BIO-BASED FILM FROM STARCH

BY

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ABSTRACT

This project aims to study the properties of biofilm from various type of starch that made by slurry method and to study operating conditions of extruder and compounding that affect properties of thermoplastic starch (TPS). The film from pure cassava, potato, and arrowroot starches and mixture of those starches with glycerol that made by slurry method were investigated. However, those biofilms were not exhibit properties that suitable to use a packaging such as soft, flexible, clear, high tensile strength and good tear resistance. Therefore, the compounding of TPS by using twin screw extruder were carried out to improve properties of biofilm from starch. The pre-mixed of cassava starch, chitosan, glycerol, and water were made in a household dough mixer. There are several trials to find the suitable ratios of those mixers that yield a good pre-mixed. The suitable formula was %wt. of cassava starch, chitosan, glycerol, and water equal 50, 3, 30 and 17, respectively. There were nineteen examples of pre-mixed were used to study effect of temperature and speed of twin screw and % of glycerol on properties of the TPS. The observed physical properties of those TPS revealed that screw speed was a significant factor. In addition. The glass transition temperature (T_g) of pre-mixed before and after passing twin screw extruder were also disclosed that the extruder could change properties of the pre-mixed starch. In addition, the DSC analysis of those examples were confirmed that the twin-screw extruder could destroy the crystallinity of starch.

Keywords: Bio-based film, Thermoplastic starch, TPS compounding, Twin-screw extruder

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols/Abbreviations	Terms
DSC	Differential Scanning Calorimetry
PLA	Polylactic Acid
PBAT	Polybutylene Adipate Terephthalate
PBS	Poly Butylene Succinate
UV	Ultraviolet
HALS	Hindered Amine Light Stabilizers
NOR-HALS	Aminoxyamine Hindered Amine Light Stabilizers
UVA	UV Absorbers
PVC	Polyvinyl Chloride
τ	Shear Stress
η	Viscosity
$\dot{\gamma}$	Shear Rate
t	Time
ΔT	Change in Temperature
C_p	Heat Capacity
rpm	Round per Minutes
mins	Minutes
%wt.	Weight Percent
DOE	Design of Experiment
Min.	Minimum Value
Avg.	Average Value

Symbols/Abbreviations	Terms
Max.	Maximum Value
L/D	Length-Diameter Ratio
T_g	Glass Transition Temperature
T_c	Crystallinity Temperature
#	Number
TPS	Thermoplastic Starch
MFI	Melt Flow Index

CHAPTER 1: INTRODUCTION

This chapter provides background information for starch, biodegradable plastic, and bio-based film that are used for continuing steps of works such as objectives, scope of work and expected outputs in the project.

1.1 Background

Recently, the serious negative impact of improper disposal of plastic items on soil, water, and air cause the ban of single-use plastic bag in Thailand starting from Jan; 2020. Thus, the biodegradable plastic is an alternative to substitute plastic. The biodegradable plastic was invented around 1990s. However, the usage is still small due to high cost and complicated technology to produce and processing of biodegradable plastics [1].

Agriculture is a backbone of Thailand. Farmers grow crops for domestic consumption and export as well. The major crops in Thailand are rice, rubber, cassava, glutinous rice, corn, and palm oil [2]. Therefore, finding ways to value and save environmental at the same time is a good value added to crop. The cassava is a good candidate for bioplastic from low price, and plentiful [3].

There are many research projects on modified and compounding starch to make a biofilm. However, some research use technologies that difficult to make a mass production such as casting film and some made chemical modification of starch that made higher cost of starch [4,5].

This project aims to study process to make thermoplastic compound starch which is a simple technology and could produce bio-based film in a production scale [1,6].

1.2 Objective

1) To study the properties of the starch and additives to improve properties of bio-based film from starch.
2) To study operating conditions of extruder and compounding that affect properties of thermoplastic starch.

1.3 Scope of Work

1) This project chooses only cassava starch to study and improve the desired properties by thermoplastic compounding.
2) The S1-KRC Kneader twin-screw extruder is used to find operating conditions for compounding.
3) Differential Scanning Calorimetry (DSC) will be used to study crystalline structure of compounds before and after compounding.

1.4 Expected Output

1) To be able to learn and understand properties of additive on thermoplastic starch.
2) To understand and find suitable operating condition of twin-screw extruder to compounding thermoplastic starch.

CHAPTER 2: THEORY AND LITERATURE REVIEW

This chapter consists of information about starch, biopolymer, bioplastic, thermoplastic starch, and thermoplastic compounding starch. Furthermore, this chapter is also explained about literature review for improving properties of starch.

2.1 Starch

Starch has different size and shape and could classified by the plant that starch obtained from.

2.1.1 Types

2.1.1.1 Cassava Starch

Cassava starch originally made from cassava root and process into powder. The physical characteristics of cassava starch is white, smooth, and glossy. After mixing cassava starch with water and heat at low to medium temperature, the starch will dissolve easily and turn glossy, then get more viscous at higher temperature. Cassava starch is high in carbohydrates and starchy and contains dietary fiber. The advantage of cassava starch are granule morphology and thermal property [7].

In industrial application cassava can be used in producing glue, desserts, and paper. Cassava starch is shown in figure 2.1 [7,8].

Figure 2.1: Cassava starch [9]

2.1.1.2 Potato Starch

Potato starch made from potato. This flour when cooked will have thick texture, crystal clear color than cassava starch. The advantages are the sticky texture and when the starch mixed with water and heat up then no deformation and remain it is stickiness. Potato starch is shown in figure 2.2 [8].

Figure 2.2: Potato starch [8]

2.1.1.3 Arrowroot Starch

Arrowroot starch made from arrowroot. In Thailand, price of this starch is higher than other types of starch because arrowroot can be harvested only once a year. Moreover, the method of making flour is complicated. The characteristic of powder is white color small square grain and rough texture compared to other flour types. After ground and mixed in water then heat up, the starch will thicken viscously with quite clear crystal color. Arrowroot starch can be shown as figure 2.3 [8].

Figure 2.3: Arrowroot starch [8]

2.1.2 Starch structure

Starch is consisted of two types of polymer chains, i.e., amylose and amylopectin.

2.1.2.1 Amylose

Amylose is a polysaccharide in long chain. It forms from connecting α-D-glucose units in long chain, which in each unit connected α linkage to C-4 of the next one through glycosidic bonds. Amylose has two type of linkage in alternative consist of α and β linkage. Therefore, Amylose has more resistance of digestion than other starch molecule. The structure of amylose is shown in figure 2.4 [10].

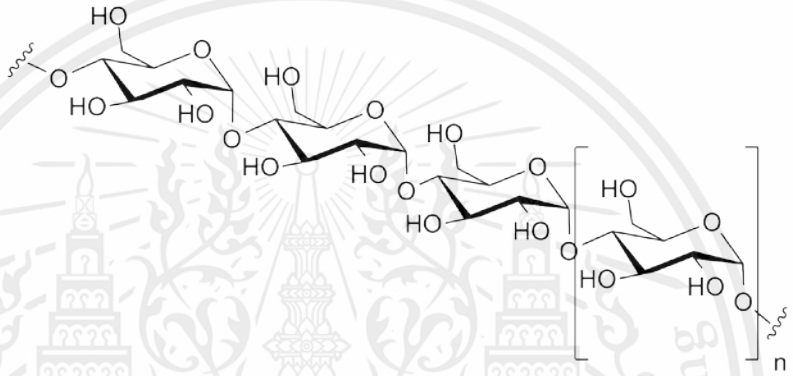


Figure 2.4: Amylose structure [10]

2.1.2.2 Amylopectin

Amylopectin is soluble in water, therefore, it could be hydrolyzed to the single disaccharide. Amylopectin as water-soluble, it has lower tendency of retrogradation (the reaction that occurs when amylose and amylopectin chains is cooked, gelatinized starch realign happens) or gelatinization during cooling. Amylopectin formed from D-glucose units with the joint is α linkage to C-4 to the next one in each unit. Nonetheless, in comparison of structure of amylopectin is more complex than amyloses [10].

Molecular weight of amylopectin shows that there are a million D-glucose units per molecule. The structure consists of highly branch which contain of many hundred short chain of around 20-25 D-glucose. Thus, in these chains is joint through C-1 to C-6 until next chain. The structure of amylose is shown in figure 2.5 [10]

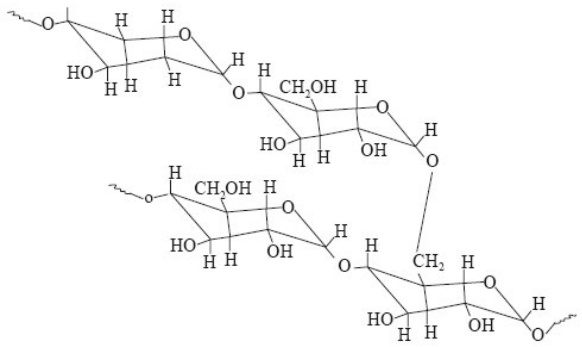


Figure 2.5: Amylopectin structure [10]

Each type of starch contains different ratio of amylose and amylopectin content as shown in table 2.1 [10].

Table 2.1: Amylose and amylopectin content (%)

Starch Type	Amylose Content (%)	Amylopectin (%)
Cassava Starch	17	83
Potato Starch	20	80
Arrowroot Starch	40.86	59.14

2.1.2.3 Crystalline

In crystalline solid particles, the molecules are arranged in linear segment of amylopectin by hydrogen bonds. The structure has high density and strongly bond together. In the other hand, it has the disadvantage of limiting in water absorption and inflation. In order to break the crystallinity, it requires heat to melt which thermal energy of the particles has to sufficient enough to overcome the internal holding force of the crystal called intracrystalline force [10]. The structure of crystalline phase can be shown in figure 2.6.

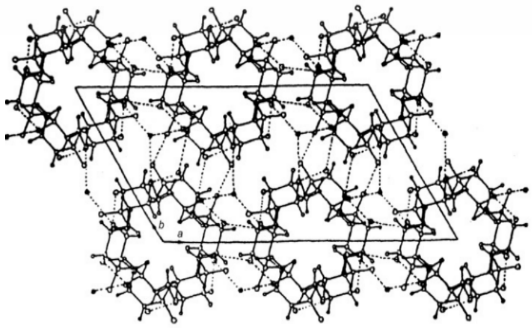


Figure 2.6: The structure of crystalline phase [10]

2.1.2.4 Amorphous

In amorphous particles, the molecules are disordered arranged. In amorphous region, it contains more amylopectin than amylose. Thus, it has less hydrogen bonding which make the amorphous form has a high reactivity more than crystalline form and good absorption. At last, in the experiment prefer to work on an amorphous phase from preferable physical properties and chemical properties [10]. The structure of amorphous phase can be shown in figure 2.7.

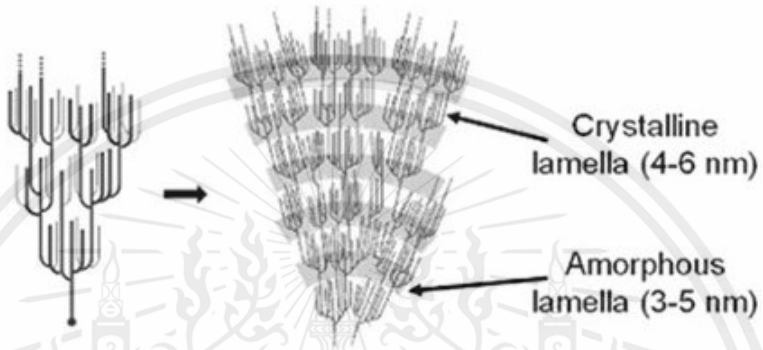


Figure 2.7: The structure of amorphous phase [10]

2.2 Bioplastic

Bioplastics are polymers produced from renewable biomass source; thus, bioplastics should be able to decompose into CO_2, H_2O, and biomass through enzymatic reaction of microorganism for instance bacteria or yeast. Due to chemical characteristics of biopolymers, it appears to require at least 50% of necessary organic composition [1].

Bioplastics based on starch made from two types of biopolymer which are amylose and amylopectin. Glucose polymers affects directly to physicochemical properties of starch, the higher amylose help in increasing of strength. In the other hand, the branch in amylopectin structure causes the film low mechanical properties, which can improve the mechanical properties by using plasticizers and glycerol as alternative [1,6].

There are three main groups of bioplastics that are popular for film and plastic bags.

2.2.1 Polylactic Acid (PLA)

Polylactic acid or known as PLA, it is thermoplastic polyester and considered as biodegradable. The chemical formula is $(C_3H_4O_2)_n$, it is included aliphatic polyesters group. PLA produced from α-hydroxy acid. The advantages of PLA are high strength and high modulus. PLA is stereochemical structure which easily to modified by polymerizing of L- or D- isomers, thus can be used for food contact products [11].

2.2.2 Polybutylene Adipate-Co-Terephthalate (PBAT)

Polybutylene adipate terephthalate or known as PBAT considered as copolymer specially in co-polyester. PBAT produced from adipic acid, 1-4 butanediol and terephthalic acid. The advantages of PBAT are flexibility with high elongation at break, good hydrophilic and processing properties. Moreover, it has been used in blown film production and membrane products [12].

2.2.3 Poly Butylene Succinate (PBS)

Poly butylene succinate or known as PBS, as a fully biodegradable thermoplastic in polyester group, however, it also included in aliphatic series polyester with the similar properties to propylene. For biodegradable film, PBS degrades better soluble of culture more than soil culture solution [13].

2.3 Thermoplastic Starch

Thermoplastic starch is a process of blending of polymers or starch with additives to improve polymers properties to be suitable for working in various situations such as light fastness, colorant, and UV stabilizer etc. [14]. Properties of starch are not suitable for producing films, so additives are needed to blend with polymers to improve their properties and reduce the environmental impact [15].

2.3.1 Additives

Additives are an organic or inorganic chemical that used in plastics resin to improve polymers properties before or during forming process. Furthermore, normal additives should be stable in working and forming process, cheap, safety and not reducing polymers properties [14,15]. Additives are divided into three types as the following:

2.3.1.1 Plasticizers

Plasticizers are a substance that added into a polymer to improve qualities such as increasing the workability, distensibility, strength and flexibility of the material.

Moreover, a great plasticizer should have a low tensile strength whereas high tensile elongation, a high flexibility at low temperatures and a low elastic modulus [16].

Example of plasticizers are

- **Glycerol**; glycerol or glycerine is a kind of polyol that has three molecules of carbon. It is a by-product from saponification reaction as shown in figure 2.8 [17]. Furthermore, it is sensitive to water, but it is good for adding in polymer as plasticizer. It has many advantages such as increase the flexibility and increase a chain mobility of polymers [18].

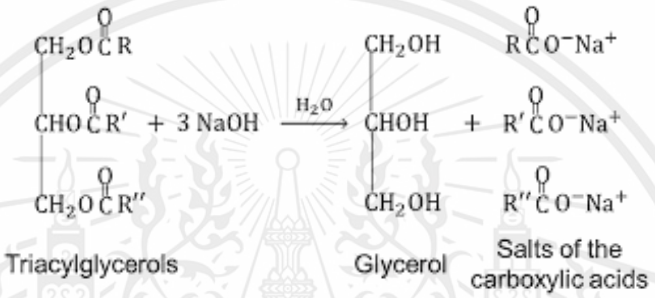


Figure 2.8: Saponification reaction [18]

- **Sorbitol;** sorbitol is a sugar alcohol that is used as sweetening agent. It is generally found in fruits and vegetables such as apple, pear, carrot and so on. It has six molecules carbon in structure as shown in figure 2.9 [17]. Sorbitol can prevent tooth decay but should not be used in a large quantity because it can cause a stomachache. In addition, when add sorbitol into films, it could improve properties of film such as low solubility, low moisture content, low water uptake ratio (WUR) and low water vapor permeability (WVP) [19].

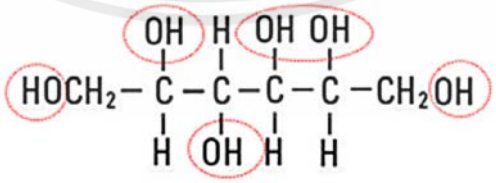


Figure 2.9: Sorbitol [19]

2.3.1.2 Fillers

Fillers are organic or inorganic powders that added into plastics for increasing volume or decreasing cost because fillers are cheaper than plastics and they

can help forming film [14]. Moreover, fillers mainly used to improve properties of the polymer in mineral forms such as chalk, talc, and china clay. Fillers which are compounded with polymers have many advantages such as enhance gelation, faster start-up, higher-impact strength and improved physical properties [15]. Examples of fillers are:

- **Keratin;** keratin is a chemical abundant in cysteine residues that are oxidized to get a strong mechanical dimension linked with keratin fiber network. In addition, keratin fibers have several characteristics such as toughness, high hydrophobicity, high length to diameter ratio, surface flexibility, low solubility, and high stability**.** From keratin properties, they can be used in food production as biodegradable films and edible films [20]. The structure of keratin is shown in figure 2.10.

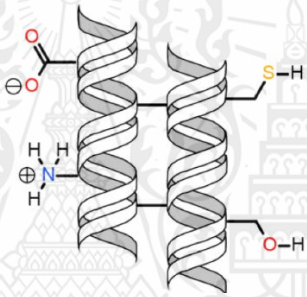


Figure 2.10: Keratin structure [20]

- **Lignin**; lignin is a kind of hydroxyl groups that acting like an interfacial compatibilizer agent. Furthermore, lignin is a key for a bio-based materials production which has a high tensile strength and a high thermoplastic polymer property so it can be used in a film production [20]. The structure of lignin can be shown in figure 2.11.

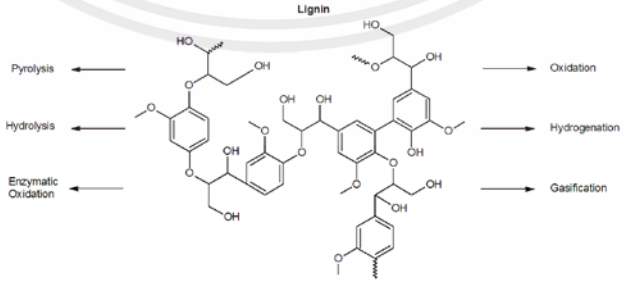


Figure 2.11: Lignin structure [20]

- **Cellulose**; cellulose is an abundant biopolymer that has a β-1,4 linked glucopyranose units relate to polymer chains by hydrogen bonds bundles of fibrils as

shown in figure 2.12. Moreover, crystalline phases alternate with amorphous phases which are called highly ordered regions and disordered domains, respectively. Cellulose fibers have several properties to increase strength of bio-based material films, give a strong interaction plasticized starch film and increase a crystallinity phases of the bio-based films from starch to give positive effect on mechanical properties [20].

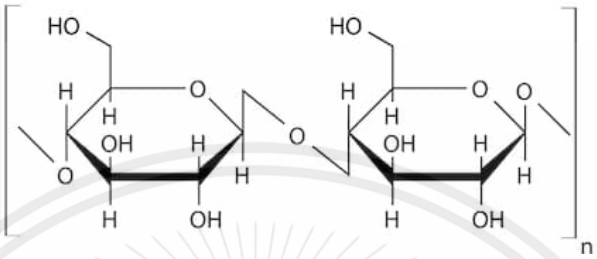


Figure 2.12: Cellulose structure [20]

2.3.1.3 Stabilizers

Polymer stabilizers are substances or additives that be added to polymeric compounds such as polyvinyl chlorides (PVC), polyethylene (PE), polypropylene (PP) and biopolymer to be produced faster with fewer defects. In addition, the main properties are used in preventing an oxidative of the elementary degradation of plastics that terminated a radical reaction from the early stage of degradation [21]. Examples of stabilizers are:

- **Chitosan;** chitosan is a nanoparticles that used as size control agent and stabilizer. In addition, chitosan has many good properties such as nontoxicity, biocompatibility, biodegradability, and antibacterial activity for producing biodegradable films with other polymers [22]. Chitosan also has a hydrophobicity and a positive effect on tensile properties of starch films [4]. The structure of chitosan is shown in figure 2.13 [22].

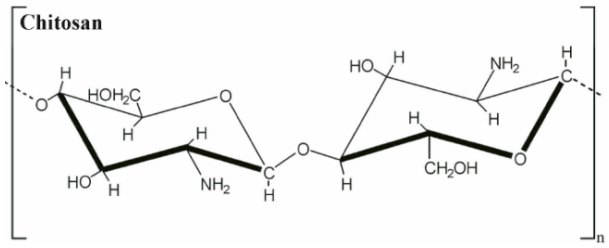


Figure 2.13: Chitosan structure [22]

- **UV stabilizers**; UV stabilizers are used for protecting polymer films from photodegradation especially for absorbing ultraviolet (UV) radiation. Furthermore, several types of UV stabilizers can be used in agricultural films such as hindered amine light stabilizers (HALS), UV absorbers (UVA), aminoxyamine hindered amine light stabilizers (NOR-HALS) and Nickle quenchers. The main advantages of these types of UV stabilizers are an extreme resistance to pesticides, protecting against chemical acid attack and still used in warmer regions [23].

- **Heat stabilizers;** heat stabilizers are used to prevent polymers from degradation by heat and to stop thermal oxidation by attacking decomposed products [24]. Moreover, heat stabilizers are usually used in polyvinyl chloride (PVC) production because PVC is a sensitive material to heat. Therefore, there are various effective types for heat stabilizers such as barium-zinc, calcium-zinc, organotin, hydrolyzed polyvinyl alcohol and bisphenol type epoxy resin. The main advantages are against a high temperature of resin during processing [25]**.**

2.4 Thermoplastic Compounding

In thermoplastic compounding process, extruders act as a mixing and pumping device that are used in various industries. Therefore, single-screw and twin-screw extruders are very important machines to compress, melt and mix several types of additives with different polymers [15].

2.4.1 Single-Screw Extruder

Single-screw extruder has a screw that is rotated inside a cylindrical barrel, so overall performance of mixing is based on the homogenization of compounding. The advantages for this type of extruder are easy to implement, few process variables and cheap for replacing worn out screws. In contrast, the single-screw extruder cannot be well dispersed due to additives that interfere with dissolution of polymers [15]. From a reason, twin-screw extruder is used instead of single-screw extruder in the project. Single-screw extruder is shown in figure 2.14.

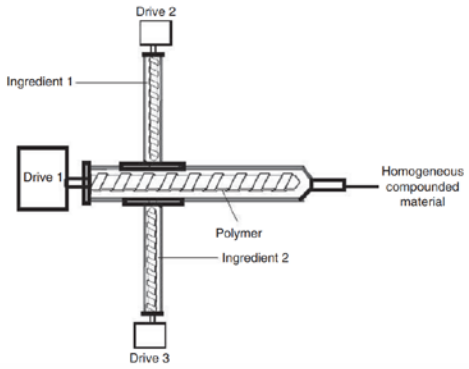


Figure 2.14: Single-screw extruder [15]

2.4.2 Twin-Screw Extruder

Twin-screw extruder has two parallel-installed screw in one barrel which uses counter-rotating and co-rotating extruders in polymer production process, so it suits for mixing, homogenizing, and melting of solid polymer materials. Moreover, there are two common types of screw accessories that are composed of kneading blocks and conveying elements, but the project focuses only on kneading blocks. The advantages of this extruder are a better ability to control distributive and dispersive blending, an ability to feed larger volumes and high-density material and a good transport flexibility for ventilation [15]. Twin-screw extruder is shown in figure 2.15.

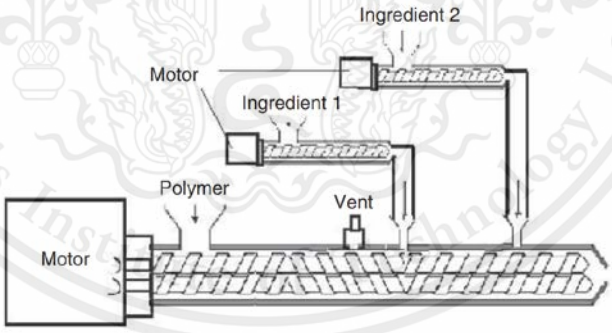


Figure 2.15: Twin-screw extruder [15]

2.4.3 Extrusion and Process

Extrusion is one of the important processing using in thermoplastics processing when applying the extruder with the polymers granule which fed into the extruder [26]. The screw rotation will drag the polymer through extruder. The heat from friction with the extruder walls and the external heat source melts down the polymer, and the screw movement mixes polymer to homogenizes. Lastly, the product leaves the extruder

through different shape die depends on the final product (e.g., film, sheet, bottle, pipe) [26].

For shaping into thick film or sheet, hot polymer moves through the outlet of extruder and get on to the cooled metal rolls to be quenched and shaped into thin film as shown in figure 2.16. As the air-cooled surfaces are rough, the polymer is cooled by the cooled rolls. The metal surface roughness is important, as slower cooling rate interior results in compressive stresses in surface layer which gives wrinkled surface [26].

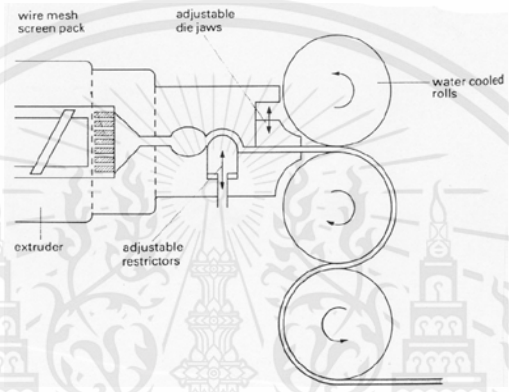


Figure 2.16*:* Extrusion in filming processes [26]

2.4.4 Effects of Processing on Polymer Properties

The processing methods affect two main thermoplastic properties, i.e., crystallinity and molecular arrangement.

2.4.4.1 Crystallinity

In crystalline region contains the chain which denser chain packing than the amorphous material, caused by the higher elastic modulus and tensile strength. Density is used to indicate the degree of crystallinity because of the geometry of the chain folding [26]. Figure 2.17 showed specific volume as function of temperature of polymer with different coating rate. Crystallization results in a significantly decrease in volume during coagulation. Crystallization in polymers follows C-curves for the transition region in the same way as the phase shift in metal and other materials [26]**.**

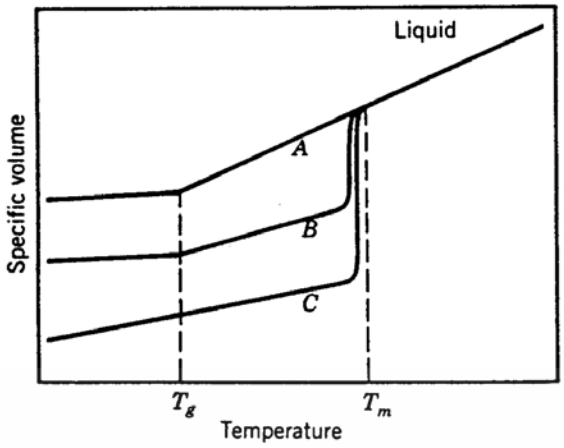


Figure 2.17: Volume / density curves for the same polymer with different cooling rates [26]

At different cooling rates of polymer start from point A, it has fast cooling rate and the structure is fully amorphous and no crystallization. At point B which is intermediate cooling rate is partially crystalline. At point C has slow cooling rate because becoming fully crystalline as much as crystalline could occur in the system. Whereas T_m is the melting point of the crystalline phase and T_G is the glass transition temperature if T_G below this the polymer chains are essentially immobile [26].

During thermoplastic processing, thick parts tend to be cool slowly than thin parts. Therefore, there may be a higher proportion of crystals. This leads to different shrinkage inside the component and can cause shape distortion [26].

2.4.4.2 Chain Alignment

Strength and elastic modulus increase a lot in direction of chain alignment. Chain alignment let the strong threads of polymers created which is the effect of draw-strengthening. In extensional flow leading the chain alignment to occurs due to walls friction, molecules are naturally randomly coiled (highest entropy state) and become aligned parallel to the flow direction [26].

2.5 Rheology

Rheology is the Science study about the deformation and flow of material. The science of flow that applied to physics, chemistry, engineering, medicine, dentistry, pharmacy and biology. The theory of elasticity assumes that the elastic solid is consistent according to Hooke's law [27].

Rheology has two purpose in science, first is to define the relationship between stress and time transformation, second is determining the molecular structure and the relationship between viscosity properties and materials structure. The dependance of time and temperature of polymer properties is significant when compared to other materials such as metals and ceramics. This strong dependance is due to the nature of polymers viscosity [27].

2.5.1 Newtonian fluid

The Newtonian fluid is the relation between shear stress and shear rate as linearly relationship and the constant of proportion on being the coefficient of viscosity. The relationship is known as Newton's law can be described as following eq. 2.1 [28]:

$$\tau = \eta \, x \, \dot{\gamma} \qquad \text{Eq.2.1}$$

Where:

τ = shear stress

η = viscosity

$\dot{\gamma}$ = shear rate

Figure 2.18 shows the viscosity of Newtonian fluid stays constant, which means that the viscosity of the Newtonian fluid will not change under velocity it forced to flow through the tube or pipe [28].

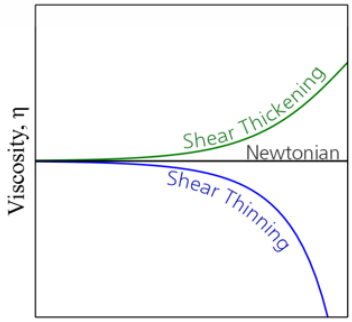


Figure 2.18: Viscosity of Newtonian, thinning and shear thickening fluids [28]

2.5.2 Non-Newtonian Fluid

In the Non-Newtonian fluid, the relationship between shear stress and shear rate is different. liquids can exhibit viscosity depending on time. Therefore, the constant viscosity coefficient cannot be determined [28].

Most fluids are Non-Newtonian fluid which their viscosity depends on shear rate. Non-Newtonian behavior caused by several factors that related to structural rearrangement of fluid molecule due the flow. In polymer melts and solutions, there is high anisotropic chains aligned and resulting in velocity decrease. Fluid generally depends on viscosity while non-Newtonian fluid can be determined by the flow characteristics [28].

In addition, the Non-Newtonian fluid has the characteristic that this fluid behaved like a solid for a short moment before returned to a liquid again. Therefore, the Non-Newtonian fluid is not following the rule of liquids take on the shape of the container they are poured into. Not all the Non-Newtonian Fluids behave in the same way when stress is applied because some fluids become more solid, others more fluid [29].

2.6 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a method used to examine the response of polymer to heating. Therefore, DSC can be used to study the melting of crystalline polymers or glass transition. The temperature different rate as a given amount of heat varies between the two pans, where the temperature difference depends on the composition of the pan and physical changes for instance phase changes. Heat flux is used in the laboratory, the system varies the heat given to one of the pans to maintain both pans temperature the same [30]. Thus, result can be plotted with the different of heat (q) and temperature (T). The thermal properties of polymer are described as following:

2.6.1 Heat Capacity

The heat capacity (C_p) of system means the heat needed raise the temperature, generally unit is in Joules/^oC. Therefore, heat capacity can be found from the heat flow and heating rate by eq.2.2-eq.2.3 [30].

$$Heat\ flow = \frac{heat}{time} = \frac{q}{t} \qquad \text{Eq.2.2}$$

and $$Heating\ rate = \frac{\Delta T}{t}$$ Eq.2.3

Where:

t = time

ΔT = change in temperature

Therefore, the heat capacity can be calculated from eq.2.4 as following:

$$C_p = \frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T}$$ Eq.2.4

This could be described that if heat capacity of material is constant over any temperature rage, the plot of heat flow against temperature will be line in zero slope as shown in figure 2.19 [30].

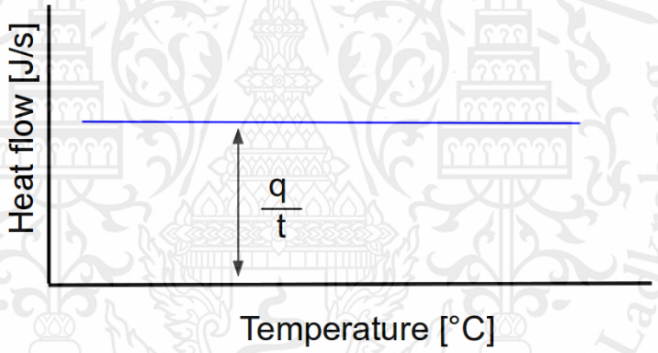


Figure 2.19: Example of plot heat flow versus temperature in condition of material that does not undergo any changes during heating [30].

2.6.2 Glass Transition

In case if polymers in the molten state is cooled at some point, it will reach the glass transition temperature (T_g). At this point, the mechanical properties of polymer change from flexible material to brittle material due to the chain mobility changes. The change can be observed from figure 2.20 which shown the sample of heat flow versus temperature at glass transition temperature of two different point A and B as followed: Picture A). In a plot of heat flow versus temperature it is a gradual transition that occurs over a range of temperatures.

Picture B). The glass transition temperature is taken to be the middle of the sloped region.

The heat capacity of polymer generally higher than T_g. The transition occurs by over a range of temperature but not suddenly at one temperature [30].

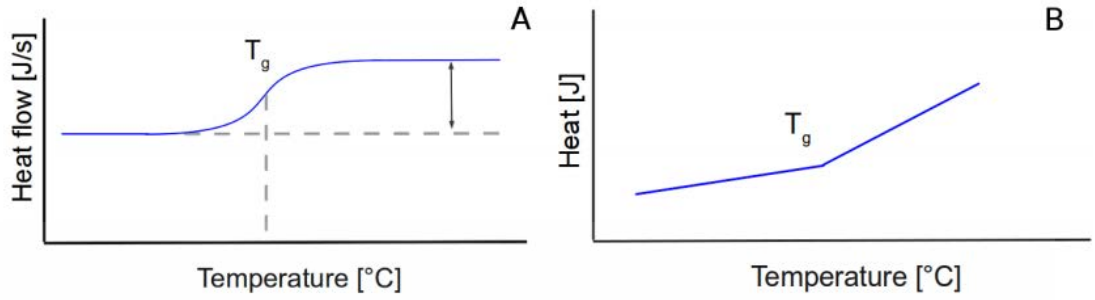


Figure 2.20: Example of plot of heat flow versus temperature in glass transition [30].

2.6.3 Crystallization

At temperature above the temperature of T_g the chains of polymer have high mobility. For crystallization, it is the exothermic process which the heat will released into surroundings. Therefore, less heat is required to keep the sample pan heating rate the same as the reference pan. If refer to the "exothermic-down" convention, then the result is dipped into the heat flow scheme, which relative to the temperature as shown in figure 2.21 [30].

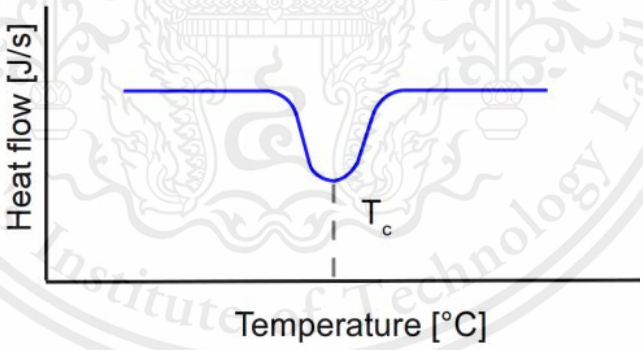


Figure 2.21: Example of a crystallization 'peak' in a plot of heat flow against temperature [30].

Crystallization is an exothermic process, so the heat flow to the sample must be decreased to maintain a constant heating rate [30].

For crystallization peak, is used to confirm that crystallization occurs in the sample. The crystallization can be observed from the crystallization temperature (T_c) then determine the latent heat of crystallization. Where the point at the lowest point of

dip is defined to be crystallization temperature. The latent heat (enthalpy) of crystallization can find from the area under the curve [30].

2.6.4 Melting

At melting point (T_m), the chain of polymers moves freely and without order arrangements. Melting is an endothermic process, by absorbing the heat. The energy added during this time is used to melt the crystalline regions and does not increase the average kinetic energy of the chains that are already in the melt [30].

From a plot of heat flow versus temperature shown in figure 2.22, it can be used to calculate the area of melting peak. The temperature increases slower than before due to the heat capacity of a polymer in melting is higher than solid crystalline polymer [30]. In example shows that the heat flow to the sample must be increased to keep the heating rate constant, resulting in a discontinuity in the plot of heat versus temperature.

Picture A). This appears as a peak if the heat flow is plotted against temperature.

Picture B). The area under the curve can be used to calculate the latent heat of melting.

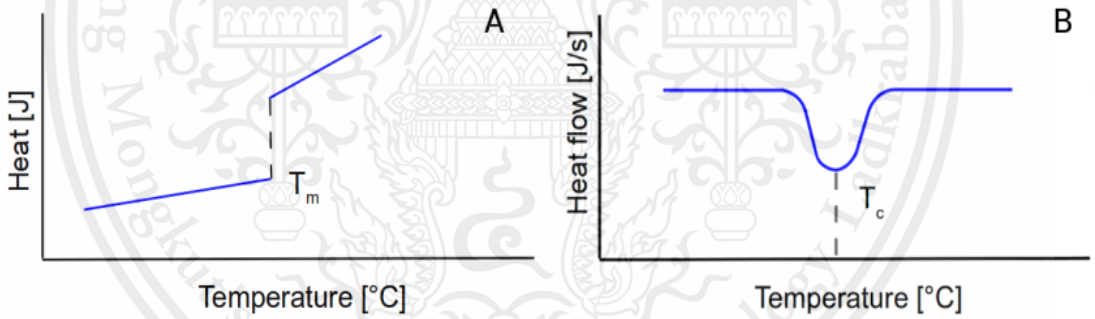


Figure 2.22: Example of endothermic process at melting point [30].

2.6.5 Comparing T_g, T_c, and T_m

In condition of polymers which form crystals could be observed from the peaks of crystallization (T_c) and melting (T_m). In case of pure amorphous polymers can see from glass transition (T_g). As a conclusion, the amorphous only undergoes the glass transition while the crystalline regions only undergo melting. The parameter which affects to temperature at which the polymer chains undergo in this region is the structure of polymer. The example plot of a heat flow versus temperature plot for a polymer can be shown in figure 2.23 [30].

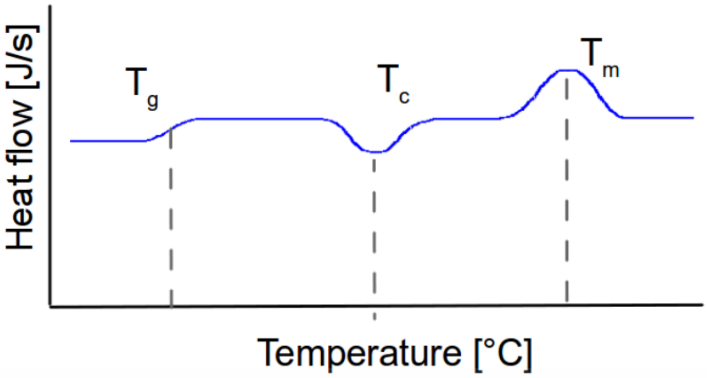


Figure 2.23: Example plot of a heat flow versus temperature plot for a polymer that under-goes a glass transition, crystallization and melting [30].

2.7 Literature Review

The main objective of studies was to observe the mechanical and chemical properties of different types of starch and applied the mixture contents to meet the required properties of the biodegradable film and bio-based film from starch.

Pelissari, F.M.; et al [4], the purpose of this research was to evaluate the attempt of cassava starch, glycerol, and chitosan concentrations on the water vapor barrier properties, optical and mechanical of films. This study can be concluded that the interactions of starch, glycerol, and chitosan concentrations can improve properties in a good way to produce films in food packaging. For example, the concentrations of cassava starch, glycerol, and chitosan had the interactions that influenced the mechanical and optical properties of the films. The addition of glycerol concentration enhanced the flexibility and decreased the Young's modulus of films. Moreover, the addition of chitosan increased the mechanical properties and decreased water vapor barrier properties of starch films.

Huntrakul, K; et al [5], the objective of this project was to improve properties of cassava starch films with plasticizers by combination with protein and barrier properties for oil-based food products. The protein in this study was a pea protein isolate which dispersed crystallinity and particles. In addition, pea protein also enhanced barrier properties such as water vapor transfer and surface hydrophobicity for cassava starch films packaging. The conventional blown-film extrusion used to develop the edible film from acetylated cassava starch (AS) and pea protein isolate (PI). This study can be concluded that increases in pea protein isolate can reduce glass transition and relaxation temperature in acetylated cassava starch and pea protein isolate blends. Moreover,

increased in pea protein isolate decreased the solubility and light transmission but it improved crystallinity and barrier properties.

Kuntima, P and Pimpilai, S; et.al [17], the objectives were to study the process of producing cassava starch film that passed ultraviolet radiation and to acquired film production with commercial production potential and increasing the variety of cassava starch to approach the use in the food industry. The results from UVc test affected the properties of cassava starch, with the film that dehumidified before or after had an effect on film brightness. Thus, the film that dehumidifies after UVc radiation had increased the oxygen penetration resistance and decrease in water solubility of the film. The film that dehumidifies at most effective time timing on 60 minutes before radiation can slow down the microbial contamination better the time less than 40 minutes. The elongation had no difference from the 3 treatments of UVc.

Khunthachai, W; et al [31], the objectives were to develop standard bill of materials for edible film formations and coating made from rice flour, to study the application of edible film and coating from rice flour to be applied in fruit toffee, to study the physical properties and test with customer acceptance by coating the fruit toffee and comparing with the commercial fruit toffee, and to approximate the shelf life of films and coating comparing with commercial toffee. Customers accepted a film made from rice flour and glycerol 0.2 g observe on color, taste, and texture with tensile strength of 1.733 mega pascal, which had a moderate tensile strength. Furthermore, sorbitol was an optional in this research because it was stable in the air and cold air and gave moisture to a product that needed some moist for instance food contact product like candy wrap.

CHAPTER 3: METHODOLOGY

From the objectives of this project, properties of starch and additives that influenced breaking of crystallization to amorphous properties can be measured by Differential Scanning Calorimetry (DSC). Therefore, experimental methods can describe as follows.

3.1 Raw Materials

1) Cassava Starch
2) Arrowroot Starch
3) Potato Starch
4) Additives
   - Glycerol
   - Chitosan

3.2 Equipment

1) Beaker
2) Cylinder
3) Wash bottle
4) Stopwatch
5) Petri dish
6) Dispensing spoons
7) Heat resistant gloves

3.3 Instrument

1) Thermometer
2) Analytical balance
3) Hot plate
4) Hot air oven
5) Dough mixer: HM-275; OTTO Kingglass
6) S1-KRC Kneader twin-screw extruder
7) Differential Scanning Calorimetry (DSC)

3.4 Procedure

The experiments were divided into two parts: 1) To study the properties of each type of starch by slurry method and 2) To study conditions of twin-screw extruder and glycerol for breaking crystalline phase.

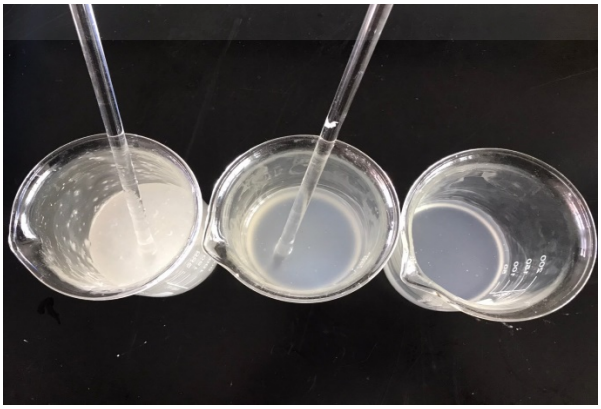
3.4.1 Study the Properties of Each Type of Starch by Slurry Method

In this experiment, there were three types of starch, i.e., cassava starch, potato starch and arrowroot starch were investigated. The steps for testing properties are

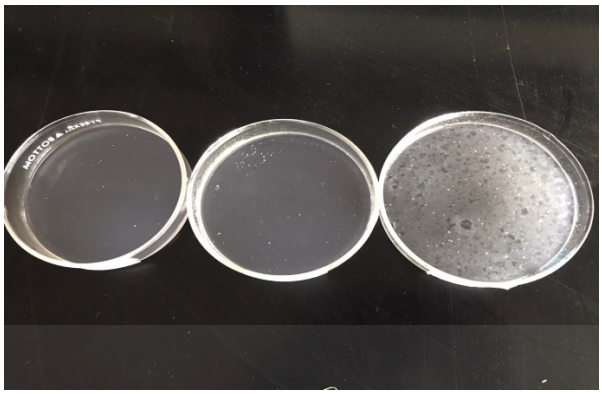
1) Weigh 5.0 g for each starch by using analytical balance.

2) Add 95.0 ml of water in each beaker and heat them until gelatinization. (Temperature 60-70 ℃)

3) Stir each beaker in room temperature for 40 minutes.



4) Pour the solutions into petri dish.



5) Bring dish in hot air oven and set temperature 45 ℃ for 8 hours.

6) Observe properties of each starch and compare them.

3.4.2 Study Conditions of Twin-Screw Extruder and Glycerol for Breaking Crystalline Phase

Workflow diagram can show the steps of experiment for the project as figure 3.1.

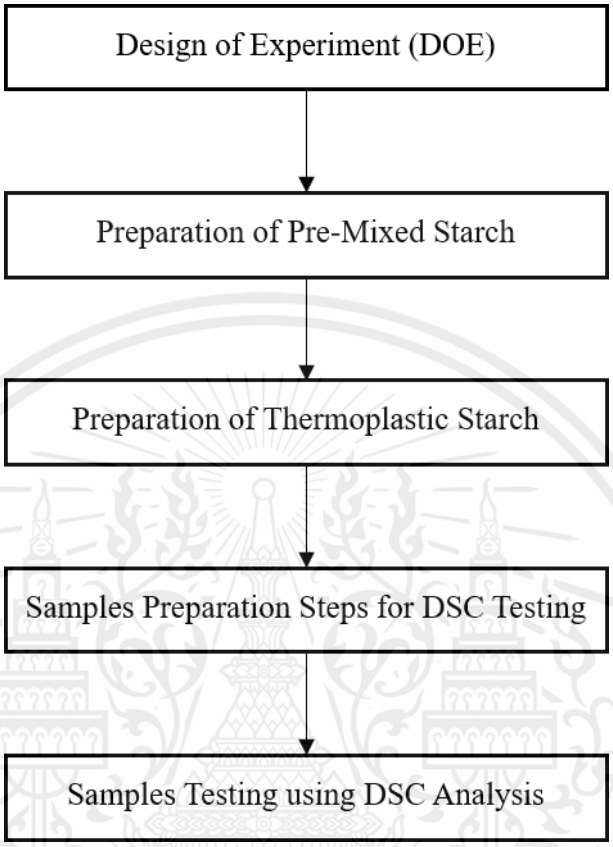


Figure 3.1: Workflow diagram for the project

3.4.2.1 Design of Experiment (DOE)

This experiment uses 2^3 full factorial design with two replications and three center points to design experiment. The total of 19 experiments will be carried out. The three variables were varied in experiments that were listed as codes in table 3.1. Similarly, the amount of three ingredients in each experiment are shown in table 3.2.

Table 3.1: List of codes for minimum, average, and maximum values of three variables

Factors	Minimum	Average	Maximum
Temperature (°C)	100	115	130
Screw Speed (rpm)	81	121.5	162
Glycerol (%wt.)	28	30	32

Table 3.2: The amount of three ingredients in each experiment

Batch #	Temperature (°C)	Screw Speed (rpm)	Glycerol (%wt.)
1	100	81	28
2	130	81	28
3	100	162	28
4	130	162	28
5	100	81	32
6	130	81	32
7	100	162	32
8	130	162	32
9	100	81	28
10	130	81	28
11	100	162	28
12	130	162	28
13	100	81	32
14	130	81	32
15	100	162	32
16	130	162	32
17	115	121.5	30
18	115	121.5	30
19	115	121.5	30

3.4.2.2 Preparation of Pre-Mixed Starch

The raw materials were blended by the HM-275; OTTO Kingglass dough mixer to prepare a pre-mixed starch. The steps of blending were shown in figure 3.2 and the picture of the HM-275; OTTO Kingglass dough mixer was shown in figure 3.3.

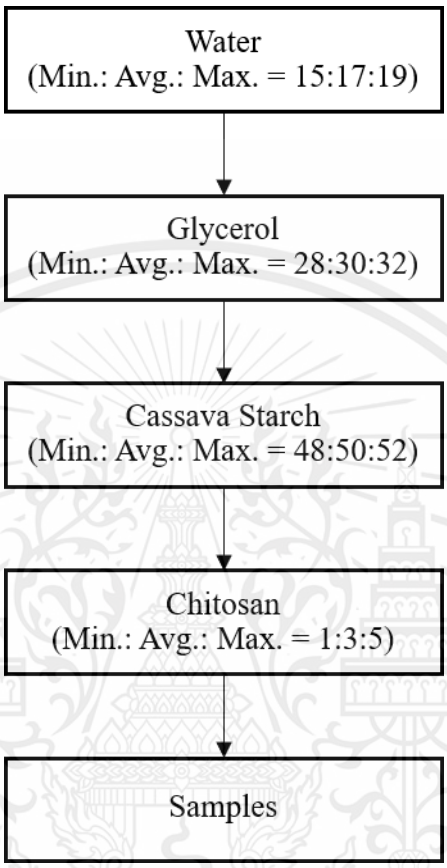


Figure 3.2: The steps for blending in the HM-275; OTTO Kingglass dough mixer

Figure 3.3: Figure of HM-275; OTTO Kingglass dough mixer [32].

3.4.2.3 Preparation of Thermoplastic Starch

Samples were blended and heated by the S1-KRC Kneader twin-screw extruder to break a crystallinity of the substances.

In addition, S1-KRC Kneader was selected in the research because it has great characteristics such as long residence time, low power for dispersion capability, short L/D, high capacity of production and easy for cleaning [33]. Furthermore, specifications and conditions in S1 KRC Kneader are shown in table 3.3 and figure of S1 KRC Kneader was shown in figure 3.4 [34].

Table 3.3: Specifications and conditions in S1-KRC Kneader [33,34]

Specifications	Values
Machine size	25 mm (D) x 255 mm
L/D	10.2
Rotating speed	96-384 min^{-1}
Paddle revolution	360-480 rpm
Motor capacity	1.5 kW
Weight	500 kg
Maximum heat temperature	300 ℃
Effective volume	120 cm3
Drive unit	0.4 kW
Material	Barrel: SUS316 Screw and paddle: SCS314
Barrel structure	Split barrel

Figure 3.4: The S1-KRC Kneader twin-screw extruder [34]

3.4.2.4 Samples Preparation Steps for DSC Testing

The steps for preparing the samples prior to testing by using the Differential Scanning Calorimeter (DSC) were shown in figure 3.5.

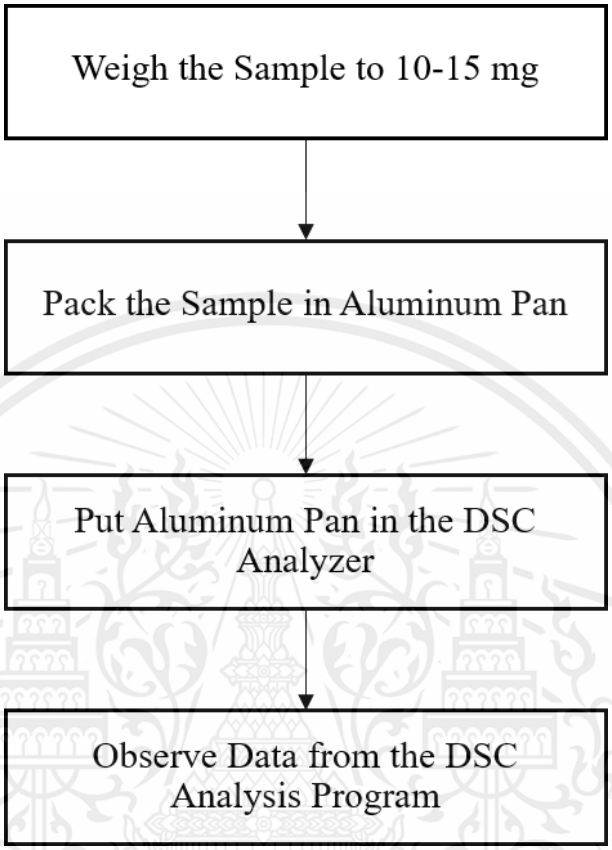


Figure 3.5: The samples preparation steps for testing

3.4.2.5 Samples Testing using DSC Analysis

The samples were analyzed by using Differential Scanning Calorimetry (DSC) analysis to characteristics properties such as crystallinity, latent heat (enthalpy) of crystallinity, and glass transition temperature. Therefore, all experimental data can be explained in graph for DSC analysis.

CHAPTER 4: EXPERIMENTAL RESULT

This chapter described the results and discussion.

4.1 The Properties of Starch Film prepared by Slurry Method

From the slurry method, the three types of starch were investigated. There are cassava starch, potato starch, and arrowroot starch. The properties of these three starches were compared by observing physical properties such as viscosity, flexibility, and strength.

4.1.1 Properties of Film from Pure Starch

After heating cassava starch and water in a hot plate, slurry appears translucent and moderated viscous. A film that cast on a petri dish looks clear with a little white powder disperses on its matrix. Picture of cassava starch solution and film before drying is shown in figure 4.1.

After drying in an oven, film turns clear, colorless, and sticking on petri dish. Picture of cassava starch film after drying is shown in figure 4.2.

Figure 4.1: Cassava starch slurry and film before drying

Figure 4.2: Cassava starch film after drying

For potato starch, solution look milky white and high viscous. Film on petri dish look cloudy and has several clear pieces like jelly disperse in a film. Picture of potato starch solution and film before drying is shown in figure 4.3.

After drying, film looks transparent and easy to break. Picture of potato starch film after drying is shown in figure 4.4.

Figure 4.3: Potato starch slurry and film before drying

Figure 4.4: Potato starch film after drying

For arrowroot starch, solution look milky, and viscosity are highest. Film on petri dish look clear. Picture of arrowroot starch solution and film before drying is shown in figure 4.5.

After drying, film turns white and flaky. Picture of arrowroot starch film after drying is shown in figure 4.6.

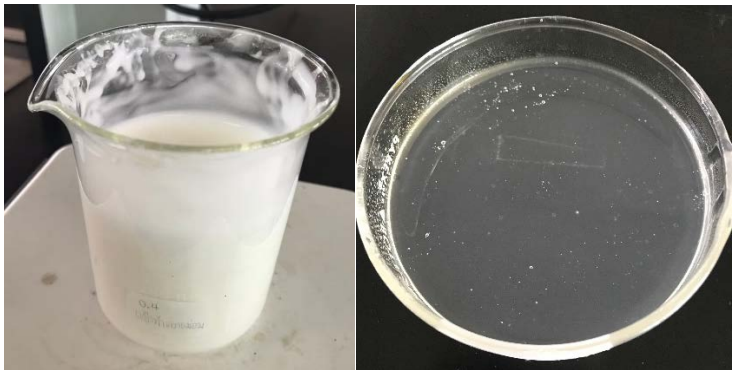


Figure 4.5: Arrowroot starch slurry and film before drying

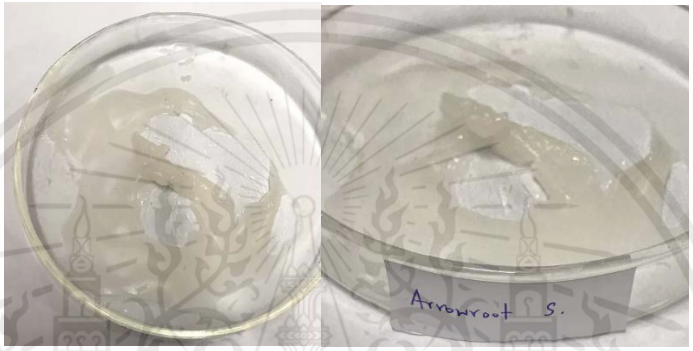


Figure 4.6: Arrowroot starch film after drying

The comparison of solution properties of these pure starches revealed that the arrowroot starch had the highest viscosity and strength. However, all these starches were not suitable to produce a bio-based film because starches since film turned translucent or white and flaky. Therefore, additives are required to improve the properties of the starches.

4.1.2 Properties of Film from Starch with Glycerol as Additive

For this experiment, the additive was added in the solution to improve properties of the starches. Glycerol was one of the additives that can increase the flexibility and chain mobility of polymers so, glycerol was added into the starch solutions to improve the features.

The solution of mixture of cassava starch and glycerol are light grey, translucent, and low viscous. Film on petri dish look clear. Picture of cassava starch with glycerol solution and film before drying is shown in figure 4.7.

After drying, film turns to a thin sheet and easy to tear. This film also has low strength and low flexibility. Picture of cassava starch with glycerol film after drying is shown in figure 4.8.

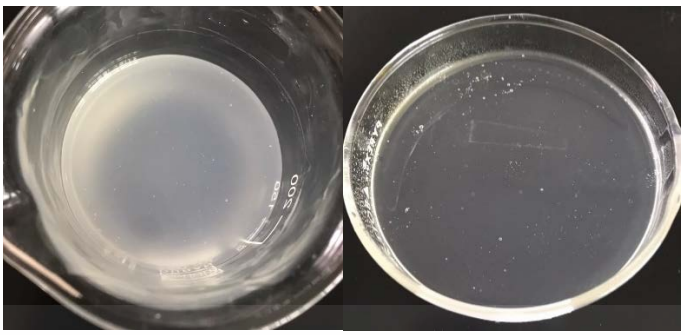


Figure 4.7: Cassava starch with glycerol slurry and film before drying

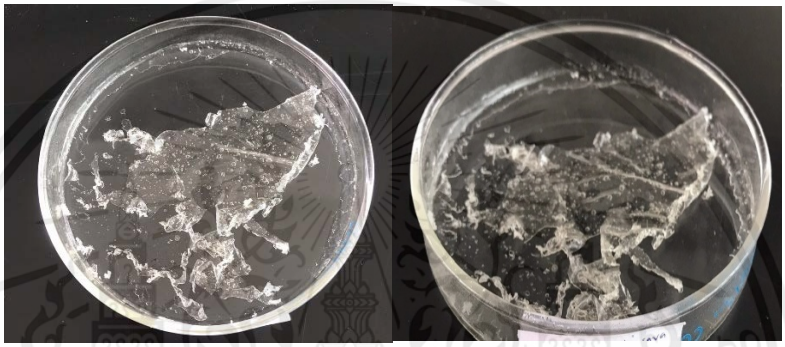


Figure 4.8: Cassava starch with glycerol film after drying

The solution of mixture of potato starch and glycerol are grey with bubbles and translucent. The mixture solution has a higher viscous than cassava starch in the previous solution. Picture of potato starch with glycerol solution and film before drying is shown in figure 4.9.

After drying, film turns to a thicker sheet than cassava starch. This film also has higher strength and flexibility than cassava starch in the previous one. Picture of potato starch with glycerol film after drying is shown in figure 4.10.

Figure 4.9: Potato starch with glycerol slurry and film before drying

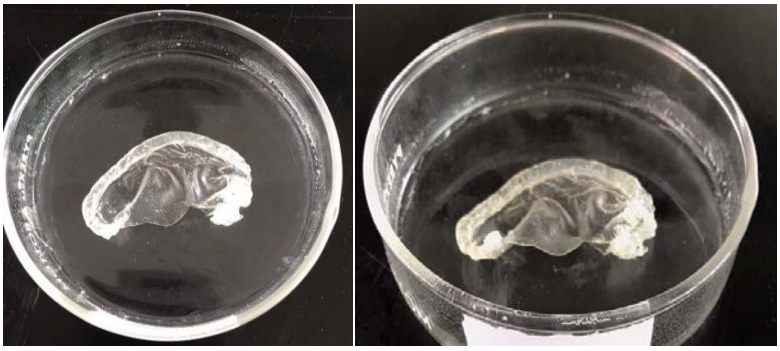


Figure 4.10: Potato starch with glycerol film after drying

The solution of mixture of arrowroot starch and glycerol are look milky and viscosity are highest. Film on petri dish look clear. Picture of arrowroot starch with glycerol solution and film before drying is shown in figure 4.11.

After drying, the film turns to a thick sheet. This film also has the highest strength and flexibility. Picture of arrowroot starch with glycerol film after drying is shown in figure 4.12.

Figure 4.11: Arrowroot starch with glycerol slurry and film before drying

Figure 4.12: Arrowroot starch with glycerol film after drying

When added glycerol into starch, the arrowroot had also the highest in flexibility, strength, and viscosity. However, the quality of all starches film is not good to produce packaging films. Therefore, the melting process in thermoplastic starches was one way to improve the properties of the bio-based film by using a twin-screw extruder.

4.2 Effect of Amount of Ingredients on Pre-Mixed Starch

The pre-mixed starch consisted of water, glycerol, cassava starch, and chitosan were mixed in HM-275; OTTO Kingglass dough mixer. The pre-mixed was a required step prior to send to twin-screw extruder. There were several trials to find a right amount of ingredient that yield suitable flowed properties to feed into twin-screw extruder.

From literature review, the weight ratio of cassava starch, chitosan, glycerol, and water were 58, 2, 25, and 15, respectively. Table 4.1 showed weight ratio of the 8 formulas.

Table 4.1: The weight ratio of the 8 formulas

Batch #	% wt.			
	Cassava Starch	Chitosan	Glycerol	Water
1	65	3.5	16.5	15
2	56.5	3.5	16.5	23.5
3	56.5	3.5	10	30
4	45	3	25	27
5	45	3	27	25
6	45	3	32	20
7	50	3	30	17
8	55	3	25	17

The batch #1 yield a pre-mixed that not integrated. It was clearly separated as loose soil as shown in figure 4.13. This might cause from very high amount of starch and less water to hold all ingredients together.

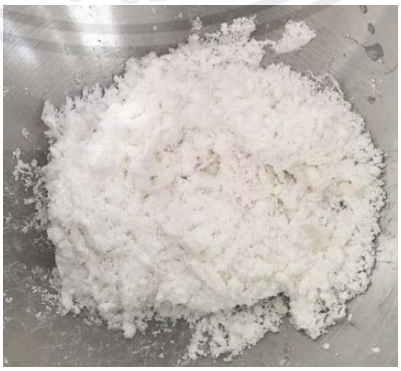


Figure 4.13: The sample in the first pre-mixing process

Batch #2, starch amount was reduced, and more water was added but still not enough to hold all ingredient. The pre-mixed was clearly aparted similar to batch #1 as shown in figure 4.14.

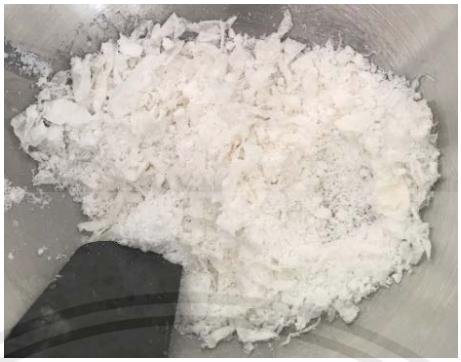


Figure 4.14: The sample in the second pre-mixing process

Batch #3, starch and chitosan amounts are same as batch #2. However, water was increased to 30 %wt. However, the pre-mixed was still not integrated as shown in figure 4.15.

Figure 4.15: The sample in the third pre-mixing process

Batch #4, the amount of starch was decreased to 45 %wt., and 25 %wt. and 27 %wt. of glycerol and water, respectively. The pre-mixed was in slurry form as shown in figure 4.16. This formula flowed like liquid and not appropriated to feed into twin-screw extruder.

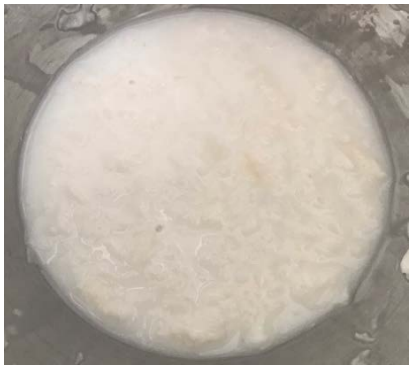


Figure 4.16: The sample in the fourth pre-mixing process

Batch #5, the amount of cassava starch and chitosan was same as batch #4. However, amount of glycerol and water was 27 and 25 %wt., respectively. The pre-mixed exhibits as high viscous liquid slurry as batch #4 as shown in figure 4.17.

Figure 4.17: The sample in the fifth pre-mixing process

Batch #6, the amount of starch and chitosan was same as batch #4 and 5. However, amount of glycerol and water was changed to 32 and 20 %wt., respectively. The pre-mixed started to form solid-like mixture but still too wet to put into an extruder as shown in figure 4.18. The result showed that increasing amount of glycerol yield a better pre-mixed.

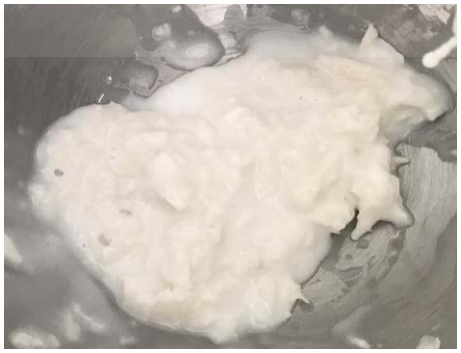


Figure 4.18: The sample in the sixth pre-mixing process

Batch #7, the amount of starch was increased to 50 %wt. and varied amount of glycerol and water to 30 and 17 %wt., respectively. For this weight ratio, the pre-mixed looked like a dough that was not too hard. When kneading, a sample would be hard and form a solid mass. However, after the pre-mixed loosened and flowed as a liquid. The pre-mixed of batch #7 is shown in figure 4.19.

Figure 4.19: The sample in the seventh pre-mixing process

Batch #8, the amount of starch was increased to 55 %wt. and decreased amount of glycerol to 25 %wt. The pre-mixed was turned back to a solid form that ingredient was not integrated as batch #1-3. Figure 4.20 showed a pre-mixed from batch #8. It was cleared that %wt. of starch more than 50 %wt. was not suitable to prepare a pre-mixed.

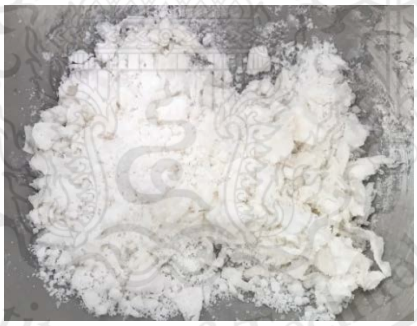


Figure 4.20: The sample in the eighth pre-mixing process

Based on the total of eight experiments, the batch #7 showed the suitable formula for pre-mixed.

4.3 Effect of Twin-Screw Extruder Condition on Thermoplastic Starch

In this part, the suitable formula from the pre-mixed process fed into twin-screw extruder to determine suitable conditions on thermoplastic starch (TPS).

Moreover, there were three parameters, i.e., temperature, screw speed of twin-screw extruder, and weight ratio of glycerol that were changed the conditions to

compare the physical properties of 19 samples. The range of parameters consists of minimum, center, and maximum value of three parameters.

The physical properties of TPS that were observed in each experiment. There are color, flexibility, strength, and texture. Table 4.2 showed the overall physical properties of the 19 experiments

Table 4.2: The overall physical properties of 19 experiments that was changed with different conditions

Batch #	Temperature (°C)	Screw Speed (rpm)	Glycerol (%wt.)	Observed Physical Properties of TPS				
				Color	Texture	Strength	Flexibility	Viscosity
1	100	81	28	Light Brown	Fine	Low	High	Low
2	130	81	28	Dark Brown	Fine	Low	High	Low
3	100	162	28	Light Brown	Rough	High	Low	Low
4	130	162	28	Dark Brown	Rough	High	Low	Low
5	100	81	32	Light Brown	Fine	Low	High	High
6	130	81	32	Dark Brown	Fine	Low	High	High
7	100	162	32	Light Brown	Rough	High	Low	High
8	130	162	32	Dark Brown	Rough	High	Low	High
9	100	81	28	Light Brown	Fine	Low	High	Low
10	130	81	28	Dark Brown	Fine	Low	High	Low
11	100	162	28	Light Brown	Rough	High	Low	Low
12	130	162	28	Dark Brown	Rough	High	Low	Low
13	100	81	32	Light Brown	Fine	Low	High	High
14	130	81	32	Dark Brown	Fine	Low	High	High
15	100	162	32	Light Brown	Rough	High	Low	High
16	130	162	32	Dark Brown	Rough	High	Low	High
17	115	121.5	30	Brown	Fine	Low	High	Low
18	115	121.5	30	Brown	Fine	Low	High	Low
19	115	121.5	30	Brown	Fine	Low	High	Low

Batch #1 and 9 are replicated experiment. The conditions are minimum value of temperature, screw speed, and %wt. of glycerol. The physical properties of batch #1 and 9. are identical The TPS that came out the extruder were light brown color, fine texture, low strength, high flexibility, and low viscosity. Photos of TPS from batch #1 and 9 are shown in figure 4.21.

Batch #1 Batch #9

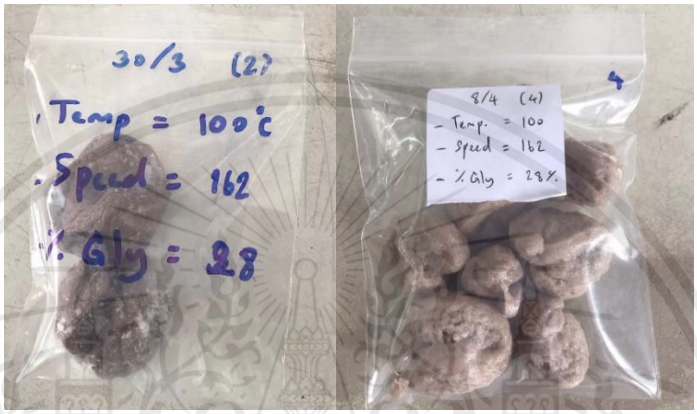
Figure 4.21: The TPS from batch #1 and 9

Batch #2 and 10 are also a duplicated experiment. Temperature of these batches are maximum while screw speed and %wt. of glycerol were same as batch #1 and 9. Most of properties were similar to batch #1 and 9, except color that was dark brown. Photos of these TPS are shown in figure 4.22. The increasing temperature affected only on color of TPS.

Batch #2 Batch #10

Figure 4.22: The TPS from batch #2 and 10

Batch #3 and 11, the screw speed of the twin-screw extruder is maximum at 162 rpm. However, other variables that consisted of temperature and %wt. of glycerol were same as batch #1 and 9. The three properties of TPS were changed. Texture was shifted from fine to rough while strength and flexibility were changed from low and high to high and low. The viscosity was unchanged. The increasing of screw speed was contributed to physical properties than temperature. Photos of TPS from batch #3 and 11 are shown in figure 4.23.



Batch #3 Batch #11

Figure 4.23: The TPS from batch #3 and 11

Batch #4 and 12, both temperature and screw speed were changed to the maximum conditions that were 130 ℃ and 162 rpm, respectively. Properties of these TPS are similar to batch #3 and 11, except the color. The TPS of these batches showed that temperature is only affected color of TPS. While screw speed affected on texture, strength, and flexibility. Photos of TPS from batch #4 and 12 are shown in figure 4.24.

Batch #4 Batch #12

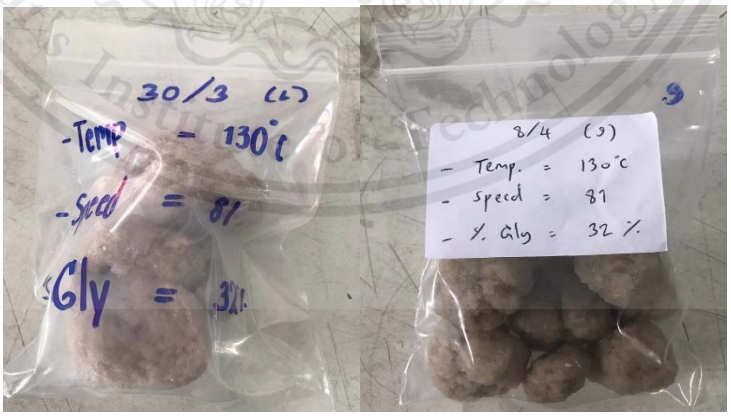
Figure 4.24: The TPS from batch #4 and 12

Batch #5 and 13, the condition of weight ratio of glycerol was changed to 32%wt. However, other conditions of temperature and screw speed were the same as batch #1 and 9. Properties of these TPS were similar to batch #1 and 9, except the viscosity. The increasing of weight ratio of glycerol was changed the viscosity of samples from low to high. The photos of TPS from of batch #5 and 13 are shown in figure 4.25.

Batch #5 Batch #13

Figure 4.25: The TPS from batch #5 and 13

Batch #6 and 14, Condition of these batches were almost same as batch #5 and 13, except for the temperature that changed to the highest at 130 ℃. The thermoplastic starch properties were similar to batch #5 and 13, except the color. These results also confirmed affected of temperature on TPS. Photos of these TPS are shown in figure 4.26.



Batch #6 Batch #14

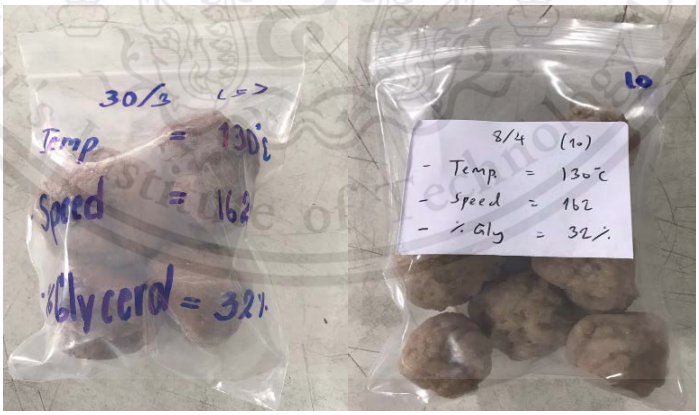
Figure 4.26: The TPS from batch #6 and 14

Batch #7 and 15, the conditions were the same as batch #5 and 13, except the screw speed that changed to 162 rpm while color and viscosity were same as batch #5 and 13. The 3 physical properties of batch #7 and 15 were different from batch #5 and 13. They showed rough texture, high strength, and low flexibility. The photos of TPS from batch #7 and 15 are shown in figure 4.27.

Batch #7 Batch #15

Figure 4.27: The TPS from batch #7 and 15

Batch #8 and 16, the temperature was increased to 130 °C from batch #7 and 15. Furthermore, the 4 physical properties of batch #8 and 16 were same as batch #7 and 15, except the color that changed to dark brown. Photos of these TPS are shown in figure 4.28.



Batch #8 Batch #16

Figure 4.28: The TPS from batch #8 and 16

For the center points, the conditions in batch #17 to 19 of the three variables that consisted of temperature, screw speed, and weight ratio of glycerol were 115 ℃, 121.5 rpm, and 30 %wt., respectively. The physical properties of thermoplastic starch were similar to batch #1 and 9. However, the color of center point conditions was changed from light brown to brown color. Photos of these TPS are shown in figure 4.29.

Batch #17 Batch #18 Batch #19

Figure 4.29: The TPS from batch #17, 18, and 19

The observed physical properties of the 19 batches informed that when varied speed from 81 to 121.5 rpm, and %wt. of glycerol from 28 to 30 %wt., texture, strength, flexibility, and viscosity were unchanged.

However, when increased screw speed to 162 rpm, texture, strength, and flexibility were shifted significantly. The changed in temperature from 100 to 115 and 130 ℃ caused the shifted of color from light brown to brown and dark brown, respectively. In addition, the highest %wt. of glycerol yield TPS to high viscosity.

4.4 Effect of Twin-Screw Extruder Condition on Crystallinity of TPS

Some samples of pre-mixed starch and TPS were analyzed by the Differential Scanning Calorimetry (DSC) to characterize crystallization, and latent heat (enthalpy) of crystallization, glass transition temperature (T_g), and heat flow.

Those samples were analyzed by using different heating method. The first one is heat from -80 to 80 ℃ to study the glass transition temperature (T_g). The second is heat from 25 to 250 ℃ to study crystallization and enthalpy.

Table 4.3 showed the glass transition temperature (T_g) of the 5 samples at different conditions in the twin-screw extruder. Furthermore, the graph of DSC analysis of the first heating method is shown in figure 4.30.

Table 4.3: The glass transition temperature (T_g) of samples

Batch #	Glycerol (%wt.)	Time in Twin Screw Extruder (Minutes)	Keep in Room Temperature for one week	T_g (°C)	Heat Flow (W/g)
1	30	0	No	19.86	-0.089
2	30	10	No	39.25	-0.159
3	30	30	No	52.85	-0.121
4	30	30	Yes	53.50	-0.080
5	32	30	No	23.78	-0.095

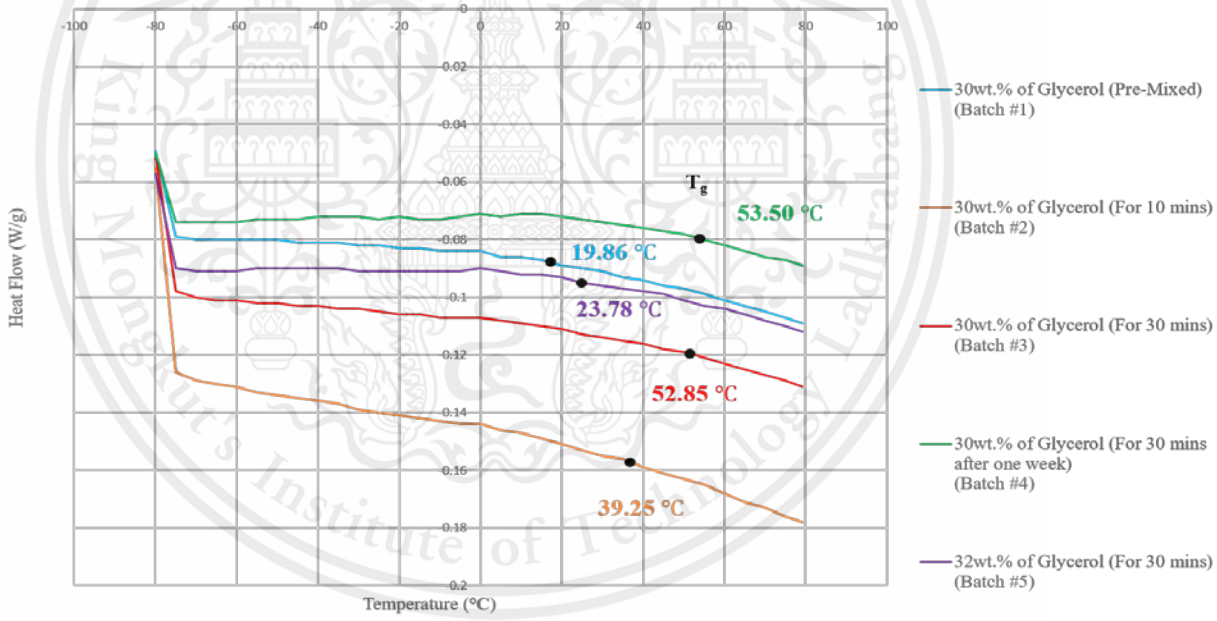


Figure 4.30: The graph of DSC analysis of the -80 °C to 80 °C

From the results of -80 to 80 °C heating method, it showed that batch #1 or the pre-mixed that not pass the extruder had lowest T_g at 19.86 °C. Batch #2 and 3 were same formula as batch #1. It was processed in an extruder at same condition as batch #17-19 in previous section.

The time in an extruder were investigated. The results revealed that the longer time yield a higher T_g. T_g of TPS when processed for 10 and 30 mins were 52.85 and 53.50 ℃, respectively.

Batch #4 were processed at same condition as batch #3 but kept at room temperature before analysis. The result showed that T_g was slightly increased to 53.50℃.

Batch #5 was TPS that increased %wt. of glycerol to 32 % and processed at same condition as batch #3. The result revealed that the increasing of glycerol yielded the lower T_g. The T_g of TPS was decreased to 23.78 ℃.

Figure 4.30 showed the heat flow (W/g) and T_g of these samples from -80 to 80 ℃.

Those curves showed different characteristic of each samples. Batch #5 with had 32 %wt. of glycerol, T_g that closer to pre-mixed (batch #1), batch #3 and batch #4, showed significant changed of heat flow due to different time in screw extruder.

For the second heating method, there are 3 samples that were analyzed to find crystallization temperature (T_c) and enthalpy. The results were shown in table 4.4 and figure 4.31. Those samples were processed similar to batch #1, 3 and 4 in table 4.3.

Table 4.4: The crystallization temperature (T_c) and enthalpy of samples in the second heating method

Batch #	Glycerol (%wt.)	Time in Twin-Screw Extruder (Minutes)	Keep in Room Temperature for one week	T_c (℃)	Enthalpy (J/g)
1	30	0	No	175.18	501.90
3	30	30	No	137.25 & 150.86	4.62 & 4.32
4	30	30	Yes	156.17	210.84

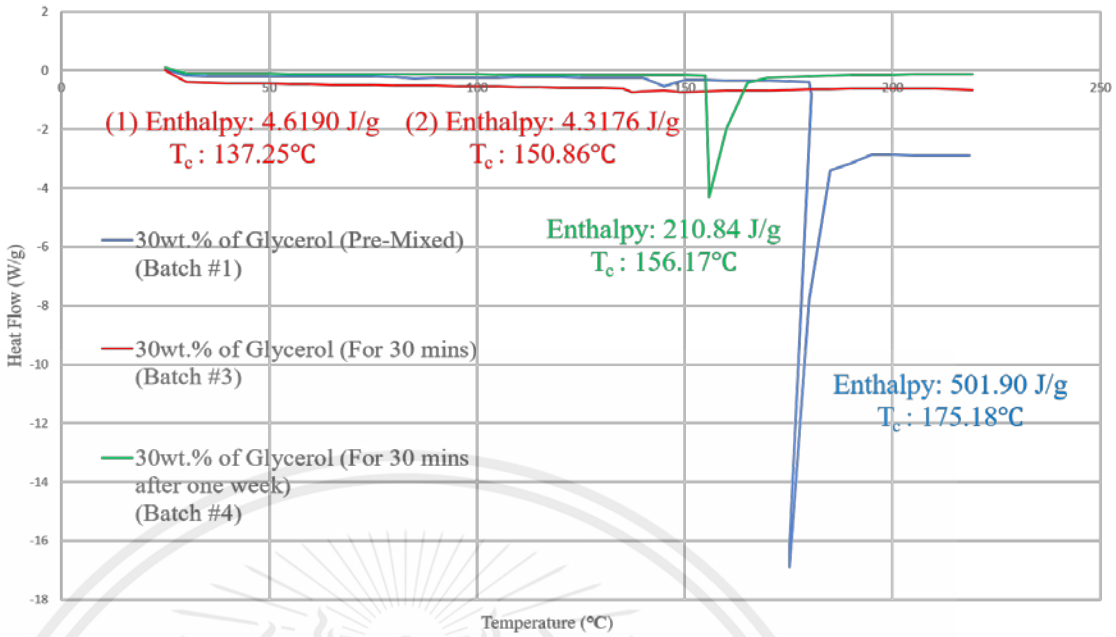


Figure 4.31: The graph of DSC analysis of the 25 ℃ to 250 ℃

From figure 4.31, the peak that show during increasing temperature revealed that the pre-mixed had higher % of crystallinity and T_c at 175.18 ℃. However, after passing through an extruder foe 30 mins, there are very small peak showed at 137.25 and 150.86 ℃. This confirmed that torque and heat in an extruder could destroy crystallinity in TPS.

However, the condition in screw extruder could not completely destroy crystallinity of starch. The batch #4 revealed that crystallinity in starch came back after kept sample for one week before analysis. The small peak was shown during was shown during DSC scanning.

The DSC analysis of these samples showed significant effect of extruder condition on properties of TPS. The process in extruder could increase T_g and destroy crystallinity of starch. When leave sample at room temperature for a week, T_g will slight change. However, crystallinity will come back.

CHAPTER 5: CONCLUSION

This chapter concluded the results and discussion from all experiments in chapter 4. Furthermore, there were five parts of experimental data results and recommendation that can be shown as the following:

5.1 The Properties of each Starch Film prepared by Slurry Method

When comparison a film that casting from cassava, potato, and arrowroot, film of the pure arrowroot starch had the highest viscosity and the highest strength. However, all these starches were not suitable to produce a bio-based film since easy to break. Therefore, adding the additives was one way to improve the properties of the starches.

When added glycerol into starch, the arrowroot film had also the highest in flexibility, strength, and viscosity. However, the quality of all starches film is not good to produce packaging films. Therefore, the melting process in thermoplastic starches was the way to improve the properties of the bio-based film by using a twin-screw extruder.

The slurry method could be used in the laboratory scale, but their films did not have enough flexibility and strength to produce a film in commercial scale.

5.2 Effect of Amount of Ingredients on Pre-Mixed Starch

An appropriate weight % of starch, chitosan, glycerol, and water were studied in the pre-mixing process was found by 8 trials.

The results showed that suitable ratios were %wt. of cassava starch, chitosan, glycerol, and water equal 50, 3, 30 and 17, respectively. This formula created a mixer that integrated in solid form but still able to flow like a dough. These experiments were also provided an upper bounded and lower bounded of each ingredient.

5.3 Effect of Twin-Screw Extruder Condition on Thermoplastic Starch

Effect of temperature, screw speed, and the weight ratio of glycerol on the physical properties of TPS were investigated. The total of 19 experiments were performed by using formula from previous section.

The properties such as color, texture, strength, viscosity, and flexibility were observed. The results show that screw speed was affected texture, strength, and

flexibility of TPS. Temperature and %wt. of glycerol were only affected on color and viscosity, respectively. The varied of speed from 81 to 121.5 rpm and %wt. of glycerol from 28 to 30 % did not change the properties of TPS.

5.4 Effect of Twin-Screw Extruder Condition on Crystallinity of TPS

The DSC analysis was used to observe the glass transition temperature, the latent heat of crystallinity, and the crystallinity of samples before and after passed through the S1-KRC Kneader twin-screw extruder. There were two heating methods in DSC analysis that consisted of the heating method from -80 to 80℃ and the heating method from 25 to 250℃, respectively.

In the -80 to 80 ℃ heating method, the results revealed that time in an extruder affected on T_g. The T_g for pre-mixed, 10 and 30 mins in an extruder were 19.86, 39.25 and 52.85 ℃, respectively. When left sample at room temperature for a week before analysis, T_g was slightly increased. The increasing of %wt. of glycerol showed slightly increased in T_g.

The 25 to 250 ℃ heating method revealed that the pre-mixed had high crystallinity and crystallinity temperature at 175.18 ℃. When processed the same pre-mixed in an extruder for 30 mins, the crystallinity was disappeared. However, if leave the TPS from extruder at room temperature for a week before analysis, the crystallinity will come back. These results revealed that process in a twin-screw extruder could lead to higher T_g in TPS and destroy crystallinity in TPS.

5.5 Recommendation

In this research project, the properties of TPS should be continued to investigate by using the Melt Flow Index (MFI) tester. The MFI tester can determine the flow behavior and the viscosity of the TPS at different temperatures that are found the most suitable formula to test whether TPS could be used in a blow film process.

REFERENCES

[1] M. Lackner, "Bioplastics," *Kirk-Othmer Encyclopedia of Chemical Technology*, pp. 1–41, 2015.

[2] S. Omondi, (2019). *What Are The Major Natural Resources Of Thailand?*. Retrieved 14 November 2020, from https://www.worldatlas.com/articles/what-are-the-major-natural-resources-of-thailand.html

[3] C. Ratanawaraha, (1999). *A review of cassava in Asia with country case studies on Thailand and Viet Nam*. Retrieved 20 November 2020, from http://www.fao.org/3/y1177e/Y1177E04.htm

[4] F. M. Pelissari, et al., "Constrained mixture design applied to the development of cassava starch–chitosan blown films," *Journal of Food Engineering*, vol. 108, no. 2, pp. 262–267, 2012.

[5] K. Huntrakul, et al., "Effects of pea protein on properties of cassava starch edible films produced by blown-film extrusion for oil packaging," *Food Packaging and Shelf Life*, vol. 24, p. 100480, 2020.

[6] S. Kumar, and K. Thakur, "Bioplastics - classification, production and their potential food applications," *Journal of Hill Agriculture*, vol. 8, no. 2, p. 118, 2017.

[7] K. Sriroth, et al., "Cassava starch granule structure–function properties: influence of time and conditions at harvest on four cultivars of cassava starch," *Carbohydrate Polymers*, vol. 38, no. 2, pp. 161–170, 1999.

[8] A. H. D. Abdullah, et al., "Physical and chemical properties of corn, cassava, and potato starchs," *IOP Conference Series: Earth and Environmental Science*, vol. 160, p. 012003, 2018.

[9] S. Brooks, (2016). *Cassava Starch Processing and Production*. Retrieved 20 November 2020, from https://www.streambrooks.com/post-6/

[10] R. T. Morrison, and R. N. Boyd, (1992). *Organic Chemistry, 6th Edition* (6th ed.). Prentice Hall.

[11] D. Garlotta, "A literature review of poly(lactic acid)," *Journal of Polymers and the Environment*, vol. 9, no. 2, pp. 63–84, 2001.

[12] Y. X. Weng, et al., "Biodegradation behavior of poly(butylene adipate-co-terephthalate) (PBAT), poly(lactic acid) (PLA), and their blend under soil conditions," *Polymer Testing*, vol. 32, no. 5, pp. 918–926, 2013.

[13] J. Huang, et al., "A study on degradation of composite material PBS/PCL," *Polymers and Polymer Composites*, vol. 24, no. 2, pp. 143–148, 2016.

[14] PTT Public Company Limited. (2010). *Petroleum and Alternative Energy Encyclopedia*. Retrieved 25 November 2020, from https://www.thailand- energ y- academy.org/th/energy/detail/2

[15] M. N. Subramanian, *Introduction to polymer compounding: machinery and technology*. Shropshire, England: Smithers Rapra Technology, 2015.

[16] A. Lindström, *Environmentally friendly plasticizers for PVC: improved material properties and long-term performance through plasticizer design*. Stockholm: Fiber- och polymerteknologi Fibre and Polymer Technology, 2007.

[17] S. Kantima, and S. Phimphilai, (2555). Effect of Glycerol and Potassium Sorbate on Properties of Tapioca Starch Films Treated with Ultraviolet Radiation. *Maejo University.*

[18] J. R. Rodríguez-Núñez, et al., "Chitosan/hydrophilic plasticizer-based films: preparation, physicochemical and antimicrobial properties," *Journal of Polymers and the Environment*, vol. 22, no. 1, pp. 41–51, 2013.

[19] A. I. Balqis, et al., "Effects of plasticizers on the physicochemical properties of kappa-carrageenan films extracted from Eucheuma cottonii," *International Journal of Biological Macromolecules*, vol. 103, pp. 721–732, 2017.

[20] R. Bodirlau, C.-A. Teaca, and I. Spiridon, "Influence of natural fillers on the properties of starch-based biocomposite films," *Composites Part B: Engineering*, vol. 44, no. 1, pp. 575–583, 2013.

[21] M. Sapper, P. Talens, and A. Chiralt, "Improving functional properties of cassava starch-based films by incorporating xanthan, gellan, or pullulan gums," *International Journal of Polymer Science*, vol. 2019, pp. 1–8, 2019.

[22] T. T. V. Phan, et al., "Chitosan as a stabilizer and size-control agent for synthesis of porous flower-shaped palladium nanoparticles and their applications on photo-based therapies," *Carbohydrate Polymers*, vol. 205, pp. 340–352, 2019.

[23] "Stabilizing agricultural films: a question of balance," *Plastics, Additives and Compounding*, vol. 5, no. 4, pp. 20–23, 2003.

[24] V. Ambrogi, et al., "Additives in polymers," *Modification of Polymer Properties*, pp. 87–108, 2017.

[25] V. R. Sastri, “Commodity thermoplastics,” *Plastics in Medical Devices*, pp. 73–120, 2014.

[26] B. A. Strong, (2005). *Plastics: Materials and Processing (3rd Edition)* (3rd ed.). Pearson.

[27] H. Murata, (2012). *Rheology - Theory and Application to Biomaterials*. Retrieved 19 April 2021, from https://www.intechopen.com/books/polymerization/rheology-theory-and-application-to-biomaterials

[28] RheoSense. *Viscosity of Newtonian and Non-Newtonian Fluids*. Retrieved 5 May 2021, from https://www.rheosense.com/applications/viscosity/newtonian-non-newtonian

[29] *Non- Newtonian fluids*. Retrieved 5 May 2021, from https://www.sciencelearn.org.nz/resources/1502-non-newtonian-fluids

[30] *Investigation of Polymers with Differential Scanning Calorimetry*. Retrieved 5 May 2021, from https://docplayer.net/23045605-Investigation-of-polymers-with-differential-scanning-calorimetry.html

[31] W. Khunthachai, (2012). *Development edible films and coatings based on rice flour and application of Toffee fruit.* Retrieved 5 May 2021, from http://fic.nfi.or.th/knowlegdedatabankResearch-detail.php?id=810

[32] *HM- 275; OTTO Kingglass dough mixer.* Retrieved 19 January 2021, from https://www.otto.co.th/product/24250-19850/%

[33] N. Kitahorie, (2014). *KRC Kneader -Twin Screw Continuous Kneader.* Retrieved 19 January 2021, from http://www.kurimoto.co.jp/worldwide/en/product/item/07pw/010.php

[34] N. Kitahorie, (2019). *Continuous Compact Kneading (Reacting) Processor for Research and Development S1KRC Kneader.* Retrieved 19 January 2021, from http://www.kurimoto.co.jp/worldwide/en/product/item/07pw/020.php

APPENDICES

APPENDIX A

The Pure Data from DSC Analysis

From the first heating method: -80℃ to 80℃

Appendix Table A.1: The first heating method of batch #1

Fresh Raw Materials	
Temperature	Heat Flow
°C	W/g
-80.05	-0.05
-80	-0.049
-75	-0.079
-70	-0.08
-65	-0.08
-60	-0.08
-55	-0.08
-50	-0.08
-45	-0.081
-40	-0.081
-35	-0.081
-30	-0.082
-25	-0.082
-20	-0.083
-15	-0.083
-10	-0.084
-5	-0.084
0	-0.084
5	-0.086
10	-0.086
15	-0.087
20	-0.089
25	-0.09
30	-0.091
35	-0.093
40	-0.094
45	-0.096
50	-0.097
55	-0.099
60	-0.101
65	-0.103
70	-0.105
75	-0.107
79.22	-0.109

Appendix Table A.2: The first heating method of batch #2

30 wt.% of Glycerol (For 10 minutes)	
Temperature	Heat Flow
°C	W/g
-80.05	-0.056
-80	-0.055
-75	-0.126
-70	-0.129
-65	-0.13
-60	-0.131
-55	-0.133
-50	-0.134
-45	-0.135
-40	-0.136
-35	-0.137
-30	-0.139
-25	-0.14
-20	-0.141
-15	-0.142
-10	-0.143
-5	-0.144
0	-0.144
5	-0.146
10	-0.147
15	-0.149
20	-0.151
25	-0.153
30	-0.155
35	-0.156
40	-0.159
45	-0.161
50	-0.163
55	-0.165
60	-0.168
65	-0.171
70	-0.173
75	-0.176
79.2	-0.178

Appendix Table A.3: The first heating method of batch #3

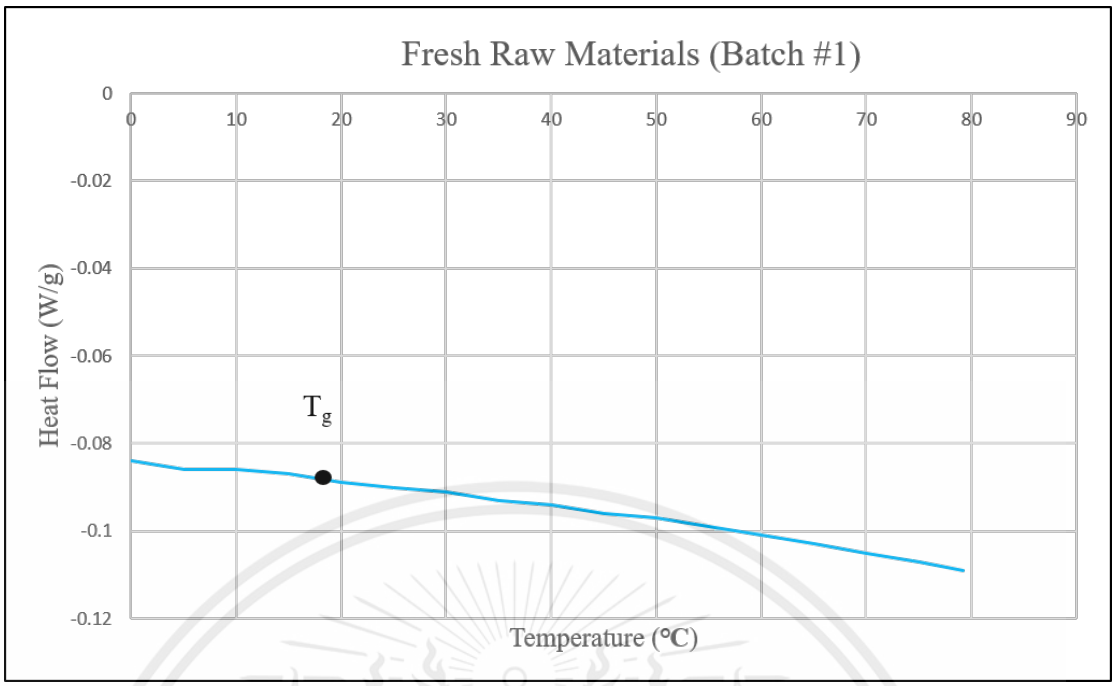
30 wt.% of Glycerol (For 30 minutes)	
Temperature	Heat Flow
°C	W/g
-80.05	-0.052
-80	-0.05
-75	-0.098
-70	-0.1
-65	-0.101
-60	-0.101
-55	-0.102
-50	-0.102
-45	-0.103
-40	-0.103
-35	-0.104
-30	-0.104
-25	-0.105
-20	-0.106
-15	-0.106
-10	-0.107
-5	-0.107
0	-0.107
5	-0.108
10	-0.109
15	-0.11
20	-0.111
25	-0.113
30	-0.114
35	-0.115
40	-0.116
45	-0.118
50	-0.119
55	-0.121
60	-0.123
65	-0.125
70	-0.127
75	-0.129
79.21	-0.131

Appendix Table A.4: The first heating method of batch #4

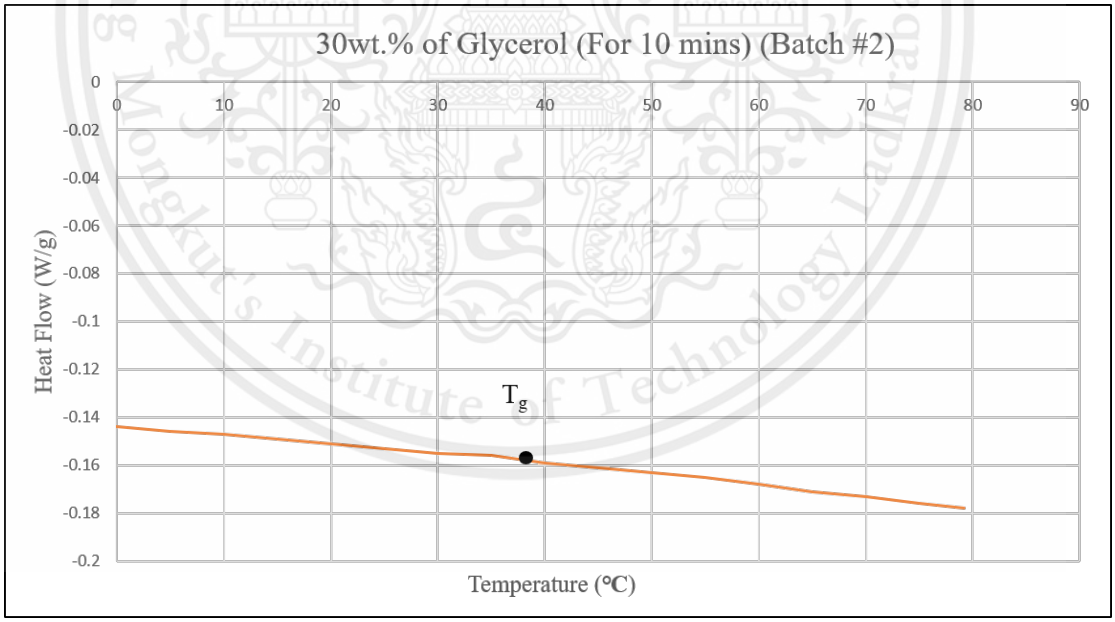
30 wt.% of Glycerol (For 30 minutes after one week)	
Temperature	Heat Flow
°C	W/g
-80.05	-0.051
-80	-0.05
-75	-0.074
-70	-0.074
-65	-0.074
-60	-0.074
-55	-0.073
-50	-0.073
-45	-0.073
-40	-0.072
-35	-0.072
-30	-0.072
-25	-0.073
-20	-0.072
-15	-0.073
-10	-0.073
-5	-0.072
0	-0.071
5	-0.072
10	-0.071
15	-0.071
20	-0.072
25	-0.073
30	-0.074
35	-0.075
40	-0.076
45	-0.077
50	-0.078
55	-0.08
60	-0.082
65	-0.084
70	-0.086
75	-0.087
79.22	-0.089

Appendix Table A.5: The first heating method of batch #5

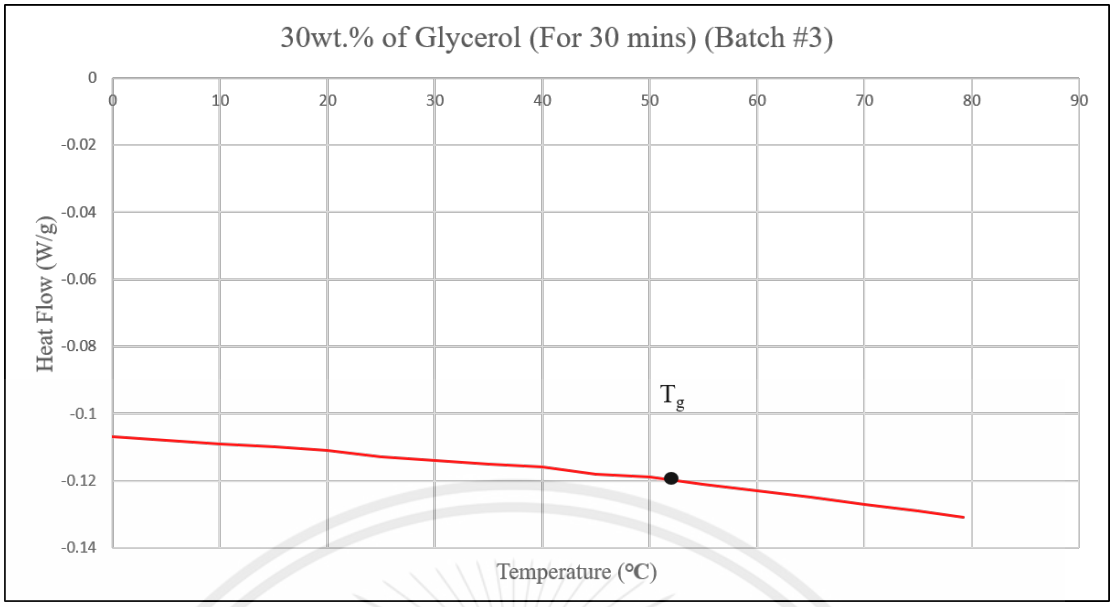
32 wt.% of Glycerol (For 30 minutes)	
Temperature	Heat Flow
°C	W/g
-80.05	-0.057
-80	-0.057
-75	-0.09
-70	-0.091
-65	-0.091
-60	-0.091
-55	-0.09
-50	-0.09
-45	-0.09
-40	-0.09
-35	-0.09
-30	-0.091
-25	-0.091
-20	-0.091
-15	-0.091
-10	-0.091
-5	-0.091
0	-0.09
5	-0.091
10	-0.092
15	-0.092
20	-0.093
25	-0.095
30	-0.096
35	-0.097
40	-0.098
45	-0.099
50	-0.101
55	-0.103
60	-0.104
65	-0.106
70	-0.108
75	-0.11
79.22	-0.112



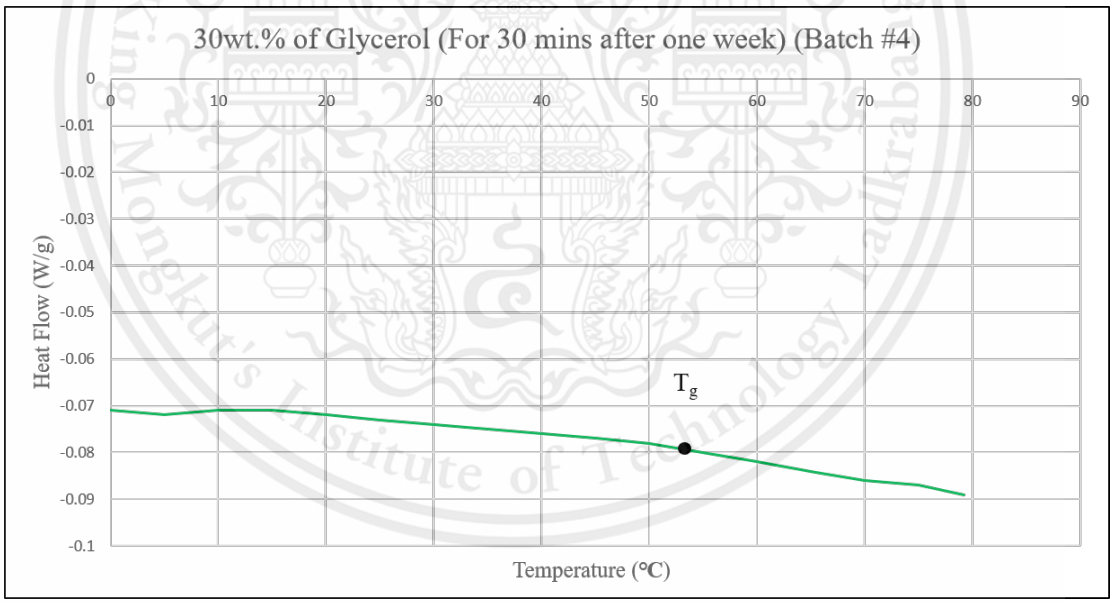
Appendix Figure A.1: The first heating method of batch #1



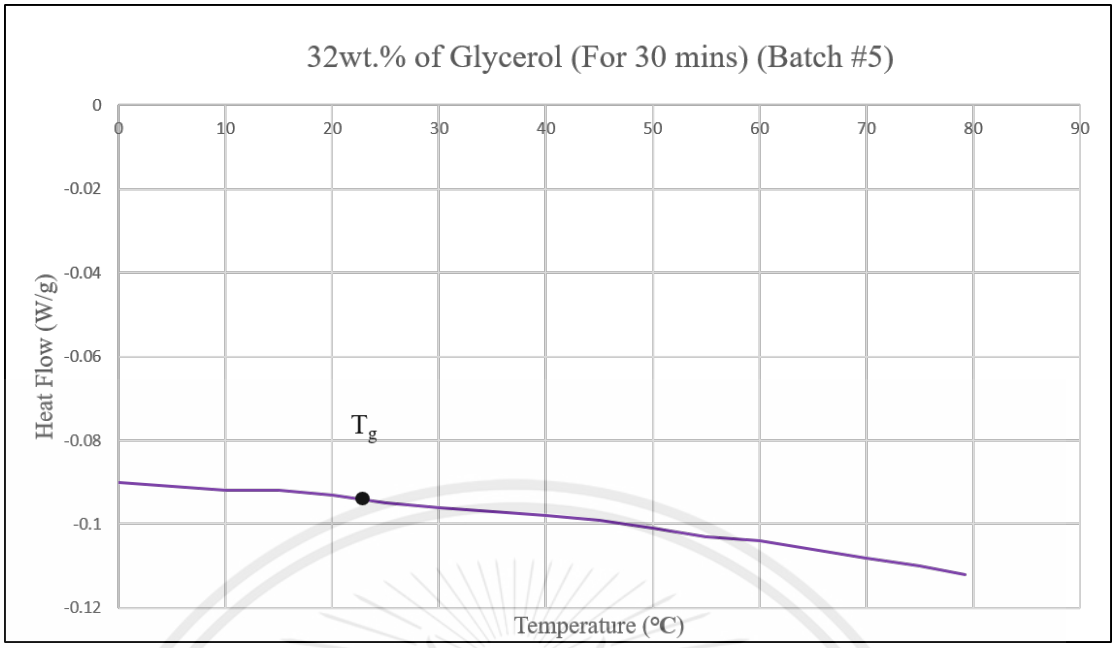
Appendix Figure A.2: The first heating method of batch #2



Appendix Figure A.3: The first heating method of batch #3



Appendix Figure A.4: The first heating method of batch #4



Appendix Figure A.5: The first heating method of batch #5

From the second heating method: 25℃ to 250℃

Appendix Table A.6: The second heating method of batch #1

Fresh Raw Materials	
Temperature	Heat Flow
°C	W/g
24.98	0.044
25	0.022
25	0.021
30	-0.181
35	-0.186
40	-0.188
45	-0.191
50	-0.193
55	-0.195
60	-0.198
65	-0.201
70	-0.203
75	-0.208
80	-0.22
85	-0.26
90	-0.243
95	-0.242
100	-0.242
105	-0.238
110	-0.23
115	-0.229
120	-0.232
125	-0.234
130	-0.244
135	-0.245
140	-0.251

Appendix Table A.7: The second heating method of batch #1 (Continued)

Fresh Raw Materials	
Temperature	Heat Flow
°C	W/g
145	-0.534
150	-0.319
155	-0.322
160	-0.333
165	-0.343
170	-0.353
175	-0.365
180	-0.392
180.5	-0.804
175.3	-16.136
175.27	-16.262
175.24	-16.374
175.15	-16.748
175.14	-16.792
175.14	-16.856
175.14	-16.893
179.99	-7.802
185	-3.408
190	-3.143
195	-2.863
200	-2.859
205	-2.875
210	-2.893
215	-2.89
218.43	-2.889

Appendix Table A.8: The second heating method of batch #3

30 wt.% of Glycerol (For 30 minutes)	
Temperature	Heat Flow
°C	W/g
24.98	0.029
25	-0.009
25	-0.011
25	-0.012
30	-0.398
35	-0.42
40	-0.431
45	-0.441
50	-0.45
55	-0.459
60	-0.468
65	-0.478
70	-0.486
75	-0.496
80	-0.505
85	-0.514
90	-0.522
95	-0.531
100	-0.54
105	-0.549
110	-0.557
115	-0.566
120	-0.576
125	-0.587
130	-0.6
135	-0.623
136.87	-0.72
136.99	-0.728
137.04	-0.73
137.84	-0.734
140	-0.711
145	-0.694

Appendix Table A.9: The second heating method of batch #3 (Continued)

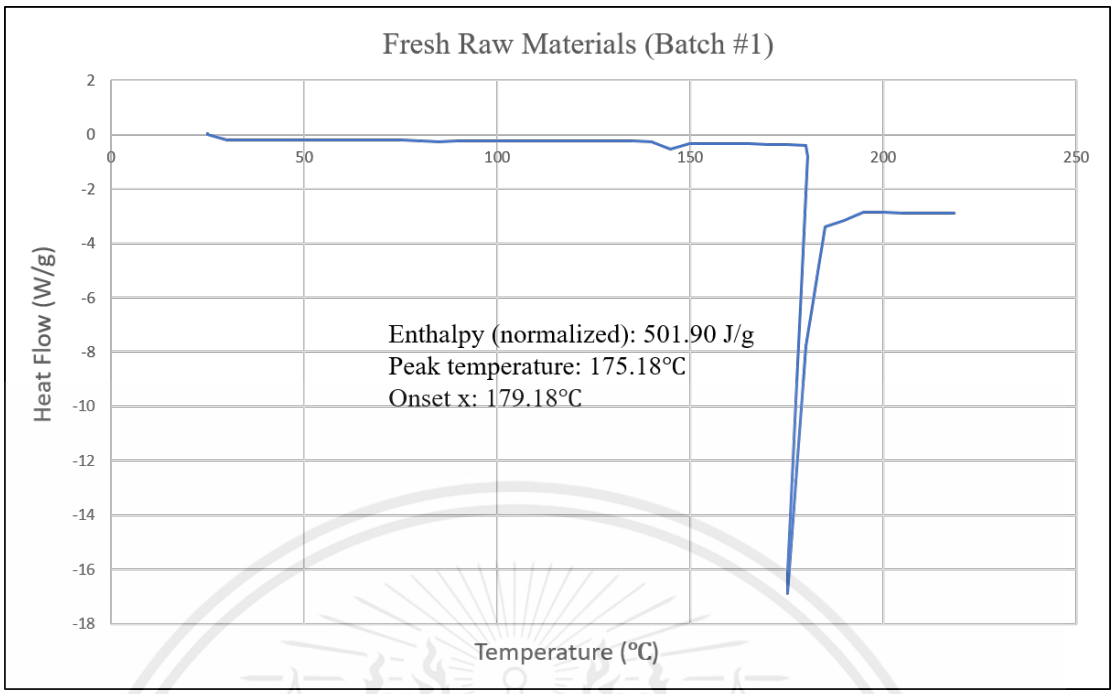
30 wt.% of Glycerol (For 30 minutes)	
Temperature	Heat Flow
°C	W/g
147.56	-0.7
148.73	-0.728
149.46	-0.733
149.95	-0.738
149.97	-0.74
150	-0.744
155	-0.722
160	-0.694
165	-0.683
170	-0.677
175	-0.671
180	-0.645
185	-0.628
190	-0.619
192.47	-0.618
194.26	-0.617
195.44	-0.618
196.11	-0.619
196.46	-0.62
196.83	-0.621
200	-0.62
205	-0.618
210	-0.621
215	-0.633
219.14	-0.651

Appendix Table A.10: The second heating method of batch #4

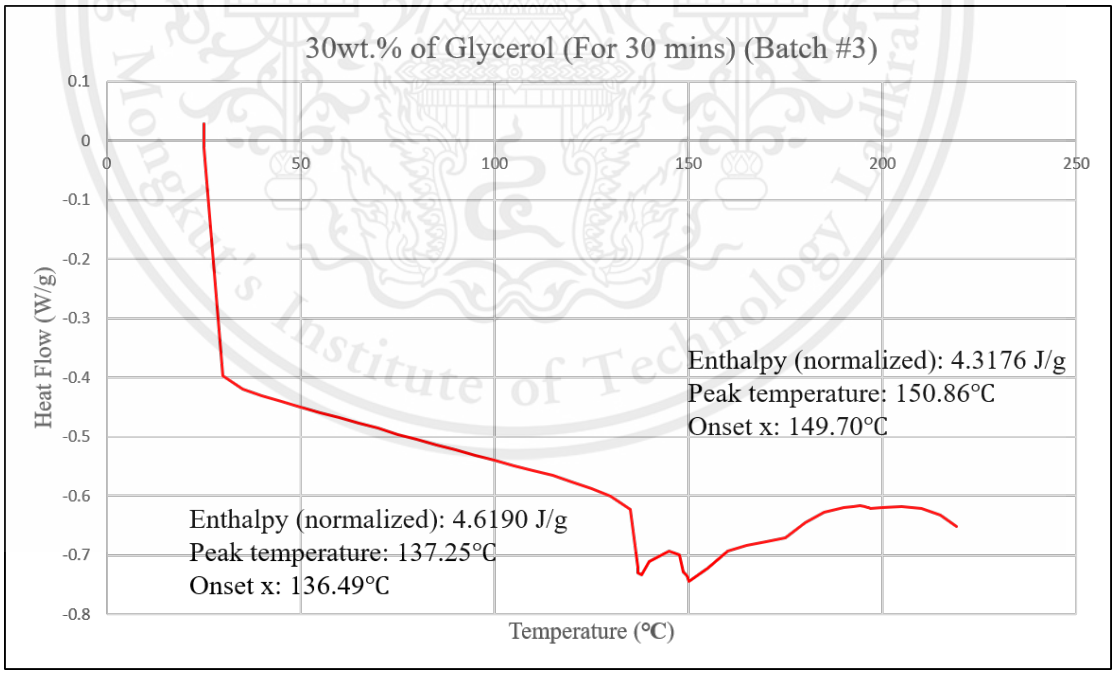
30 wt.% of Glycerol (For 30 minutes after one week)	
Temperature	Heat Flow
°C	W/g
25.03	0.096
30	-0.097
35	-0.106
40	-0.108
45	-0.11
50	-0.111
55	-0.113
60	-0.115
65	-0.117
70	-0.12
75	-0.122
80	-0.124
85	-0.126
90	-0.127
95	-0.129
100	-0.133
105	-0.141
110	-0.149
115	-0.15
120	-0.148
125	-0.143
130	-0.143

Appendix Table A.11: The second heating method of batch #4 (Continued)

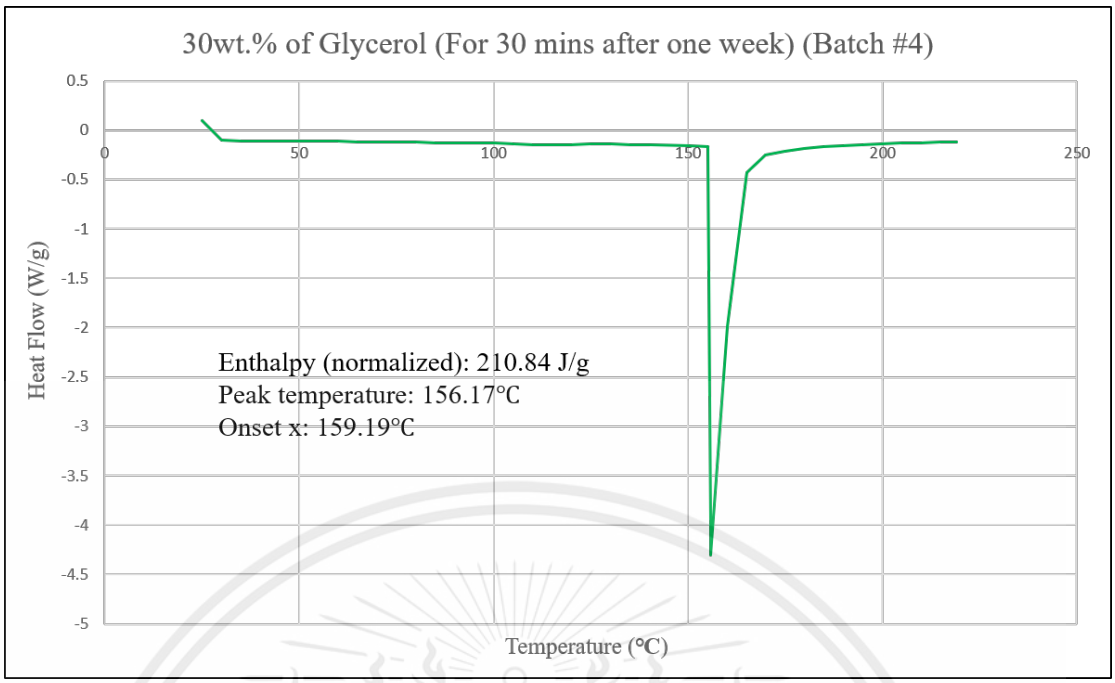
30 wt.% of Glycerol (For 30 minutes after one week)	
Temperature	Heat Flow
°C	W/g
135	-0.148
140	-0.151
150	-0.16
155	-0.168
155.87	-3.96
155.87	-4.304
160	-1.99
165	-0.426
170	-0.252
175	-0.214
180	-0.188
185	-0.17
190	-0.156
195	-0.145
200	-0.137
205	-0.13
210	-0.127
215	-0.124
219.14	-0.121



Appendix Figure A.6: The second heating method of batch #1



Appendix Figure A.7: The second heating method of batch #3



Appendix Figure A.8: The second heating method of batch #4

APPENDIX B

The Sample Color Comparison through Twin-Screw Extruder

The samples at center point after passed through the S1-KRC Kneader twin-screw extruder in different time

(A) (B) (C) (D)

Appendix Figure B.1: The different color of the samples after had passed through the S1-KRC Kneader twin-screw extruder

(A) The sample had passed through the twin-screw extruder only one time.
(B) The sample had passed through the twin-screw extruder for 10 minutes.
(C) The sample had passed through the twin-screw extruder for 20 minutes.
(D) The sample had passed through the twin-screw extruder for 30 minutes.

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