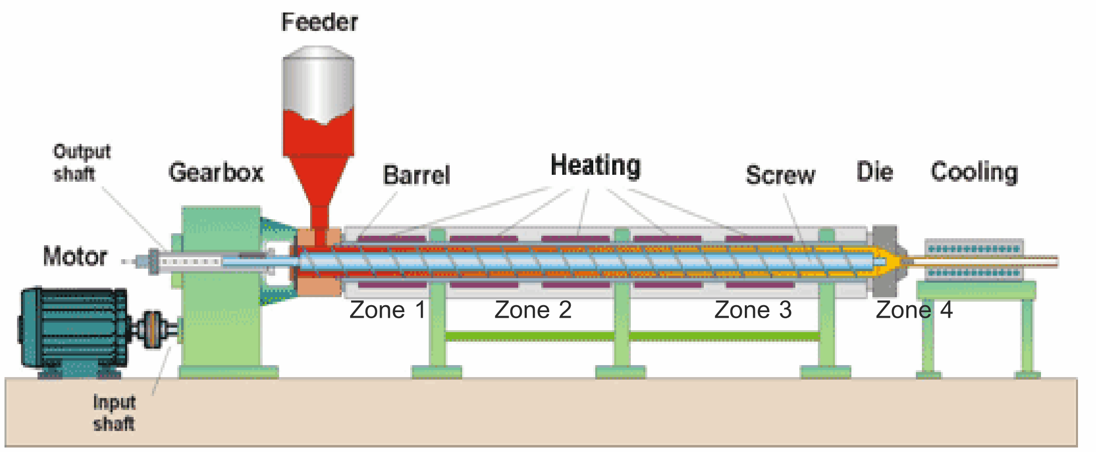
Code	weight %		Code	weight %	
	triethyl citrate	PLA		tributylacetyl citrate	PLA
PE05	5	95	PB05	5	95
PE10	10	90	PB10	10	90
PE15	15	85	PB15	15	85

3.3.3 Preparation of PLA/TPS blends

TPS and PLA were mixed at various compositions (Table 3.3) in a high speed mixer at 3000 rpm for 10 minutes. Each mixture was then dried in a vacuum oven at 60 °C for 4 hours prior to use in the extrusion process. The dried mixture was extruded through a single screw extruder at the mixing speed of 10 rpm using isothermal processing temperature of 150°C along the feed zone to die. The extruded was allow to cool to room temperature and chopped into granules using a palletizer and subsequently dried at 80°C in oven for 3 hours and then kept at ambient condition before sample preparation for further study and testing.

Table 3.3 Formulation of PLA/TPS blends and sample codes

Code	weight %	
	Plasticized PLA	TPS
3PE05/7SF35	30	70
4PE05/6SF35	40	60
5PE05/5SF35	50	50
3PE10/7SF35	30	70
4PE10/6SF35	40	60
5PE10/5SF35	50	50
3PE15/7SF35	30	70
4PE15/6SF35	40	60
5PE15/5SF35	50	50
3PB05/7SF35	30	70
4PB05/6SF35	40	60
5PB05/5SF35	50	50
3PB10/7SF35	30	70
4PB10/6SF35	40	60
5PB10/5SF35	50	50
3PB15/7SF35	30	70
4PB15/6SF35	40	60
5PB15/5SF35	50	50



Zone 1: feed zone (150°C); Zone 2: compression zone (150°C); Zone 3: metering zone (150°C); Zone 4: screen changer (150°C)

Figure 3.6. Drawing of single screw extruder.

3.4 Thermal analysis

3.4.1 Differential scanning calorimeter (DSC)

DSC thermograms of the plastic samples were recorded by a differential scanning calorimeter (DSC, Figure 3.7). A sample (20 mg) was cut in a small circular disc and weighed accurately into an aluminum pan. Measurements were carried out under a nitrogen flow using an empty pan as the reference. The temperature ranges were -20 to 100°C for TPS and -50°C to 200°C for TPS/PLA blend samples with a heating rate of 10°C / minute. The melting and glass transition temperature (T_m and T_g) were recorded in the second heating cycle.

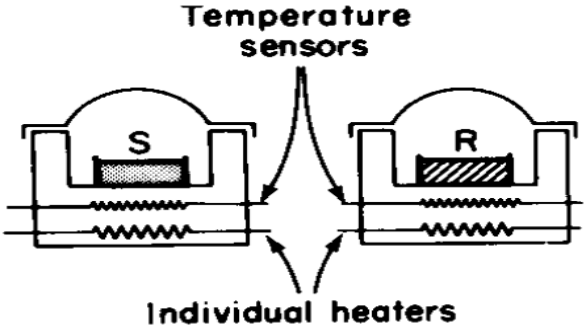


Figure 3.7. Drawing of typical DSC cells showing the sample(S) and reference(R).

3.5 X-ray diffractometry

The samples were conditioned at room temperature and 53% relative air humidity (RH) for 30 days before the measurements. Diffractograms were recorded on a Rigaku diffractometer. Scattered radiation was detected in the angular range of 3–40°(2θ) at a speed of 2° (2θ)/min. The extent of crystallinity was estimated by the height ratio between the diffraction peaks and the calculation of crystallinity can be calculated as Figure 3.8.

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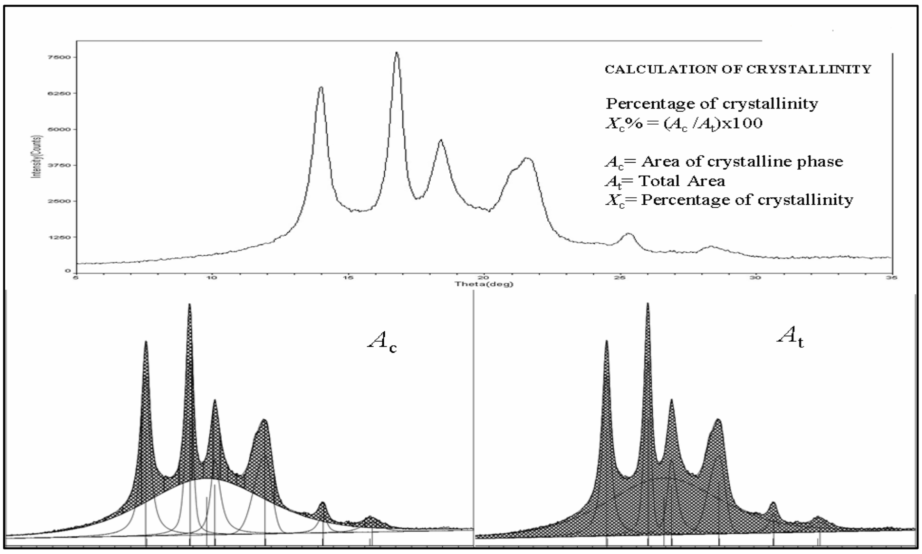


Figure 3.8. Calculation of crystallinity.

3.6 Morphological observation

The morphology of TPS/PLA blends was assessed by the observation of microtomed surfaces using scanning electron microscopy (SEM). The plastic samples were coated with gold sputtering before the analysis. The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.

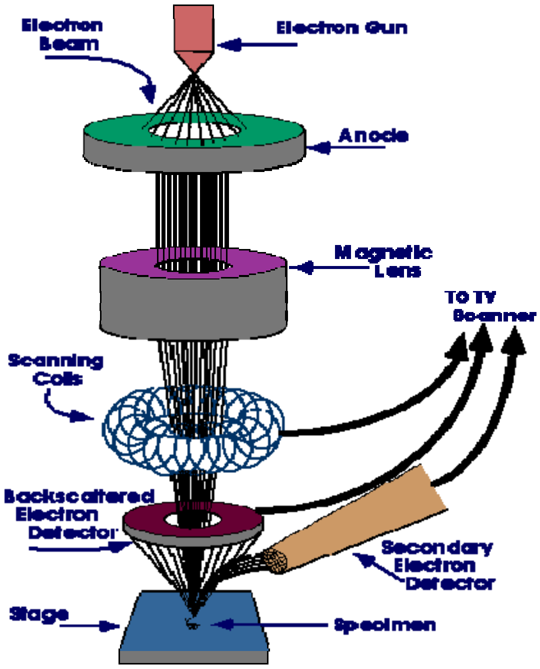


Figure 3.9. The scanning electron microscopy works.

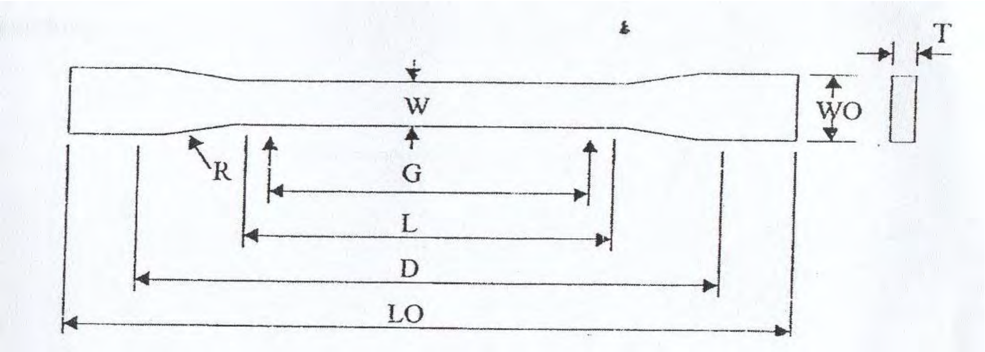
3.7 Mechanical properties

3.7.1. Tensile testing of TPS

The tensile testing of TPS was conducted in accordance with ASTM D638 using a universal testing machine. A sample stick with a diameter of 3 mm and 8 cm in length were cut from an extruded strip. The crosshead speed of 10 mm/min was used for tensile testing. The tests were performed on five specimens of the samples from every formulation of TPS and the data were reported as the average values ± 1 SD.

3.7.2 Tensile testing of PLA/TPS blends

A dumbbell specimen for the tensile measurement was prepared according to ASTM D4101. The universal testing machine was used in accordance with ASTM D638. The sample was pulled by the tensile testing machine from both ends with a load cell of 5 kN at a crosshead speed of 500 mm/min and a gauge length of 115 mm as shown in Figure 3.10. The force required for pulling the specimen apart and the length of the sample were recorded. The tests were performed on specimens of the samples from every formulation of TPS.



W: Width of narrow section	13 mm.	G: Gauge length	50 mm.
L: Length of narrow section	57 mm.	D: Distance between grips	115 mm.
WO: Width overall	19 mm.	R: Radius of fillet	76 mm.
LO: Length overall	165 mm.	T: Thickness	3.2 mm.

Figure 3.10. Tensile test specimen.

3.7.3 Izod impact strength testing

The impact resistance was determined with an impact tester (Model BPI, Atlas, England) according to the standard method of ASTM D256. The testing specimen is 64 x 12.7 x 3.2 mm. A pendulum swings on its track and strikes a notched plastic sample. The energy lost (required to break the sample) is measured from the distance of its follow through. Izod impact testing machine shown in figure 3.11.

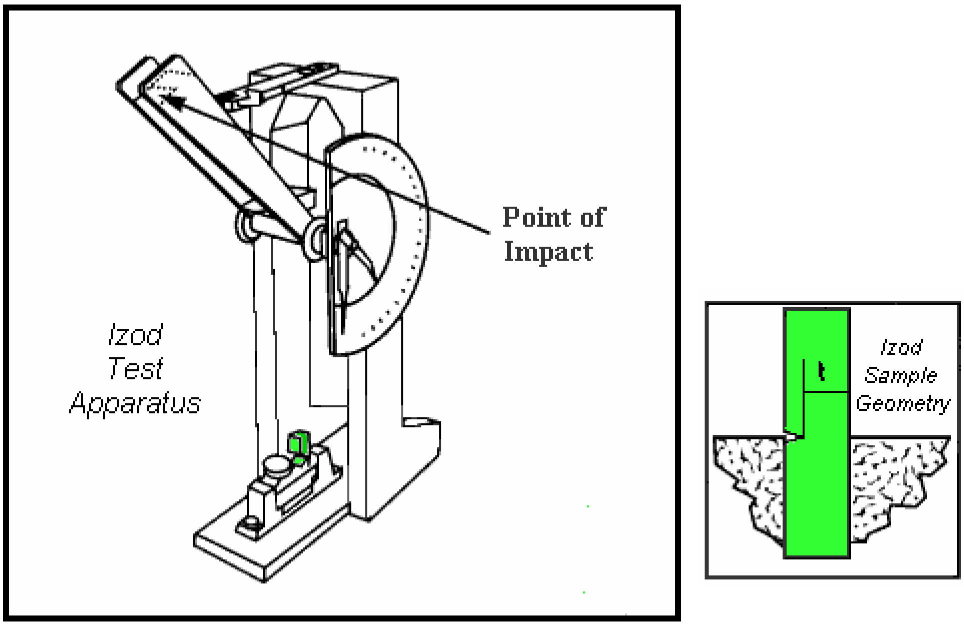


Figure 3.11. Izod impact strength apparatus and test specimen.

CHAPTER IV

RESULTS AND DISCUSSION

The results and discussion is divided into two main parts: the preparation of thermoplastic starch (TPS) discussed in section 4.1 and the preparation of PLA/TPS blends discussed in section 4.2. In the preparation of TPS, formamide and water were tested as plasticizers of cassava starch. In the preparation of blends, tributylacetyl citrate and triethyl citrate were used as compatibilizers. The effects of compatibilizers on the mechanical properties and physical properties of the blends were investigated.

4.1 Characterization of thermoplastic starch (TPS)

In the preparation of TPS, cassava starch was gelatinized with various compositions of formamide and water. The TPS was evaluated by tensile testing, differential scanning calorimetry (DSC) and powder X-ray diffraction to decide on which composition of plasticizer to be used for preparation of TPS in PLA/TPS blends.

4.1.1 Mechanical properties of TPS

As referred to previous study, Martin [2001], it was mentioned that the ratio of starch and plasticizer of 65:35 is suited to represent good mechanical properties of TPS. Moreover, he stated that the properties of TPS also depended on what kind of plasticizer would be used. As a result, the ratio of starch and formamide/water plasticizer of 65:35 was selected and investigated in this study. The TPS were formulated from 65 wt% of cassava starch and 35 wt% of various ratios of formamide/water plasticizer. The tensile strength and elongation at break of TPS is shown in Table 4.1.

Table 4.1 Mechanical properties of TPS with various plasticizer concentrations

Sample Code	Composition (wt %) (Starch/formamide/water)	Tensile strength (MPa)	Elongation (%)
SF10	65/10/25	very brittle	very brittle
SF25	65/25/10	0.28	25
SF35	65/35/0	1.6	37

TPS containing with 35% formamide and no water (SF35) showed the highest tensile strength and elongation percentage at 1.6 MPa and 37%, respectively. The Increase of water content with an expense of formamide resulted in weaker tensile and lower elongation at break as observed for SF25 and SF10. SF10 was so brittle that the preparation of the dumbell specimen for tensile test was not possible. The lost of the water during storage prompts re-crystallization of starch chain in the TPS formulated with water content that embrittles the materials. The superiority in plasticization of formamide over water is probably due to both its relatively higher boiling point and the strong hydrogen bonds with hydroxy groups of starch molecules. SF35 can also be stored for several months without significant change of its physical properties suggesting that there were no evaporation of formamide to cause recrystallization or delocalization of formaide molecules to cause any phase separation.

4.1.2 Thermal properties of TPS

Figure 4.1 shows the DSC thermograms of TPS containing three levels of formamide contents, 10% (SF10), 25% (SF25) and 35% (SF35). The glass transition temperature (T_g) decreased as the formamide content increased with SF10 showing the highest T_g of 56.4°C and SF35 having the lowest T_g of 43.3°C. The increase in the glass transition temperature (T_g) suggests the higher degree of crystallization with the increase of water content. As the glass transition temperatures of all TPS samples were above room temperature, they appeared as hard and brittle plastics at room temperature.

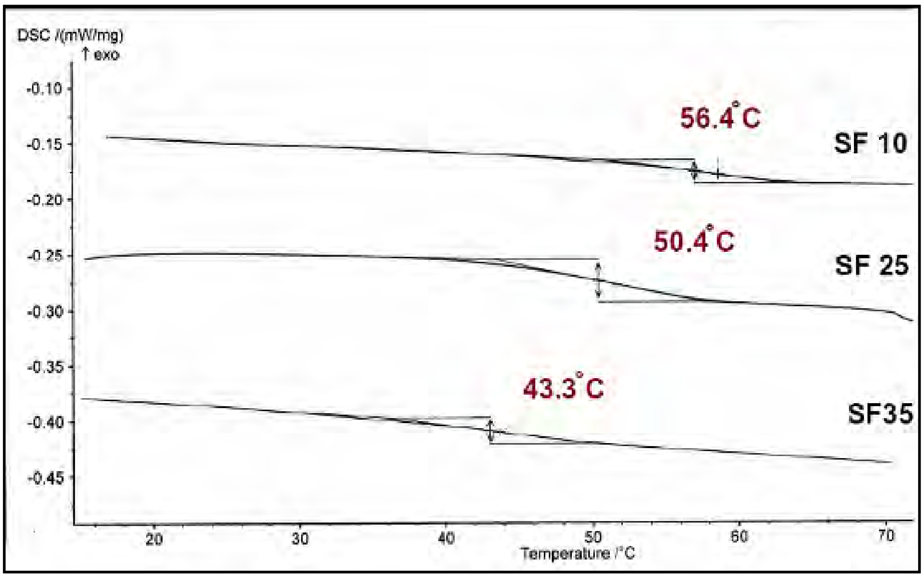


Figure 4.1. DSC thermograms of TPS containing formamide 10%, 25% and 35 % (w/w).

The decreases of T_g upon the addition of formamide may be well explained by the intercession of hydrogen bond formation among the starch chains by the formamide molecules. The inclusion of formamide, a small mobile organic compound, makes the thermal movement of the long starch chains in TPS more viable. Due to their superior mechanical and plasticized properties, only SF35 was used in further investigation for PLA/TPS blends.

4.1.3 X-ray diffraction analysis of TPS

The X-ray diffractograms of cassava starch and TPS plasticized with different formaimide/water ratios, which stored for 30 days, are shown in Figure 4.2. The degree of crystallinity can be determined from the ratio of diffraction peak area and total diffraction area as shown below.

$$X_c = (A_c/A_t) \times 100$$

Where A_c= Area of crystalline phase

A_t= Total area

X_c= Percentage of crystallinity

The diffractograms show the higher degree of crystallinity of cassava starch in comparison to TPS. The TPS containing 35% formamide and no water (SF35) has the lowest crystallinity of 12.5%, while high water content as plasticizers of TPS (SF10) has the highest crystallinity of 15.50%.

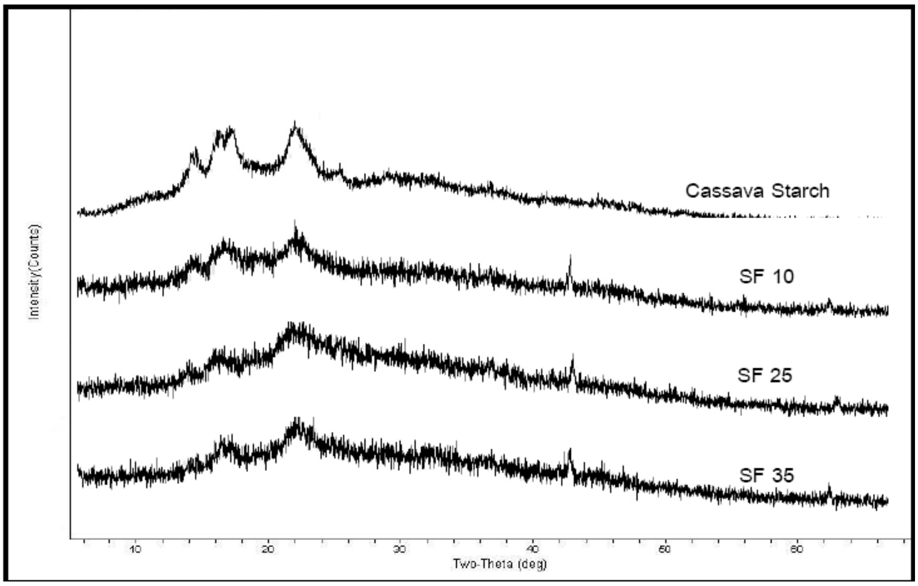


Figure 4.2. X-ray diffractograms of cassava starch and plasticized TPS after being stored for 30 days.

Table 4.2 Degree of crystallinity of cassava starch and plasticized TPS

Sample Code	Composition (wt %) (Starch/formamide/water)	Degree of crystallinity (%)
Cassava starch	100/0/0	20.28
SF10	65/10/25	15.50
SF25	65/25/10	14.22
SF35	65/35/0	12.50

Van Soest & Knooren (1996) have reported that TPS was likely to re-crystallization and became brittleness after being stored for a period of time because the plasticizers might be evaporated or dislocated from starch chains. The re-crystallization or retrogradation of TPS is thus greatly dependent on the strength of hydrogen bonds forming between plasticizer molecules and starch chains. As the result, TPS plasticized with formamide aqueous solutions tended to have a higher degree of crystallinity than the TPS plasticized with pure formamide presumably due to the lost or dislocation of water molecules.

4.2. Characterization of PLA/TPS blends

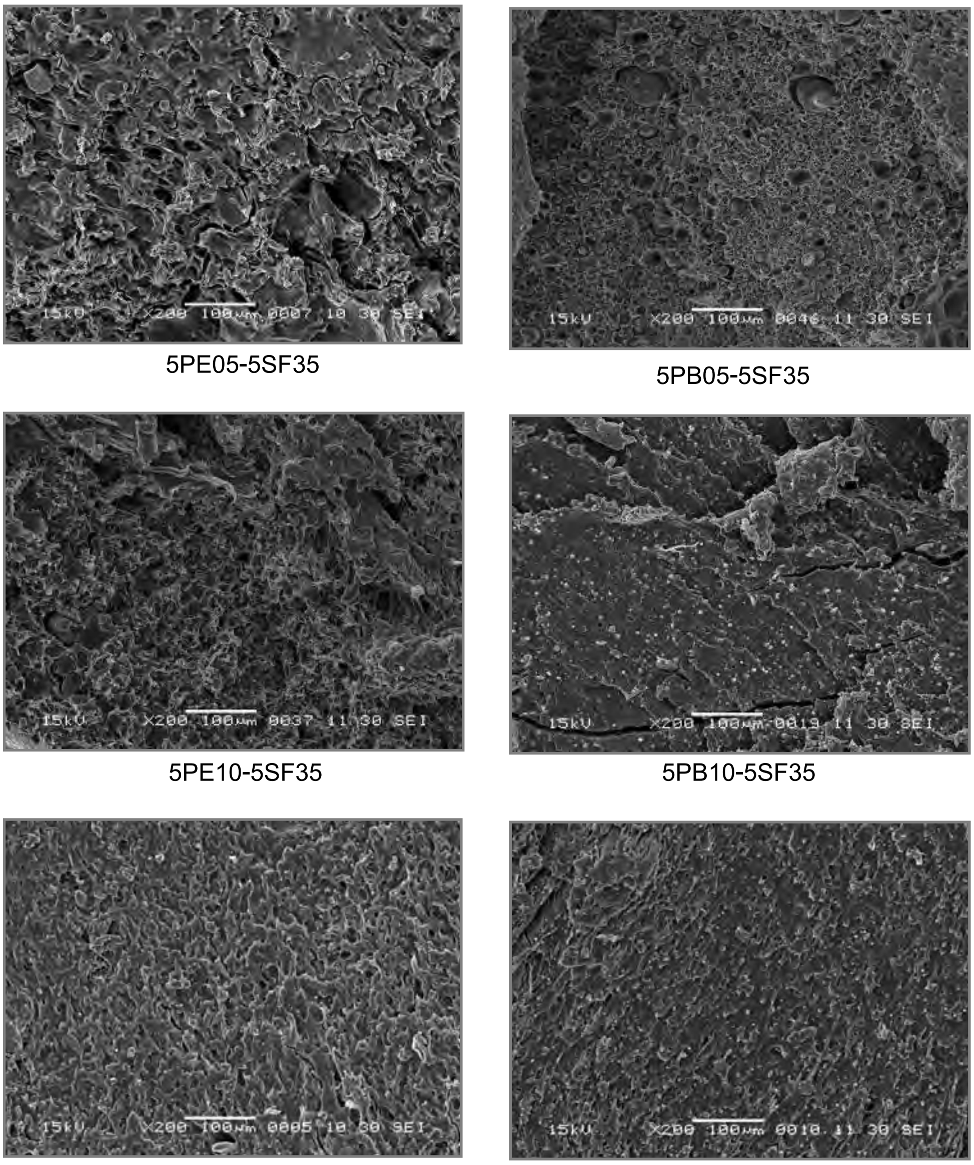
PLA was plasticized by triethyl citrate and tributylacetyl citrate to give two plasticized PLA, namely PE and PB, respectively. The number after PE and PB is the weight percentage of the plasticizer used in the preparation of plasticized PLA. The plasticized PLA was then blended with TPS (SF35) at various weight ratios. To decide for the optimal formulation, morphology, thermal properties and mechanical properties of the blends were investigated. The numbers in front of PE, PB and SF35 in the sample codes are the weight percentage of plasticized PLA or TPS.

4.2.1 Blend morphology

The morphology of polymer blends is very important information for understanding properties of the polymer blends, especially the mechanical properties. The morphology of PLA/TPS blends was thus explored by scanning electron microscope (SEM).

- Effects of compatibilizers in PLA/TPS blends

Figure 4.3 shows the SEM micrographs of 50/50 wt% PLA/TPS blends with different weight percentages of the citrate compatibilizers. At the same weight percentages, the blends using tributylacetyl citrate (PB series) showed less starch granules and voids than those using triethyl citrate (PE series) signifying greater compatibilizing effect of tributylacetyl citrate. The increase of compatibilizer content can also enhance the homogeneity of the blends as the blend containing 5 wt% of the compatibilizer showed significantly more voids, granules and cracks than the blends containing 10 and 15 wt% of the compatibilizer. The micrographs showed that the PLA/TPS (50/50 w/w) blends with a good homogeneity can be obtained by using 15% tributylacetyl citrate as a compatibilizer.



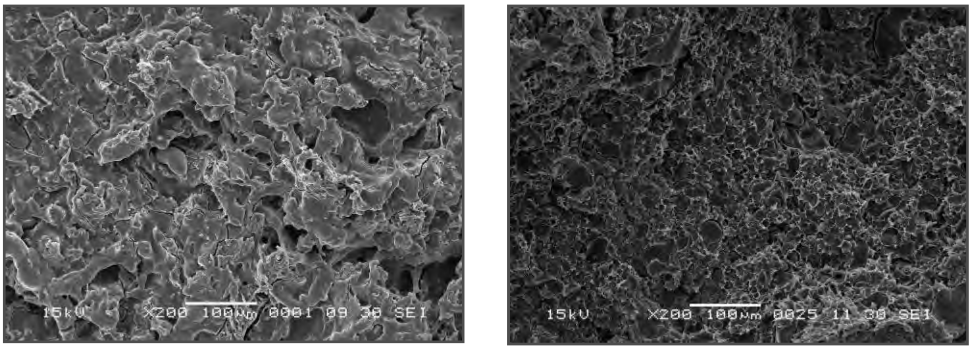
5PE05-5SF35 5PB05-5SF35

5PE10-5SF35 5PB10-5SF35

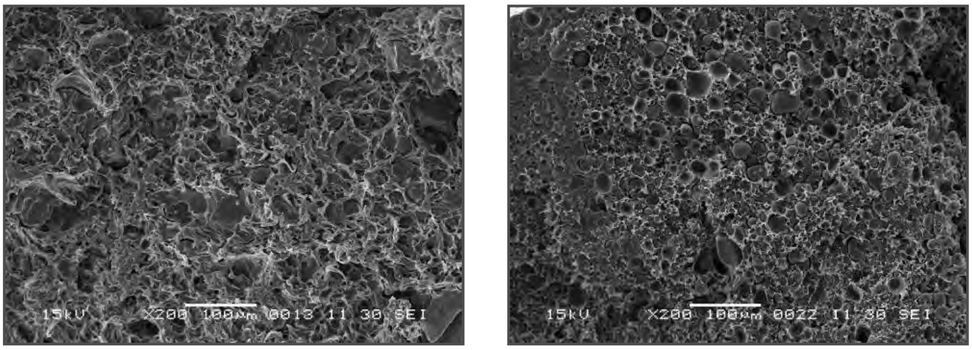
5PE15-5SF35 5PB15-5SF35

Figure 4.3. SEM images of 50/50 wt% PLA/TPS blends using 5, 10 and 15 wt% of triethyl citrate (5PE05-5SF35, 5PE10-5SF35 and 5PE15-5SF35) and tributylacetyl citrate (5PB05-5SF35, 5PB10-5SF35 and 5PB15-5SF35) as the compatibilizers. The scale bar is 100 µm.

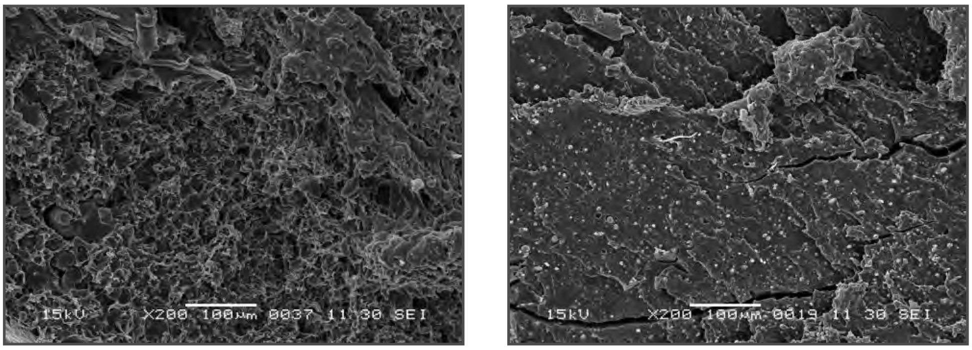
The morphologies of PLA/TPS blends with different weight ratios of tributylacetyl citrate and the triethyl citrate as compatibilizers are presented in Figure 4.4. The PLA/TPS blends comprise of 50, 60 and 70 wt% of TPS with 10 wt% of compatibilizers. All the SEM images in Figure 4.4 shows the large and non-uniform holes where TPS is a continuous phase and PLA is separated coarse phase. However, using 10 wt% tributylacetyl citrate and 10 wt% triethyl citrate were found that tributylacetyl citrate gave the better result than triethyl citrate. As seen in Figure , using 10 wt% tributylacetyl citrate would give nearly spherical and relatively homogeneous as well as small tufts of the SEM. Comparing between triethyl citrate and tributylacetyl citrate at each PLA/TPS weight ratio, tributylacetyl citrate seems to be the better compatibilizer as it produces more homogeneous blends with smaller starch granules and voids. Moreover, the presence of tributylacetyl citrate can reduce interfacial tension in PLA/TPS blends more than triethyl citrate. The result indicated that tributylacetyl citrate gave the blends with the better interface than those of the blends using triethyl citrate. The results may be attributed to the fact that the molecule of tributylacetyl citrate has more carbonyl groups and longer aliphatic chain comparing with triethyl citrate. The tributylacetyl citrate having four carbonyl groups and aliphatic chain could form bonding with starch molecule and poly (lactic acid) more effective than triethyl citrate.



3PE10-7SF35 3PB10-7SF35



4PE10-6SF35 4PB10-6SF35

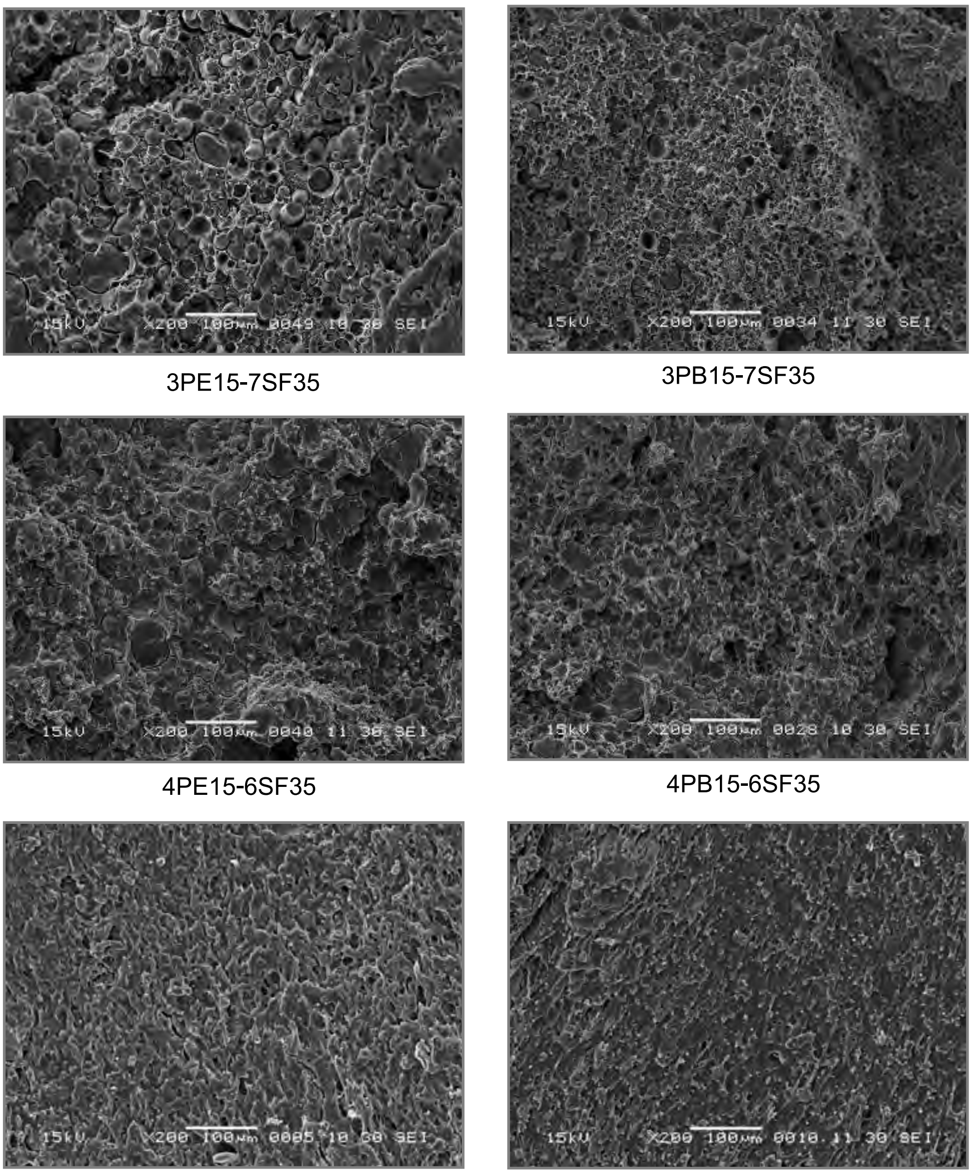


5PE10-5SF35 5PB10-5SF35

Figure 4.4. SEM images of 30/70, 40/60 and 50/50 wt% PLA/TPS blends using 10 wt% triethyl citrate (3PE10-7SF35, 4PE10-6SF35 and 5PE10-5SF35) and tributylacetyl citrate (3PB10-7SF35, 4PB10-6SF35 and 5PB10-5SF35) as the compatibilizers. The scale bare is 100 μm.

- Effects of TPS content in PLA/TPS blends

The SEM micrographs of PLA/TPS blends comprised of different TPS contents (50, 60 and 70 wt %) and 15 wt% of citrate compatibilizers as shown in Figure 4.5. When 50 wt% TPS was being used, the smooth fracture structure, nearly spherical and relatively homogeneous of the blends would be occur as shown in 5PE15-5SF35 and 5PB15-5SF35. On the other hand, if 60 and 70 wt% TPS were added in the PLA/TPS blends, the two-phase polymer blend structure would be appear and their particles would be larger and had irregular shapes. Moreover, the dark holes in Figure 4.5 caused from removed PLA from PLA/TPS blends. Particularly, at the 70 wt% TPS the sample surface was quite rugged. Meanwhile, PLA was removed from their surfaces and left some cavities in the fracture surface. These are because they have the high interfacial tension between hydrophilic TPS and hydrophobic polymer. As increased TPS content, the interfacial adhesion between the TPS and PLA would be poor and the phase would be obviously separated out from the surface.



3PE15-7SF35

3PB15-7SF35

4PE15-6SF35

4PB15-6SF35

5PE15-5SF35

5PB15-5SF35

Figure 4.5. SEM images of 30/70, 40/60 and 50/50 wt% PLA/TPS blends using 15 wt% triethyl citrate (3PE15-7SF35, 4PE15-6SF35 and 5PE15-5SF35) and tributylacetyl citrate (3PB15-7SF35, 4PB15-6SF35 and 5PB15-5SF35) as the compatibilizers. The scale bare is 100 μm.

4.2.2. Thermal properties of PLA/TPS blends

The thermal characteristics of PLA/TPS blends were determined by DSC. The thermal transitions of blends are useful in that they reveal the interactions between respective polymers. Practically, in a binary polymer blend, some level of compatibility may be inferred when the two observed the glass transition temperature (T_g) are shifted toward each other. In addition, a significant decrease in the melting temperature(T_m) is a direct result of reducing crystalline domains.

Table 4.3 shows the melting temperature(T_m) of PLA/TPS blends systems with different compatibilizer contents. The results indicate that the melting point of the pure PLA is 149.9°C. The addition of the compatibilizers to PLA/TPS blends reduced crystallization. It can be seen that the T_m of blends decreased as the compatibilizers content increased and the PLA/TPS blends show significantly lower the T_m in comparison to virgin PLA. As the same time, a small effect of the PLA content on T_m of PLA/TPS blends was observed. The T_m of the blends designates closely to that of the PLA virgin. The matrix phase in the blends is shown in Table 4.3.

The melting temperature(T_m) of PLA/TPS blends compared to pure PLA is that triethyl citrate and tributylacetyl citrate can be regarded as the good efficient plasticizer of PLA/TPS blends.

Table 4.3 T_m of PLA/TPS blends having various triethyl citrate or tributylacetyl citrate contents

PLA/TPS	T_m (^{o}C)	PLA/TPS	T_m(^{o}C)
PLA(Virgin)	149.9	PLA(Virgin)	149.9
3PE05/7SF35	142.1	3PB05/7SF35	140.1
4PE05/6SF35	145.9	4PB05/6SF35	142.7
5PE05/5SF35	146.7	5PB05/5SF35	144.9
3PE10/7SF35	140.6	3PB10/7SF35	139.4
4PE10/6SF35	141.4	4PB10/6SF35	140.3
5PE10/5SF35	144.0	5PB10/5SF35	142.7
3PE15/7SF35	140.5	3PB15/7SF35	132.5
4PE15/6SF35	136.4	4PB15/6SF35	137.5
5PE15/5SF35	139.9	5PB15/5SF35	137.1

Data are average of two measurements

Figures 4.6 and 4.7 show the T_g of the different compatibilizers in the PLA/TPS blends. As the compatibilizers of 15 wt% were used, the T_g of 3PB15/7SF35 and 3PE15/7SF35 were 23.5 and 28.4^{o}C, respectively. When 10 wt% of the compatibilizers were added into 3PB10/7SF35 and 3PE10/7SF35, the T_g were greatly increased to 31.4 ^{o}C and 35.1^{o}C, respectively. Therefore, PLA/TPS blends with triethyl citrate compatibilizers have relatively higher the T_g than those of blends with tributylacetyl citrate. In addition, the T_g of 3PB15/7SF35 was in the rubbery state at the room temperature. As a result, it was soft and flexible.

As the original T_g of PLA was 58°C, it was decreased to 34.3°C, 31.4°C and 23.5°C when the tributylacetyl citrate was added into the PLA/TPS blends with 5, 10 and 15 wt%, respectively. In the case of triethyl citrate, the T_g of PLA/TPS blends with the same weight ratio decreased to 38.5°C, 35.5°C and 28.4°C, respectively. As a result, at low citrate compatibilizer content of 5 wt %, not only did polymer blends not have a good homogeneous but also the T_g of PLA/TPS blends had a high temperature.

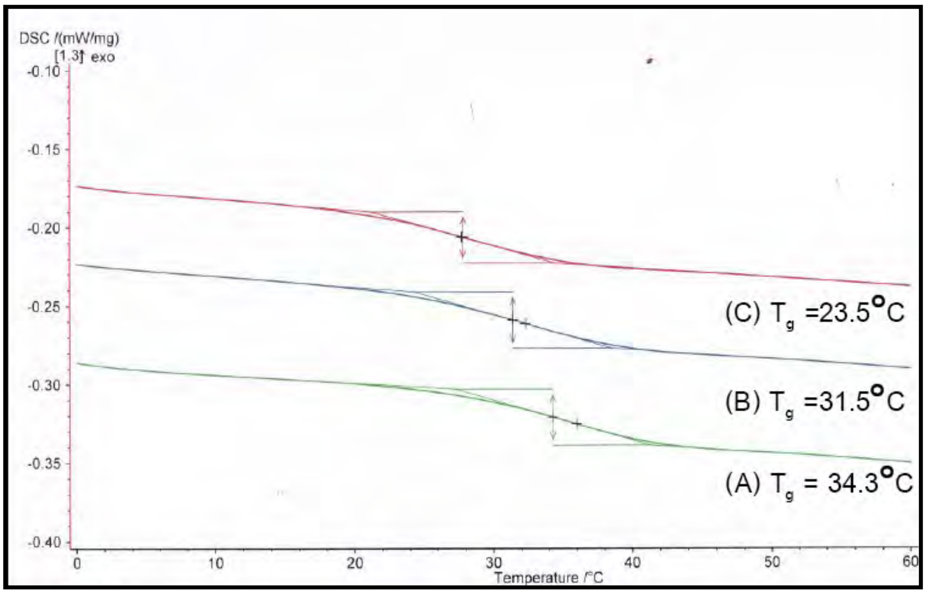


Figure 4.6. Comparison of DSC thermograms of PLA/TPS blends of (A) 3PB05/7SF35, (B) 3PB10/7SF35, (C) 3PB15/7SF35.

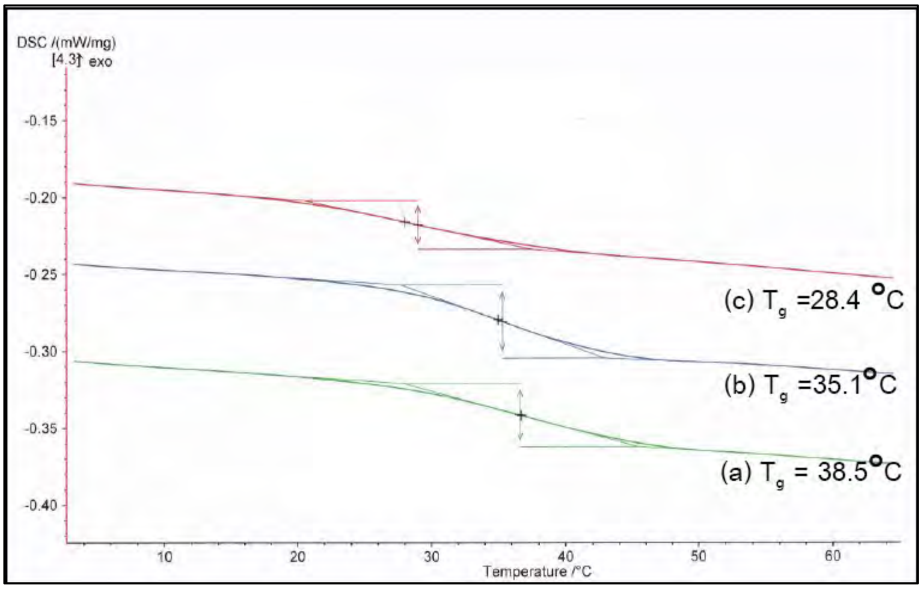


Figure 4.7. Comparison of DSC thermograms of PLA/TPS blends of (a) 3PE05/7SF35, (b) 3PE10/7SF35, (c) 3PE15/7SF35.

In the case of the decrease in the T_g of PLA/TPS blends, the situation is more complex. First of all, the starch is in a plasticized form and therefore the amylose and amylopectin macromolecules are free to move to or away from the blend’s interface. Secondly, the presence of the compatibilizers, namely tributylacetyl citrate and triethyl citrate could potentially react preferably with carbonyl group and aliphatic chain and could form bonding with starch and PLA molecule. Thirdly, residual humidity in the TPS phase may cause to reduce its reactivity.

Figure 4.8 and 4.9 show the comparisons of PLA/TPS blends with different TPS contents. The T_g of TPS (SF35) is 43.3°C and the T_g of pure PLA is about 58°C, which the T_g of PLA actually decreased from 58°C for pure PLA to 38.8, 36.3 and 35.1°C with the addition of TPS content in blends of 50, 60 and 70% at 10 wt% triethyl citrate. In case of the tributylacetyl citrate as a compatibilizer for the same weight ratio, the T_g were 35.2, 33.0 and 31.5°C, respectively. Considering the PLA/TPS blending ratio, the 50:50 wt% exhibits higher the T_g than those of higher contents of TPS. As a result, the T_g decreased gradually as the content of TPS in the blend increased.

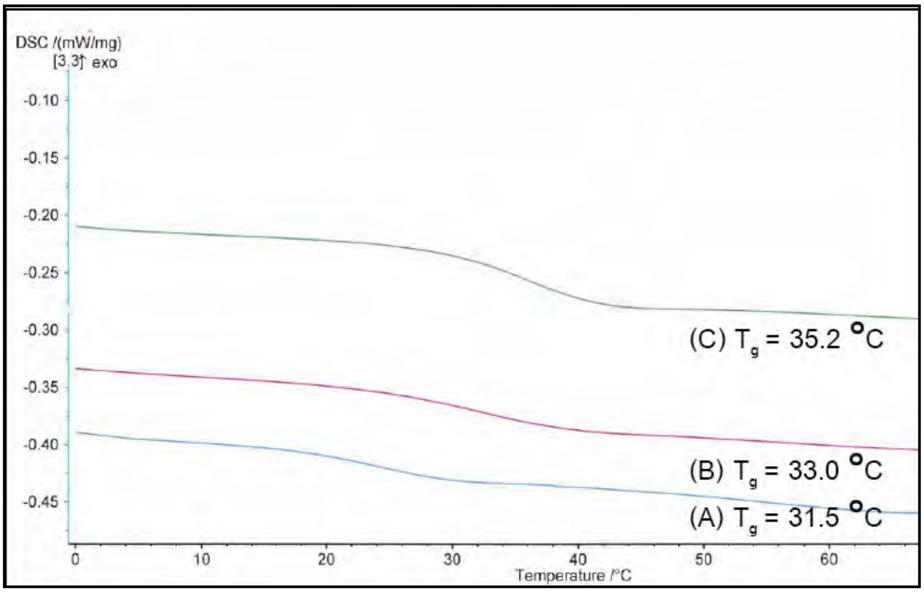


Figure 4.8. DSC thermograms of PLA/TPS blends of (A) 3PB10/7SF35, (B) 4PB10/6SF35, (C) 5PB10/5SF35.

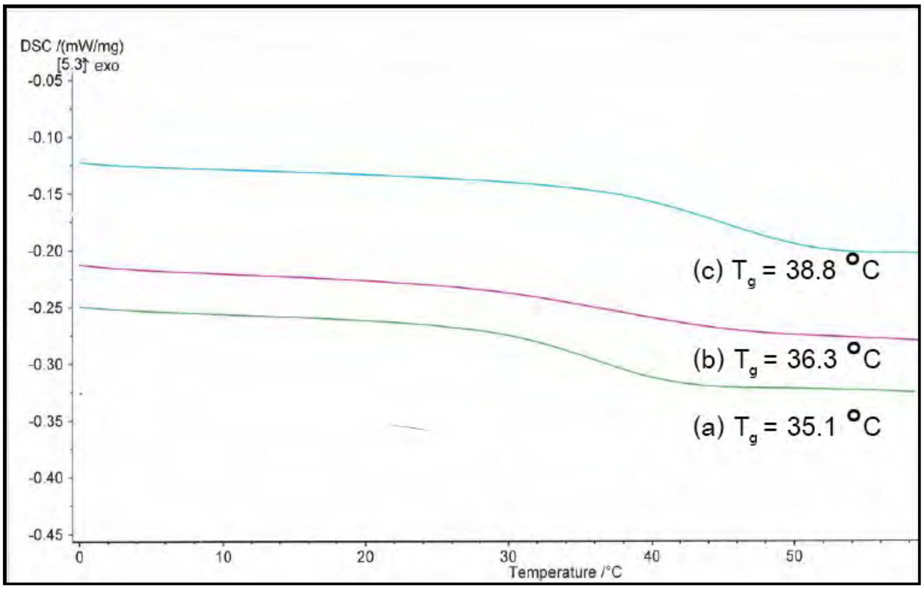


Figure 4.9. DSC thermograms of PLA/TPS blends of (a) 3PE10/7SF35, (b) 4PE10/6SF35, (c) 5PE10/5SF35.

4.2.3. Mechanical properties of PLA/TPS blends

Generally, it has been well known for a long time that immiscible polymer blends have inferior mechanical properties due to the existence of weak interfacial adhesion and poor dispersion of the component. In this study, the mechanical properties for the different weight ratios of PLA/TPS blends by using tributylacetyl citrate and triethyl citrate as compatibilizers on the impact strength and tensile strength are investigated.

4.2.3.1 Tensile strength of PLA/TPS blends

The variation in the tensile strength and elongation at break of samples with different TPS contents are also shown in Figures 4.10 and 4.11. The results indicated that at the same weight of the compatibilizers the tensile strength and elongation at break decreased as TPS contents in all samples increased. The tensile strengths of PLA/TPS blends having the TPS content of 50, 60 and 70 wt% at 5 wt% triethyl citrate were 32, 25.6 and 18 MPa and the percentage of the elongation at breaks were 4.96, 4.23, and 2.42 %, respectively. At the same weight ratio, if triethyl citrate was substituted by tributylacetyl citrate, the tensile strengths of TPS5/PLA were 33.55, 28.2 and 20.35 MPa, and the percentage of the elongation at break was found to be 9.84, 7.39 and 4.5%, respectively. All samples exhibited as a typical brittle characteristic. As compared the tensile strength of pure PLA (73.77MPa) with the tensile strength of PLA/TPS blends, they were found that the tensile strength of PLA/TPS blends dramatically decreased. That is, it may be the poor interfacial adhesion between the two phases.

The decreased tensile strength of the PLA/TPS blends can be explained by the crystallinity and hydrogen bonding in both the TPS and PLA. That is, the starch granule is highly hydrophilic, containing hydroxyl groups on their surfaces, whereas PLA is mostly non-polar. Therefore, the strong interfacial bonds such as hydrogen bonds between starch and PLA are not produced and the mechanical properties of the PLA/TPS blends are rather poor.

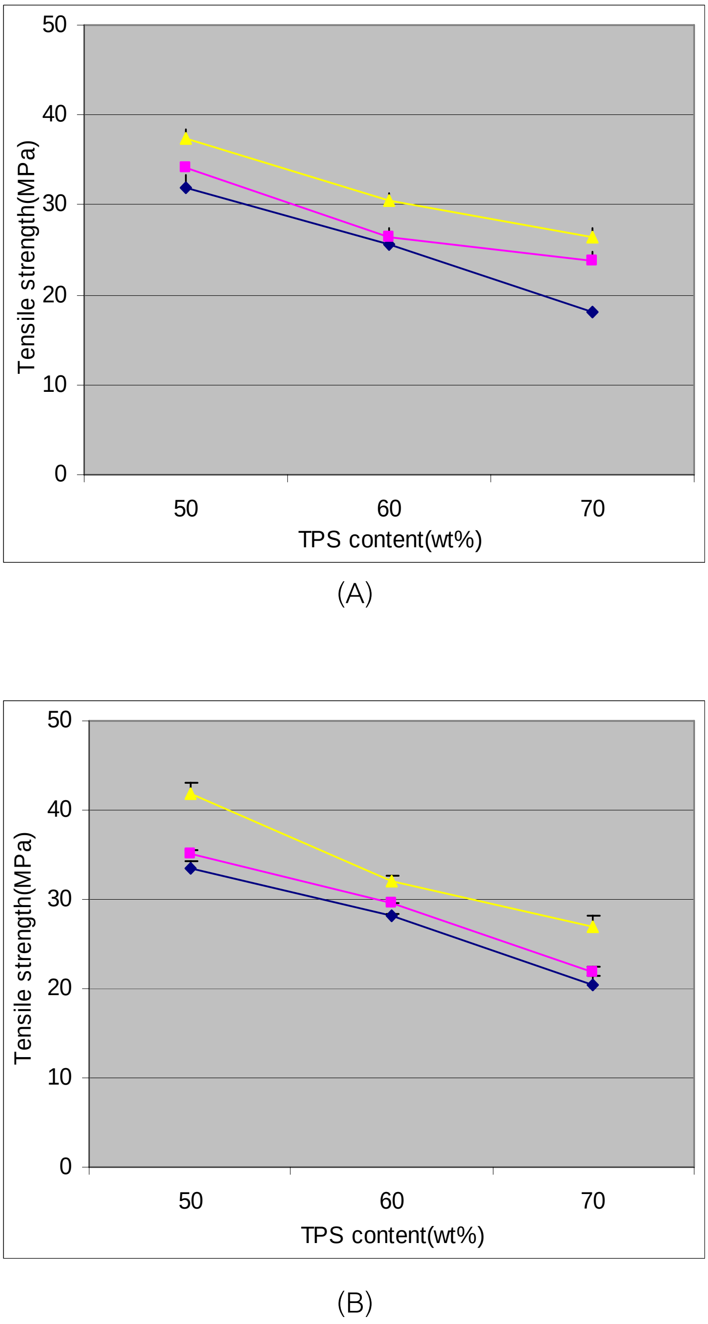
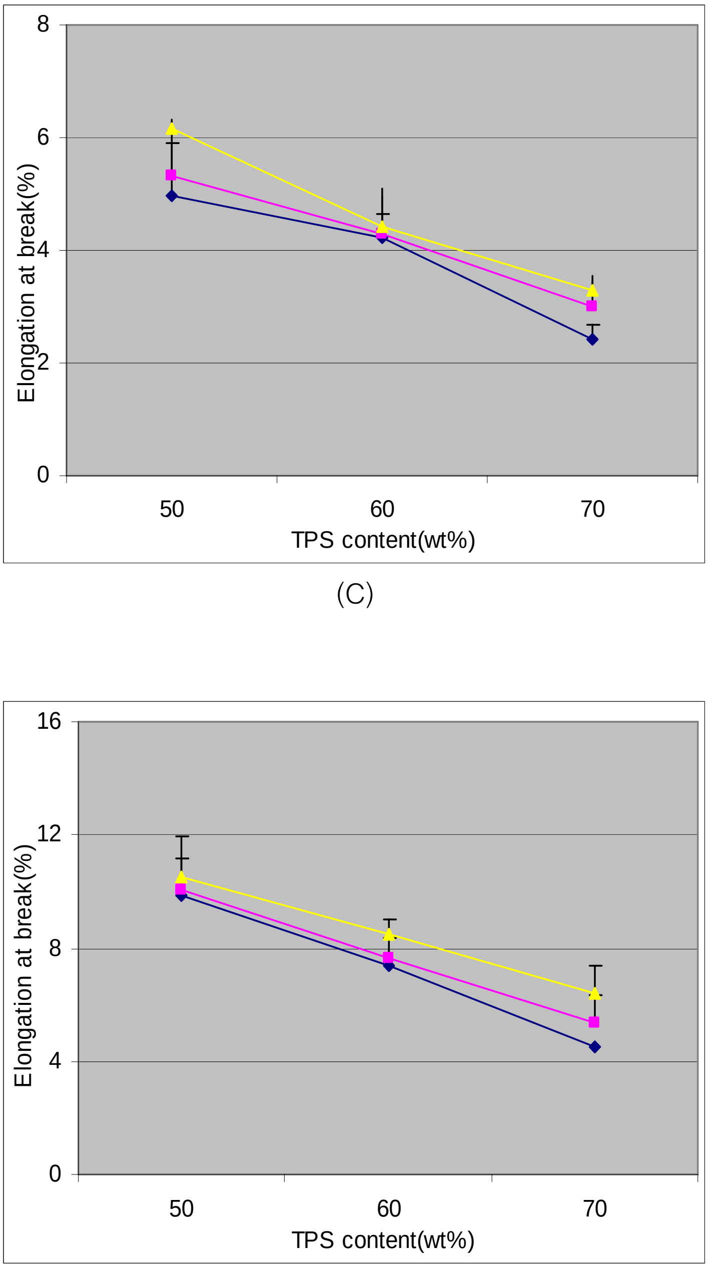


Figure 4.10. Effect of TPS contents on the tensile strength properties of PLA/TPS blends. (A) triethyl citrate as a compatibilizer, (B) tributylacetyl citrate as a compatibilizer.



(C)

(D)

Figure 4.11. Effect of TPS contents on the elongation at break properties of PLA/TPS blends. (C) triethyl citrate as a compatibilizer, (D) tributylacetyl citrate as a compatibilizer.

—◆— 5 wt%compatibilizer
—■— 10 wt%compatibilizer
—▲— 15 wt%compatibilizer

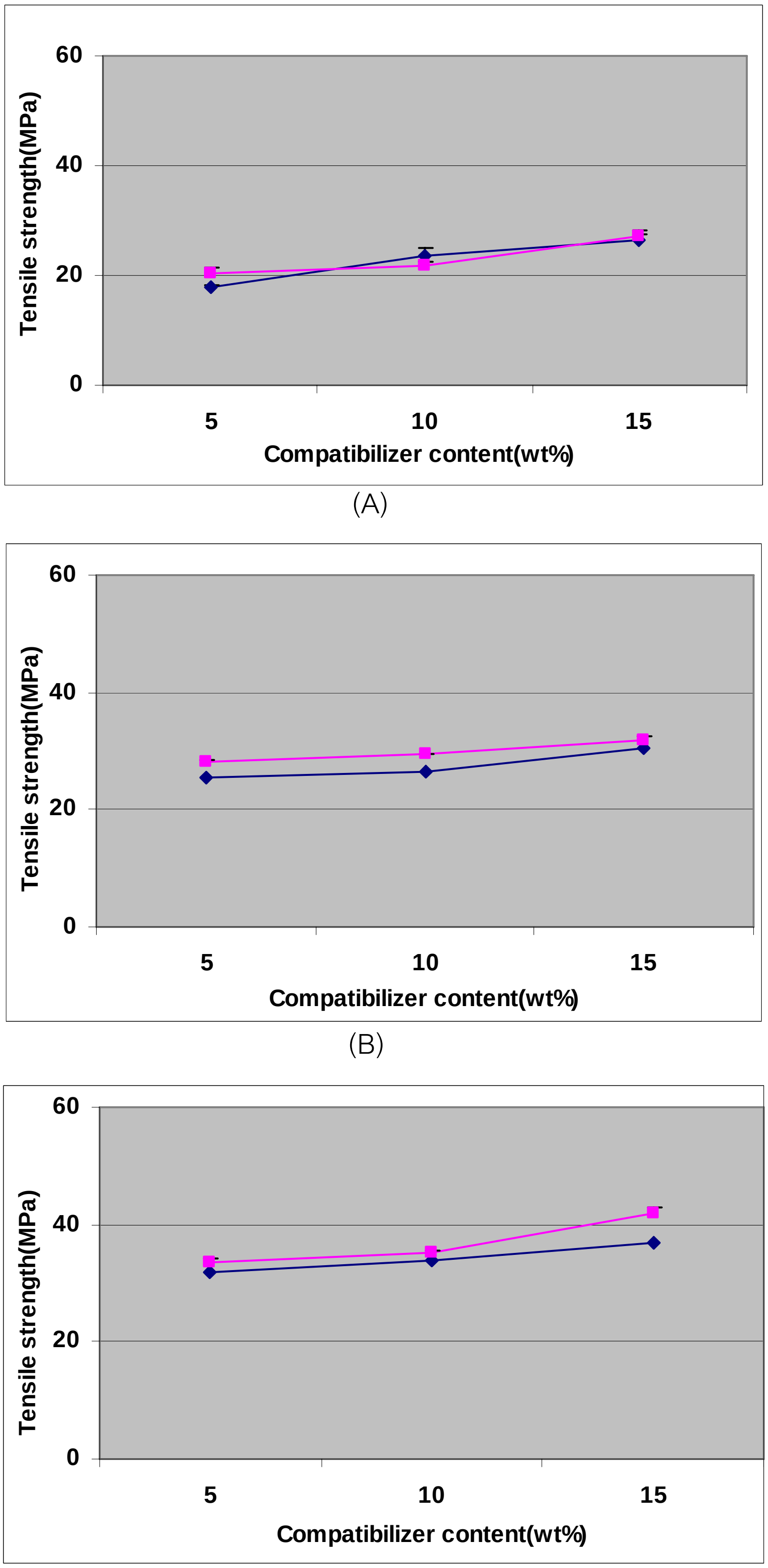
All the blends show significantly lower tensile strength along with some increment of the percent elongation at break when comparing with pure PLA. The increase of TPS content poses adverse effect on both tensile strength and percent elongation at break of the blends probably due to both poor interfacial miscibility and increased hardness as supported from the SEM images and impact strength. In order to solve this problem, the compatibilizers, tributylacetyl citrate and triethyl citrate, were added to this system. This is because they have hydrophilic–hydrophobic structures which have been known as the good compatibilizers. However, the blends with tributylacetyl citrate and triethyl citrate can improve the compatibility between PLA and TPS.

Figures 4.12 and 4.13 show that the tensile strength and elongation of the samples, at the same PLA/TPS blending ratio, both tensile strength and percent elongation at break increases with the increase of the amount of compatibilizers. These improvements could be ascribed to the increasing dispersion and compatibility between PLA and TPS.

As mentioned above, the pure PLA had an average tensile strength of 73.77 MPa and percent elongation of 3.63. When the compatibilizers were added in the PLA/TPS blends, the tensile strengths of the PLA/TPS blends trend to decrease comparing with the tensile strength of pure PLA. For example, the 5% triethyl citrate and 5% tributlyacetyl citrate caused a reduction of tensile strength of 32 MPa (5PE05/5SF35) and 33.55 MPa (5PB05/5SF35), respectively. Moreover, the elongations at break of the samples were increased to 4.96 % and 9.84 %, respectively. When all compatibilizers were used 15 wt% (5PE15/5SF35, 5PB15/5SF35) the tensile strengths increased to 37.3 and 41.85 MPa and the elongations at break increased to 6.16 and 10.49 %. It can be indicated that the less compatibilizer content has, the lower tensile strength and elongation at break of PLA/TPS blends will be.

For the poor tensile strength and percent elongation at break could be explained that the covalent linkage between PLA and TPS was not likely formed during processing. PLA is hydrophobic while starch is hydrophilic. They are thus not compatible. The presence of starch granules in the polymer matrix are just the dispersion only. More TPS incorporated would enhance the discontinuity of the blends. Furthermore, starch can easily adsorb moisture from atmosphere which cases air bubble within polymer matrix after processing and then cooling. The air bubble will decreases both tensile strength and elongation at break even more.

In addition, it could be found in all results that the blends using tributylacetyl citrate possess more favorable mechanical properties, higher tensile strength and greater percent elongation at break, comparing to the blends with triethyl citrate. To use the tributylacetyl citrate as a compatibilizer will increase the interfacial adhesion and improve the mechanical properties of the TPS/ PLA blends.



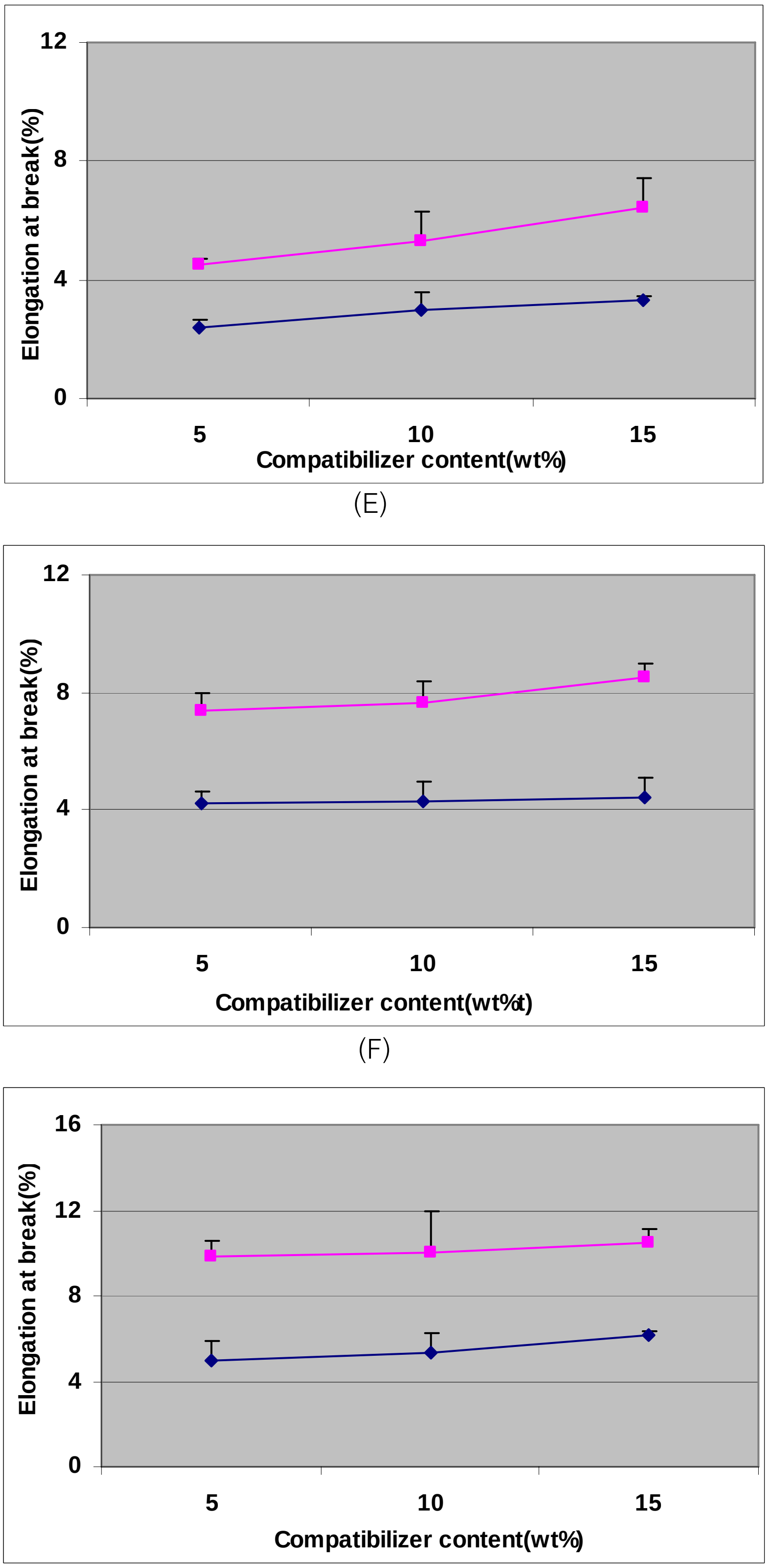
(A)

(B)

(C)

Figure 4.12. Effect of compatibilizer contents on the tensile strength properties of PLA/TPS blends. (A) 30 wt %, (B) 40 wt % and (C) 50 wt %PLA in PLA/TPS blends.

◆ Triethyl citrate as compatibilizer ■ Tributylacetyl citrate as compatibilizer



(E)

(F)

(G)

Figure 4.13. Effect of compatibilizer contents on the elongation at break of PLA/TPS blends. (A) 30 wt %, (B) 40 wt % and (C) 50 wt %PLA in PLA/TPS blends.

◆ Triethyl citrate as compatibilizer ■ Tributylacetyl citrate as compatibilizer

4.2.3.2 Impact strength of PLA/TPS blends

The impact strength data of pure PLA and all PLA/TPS blends compatibilized with triethyl citrate and tributylacetyl citrate are shown in Tables 4.4 and 4.5.

Table 4.4 Mechanical properties of PLA/TPS blends with various triethyl citrate concentrations

Sample code	(kJ/ m^2)
	Impact strength
PLA(Virgin)	3.57±2.31
3PE05/7SF35	12.0±0.29
4PE05/6SF35	11.1±0.28
5PE05/5SF35	6.9±0.29
3PE10/7SF35	13.4±0.33
4PE10/6SF35	11.1±0.28
5PE10/5SF35	11.6±0.02
3PE15/7SF35	11.9±0.05
4PE15/6SF35	10.6±0.75
5PE15/5SF35	14.0±0.37

Table 4.5 Mechanical properties of PLA/TPS blends with various tributylacetyl citrate concentrations

Sample code	(kJ/ m^2)
	Impact strength
PLA(Virgin)	3.57±2.31
3PB05/7SF35	27.1±0.36
4PB05/6SF35	10.4±0.59
5PB05/5SF35	13.8±0.45
3PB10/7SF35	17.7±0.04
4PB10/6SF35	11.3±0.12
5PB10/5SF35	13.7±0.08
3PB15/7SF35	19.9±0.14
4PB15/6SF35	14.3±0.73
5PB15/5SF35	17.9±0.19

Table 4.4 and 4.5 show that the PLA/TPS blends having the PLA content of 30, 40 and 50 wt% at 15 wt% tributylacetyl citrate had the impact strength of 19.9, 14.3 and 17.9 kJ/ m^2, respectively and the PLA/TPS blends having the same PLA contents at 15 wt% triethyl citrate had the impact strength of 11.9, 10.6 and 14.0 kJ/ m^2, respectively. It can be seen that the impact strength of PLA/TPS blends slightly increased comparing with the impact strength of the virgin PLA. Again, as referred to the Tables 4.4 and 4.5, blending of starch to PLA can significantly increase the impact strength of the plastic that may be ascribed to the hardness of TPS. In addition, these data indicated that they were a bad interfacial adhesion between the two phases. As a result, the impact strength of all the samples did not give a good result.

The 5PE15/5SF35 and 5PB15/5SF35 blends have high impact strength compared with all samples. This could be caused by the blends with 15 wt% compatibilizer. It could be improved the compatibility between PLA and TPS by the microphase of TPS performing as reinforce particle according to it has high stiffness. The tributylacetyl citrate improved the phase morphology and gave finer the dispersed phase as seen in the SEM of Figure 4.3.

The higher impact strength of the blends with higher TPS contents confirms this rationale. It is also obvious to note that, the impact resistance of the blends using tributylacetyl citrate is generally higher than those of the blends using triethyl citrate. The results underscore the importance of the interfacial miscibility improved by tributylacetyl citrate.

CHAPTER V

CONCLUSION AND FUTURE DIRECTION

5.1 Conclusion

Biodegradable plastic PLA containing at least 50 wt% of cassava starch can be prepared by blending the plasticized starch with plasticized PLA. Pure formamide is better than the formamide aqueous solution in producing amorphous thermoplastic starch (TPS). Upon blending PLA with TPS, the deformation temperature (T_g and T_m), tensile strength and %elongation at break of PLA became lower while impact strength became higher. Microscopic morphology from SEM images suggested that tributylacetyl citrate is better than triethyl citrate, as a compatibilizer for PLA and TPS blends, in improving the interfacial miscibility within the blends resulting in greater improvement in tensile strength and %elongation at break of the blends. Although the use of higher amount of tributylacetyl citrate generally gives the plastic blends with better mechanical properties, it however decreases the deformation temperature of the plastics. The results from this work suggest that the TPS/PLA blends containing at least 50 wt% of starch may be used in production of low cost biodegradable plastics with acceptable mechanical properties but their utilization should be limited for low temperature ($< 40^{\circ}C$) applications.

5.2 Future direction

In this research, the addition of tributylacetyl citrate and triethyl citrate as compatibilizers could lead to some improvements of the mechanical properties of PLA/TPS composites, nevertheless, from the SEM results, low level of compatibility was found. The further researches ought to find out other plasticizers and compatibilizers to enhance greater thermal and mechanical properties.

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APPENDIX

Figure A-1. Tensile properties of TPS with comprise of 25% formamide and 10% water.

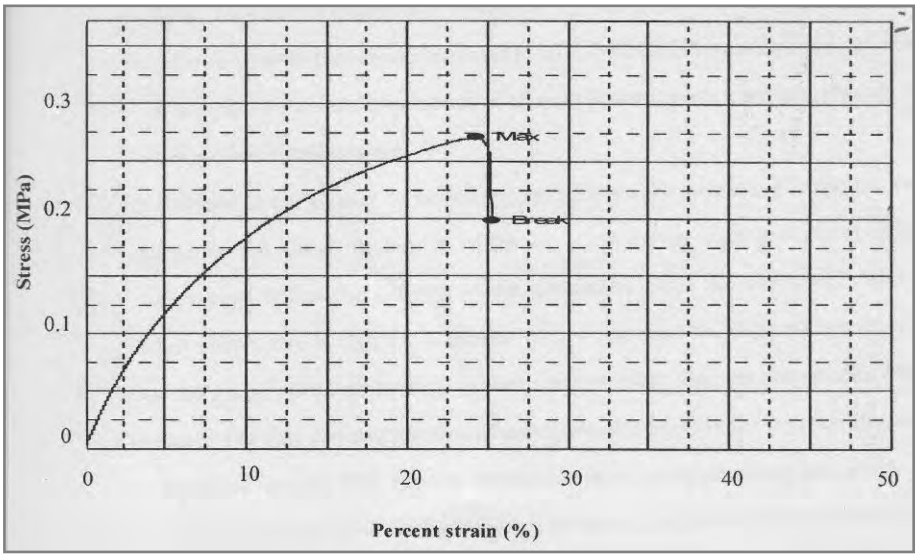


Figure A-2. Tensile properties of TPS with comprise of 35% formamide.

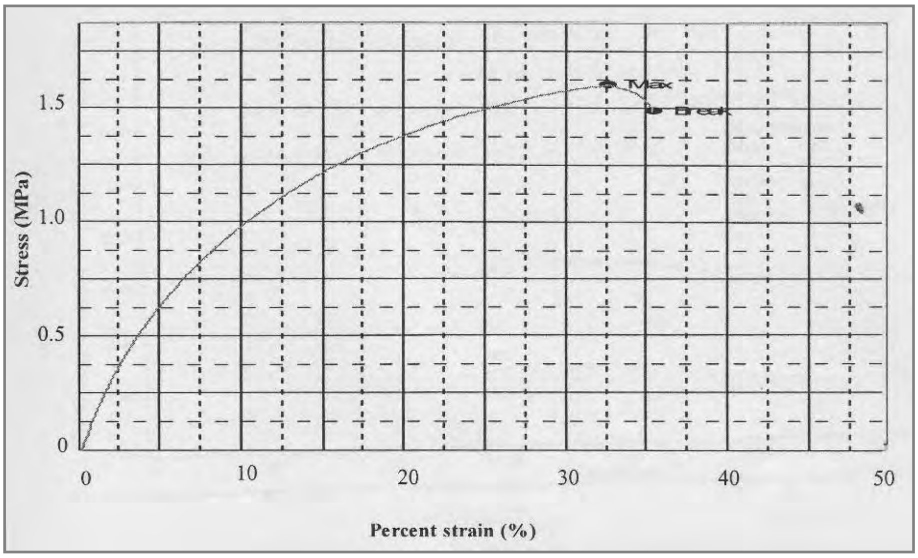


Figure A-3. X-ray diffraction patterns of cassava starch after stored for 30 days.

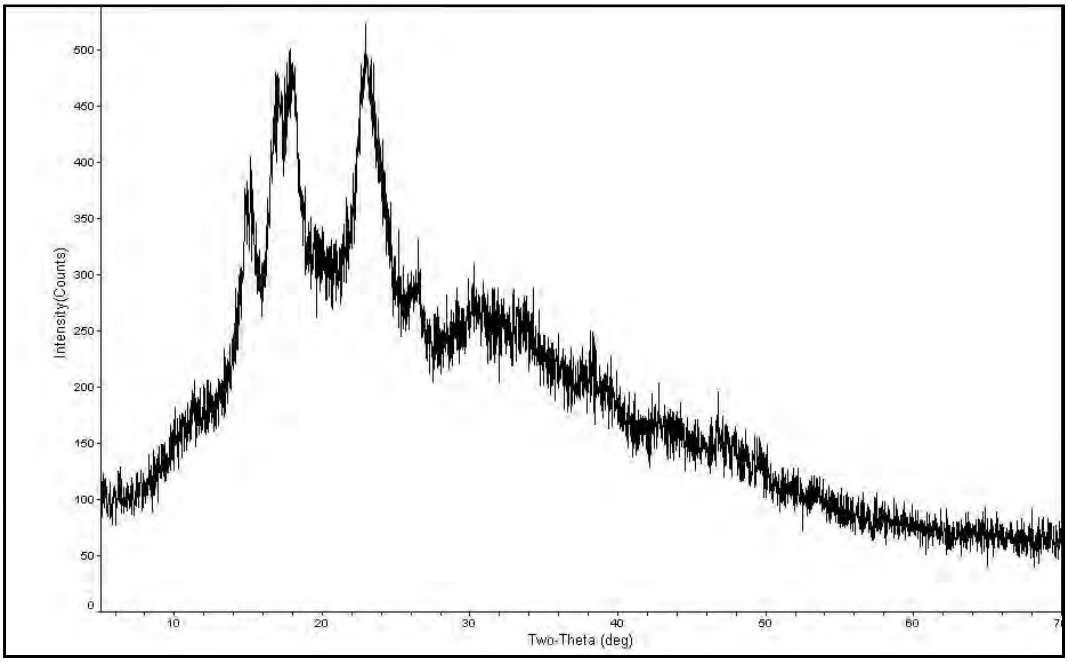


Figure A-4. X-ray diffraction patterns of SF10 after stored for 30 days.

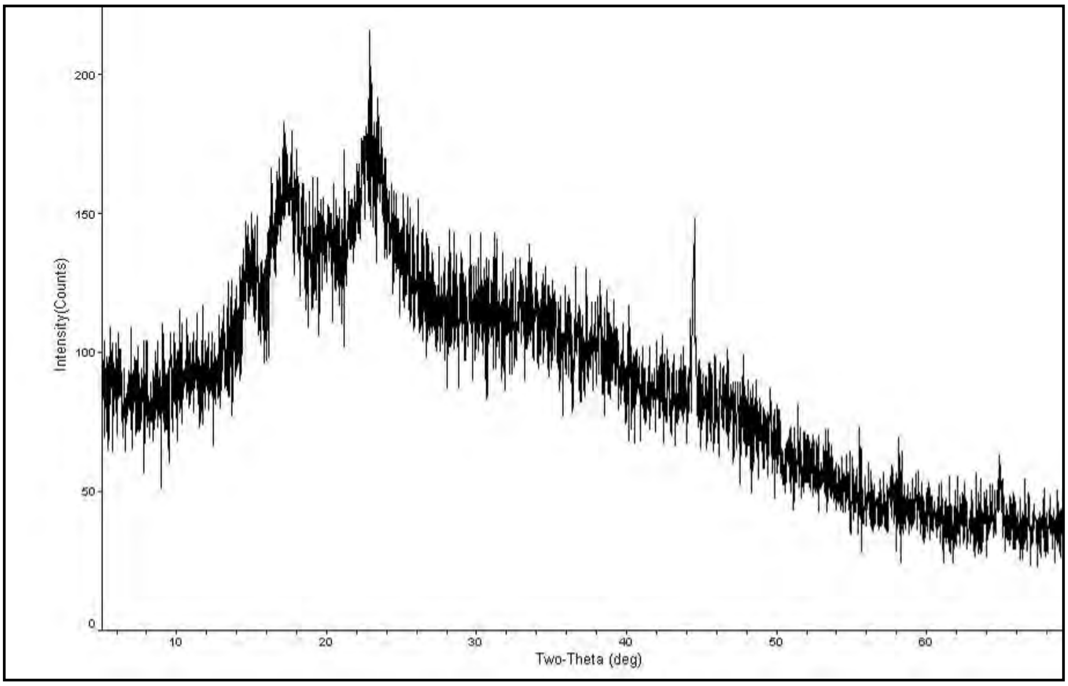


Figure A-5. X-ray diffraction patterns of SF25 after stored for 30 days.

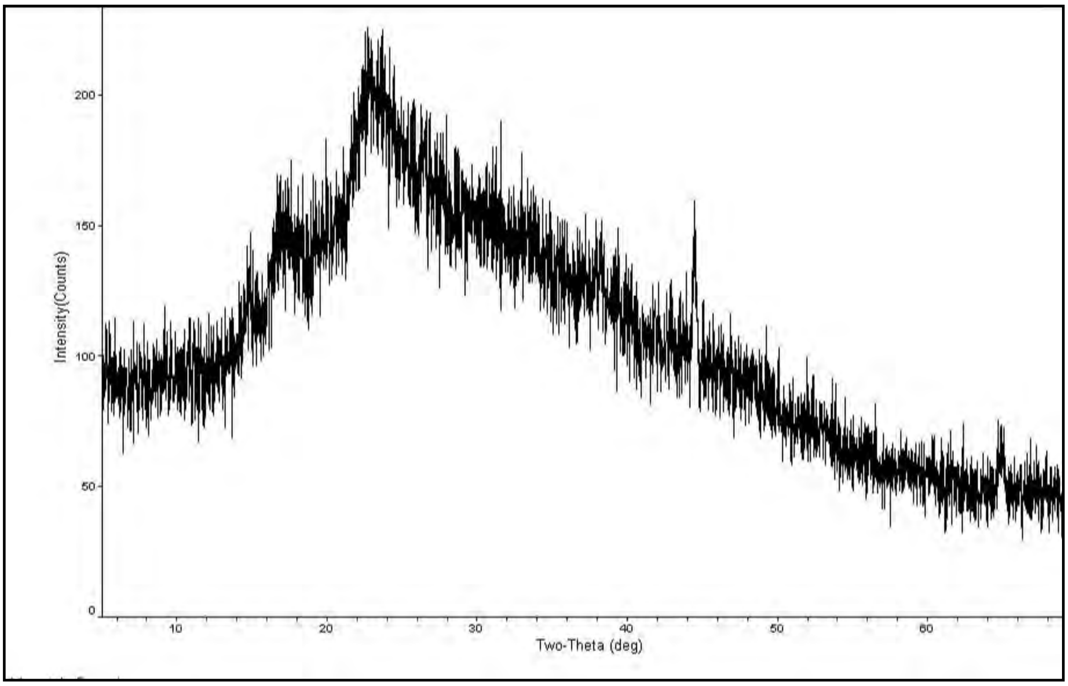


Figure A-6. X-ray diffraction patterns of SF35 after stored for 30 days.

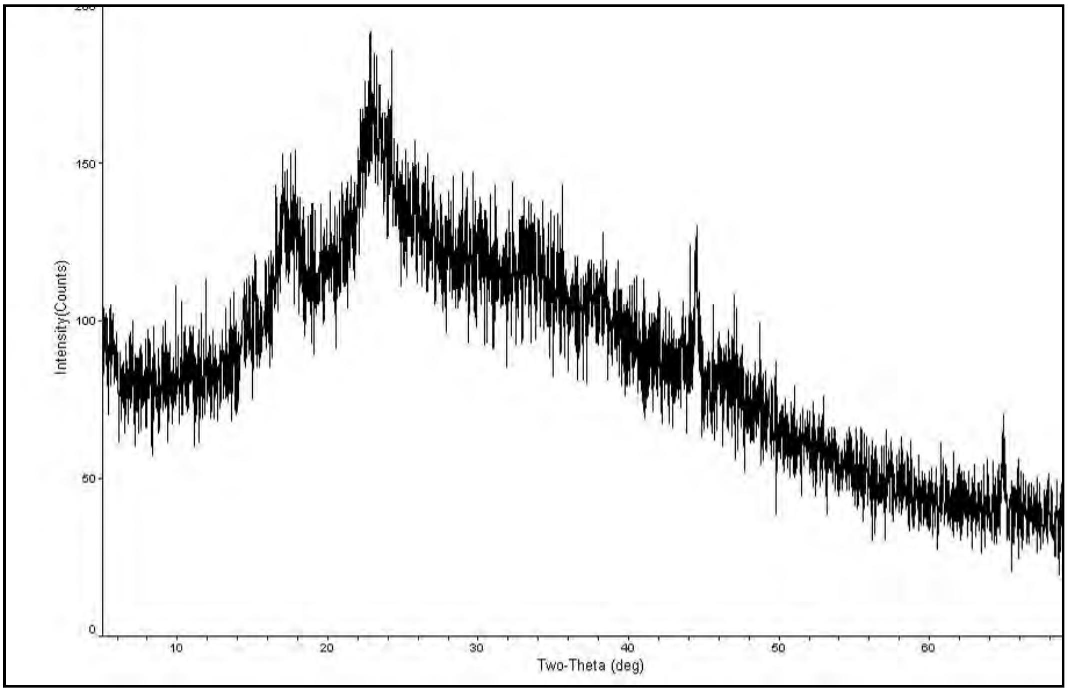
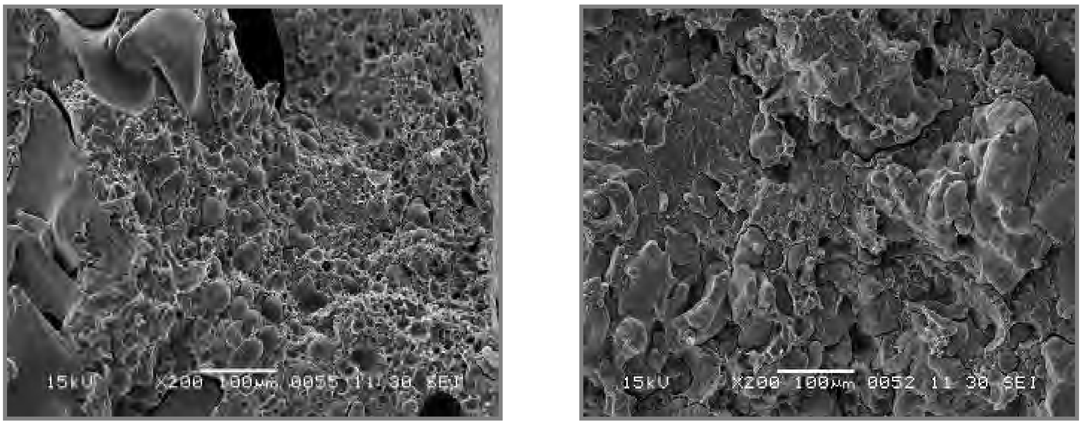
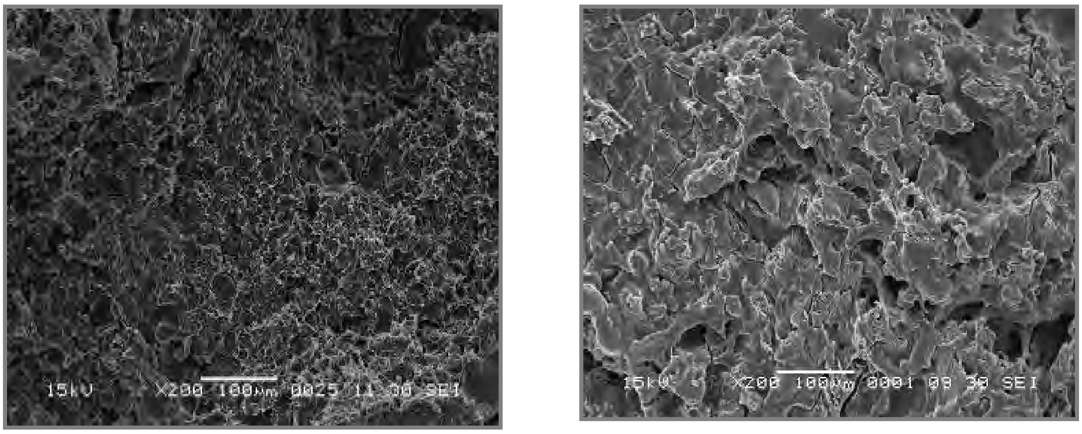


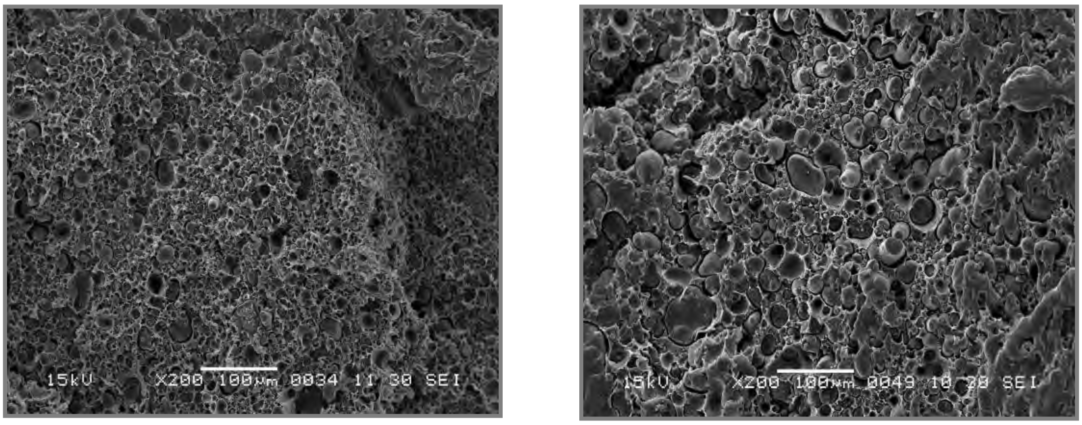
Figure A-7. SEM images of (A) 3PB05-7SF35, (B) 3PB10-7SF35, (C) 3PB15-7SF35, (a) 3PE05-7SF35,(b) 3PE10-7SF35 and (c) 3PE15-7SF35 with a blend composition of 50/50 (w/w). The scale bare is 100 µm.



(A) 3PB05-7SF35 (a) 3PE05-7SF35

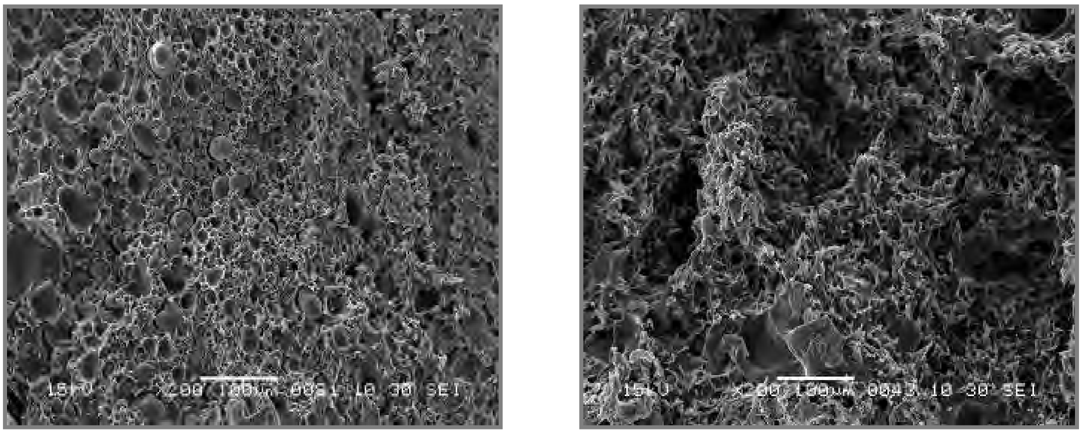


(B) 3PB10-7SF35 (b) 3PE10-7SF35

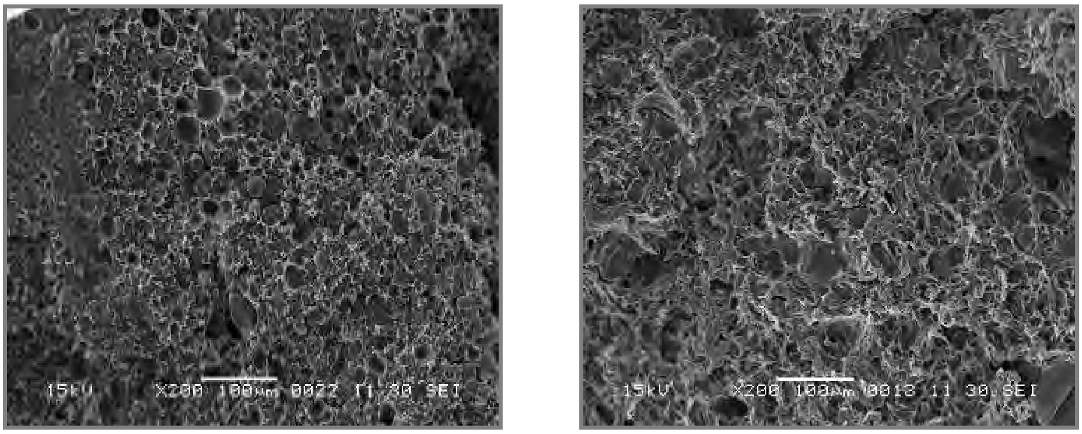


(C) 3PB15-7SF35 (c) 3PE15-7SF35

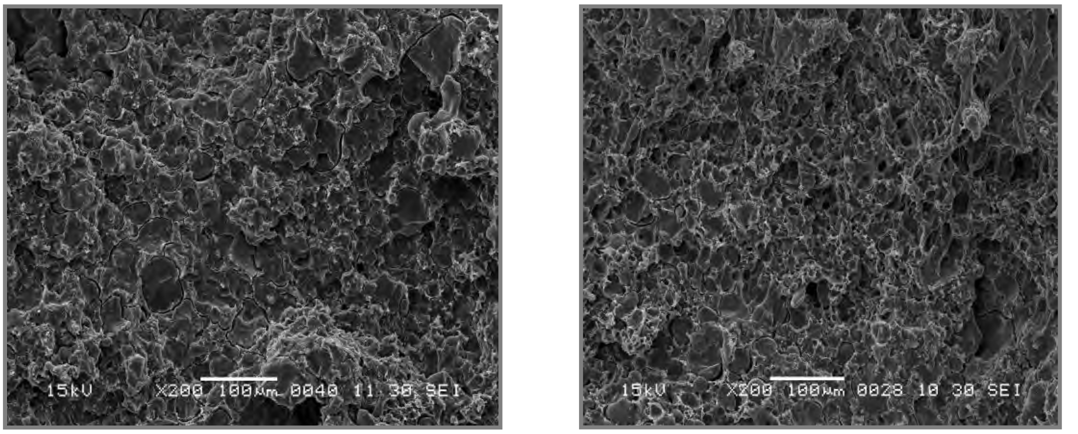
Figure A-8. SEM images of (D) 4PB05-6SF35, (E) 4PE10-6SF35, (F) 4PB15-6SF35, (d) 4PE05-6SF35, (e) 4PB10-6SF35 and (f) 4PE15-6SF35 with a blend composition of 50/50 (w/w). The scale bare is 100 µm.



(D) 4PB05-6SF35 (d) 4PE05-6SF35

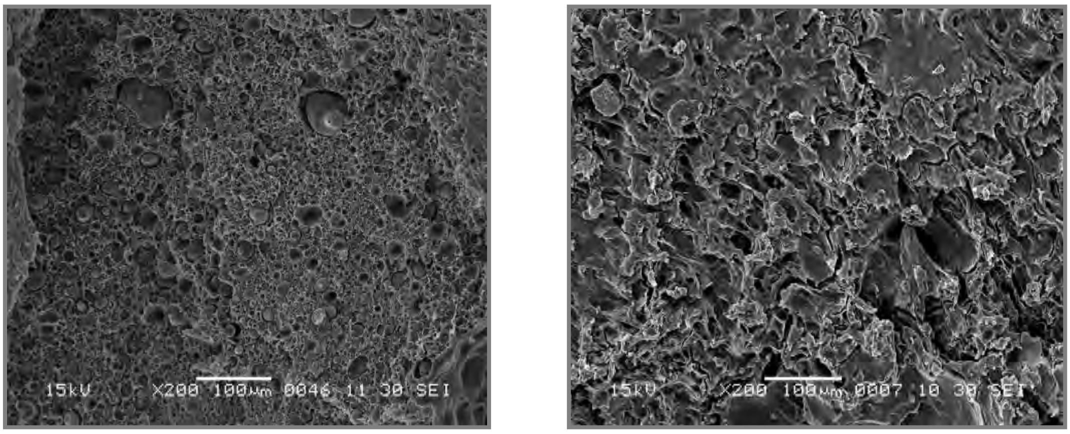


(E) 4PB10-6SF35 (e) 4PE10-6SF35



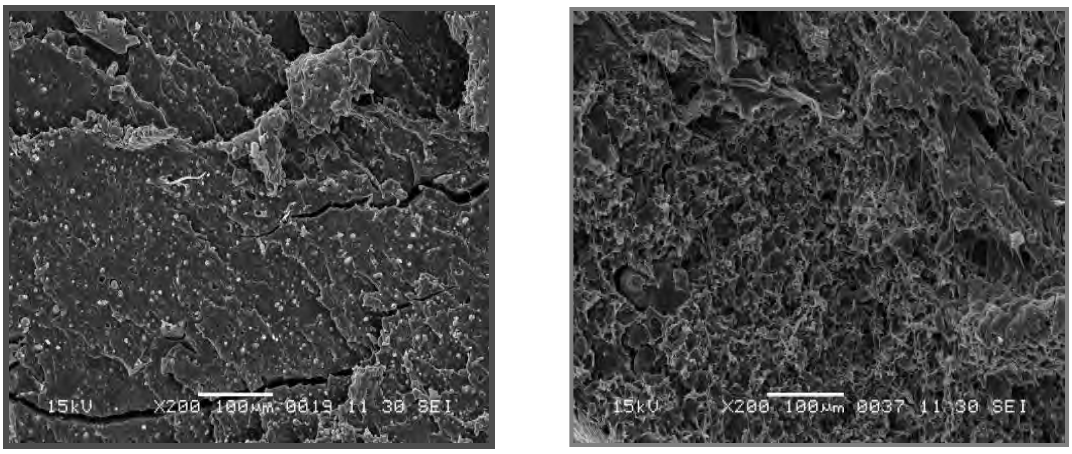
(F) 4PB15-6SF35 (f) 4PE15-6SF35

Figure A-9. SEM images of (G) 5PB05-5SF35, (H) 5PB10-5SF35, (I) 5PB15-5SF35, (g) 5PE05-5SF35, (h) 5PE10-5SF35 and (i) 5PE15-5SF35 with a blend composition of 50/50 (w/w). The scale bare is 100 µm.



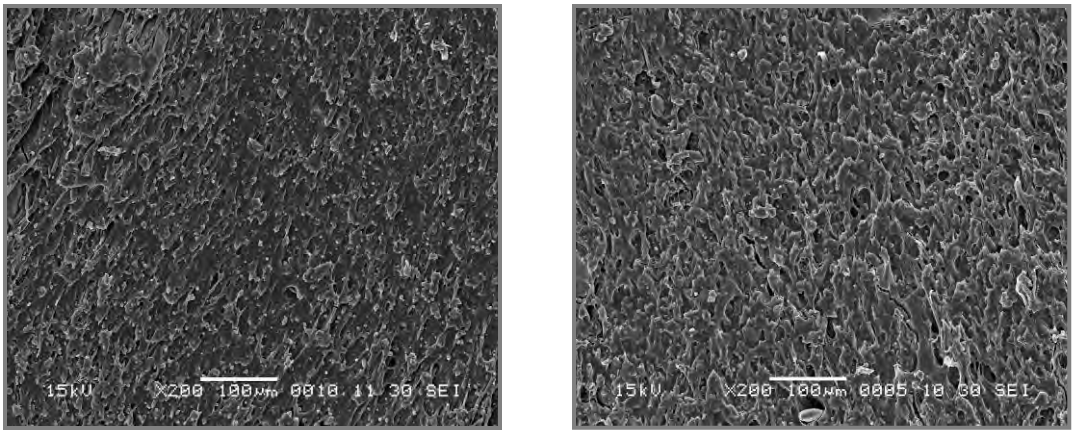
(G) 5PB05-5SF35

(g) 5PE05-5SF35



(H) 5PB10-5SF35

(h) 5PE10-5SF35



(I) 5PB15-5SF35

(i) 5PE15-5SF35

Table A-1. The glass transition temperature and melting temperature of TPS/PLA blends with various triethyl citrate contents.

TPS/PLA	(°C)	
	Tg	Tm
PLA(Virgin)	58	149.9
3PE05/7SF35	38.5	142.1
4PE05/6SF35	42.7	145.9
5PE05/5SF35	44	146.7
3PE10/7SF35	35.1	140.6
4PE10/6SF35	36.3	141.4
5PE10/5SF35	38.8	144.0
3PE15/7SF35	28.4	140.5
4PE15/6SF35	29.0	136.4
5PE15/5SF35	33.7	139.9

Table A-2. The glass transition temperature and melting temperature of TPS/PLA blends with various tributylacetyl citrate contents.

TPS/PLA	(°C)	
	Tg	Tm
PLA(Virgin)	58	149.9
3PB05/7SF35	34.3	140.1
4PB05/6SF35	35.2	142.7
5PB05/5SF35	39.4	144.9
3PB10/7SF35	31.5	139.4
4PB10/6SF35	33	140.3
5PB10/5SF35	35.2	142.7
3PB15/7SF35	23.5	132.5
4PB15/6SF35	27.8	137.5
5PB15/5SF35	29.9	137.1

Table A-3. Mechanical properties of TPS/PLA blend with various Triethyl citrate concentrations.

Sample code	MPa	%
	Tensile strength	Elongation at break
PLA (Virgin)	73.77±0.14	3.63±4.60
3PE05/7SF35	18.00±0.31	2.42±0.25
3PE10/7SF35	23.70±1.15	3.00±0.56
3PE15/7SF35	26.50±0.90	3.30±0.15
4PE05/6SF35	25.60±0.68	4.23±0.42
4PE10/6SF35	26.50±0.90	4.30±0.68
4PE15/6SF35	30.40±0.94	4.42±0.68
5PE05/5SF35	32.00±1.31	4.96±0.94
5PE10/5SF35	34.20±0.36	5.31±0.98
5PE15/5SF35	37.30±1.02	6.16±0.16

Table A-4. Mechanical properties of TPS/PLA blend with various Tributylacetyl citrate concentrations.

Sample code	MPa	%
	Tensile strength	Elongation at break
PLA (Virgin)	73.77±0.14	3.63±4.60
3PB05/7SF35	20.35±1.15	4.5±0.22
3PB10/7SF35	21.90±0.54	5.33±1.00
3PB15/7SF35	27.00±1.14	6.42±0.99
4PB05/6SF35	28.20±0.24	7.38±0.59
4PB10/6SF35	29.50±0.14	7.62±0.77
4PB15/6SF35	32.00±0.57	8.49±0.50
5PB05/5SF35	33.55±0.72	9.84±0.76
5PB10/5SF35	35.20±0.36	10.06±1.87
5PB15/5SF35	41.85±1.17	10.49±0.65

BIOGRAPHY

Miss Khwanjit Rugchad was born on March 11, 1981 at Surathani. She graduated with a Bachelor's degree of Polymer Science from Prince of Songkla University in 2004. She has worked as a R&D at Reangwa Standard Industry Co., Ltd. for 3 years. She began her master study in Petrochemistry and Polymer Science Program, Chulalongkorn University in June 2005 and completed the program in 2008.