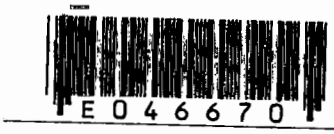
PLASTIC FILMS FROM TAPIOCA STARCH



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ABSTRACT

This special project studied about blown film molding technique of biodegradable plastic produced from tapioca starch. Biodegradable plastic was obtained from the blending of modified starch graft copolymer (MS) with low density polyethylene (LDPE). Blending studies were 11 conditions following the process line of blown film extrusion, the machine was operated to produce the plastic films. From the study, it was found that the 2nd condition (LDPE+2%MS) and the conditions which not more than 6%MS content in LDPE were suitable composition to produce plastic films when compared with LDPE. The optimum condition of blown film extrusion, temperatures setting at the Feed Zone, Compression Zone and Metering Zone of the single-screw extruder were 140, 150 and 160 degree Celsius, respectively and the rotor speed of the screw was 95 rpm. The blown film temperature setting at Zone S-adaptor and Die Zone were 180 degree Celsius. The finished products were tested to compare with LDPE (LD1905FA). Their mechanical properties were found as (tensile strength: 4.401 N/mm^2, elongation: 396.06 %, modulus: 23.383 N/mm^2). The physical properties of water absorption were 3.76%. Their thermogravimetric analysis is shown that after added the DEG stabilizer, the products have more stable than pure modified starch.

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Abbreviations

AGU	:	Anhydroglucose unit
ASTM	:	American standard test method
CAN	:	Ceric ammonia nitrate
CMC	:	Critical micelle concentration
CMS-g-AM	:	Carboxymethyl starch graft acrylamide
DEG	:	Diethylene glycol
DOP	:	Dioctyl phthalate
EB	:	Elongation at break
FT-IR	:	Fourier transform infrared spectrometer
HDPE	:	High density polyethylene
LDPE	:	Low density polyethylene
LDPE1905FA	:	Low density polyethylene (blown film grade 1905FA)
LLDPE	:	Linear low density polyethylene
MA	:	Methyl acrylate
MS	:	Modified starch
PE	:	Polyethylene
PEG 400	:	Polyethylene glycol 400
PPG 2000	:	Polypropylene glycol 2000
SDS	:	Sodium dodecyl sulfate
SEM	:	Scanning electron microscope
SS	:	Sago starch
TGA	:	Thermal gravimetric analysis
TMP	:	Trimethylol propane
TPNR	:	Thermoplastic natural rubber

Chapter 1
Introduction

Plastics have become an integral part of everyday life, and have been used for a multitude of purposes. They are ordinarily light weight, durable, and easily molded into a variety of forms. Plastics have also achieved a dominant position in agriculture which has the new description "plasticulture" to describe the use of plastics in greenhouses, in protective covers for crops (mulching films), etc.

Plastics will double in usage volume during the next decade if raw materials are available. In recognition of this growth potential, interest has increased in the use of natural polymers as extenders for plastics and as total replacements for certain types of plastics. Not only is it the renewable aspect of raw material of such natural polymers to impart biodegradability to fabricated materials. Because of concern over buildup in the environment of discarded plastic goods due to their resistance to microorganisms, the plastics industry is giving considerable attention to this area. If plastics can be made readily biodegradable, new markets for such materials would materialize, and the growth for plastics would likely exceed even the most liberal estimates.

The increasing use of plastics means ever increasing disposal problems of plastic waste. Although the amount of plastic waste in the waste stream is small, but it is increased accumulated because of its inability to degradable. In terms of weight, they only make up 8% of solid waste stream, but in volume terms their proportion comes to about 30%.

This is due to the relatively low bulk density of polymers in comparison to the other materials. At present possible role to solve the problem of waste are as followed:

1. Landfill is one of the most effective methods in the past because of its low cost. However, when considering burial in a landfill, volume percent is more important than weight percent, since the amount of space a material takes up in a landfill is more important than the weight of the material. Landfill burial costs are increasing as a result of the diminishing space and newly introduced treatment cost. Besides, they can result in environmental problems such as polluted soil and groundwater.

2. Incineration of plastic waste via clean and controlled combustion for energy generation is another way but the disadvantages are as followed:
- Creation of permanent environmental contamination.
- The cost for construction a large plant would be high.
- Prevention of emission from waste incineration plants is difficult.
- Incineration has no ecological advantages.

3. Recycle is simple and widely used today. In general, there are two possible recycling methods for this type of waste. The first one emphasizes on the process of cleaning and separation, so that the end result of the processing is a re-granulate which is close to the pure material in all its properties. The second recycling method gets round the high costs associated with cleaning and separation. The result is a raw material for the manufacture of mixed plastic products. The advantage of this process is low cost of the technological operation. But the disadvantage is the fact that a recycled plastic is of lower quality. Even if it is possible to produce short lived objects from this

kind of recycled materials, which will soon be waste again. That means we still have face the problem of what the final method for the recycling of the waste should be [1].

Polyethylene plastic is among the most dominant packaging materials in today's society. Similar to other packaging products, when products from polyethylene reach the end of their useful life, most are discarded in open dumps, landfills, or as simple litter. These materials have the disadvantage of not being degradable.

However, in some practical applications it is advantageous to have materials that decompose after either a longer or shorter time following completion of their use. Obviously, there is a need for biodegradable plastics which is environmentally friendly material.

Biodegradable plastics have branched into several district areas. Graft polymerization of thermoplastic polymers onto natural polymer such as starch is the most interesting one. An important advantage of graft copolymerization is the fact that natural and synthetic components are held together by chemical bonding rather than existing merely as a physical mixture. The two dissimilar polymers therefore tend to be more intimately associated and separation of the two polymer phases can not occur.

The ideal solution of "Plastics Degradability" has been introduced as a method to solve the disposal problem of plastics as well as other products used frequently. Degradable plastics are the new type of "Environmentally-friendly" packaging material that used to erase the pollution of natural environments, which is caused by uncontrolled solid waste disposal.

1.1 Objectives

1.1.1 To produce biodegradable plastics that could be environmental friendly.
1.1.2 To study the blown film processing of the biodegradable plastic product produced from tapioca starch.
1.1.3 To characterize the biodegradable plastic film properties produced from tapioca starch.

1.2 Scope of This Work

Producing the thermoplastic polyethylene film from chemical modification tapioca starch to find the ratio of the modified tapioca starch blended with polyethylene plastic. To investigate the mechanical properties such as tensile, elongation at break, modulus properties and characterization of tapioca starch graft copolymer. Also includes to study a biodegradation of plastic films. To characterize biodegradable plastic film by using scanning electron microscope (SEM), fourier transform infrared spectrometer (FT-IR), and thermogravimetric analysis machine (TGA).

Chapter 2
Related Literatures

2.1 Starch

Starch is one of the most abundant plant materials in the world. It is polysaccharide of repeating glucose units. Starch is extracted from plant sources as discrete granules that range in diameter from about 5 to 40 micrometer. Starch granules are insoluble in water at room temperature. They vary in size and shape depending on the plant source.

2.1.1 Chemical Structure and Composition of Starch [2]

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 as an empirical formula of $C_6H_{10}O_5$, placing in the class of carbohydrate. It is a condensation polymer of glucose. Starch is granular form is generally composed of two types of molecules, amylose and amylopectin. It is a mixture of linear and branched polymers of 1, 4-α-D-glucopyranosyl (anhydroglucose [AGU]) units.

Amylose is a linear polymer in which the anhydroglucose units are liked together by α-D (1→4) glucosidic bonds. Amylose has a molecular weight of the order of several hundred thousand. The level of amylose found in starch varies depending upon the starch source. Most starches contain about 18 to 28% amylose (Figure 2.1).

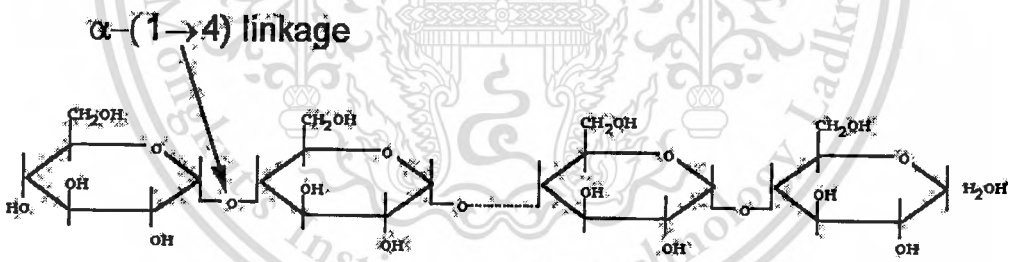


Figure 2.1 Representative structure of linear amylose

Amylopectin is a branched component of starch, it forms major constituent with a molecular weight of several million. Amylopectin considering like amylose of mostly α-D (1→4) glucosidic bonds but branching occurs at the carbon-6 position. These branches are linked to C6 atom by α-D (1→6) glucosidic bonds at about 1 in every 25 anhydroglucose units (Figure 2.2).

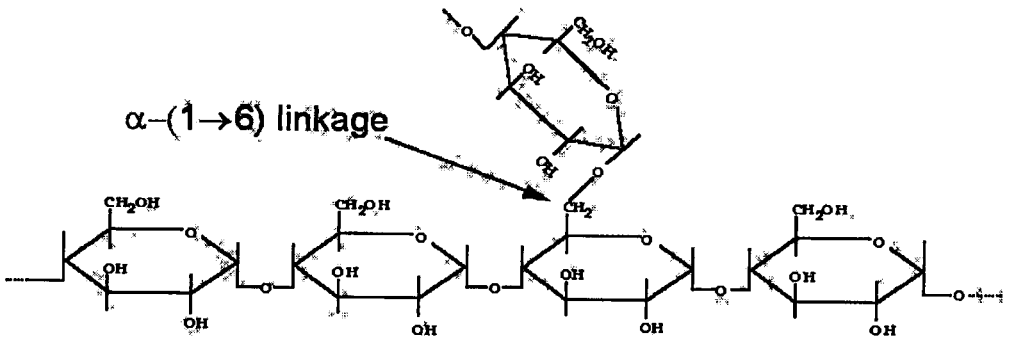


Figure 2.2 Representative structure of amylopectin, including (1, 6)-α-D branch point

2.1.2 Properties of starch [3]

Physicochemical Properties

Undamaged starch granules are insoluble in cold water, but can reversibly absorb water and swell when their aqueous dispersion is heated. In water at 25°C, the percentage increase in granule diameter ranges from 9.1% for normal (native) corn starch to 22.7% for waxy (100% amylopectin) corn starch. As temperature is increased, the molecules in the starch granule vibrate vigorously, breaking intermolecular bonds, thus allowing increased interaction with water molecules. This penetration of the starch chains increases randomness and decreases crystallinity in the granule. Continued heating in the presence of free water results in complete loss of crystallinty, as evident by loss of birefringence of the starch granules. The temperature range over which birefringence disappears is called the gelatinization temperature range (Table 2.1).

Table 2.1 Diameter and gelatinization temperature of starch granules

Source	Mean diameter, μm	Gelatinization temperature, °C
Corn	15	62-71
Wheat	20-22	53-64
Rice	5	65-73
White potato	33	62-68
Sweet potato	25-50	82-83
Tapioca	20	59-70

Gelatinization usually occurs over a small temperature range with larger starch granules generally gelatinizing first and smaller granules later. During gelatinization, granules swell extensively (Figure 2.3). Thus, one percent starch slurry in cold water has low viscosity, but on heating a thick paste is produced wherein almost all the water has entered the granules and combined with them. This causes the granules to press tightly against each other. The viscosity of the paste results from resistance to the flow of the swollen granules that now occupy nearly the entire volume. Highly swollen granules are fragile and disintegrate on mild stirring. This causes a significant decrease in paste viscosity.

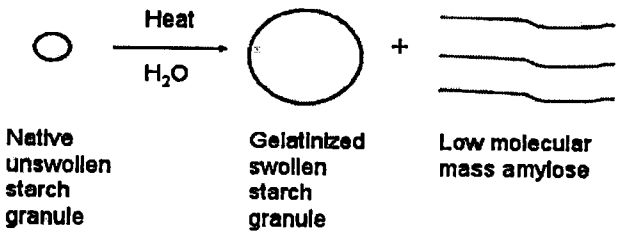


Figure 2.3 Representation of starch gelatinization process

2.2 Polyethylene [4]

The basic structure of polyethylene (PE) is the chain of ethylene monomers $(CH_2=CH_2)_n$ by addition polymerization reaction. The chemical structure is shown in figure 2.4.

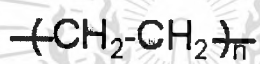


Figure 2.4 Polyethylene structure

In commercial polyethylene, "n" may be between about 400 and above 50,000; alkyl constituent, called short-chain branches, are usually present on the chain back-bones.

Polyethylene is divided into 3 groups:
1. Low Density Polyethylene (LDPE)
2. Linear Low Density Polyethylene (LLDPE)
3. High Density Polyethylene (HDPE)

2.2.1 Properties of Polyethylene

Polyethylene was introduced initially as a special purpose dielectric material of particular value for high frequency insulation. With increasing availability the polymer subsequently began to be used for chemical plant and to a small extent, for water piping. The present position of polyethylene as a general purpose thermoplastic material is due to the characteristics of polyethylene, which lead to its widespread use, may be summarized as follows: low cost, easy process ability, excellent electrical insulation and chemical resistance, toughness and flexibility even at low temperatures, reasonable clarity of the films, free from odor and toxicity, and sufficiently low water vapor permeability for many packaging.

The limitations of polyethylene are the susceptibility of low molecular weight grades to environmental stress cracking, the low softening point, and the susceptibility to oxidation (however polyethylene is better in this respect than many other polymers), the opacity of the material in bulk, the wax-like appearance, the poor scratch resistance, the lack of rigidity (a limitation in some applications but a virtue in others), the low tensile strength and the high gas permeability. For many purposes these limitations are not serious whilst in other treatment can help considerably (Brand up, 1975).

2.2.2 Low Density Polyethylene (LDPE)

Low density polyethylene includes polymers made by free-radical polymerizations: homopolymers with densities 0.915-0.930 g/cm^3, containing alkyl substitutes with 2-8 carbon atoms (most often 4) with long branches, formed during synthesis.

2.2.3 High Density Polyethylene (HDPE)

High density polyethylene includes polymers made with Phillips or Ziegler-type catalysts: homopolymer of densities 0.960-0.970 g/cm^3, including so called high molecular weight polyethylene (HMW-PE), and α-olefin copolymers of densities 0.940-0.958 g/cm^3.

2.3 Biodegradation of Plastics [4]

Degradation is a change in the chemical structure of a plastic, involving a deleterious change in properties.

Degradable plastics are plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which is reasonably accelerated as compared to a control, and which leads to fragmentation or disintegration of the plastics.

2.3.1 Photodegradable Plastics

Photodegradable plastics are degradable plastics where primary mechanism of degradation is through the action sunlight. One of the simplest ways to modify polymers for increased degradability is to accelerate processes already taking place. Most polymers are subject to photo oxidative degradation upon exposure to sunlight, where additives and impurities catalyze the breaking of the polymer chains by series of UV-initiated free radical reactions and loss in structural integrity. Photooxidation results in carbonyl end formation in the polymer chains, which increases the further biological breakdown of the polymer.

2.3.2 Biodegradable Plastics

Biodegradable plastics are degradable plastics where primary mechanism of degradation is through the action of microorganisms such as bacteria, fungi, algae, and yeast. A different approach is the production of new polymers from microbiology derived materials by fermentation that demonstrate high degradation rates.

2.4 Graft Copolymerization [5]

Copolymerization is the polymerization process in which two or more monomers are simultaneously polymerized to form polymeric products is termed a copolymer. The properties of copolymers depend on the type and composition of feed monomers.

Graft copolymer is one type of copolymer which is a branched structures containing a long sequence of one monomer with one or more branches consisting of long sequence of a second monomer.

2.4.1 Emulsion Polymerization

Emulsion polymerization is one of the most important techniques for the commercial production of polymers. It is a heterogeneous system containing two liquid phased in which unsaturated monomers or monomer solutions are dispersed as droplets in a continuous phase and polymerized with free-radical initiators.

This process is quite similar to suspension polymerization but differ from the type and smaller size of the droplets in which polymerization occurs. The initiator is soluble in the aqueous phase and so can diffuse through it. The monomer droplets are held in a stable emulsion by using surfactants, i.e. emulsifiers. This produces after agitation the product, a colloidal dispersion of the polymer or polymer solution rather like milk is called latex.

Emulsion polymerization process has several technological advantages over other polymerization which accounts for its widespread use. These include:

1. The physical state of the emulsion system makes it easy to control the process. Reduce thermal and viscosity problems of the process by using water as the dispersing medium.

2. The product of an emulsion polymerization is synthetic latex can in many instances be used directly without further separations such applications as coatings or paints.

3. Possibility of conduction the polymerization at high rate while at the same time obtaining a polymer of high molecular weight.

However, significant shortcomings of emulsion polymerization should not be forgotten, namely:

1. Necessity of introducing an additional operation for separation of the polymer.

2. Unavoidable contamination of the polymer with residues of the emulsifying agent and other components of the system.

2.4.2 Components and Their Locations

The main components for a typical emulsion polymerization system include the continuous phase, usually water; monomer; emulsifiers; water-soluble initiators and less important ingredients such as chain-transfer agent and buffers. The action of the emulsifier (also referred to as surfactant or soap) is due to its molecules having both hydrophilic and hydrophobic segments.

The physical picture of emulsion polymerization which is presented here, is based on the original qualitative picture of Harkins (1974) and the quantitative treatment of Smith and Ewart (1984). This system is for monomers with low water solubility such as styrene.

The largest portion (>95%) monomer is dispersed as monomer droplets, but very small fraction depending on water solubility dissolved in the continuous phase and some is solubilized in micelles.

Emulsifier is partly dissolved in the continuous phase. If concentration is exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate together to form micelles: and some is absorbed on monomer droplets to stabilize them. Initiator is dissolved in the continuous phase known as water-soluble initiators are usually used.

2.5 Plasticization of Polymers

The most graft copolymerization of styrene onto tapioca starch may have a T_g too high for such purposes. The addition of low molecular weight materials to a polymer to make it more flexible is known as plasticization and the diluent is called a plasticizer. American Standard Test Method (ASTM D-883) adapted the following definition, a plasticizer is a material incorporated in a plastic to increase its workability and flexibility or distensibility. The major function of the plasticizer is to impart flexibility and workability; it also has a major effect on cost and other properties. The addition of a plasticizer may lower the melt viscosity, hardness, modulus and glass transition temperature of a plastic and higher elongation friction and abrasion loss. All of which pointed to a mechanism which involved penetration tack tensile elongation and tearing as steps on the process of friction and wear.

The basic requirements to make a good plasticizer are compatibility and permanence. It should not interact with the polymer too strongly; tight association of its molecules with the chain may even stiffen it. The plasticizing effect must last for a long time, often for many years. Hence, the volatility of the material and its diffusivity must be low to prevent it from escaping from the polymer.

Many copolymers are said to be internally plasticized because of the flexibilization brought about by the presence of a second repeating unit in the polymer chain. In contrast other liquid plasticizers are said to be external plasticizers. The presence of bulky pendant groups on the polymer increases segmental motion and the flexibility of the polymer increases as the size of the pendant group increase.

2.5.1 Mechanism of Plasticization [6]

Three mechanisms have been proposed to provide an understanding of the theoretical factors controlling plasticizer compatibility and effectiveness in polymer.

1. The lubricity theory was popular many years ago when earlier workers assumed that the insertion of plasticizers between polymer molecules. It was reasoned that since the major force resisting deformation of a thermoplastic polymer is inter molecular friction, the plasticizer would act as an internal lubricant separation the polymer chains and essentially lowers the resistance of one polymer molecule moving past the other.

2. The gel theory is based on the proposition that the rigidity of thermoplastic polymer results from an internal three-dimensional gel structure base on crystallinities molecular tie bonds and plasticizer-polymer interaction forces.

3. The free volume theory originated from consideration of the nature of the glass transition in super cooled liquids and amorphous polymers. It is the most fundamental and widely accepted theory offered to explain plasticization. It is assumed that the addition of a plasticizer increases the free volume of a polymer and that the free volume is identical for polymers at T_g.

2.6 Polymer Processing [7]

2.6.1 Blow Film Molding

One of the most common methods of film manufacture is Blown Film Extrusion. The process involves extrusion of a plastic through a circular die, followed by "bubble-like" expansion. The principal advantages of manufacturing film by this process include the ability to:

1. produce tubing in a single operation
2. regulation of film width and thickness by control of the volume of air in the bubble, the output of the extruder and the speed of the haul-off
3. eliminate end effects such as edge bead trim and non uniform temperature that can result from flat die film extrusion
4. capability of biaxial orientation (allowing uniformity of mechanical properties)

The Process

Plastic melt is extruded through an annular slit die, usually vertically, to form a thin walled tube. Air is introduced via a hole in the centre of the die to blow up the tube like a balloon. Mounted on top of the die, a high-speed air ring blows onto the hot film to cool it. The tube of film then continues upwards, continually cooling, until it passes through nip rolls where the tube is flattened to create what is known as a "lay-flat" tube of film. This lay-flat or collapsed tube is then taken back down the extrusion "tower" via more rollers. On higher output lines, the air inside the bubble is also exchanged. The lay-flat film is then either kept as such or the edges of the lay-flat are slit off to produce

two flat film sheets and wound up onto reels. If kept as lay-flat, the tube of film is made into bags by sealing across the width of film and cutting or perforating to make each bag. This is done either in line with the blown film process or at a later stage.

Applications

Blown film can be used either in tube form (e.g. for plastic bags and sacks) or the tube can be slit to form a sheet. Typical applications include industry packaging (e.g. shrink film, stretch film, bag film or container liners), consumer packaging (e.g. packaging film for frozen products, shrink film for transport packaging, food wrap film, packaging bags, or form, fill and seal packaging film), laminating film (e.g. laminating of aluminium or paper used for packaging for example milk or coffee), barrier film (e.g. film made of raw materials such as polyamides and EVOH acting as an aroma or oxygen barrier used for packaging food, e. g. cold meats and cheese), films for the packaging of medical products, agricultural film (e.g. greenhouse film, crop forcing film, silage film, silage stretch film).

2.7 Related Literature

Chutamas P., Sorayut K. and Teeradej N. (2004) studied injection molding technique of biodegradable plastic produced from tapioca starch. Biodegradable plastic was obtained from the mixing tapioca starch graft copolymer HDPE or LDPE and TPNR. The study showed that the condition (MS+PEG400, 4%) + (TPNR+DOP4%) + HDPE in proportion of 1: 0.5: 1.5 by weight was suitable composition to produce plastic articles when compared with HDPE. The optimum condition of injection machine, temperatures of the nozzle, zone 1, zone 2, zone 3 were 160, 160, 150 and 140 degree Celsius, respectively. The injection molding time at the first, the second, the third stages and the cooling times were 50, 45, 30 and 150 seconds, respectively. The injection molding speed was 20 mm/second [8].

Supattra C. (2003) studied the injection molding technique of biodegradable plastic formed from tapioca starch graft copolymers. Tapioca starch graft copolymers were synthesized by react a mixture of tapioca starch with styrene and butyl acrylate monomers by emulsion polymerization using potassium persulfate as an initiator. With different conditions were tested the results showed that the temperatures of the nozzle, zone 1, zone 2 and zone 3 were 150, 140, 130 and 120 degree Celsius, respectively. The injection molding time at the first, the second, the third stages and the cooling time were 45, 40, 35 and 50 seconds, respectively. The injection molding speed was 20 mm/second. The test results suggested that the tapioca starch graft copolymers were not safe for food packaging according to the notification of the ministry of public health no.111 (B.E. (1988)) [9].

Cao, et al. (2002) synthesized water absorption resins of carboxymethyl starch graft acrylamide (CMS-g-AM) by a free radicals initiating process. The free radicals were produced by the chemical initiation method in which ceric ammonium nitrate was used as an initiator. Firstly, sample of mize starch and chloroacetic acid in solution with acrylamide. The evidence of carboxymethyl starch was incorporated in graft polymerization with acrylamide. The evidence of graft copolymers was investigated by using infrared spectra. The effect of the preparation conditions on the substitution

degree of starch and the water absorption capacities of carboxymethyl starch graft acrylamide were investigated. The results showed that substituted degree of starch first increased remarkable and then gradually with increased addition capacity of carboxymethyl starch graft acrylamide is 350 g./g. and the corresponding substient degree is 0.74 [10].

Lahman, et al. (2000) carried out the graft copolymerization by methyl acrylate with sago starch in which ceric ammonium nitrate was used as an initiator based on a free radical reaction. The effect of concentration of ceric ammonia nitrate (CAN), concentration of methyl acrylate (MA), sago starch (SS), studied in terms of the percentages of grafting, grafting efficiency, and rate of grafting. The optimum yield of grafting was obtained when the concentration of CAN, MA, SS, and H_2SO_4 were used at 8.77 x 10^{-3}, 0.803, 0.135, and 0.175 mol L^{-1}, respectively. The rate of graft polymerization was explored on the basis of experimental results and reaction mechanism. The graft copolymers were characterized by FTIR spectroscopy, TGA and DSC analysis showed that confirmation of the occurrence of polymer (methyl acrylate) onto sago starch [11].

Desai et al. (2000) studied starch as a crosslinker in polyurethane elastomers. The polyurethane elastomers were synthesized using polypropylene glycol (PPG 2000) as the polyol, starch and trimethylol propane (TMP) as the crosslinker in varying concentrations. The starch / polyurethanes were found to show better mechanical properties than TMP / polyurethanes. With increasing the NCO:OH equivalent ratio, the stress-strain properties were observed to increase. DSC thermograms of TMP / polyurethanes showed the appearance of only one glass transition, whereas thermograms of starch / polyurethane showed two, indicating phase separation. The solubility parameter from the swelling data of starch and polyurethane blends was discusses about a correlation with thermomechanical properties, and the potential for biodegradation [12].

Tanomlarp T. and Pornsak L. (1998) studied the optimum formulation, condition and sequences of mixing in compression process of cassava starch grafted copolymer with styrene and butyl acrylate to produce plastic foam. The grafted starch was prepared by emulsion polymerization with potassium persulfate as an initiator. The grafted starch was mixed with low density polyethylene and ethylene vinyl acetate copolymer which has the amount of vinyl acetate 18 percent. The optimum formulation was the amount of grafted starch was not more than 35 phr and starch's moisture was not exceed 1.66 percent with addition of stearic acid 3.1 phr, zinc oxide 2.2 phr, dicumyl peroxide 0.8 phr and polyethylene was 20 phr, respectively [13].

Jumpoon P., Wattanee S. and Visamol P. (1995) studied various quantities in percentage of monomer under constant controlled conditions to synthesized biodegradable polymer (starch graft copolymer) by the copolymerization of cassava starch with nonsoluble monomers employing a two phase reaction system. The starch graft copolymer of butyl acrylate, ethyl acrylate and 2-ethylhexyl acrylate have rubber-liked behavior with 2-ethylhexyl acrylate is the most toughness, may be used to be the filler in polymers for making the biodegradable articles [14].

Chapter 3
Experimental Details

3.1 Materials

Materials used in this study are described below.

3.1.1 Tapioca Starch and Monomers

3.1.1.1 Tapioca starch (commercial grade)
3.1.1.2 Butyl acrylate (commercial grade)
3.1.1.3 Styrene monomer (commercial grade)

3.1.2 Initiator

3.1.2.1 Potassium persulphate ($K_2S_2O_8$). The initiator solution was prepared by dissolving 27.0 g. of $K_2S_2O_8$ in 1000 ml of distilled water.

3.1.3 Emulsifier

3.1.3.1 Sodium lauryl ether sulfate (SDS)

3.1.4 Other Chemicals

3.1.4.1 Diethylene glycol (DEG, commercial grade)
3.1.4.2 Low density polyethylene (blown film grade, LDPE1905FA)
Blown film grade low density polyethylene (LD1905FA) was gifted from Thai Polyethylene Co., Ltd. Physical properties of the material are listed in Table 3.1.

Table 3.1 Physical properties of low density polyethylene (LD1905FA)

Physical Properties	Testing Method	Unit	LD1905FA
Melt flow rate	ASTM D 1238	g/10 min.	5.0
Density	ASTM D 1505	g/cm^3	0.919
Tensile strength at break	ASTM D 638	kg/cm^2	MD:210, TD:170
Elongation at break	ASTM D 638	%	MD:200, TD:720
Elmendorf tear strength	ASTM D 1922	g/25 micron	MD:370, TD:210
Dart impact strength	ASTM D 1790	g	105
Haze	ASTM D 1003	%	6
Gloss	ASTM D 2457	%	85
Flexural modulus	ASTM D 790	kg/cm^2	2,100
Hardness, Shore D	ASTM D 2240	-	46
Vicat softening point	ASTM D 1525	°C	90
Melting point	ASTM D 2117	°C	110
Brittleness temperature	ASTM D 746	°C	< -70

3.2 Instruments

The instruments used in this study are listed below:

3.2.1 Four necked 2 L glass reactor with paddle type agitator and vary rotor speed motor.
3.2.2 Hot-Air Oven
3.2.3 Granulator (BOSCO)
3.2.4 Electronic Balance
3.2.5 Tensile Testing Machine (LLOYD; 30 kN)
3.2.6 Scanning Electron Microscope, SEM (LEO 1455 VP)
3.2.7 Single-screw extruder (Polydrive with Rheomex R252HAAKE)
3.2.8 Blown film extrusion (LF-400; Lab Tech engineering company Ltd.)
3.2.9 Fourier Transform Infrared Spectrometer (Brucker IFS 28)
3.2.10 Cutting machine
3.2.11 Thermogravimetric Analysis Machine

3.3 Synthesis of Tapioca Starch Graft Copolymer

3.3.1 Graft Copolymerization

In graft copolymerization reaction, 150 g. tapioca starch in 1700 mL of distilled water was gelatinized for 1 hr. at 90°C in the 2 L four-necked glass reactor. A rotor speed was setting at 350 rpm. After cooled down to 60°C, sodium lauryl ether sulfate (10%by weight of monomer) was added and stirred until it become homogeneous solution, followed by the required amount of monomers; styrene and butyl acrylate. The mixture was stirred at the rotor speed of 450 rpm for 15 min. and then 150 mL of initiator solution was added. The reaction was allowed to stir continuously for 3 hours at 60°C. After completion of the reaction, the solution was dried with hot air oven at temperature between 55-60°C until its weight is constant.

Figure 3.1 Synthesis of modified starch graft copolymer

After dried, the modified starch graft copolymer obtained from the hot air oven was granulated by using Bosco granulator.

3.3.2 Polymer Blending Preparation

The modified starch graft copolymer was blended to the low density polyethylene and the plasticizer DEG in the ratio as listed in Table 3.2 and mixed by single-screw extruder. The extrusion temperature was set for the Feed Zone, Compression Zone, Metering Zone and Die Zone at 130°C, 140°, 140°C and 150°C respectively and the speed of screw at 15 rpm. The polymer blends were granulated by the granulator before go to the next step.

Table 3.2 The blending ratio of LDPE to the modified starch and DEG

Samples	Formula	LDPE	MS	DEG
1	LDPE	100	0	0
2	2%MS	98	2	0
3	2%MS(3%DEG)	98	2	0.06
4	2%MS(4%DEG)	98	2	0.08
5	2%MS(5%DEG)	98	2	0.10
6	4%MS	96	4	0
7	6%MS	94	6	0
8	8%MS	92	8	0
9	10%MS	90	10	0
10	20%MS	80	20	0
11	30%MS	70	30	0

3.3.3 Blown Film Extrusion

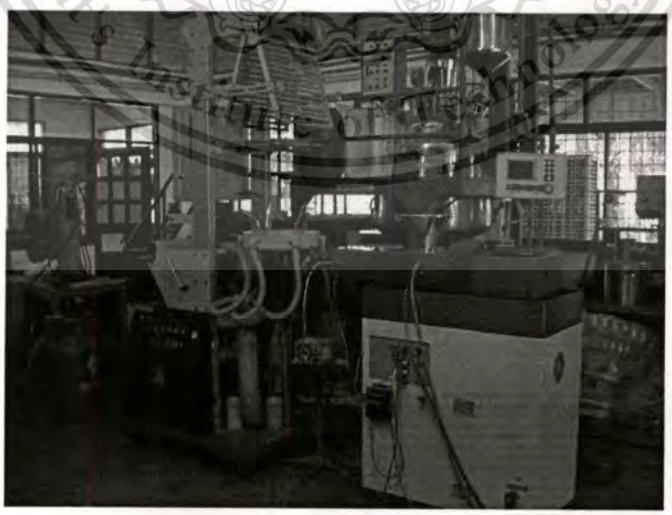


Figure 3.2 Blown film extrusion machine

The polymer blends in the Table 3.2 were blown to film by used Blown Film Extrusion LF-400 and the temperature setting at the Feed Zone, Compression Zone and Metering Zone of the single-screw extruder were 140°C, 150°C and 160°C respectively and the rotor speed of the screw was 95 rpm. The blown film temperature setting at

Zone S-adaptor and Die Zone were 180°C and the thickness of film was variable by adjusted the blown rate.

3.4 Characterizations

3.4.1 Mechanical Properties Testing [15]

3.4.1.1 Tensile Testing

Tensile specimens were prepared by using the dumbell-shaped air cutting machine. According to the ASTM D 882, the specimens were cut out into strips of 25.4 mm. wide with a gauge length of 25 mm. Five specimens were tested at the condition as followed:

-Load cell	100	N
-Test speed	5	mm./min.
-Gauge length	25	mm.

Tensile Strength

From tensile testing, tensile strength (TS) was calculated by the equation,

$$TS = F/A$$

where TS = tensile strength (MPa or N/mm^2)
F = force at yield or at break (N)
A = initial cross-sectional area of the test specimen (mm^2)

Elongation at Break

The elongation at break (EB) was obtained from the equation,

$$\%EB = ((l - l_0) / l_0) \times 100$$

where %EB = elongation at break (%)
l = the distance between gauge marks at break (mm)
l_0 = the initial distance between gauge marks or gauge length

Modulus

From the load vs. elongation curve, modulus was calculated by the equation,

$$E = F/A$$

where E = modulus (MPa)
F = load (N)
A = initial cross-section area of the test specimen (mm^2)

3.4.2 Physical Properties Testing

3.4.2.1 Water Absorption

Cut specimens in the size of 10 cm. x 10 cm. Take specimens into a hot air oven at 50°C for 24 hours. After constant weight, record their weights and then immersed in container containing water for 24 hours. After that remove the excess water and weight of specimen, record their weights again. Water absorption was calculated as follow:

$$\% \text{ water absorption} = \frac{(\text{Wet weight of sample} - \text{Dried weight of sample})}{\text{Dried weight of sample}} \times 100$$

3.4.3 Decomposition Analysis by TGA Method

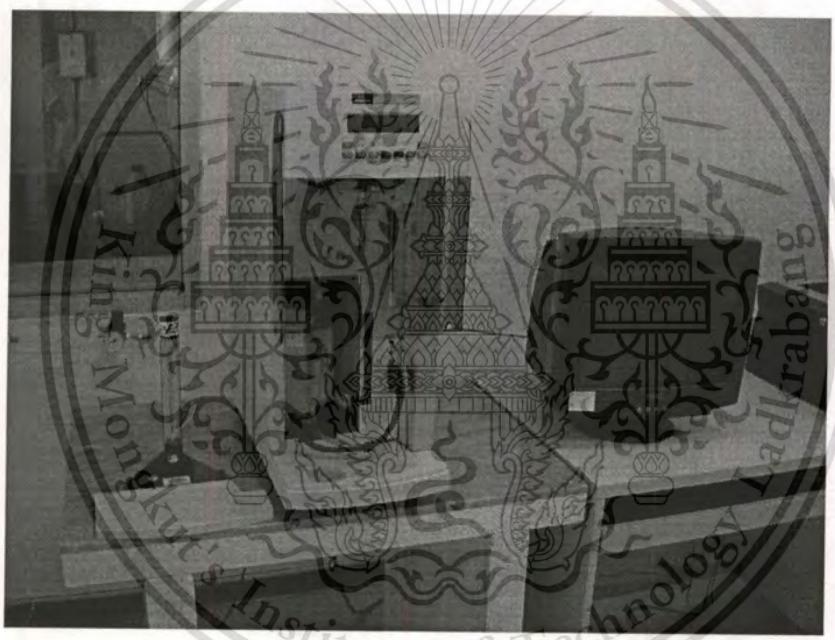


Figure 3.3 Thermogravimetric Analysis Machine

Thermogravimetric analysis (TGA) was used to determine the composition of LDPE blended with modified starch. Use nitrogen gas and air at adjust pressure approximately 40 psi. Weighed about 20 mg of sample and put into the furnace and heated it from 50°C to 800°C with heating rate of 10°C/min. The initial temperature is used at 55°C.

3.4.4 Morphology Testing

3.4.4.1 Scanning Electron Microscope (SEM)

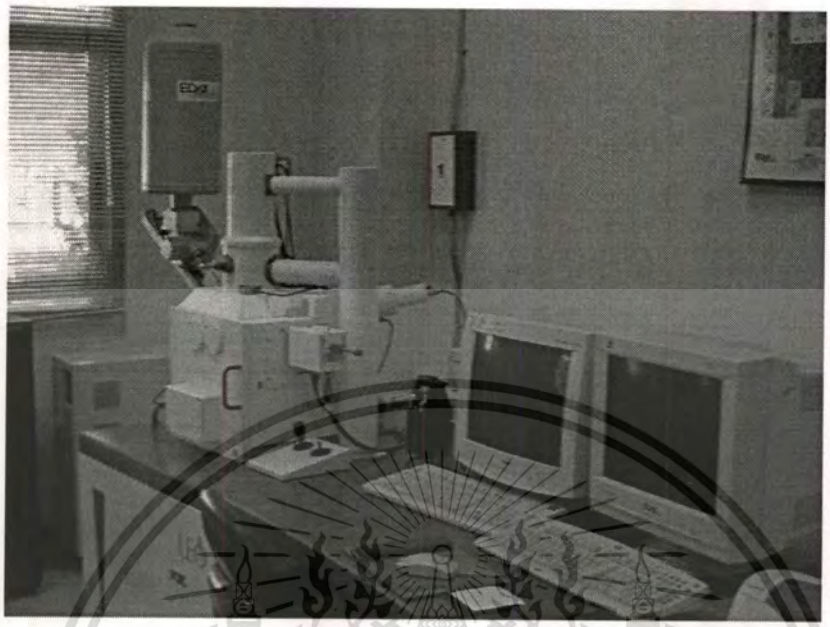


Figure 3.4 Scanning Electron Microscope

SEM was used to morphological testing of the specimens. The specimens prepared by mounting on the samples holders. Put specimens in the chamber of the sputter coater. The specimens were coated with gold in argon gas with plasma current of 18 mA for 120 seconds before tested by SEM machine. Then observed the operator acquires SEM images of specimens.

3.4.5 Identification by FT-IR

Figure 3.5 Fourier Transform Infrared Spectrometer (FT-IR)

Fourier Transform Infrared spectrophotometer (Brucker IFS 28) was used to characterize the MS-LDPE films by adsorption spectra. The samples were prepared to pellets with KBr and the IR spectra recording in the frequency range of 4000 - 400 cm^{-1}.

3.4.6 Biodegradation Testing

Prepared the area to buried specimens by choosing the area which is not annoyed by people or animals. The burial testing with composed of the garbage. Prepare the specimens in the size of 5x5 cm^2 into the soil pits. Then observed the changed of the specimens for every 10 days and recorded. The test was taken for 70 days.

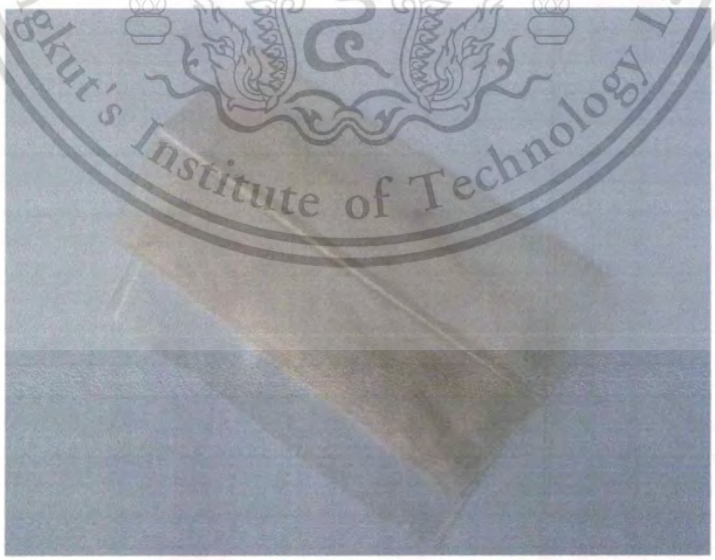
Chapter 4
Results and Discussion

4.1 Production of Blown Film Extrusion Process

The production of blown film extrusion process results in this study shown in the Table 4.1. All of samples can be process by the blown film extrusion machine with differences in quality.

The quality of blown film process can be separated by eyes observation and the ability to blowing into: very good, good, difficult to blow, and could not blow to film.

(a) Very good



(b) Good

(c) Difficult to blow

(d) Could not blown

Figure 4.1 Blown film differences

Table 4.1 The production of modified starch-filled polyethylene films

Sample	Formula	Blown Film Process
1	LDPE	Very good
2	2%MS	Good
3	2%MS(3%DEG)	Good
4	2%MS(4%DEG)	Good
5	2%MS(5%DEG)	Good
6	4%MS	Good
7	6%MS	Difficult to blow
8	8%MS	Could not blow
9	10%MS	Could not blow
10	20%MS	Could not blow
11	30%MS	Could not blow

After experiment, there were several quality differences compared with LDPE film. In this study, the blown film process can be done in good result only in the modified starch contents that lower than 4%MS. For the higher content of MS, the results have shown the difficult to blown by the blown film extrusion machine. And for the MS-content higher than 20%, the process can be done by difficulty control and the samples quite burn easily in the hot chamber zone of blown film extrusion machine.

4.2 Characterization

4.2.1 Mechanical Properties Testing

Mechanical properties of modified starch-filled polymer films are present in Figure 4.2 – 4.4. The tensile strength, elongation at break and modulus of LDPE and MS-LDPE films are shown in Table 4.2.

Table 4.2 Tensile properties of LDPE and MS-LDPE films

Sample	Formula	Tensile strength (N/mm^2)	Elongation at break (%)	Modulus (N/mm^2)
1	LDPE	7.539	422.733	28.353
2	2%MS	4.401	396.060	23.383
3	2%MS(3%DEG)	4.006	239.166	17.237
4	2%MS(4%DEG)	4.520	248.430	25.510
5	2%MS(5%DEG)	4.139	104.600	27.160
6	4%MS	4.272	235.000	23.010
7	6%MS	3.189	136.433	27.330

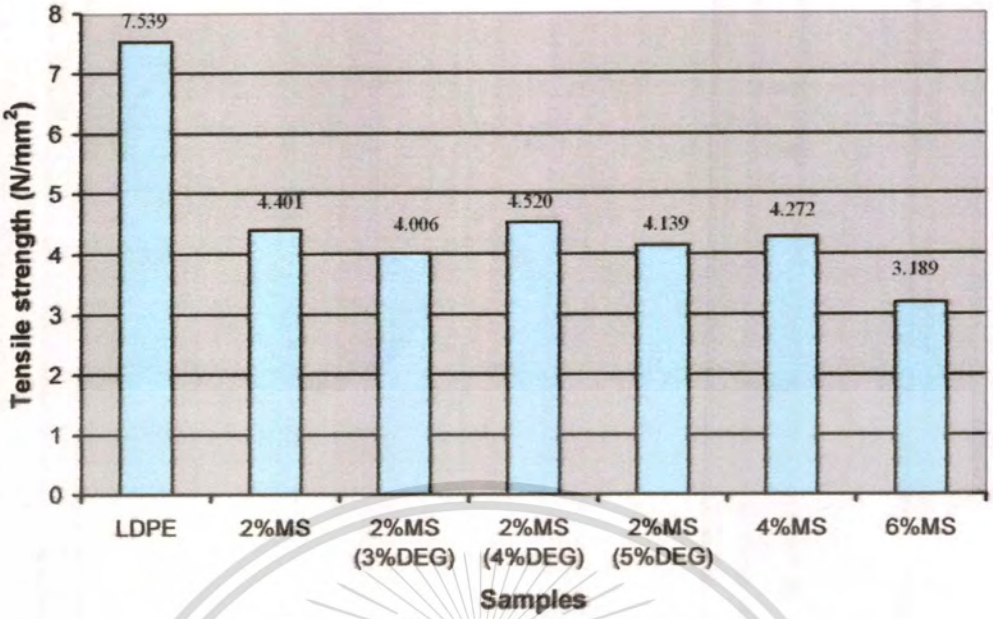


Figure 4.2 Tensile strength of MS-LDPE and LDPE films

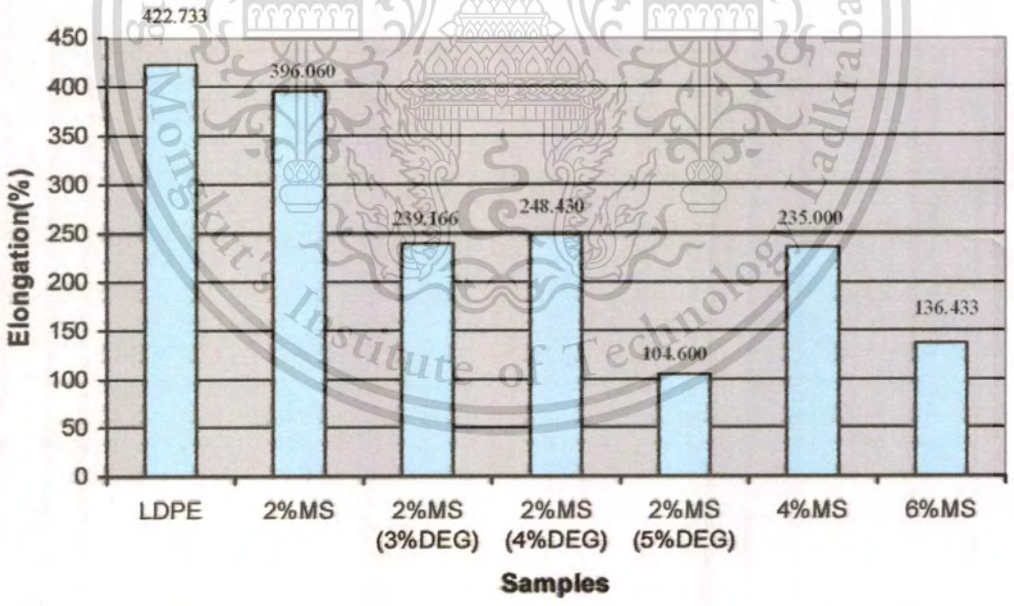


Figure 4.3 Elongation at break of MS-LDPE and LDPE films

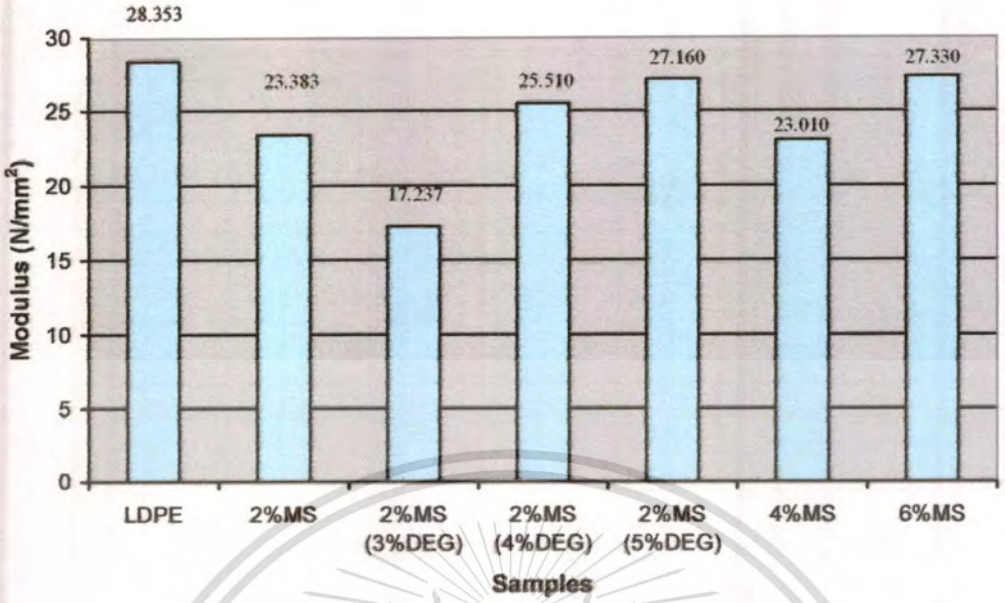


Figure 4.4 Tensile modulus of MS-LDPE and LDPE films

4.2.2 Physical Properties Testing

Physical properties of MS-LDPE films by water absorption testing in this study were presented in Figure 4.5 and the data listed in Table 4.3.

Table 4.3 The weight before and after soaking of film specimens in water

Sample	Formula	Weight of specimen (g)		Water absorption (%)
		Before soaking in water	After soaking in water	
1	LDPE	0.6108	0.6271	2.67
2	2%MS	0.6670	0.6918	3.76
3	2%MS(3%DEG)	0.6049	0.6267	3.60
4	2%MS(4%DEG)	0.6284	0.6502	3.47
5	2%MS(5%DEG)	0.7377	0.7608	3.12
6	4%MS	0.6648	0.6943	4.43
7	6%MS	0.8724	0.9339	7.05

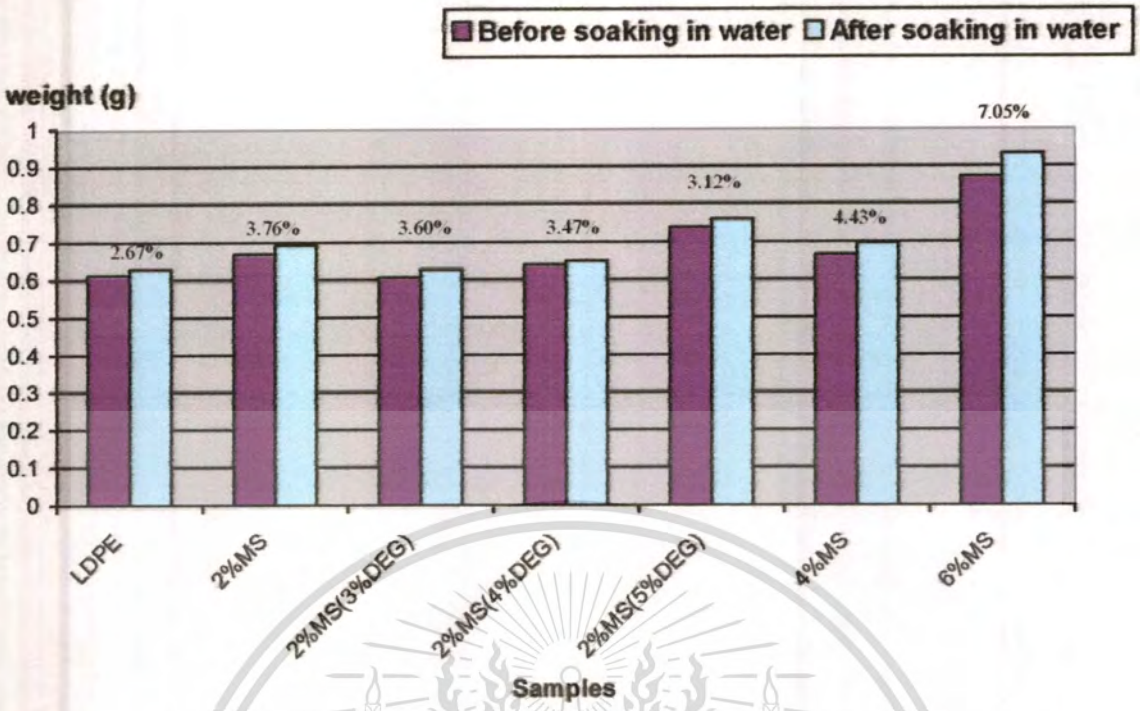


Figure 4.5 Water absorption of LDPE and modified starch-filled polyethylene films

The results have shown the percentage of water absorption after soaking the film specimens for 24 hrs in water at 25°C. This result was observed in believed that tapioca starch consists of a mixture of amylose and amylopactin that have many hydroxyl groups. The abundant of hydroxyl groups on the tapioca starch molecules impart hydrophilic properties which giving it an affinity for water absorption.

4.2.3 Decomposition Analysis by TGA Method

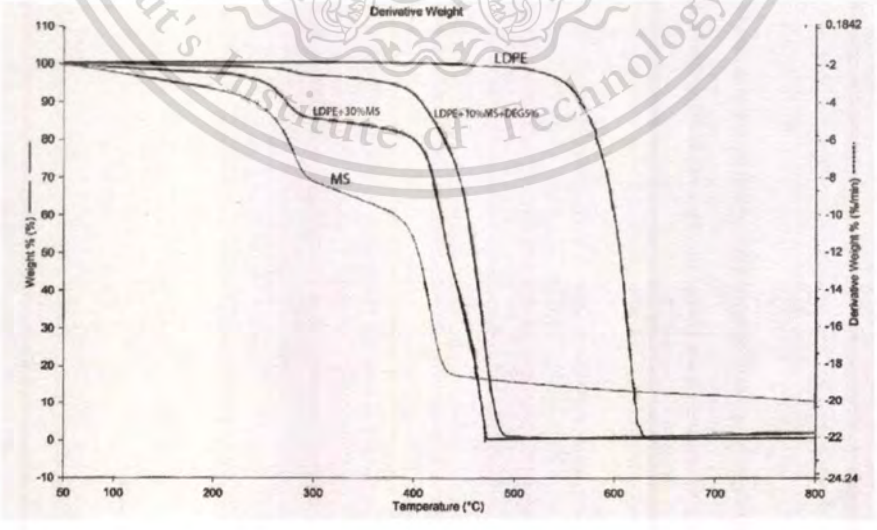


Figure 4.6 Decomposition temperature analysis by TGA

From Figure 4.6, the weight 50% loss of LDPE was at 600°C, and MS was at 430°C. After blended together, the result has shown that the decomposition temperature of both LDPE and MS was decreased from the decomposition temperature of LDPE. As in sample of 10%MS in LDPE with 5%DEG start to decompose at 468.75°C of LDPE and 450°C of MS.

The Samples which added DEG have more decomposed than the samples without DEG and stable than LDPE. It was because when we added high amount of MS into LDPE, that meant increasing –OH functional groups. DEG is used for plasticizer in blown film technique, and used for increasing stability of plastic film. The thermogram in Figure 4.6 is shown that the sample with DEG had decomposed after the samples without DEG and more stable to decompose than LDPE.

4.2.4 Morphology

The morphological testing by scanning electron microscope (SEM) of the specimens at the 100 times magnification is present in Figure 4.7 - 4.13.

From the results were shown that the distributions of rigid phase of styrene butyl acrylate on polyethylene after film proceed. In this study, the 4%MS content in LDPE have the best distribution of modified starch. The morphological appearance of 6%MS in LDPE film was just fair and had the bubble on the surface.

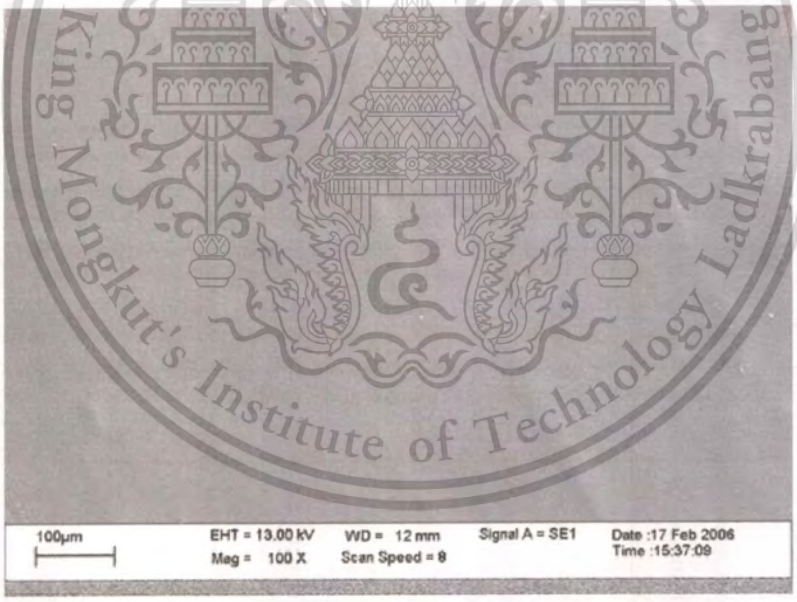


Figure 4.7 The LDPE film

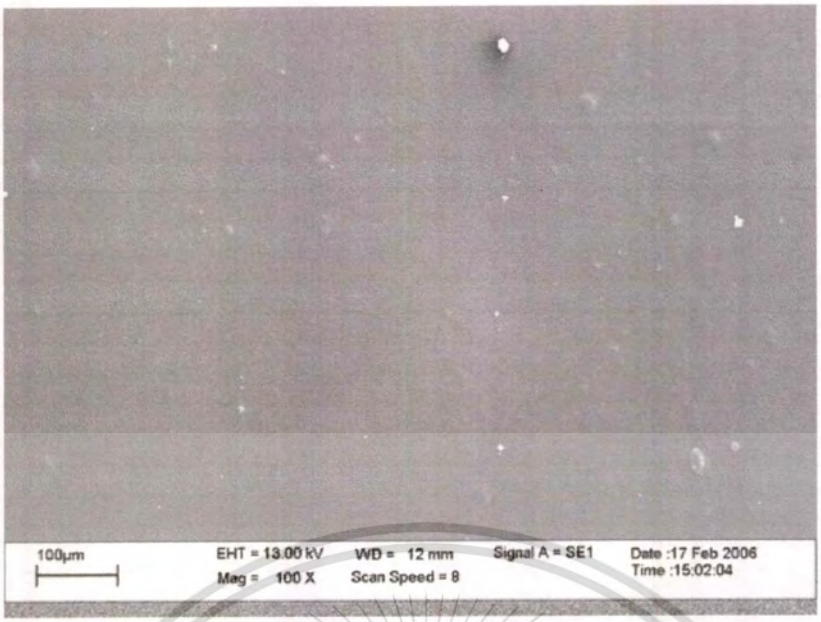


Figure 4.8 The 2%MS filled LDPE film

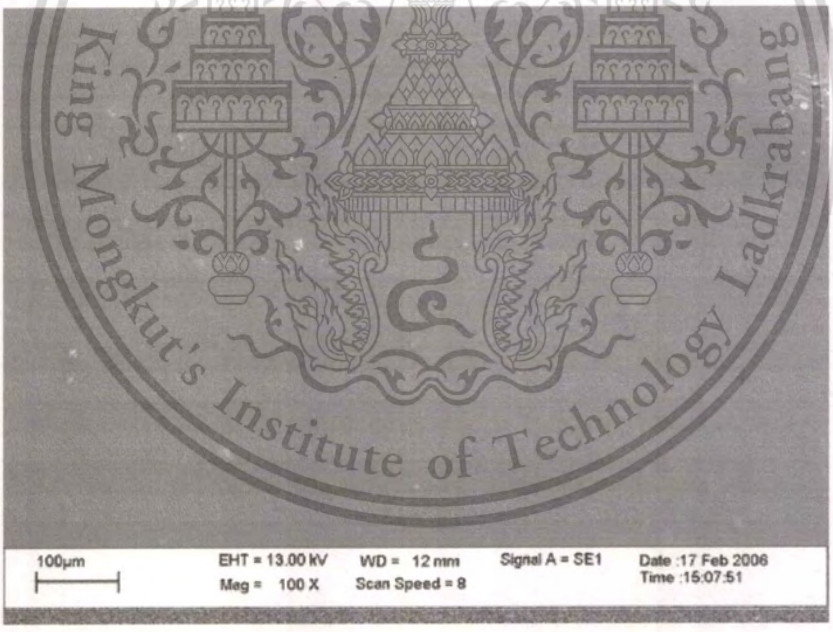


Figure 4.9 The 2%MS-3%DEG filled LDPE film

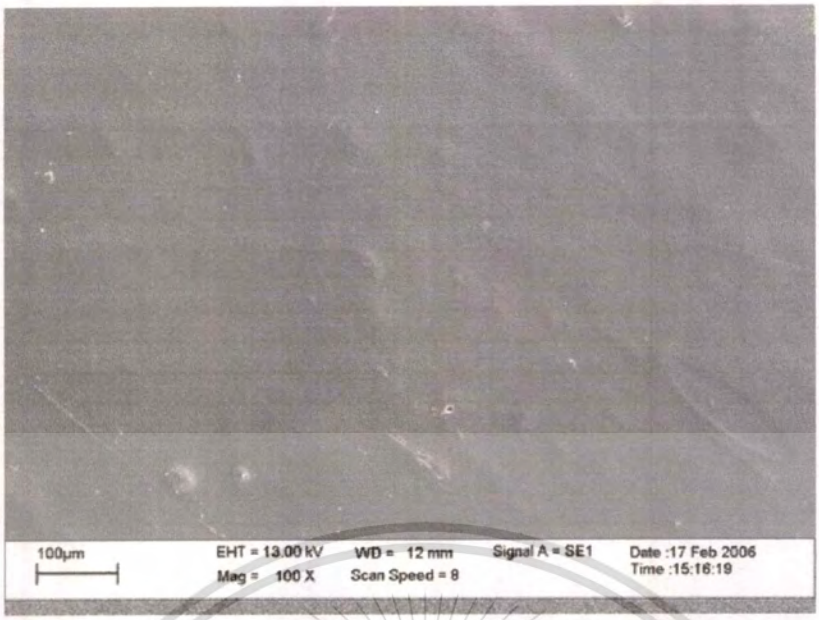


Figure 4.10 The 2%MS-4%DEG filled LDPE film

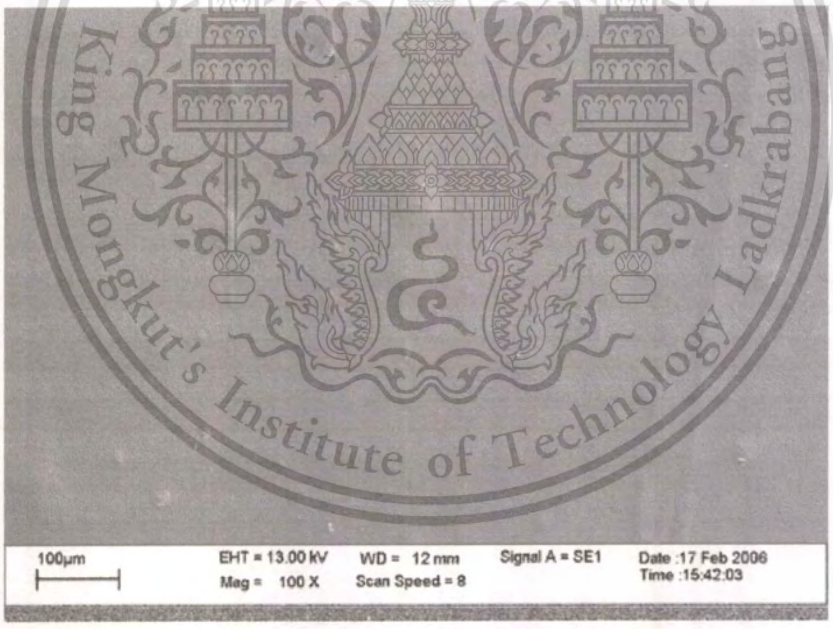


Figure 4.11 The 2%MS-5%DEG filled LDPE film

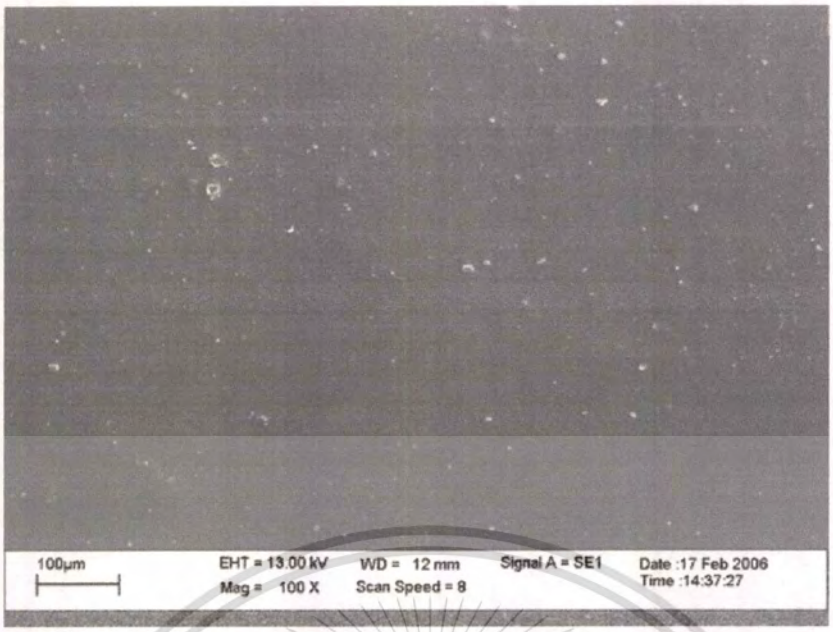


Figure 4.12 The 4%MS filled LDPE film

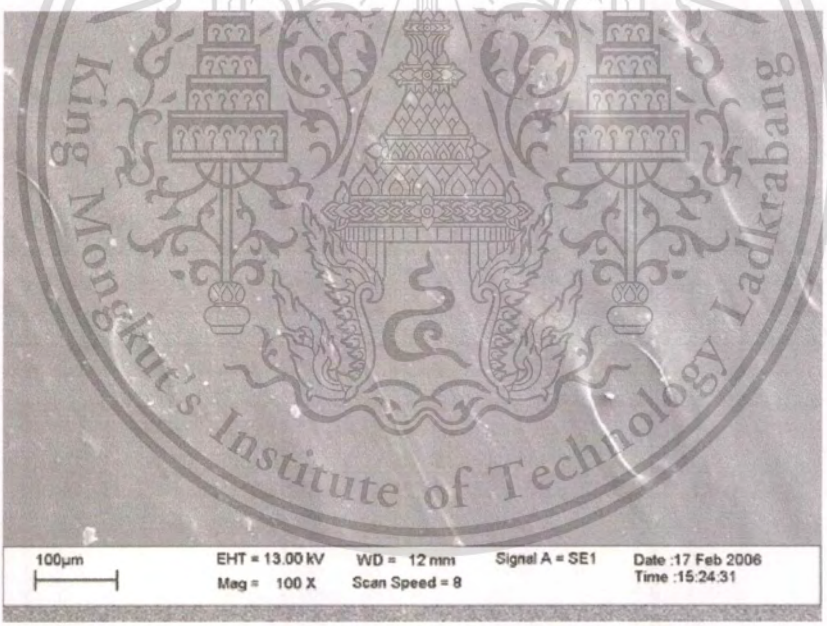


Figure 4.13 The 6%MS filled LDPE film

4.2.5 Identification by FT-IR

The MS-LDPE copolymer spectra are shown in Figure 4.14-17, respectively. The infrared spectrum was recorded in the frequency region of 4000-400 cm^{-1}. Table 4.4 summarizes the peak assignment of the infrared vibrational bands. From the results are shown the characteristic FT-IR peak of C=O of grafted butyl acrylate polymer appeared between 1730-1750 cm^{-1}.

Table 4.4 Infrared spectroscopy characterization

Wave number (cm^{-1})	Assignment
1100 - 1300	C-O stretching (C-O and C-O-H) of starch and C-O of graft butyl acrylate polymer
1600 - 1700	Multiple peak C=O aldehyde group of tapioca starch
1730 - 1750	C=O stretching of butyl acrylate polymer
2900 - 3000	C-H stretching of hydrocarbon of graft butyl acrylate polymer and C-H group of tapioca starch
3200 - 3600	O-H stretching of tapioca starch

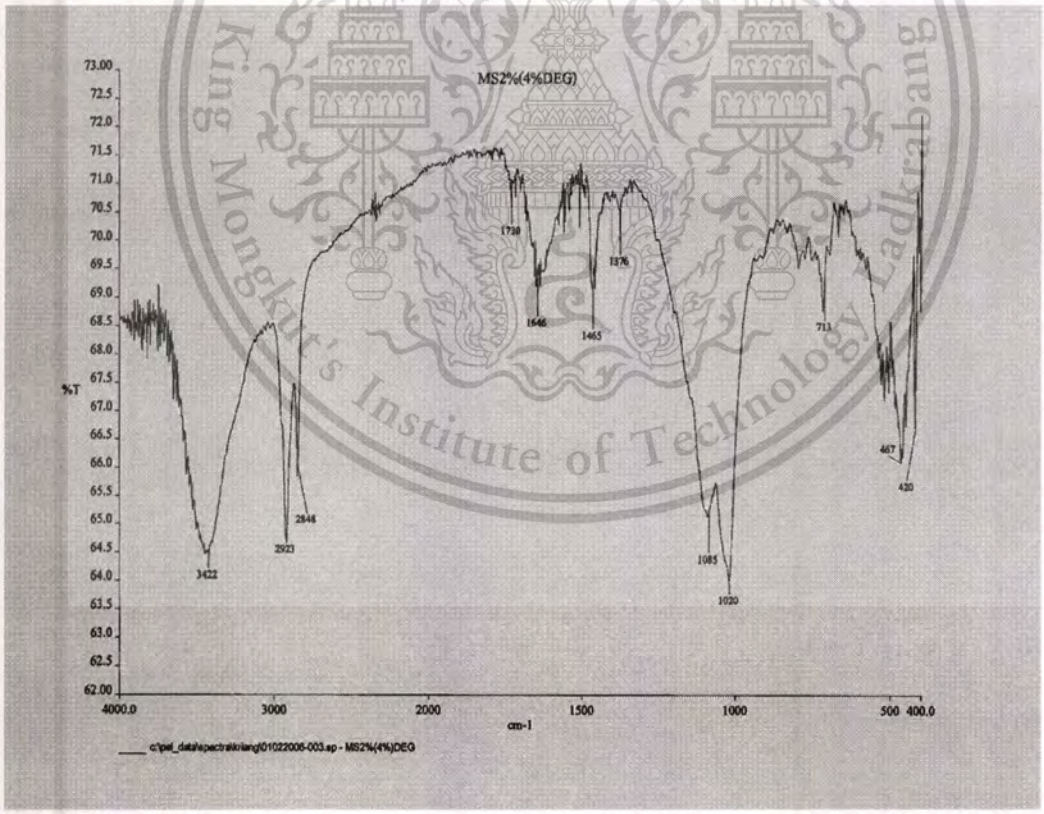


Figure 4.14 FT-IR spectra of modified starch-filled polyethylene film (2%MS with 4%DEG)

4.3 Biodegradation Testing

Degradation was thus investigated by monitoring the disappearance of plastic film, the fungi growths, and the changes in physical appearances.

Table 4.5 The biodegradable of plastic films from modified starch

Sample	Formula	Number of times (every 10 days)						
		1st	2nd	3rd	4th	5th	6th	7th
1	LDPE	0	0	0	0	0	0	0
2	2%MS	0	0	0	0	0	+	+
3	2%MS(3%DEG)	0	0	0	0	0	0	+
4	2%MS(3%DEG)	0	0	0	0	0	0	+
5	2%MS(3%DEG)	0	0	0	0	0	0	+
6	4%MS	0	0	0	0	0	+	+
7	6%MS	0	0	0	0	+	+	+
8	8%MS	0	0	0	+	+	+	++
9	10%MS	0	0	+	+	+	++	++
10	20%MS	0	+	+	+	++	++	+++
11	30%MS	0	+	+	+	++	+++	+++

where 0 = Have no changeable
\+ = Have little bit microorganism
++ = Have medium microorganism
+++ = Have more microorganisms and specimens are quite brittle

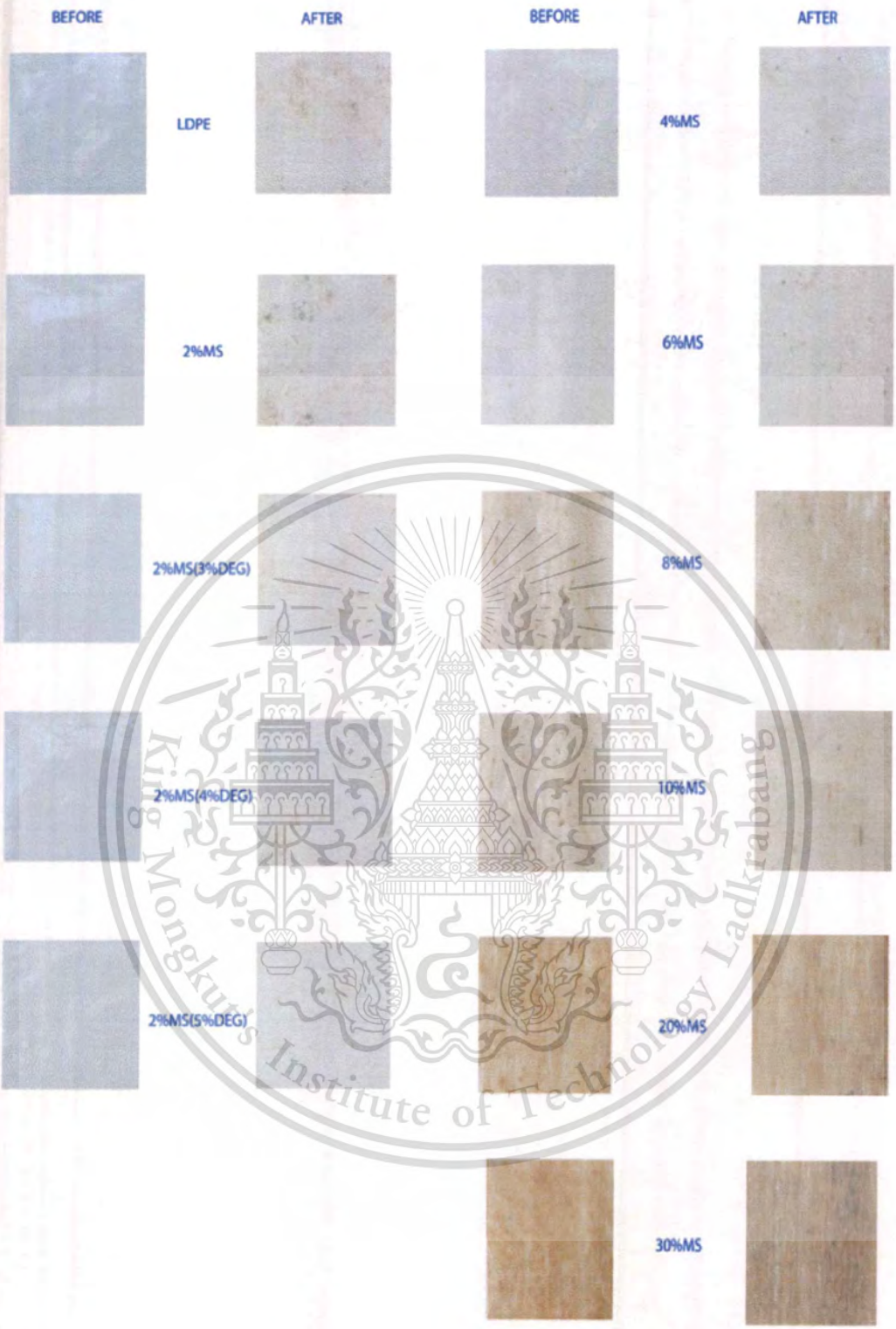


Figure 4.15 Biodegradability of modified starch-filled polyethylene films by buried in soil for 70 days

The Figure 4.15 is shown the before and after observed of film by soil burial testing in 70 days. It has seen that all samples changed in the physical appearances. The higher contents of modified starch have the higher changes than the lower modified starch contents. For the higher modified starch contents specimens, especially the Sample 11(30% MS), has the fungi growths and film changed to be more brittle.

Chapter 5
Conclusion and Suggestions

5.1 Conclusion

1. MS in this study was not suitable for film production. The films produced by blown film extrusion machine had rigid phase of modified starch which has higher melting temperature than LDPE, so the films obtained from blown film process were not homogeneous.

2. MS in this study are suitable for production of injection objects which had done by the previous study.

3. In this study, the blown film extrusion production can be done in Sample 1-7 which Sample 1 was pure LDPE film and Sample 2-5 were MS-LDPE in 2%MS-content had good result in blown film process and good film production. The Sample 7 had fairly in blowing process and the products had bubbling occurred on film surface which was the problem on film quality and the Sample 8-11 that could not be blown.

4. In this study, the best MS-content to blown film production was the Sample 6 (4%MS in LDPE) and the best sample to the blown film process was Sample 2(2%MS) which have the lowest MS-content in LDPE.

5. The MS-LDPE films have more ability to absorbed water and can be degrade in physical appearances after 70 days. After added of DEG stabilizer, there were a little bit improve of film properties but not significant.

6. For study, we expected to use MS to produce films with high content in LDPE but it could not be process in higher amount than 8%MS. This was because the limitation of the blown film extrusion machine which has ability to produce only LD1905FA grade of LDPE.

5.2 Suggestions

For further study, there are many things required to the research consideration;

1. For further study, there should be find the other olefin monomer that suitable for grafting the monomer. This study found that the mixture of styrene and butyl acrylate was not suitable graft monomers with its high glass transition temperature. Styrene and butyl acrylate monomers became styrene polymer which higher melting temperature than LDPE and made the film products not homogeneous.

2. The limitation of the machine should be at least. For this research study, the biggest problem was about the limitation of the blown film extrusion machine so that this problem also limited to the variety of polymer and also the content of MS in LDPE.

3. The results had not reached the satisfaction. The technical problem also made unreliable on the results so the next step of research projects should de made carefully consideration in experiments.

4. The biodegradability of MS-LDPE films by soil burial method should be considerate on the longer time. This study had tested on this section in only 70 days. The longer time period of testing could be gave the more physical changes to observe.

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APPENDICES

Appendix A

The Tables of Blending Data on Modified Starch-Filled Polyethylene and Characterization

Table A-1 The blending ratio of LDPE to the modified starch and DEG

Sample	Formula	LDPE	MS	DEG
1	LDPE	100	0	0
2	2%MS	98	2	0
3	2%MS(3%DEG)	98	2	0.06
4	2%MS(4%DEG)	98	2	0.08
5	2%MS(5%DEG)	98	2	0.10
6	4%MS	96	4	0
7	6%MS	94	6	0
8	8%MS	92	8	0
9	10%MS	90	10	0
10	20%MS	80	20	0
11	30%MS	70	30	0

Table A-2 The tensile strength of specimens (N/mm^2)

Sample	Formula	Tensile Strength (N/mm^2)			Average
		1	2	3	
1	LDPE	7.144	6.970	8.503	7.539
2	2%MS	3.902	5.157	4.144	4.401
3	2%MS(3%DEG)	3.427	4.344	4.249	4.006
4	2%MS(4%DEG)	4.561	4.146	4.853	4.520
5	2%MS(5%DEG)	3.350	4.771	4.295	4.139
6	4%MS	4.165	4.449	4.203	4.272
7	6%MS	3.737	2.801	3.031	3.189

Table A-3 The elongation at break of specimens (%)

Sample	Formula	Elongation at Break (%)			Average
		1	2	3	
1	LDPE	390.700	365.400	512.100	422.733
2	2%MS	338.800	469.400	380.000	396.060
3	2%MS(3%DEG)	216.900	168.100	332.500	239.166
4	2%MS(4%DEG)	190.000	252.200	303.100	248.430
5	2%MS(5%DEG)	156.900	156.900	000.000	104.600
6	4%MS	207.600	312.100	185.300	235.000
7	6%MS	155.900	103.700	149.700	136.433

Table A-4 The modulus of specimens (N/mm^2)

Sample	Formula	Modulus (N/mm^2)			Average
		1	2	3	
1	LDPE	30.710	24.820	29.530	28.353
2	2%MS	20.220	29.800	20.130	23.383
3	2%MS(3%DEG)	9.451	29.290	12.970	17.237
4	2%MS(4%DEG)	27.170	18.860	30.490	25.510
5	2%MS(5%DEG)	15.470	40.480	25.520	27.160
6	4%MS	22.720	23.200	23.110	23.010
7	6%MS	33.910	22.680	25.400	27.330

Table A-5 The mechanical properties of MS and DEG filled LDPE films

Sample	Formula	Tensile strength (N/mm^2)	Elongation at break (%)	Modulus (N/mm^2)
1	LDPE	7.539	422.733	28.353
2	2%MS	4.401	396.060	23.383
3	2%MS(3%DEG)	4.006	239.166	17.237
4	2%MS(4%DEG)	4.520	248.430	25.510
5	2%MS(5%DEG)	4.139	104.600	27.160
6	4%MS	4.272	235.000	23.010
7	6%MS	3.189	136.433	27.330

Table A-6 The weight of specimens before soaking in water (g)

Sample	Formula	Weight of specimen (g)				
		1	2	3	4	Average
1	LDPE	0.6253	0.5443	0.6297	0.6438	0.6108
2	2%MS	0.6413	0.7002	0.6571	0.6683	0.6667
3	2%MS(3%DEG)	0.5860	0.6053	0.6110	0.6132	0.6049
4	2%MS(4%DEG)	0.5526	0.6503	0.6581	0.6527	0.6284
5	2%MS(5%DEG)	0.7509	0.7207	0.7468	0.7325	0.7377
6	4%MS	0.6892	0.6510	0.6375	0.6816	0.6648
7	6%MS	0.7248	0.7370	0.9879	1.0400	0.8724

Table A-7 The weight of specimens after soaking in water (g)

Sample	Formula	Weight of specimen (g)				
		1	2	3	4	Average
1	LDPE	0.6276	0.5964	0.6372	0.6471	0.6271
2	2%MS(4%DEG)	0.6636	0.7098	0.7400	0.6791	0.6981
3	2%MS(4%DEG)	0.6052	0.6253	0.6393	0.6370	0.6267
4	2%MS(4%DEG)	0.6023	0.6333	0.6618	0.6753	0.6502
5	2%MS(4%DEG)	0.7783	0.7400	0.7695	0.7482	0.7607
6	2%MS(4%DEG)	0.7333	0.6824	0.6452	0.7162	0.6943
7	2%MS(4%DEG)	0.7462	0.7471	1.0616	1.1805	0.9339

Table A-8 The % water absorption of specimens (g)

Sample	Formula	Weight of specimen (g)		Water absorption (%)
		Before soaking in water	After soaking in water	
1	LDPE	0.6108	0.6271	2.67
2	2%MS	0.667	0.6918	3.76
3	2%MS(3%DEG)	0.6049	0.6267	3.60
4	2%MS(4%DEG)	0.6284	0.6502	3.47
5	2%MS(5%DEG)	0.7377	0.7608	3.12
6	4%MS	0.6648	0.6943	4.43
7	6%MS	0.8724	0.9339	7.05

Appendix B

FT-IR Spectra of LDPE and MS-LDPE samples

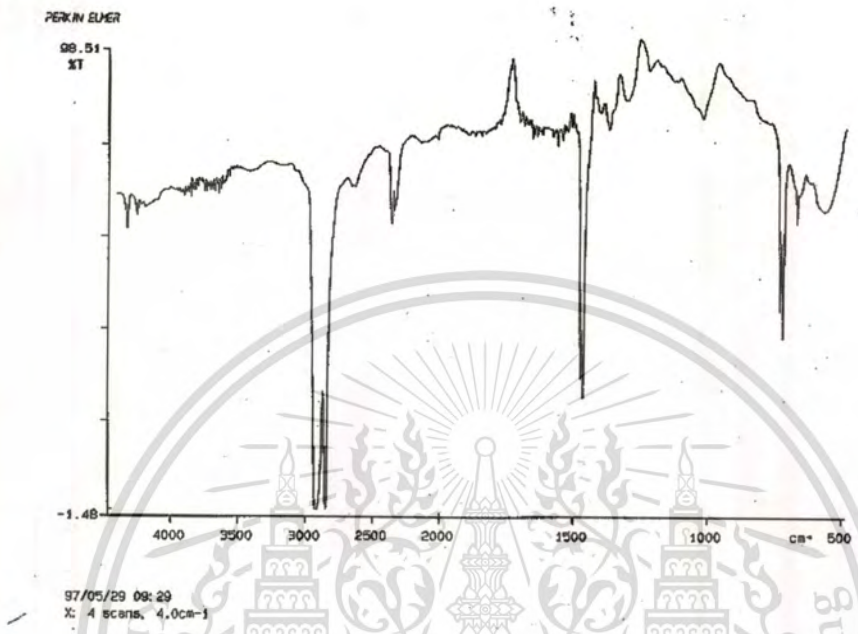

Figure B-1 FT-IR spectra of pure LDPE

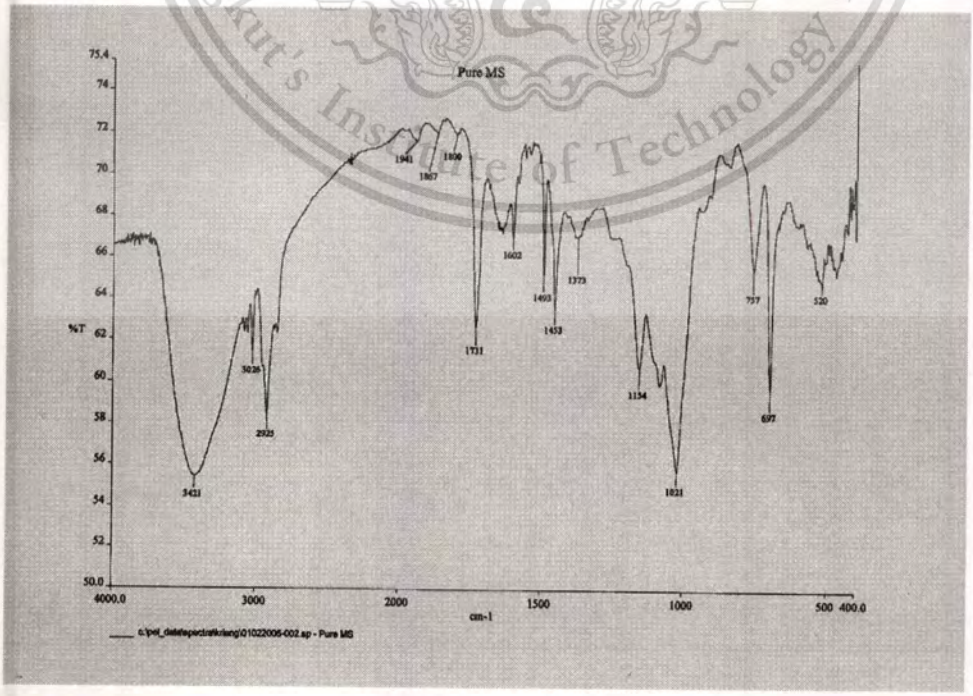

Figure B-2 FT-IR spectra of pure MS

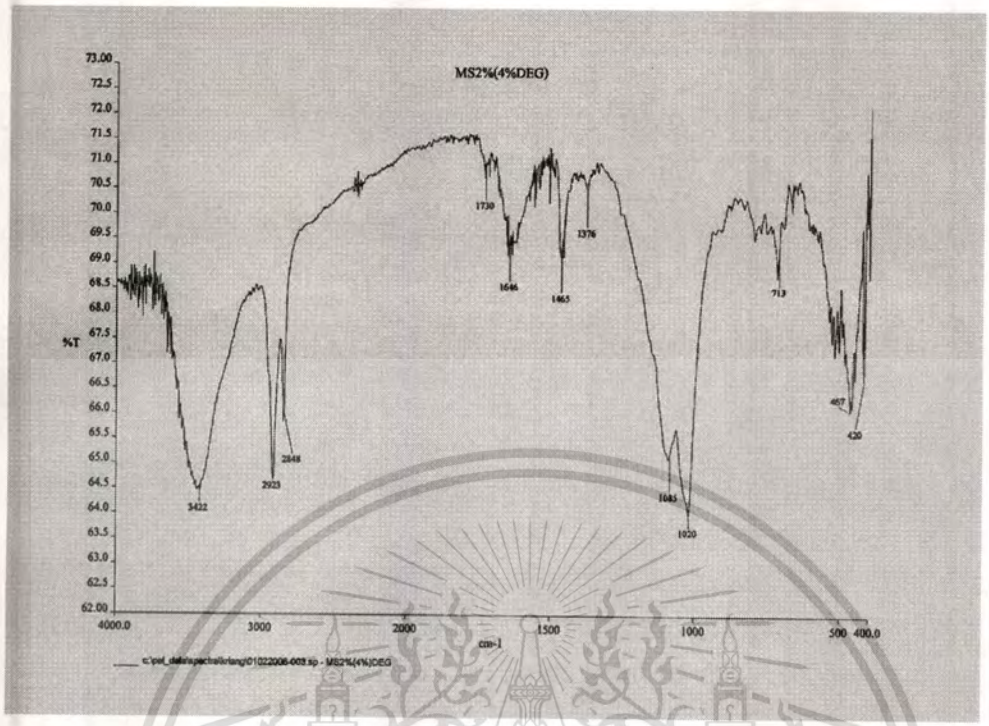

Figure B-3 FT-IR spectra of 2%MS-4%DEG filled LDPE

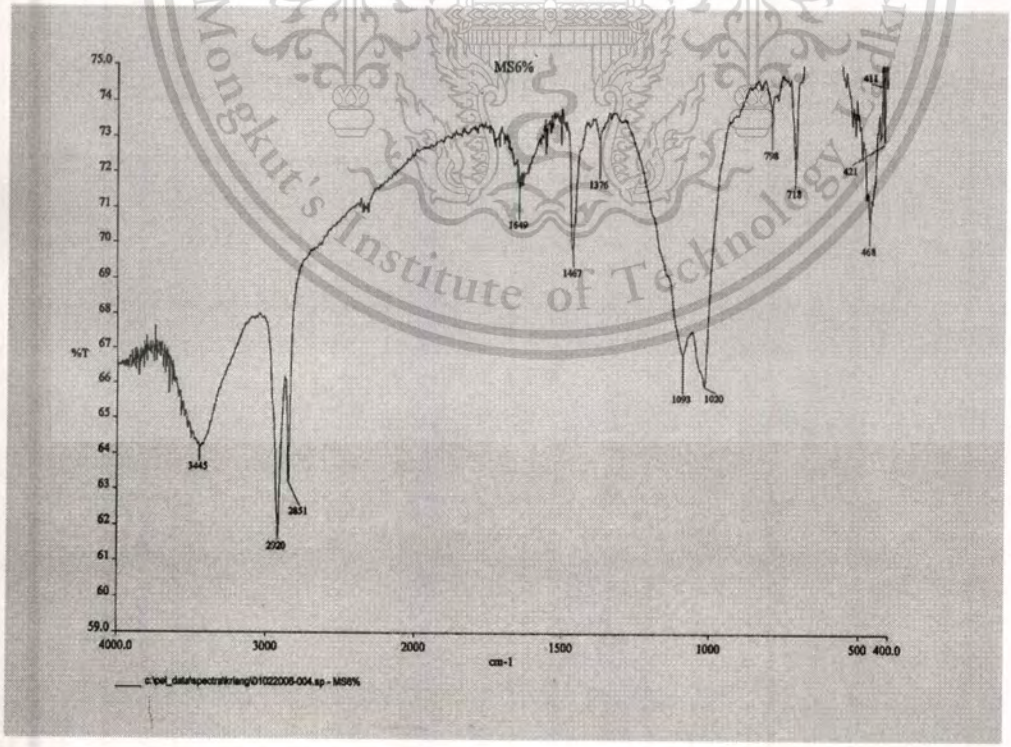

Figure B-4 FT-IR spectra of 6%MS filled LDPE

Appendix C

TGA Thermograms of LDPE and MS-LDPE samples

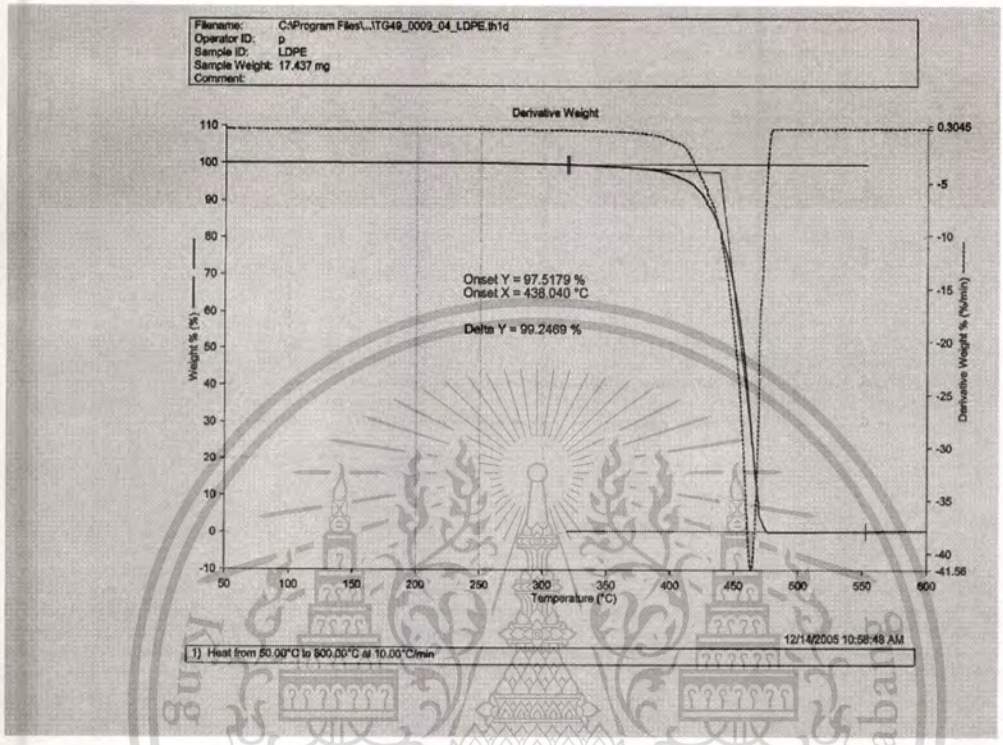

Figure C-1 TGA thermogram of pure LDPE

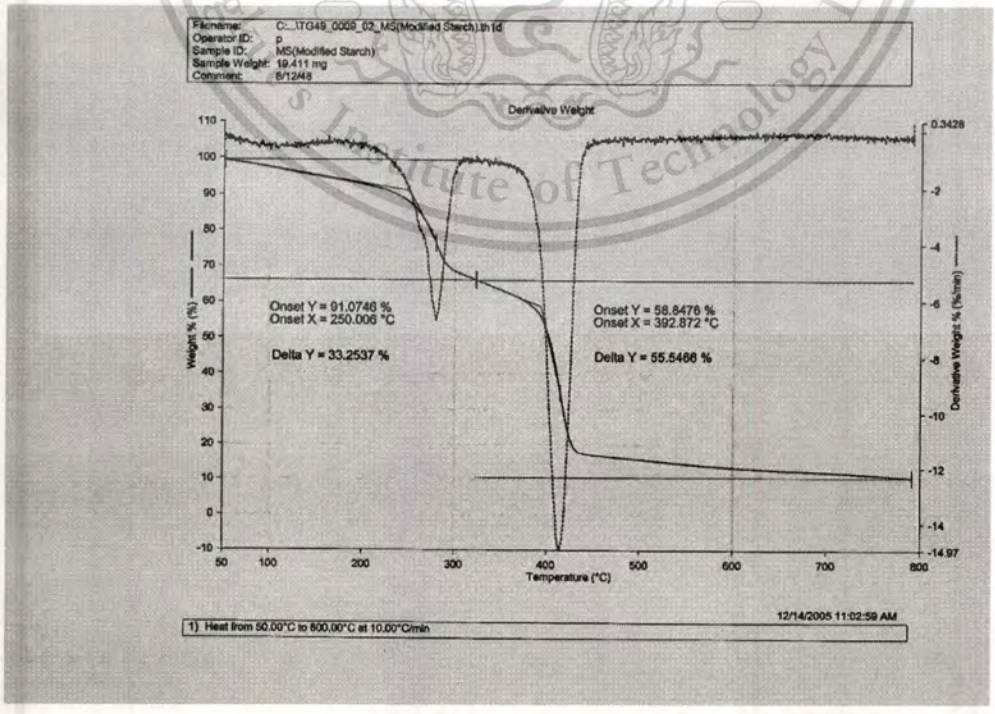

Figure C-2 TGA thermogram of pure MS

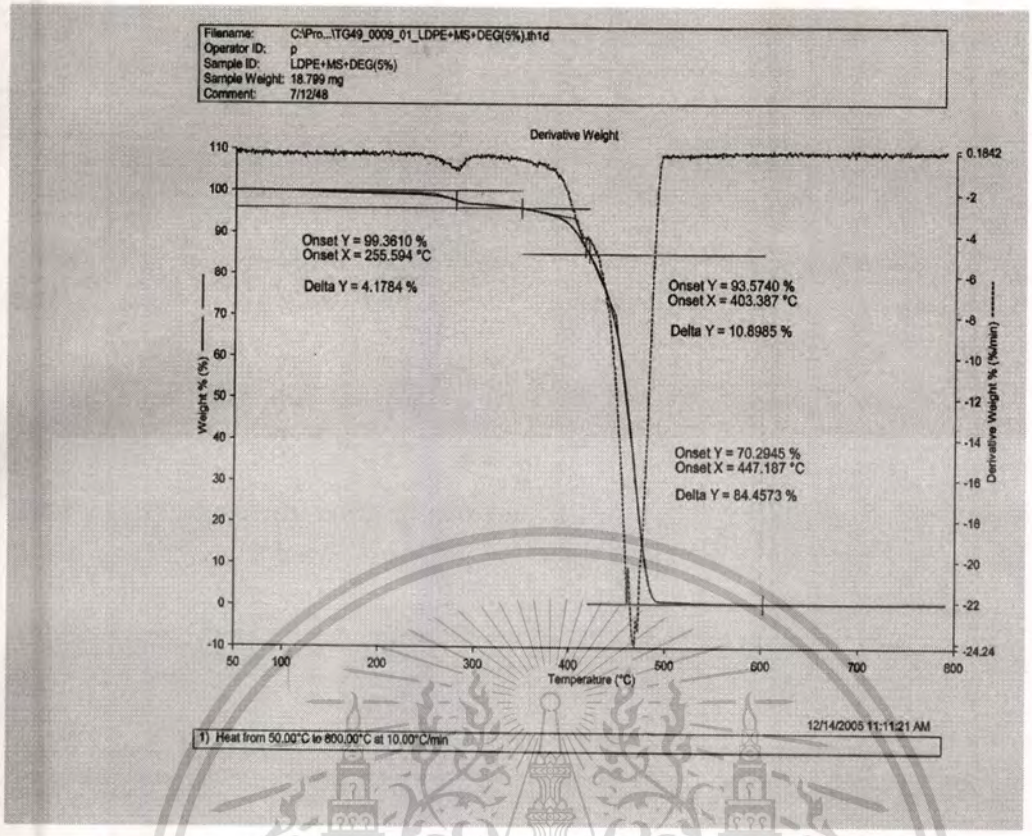

Figure C-3 TGA thermogram of 10%MS -5%DEG filled LDPE

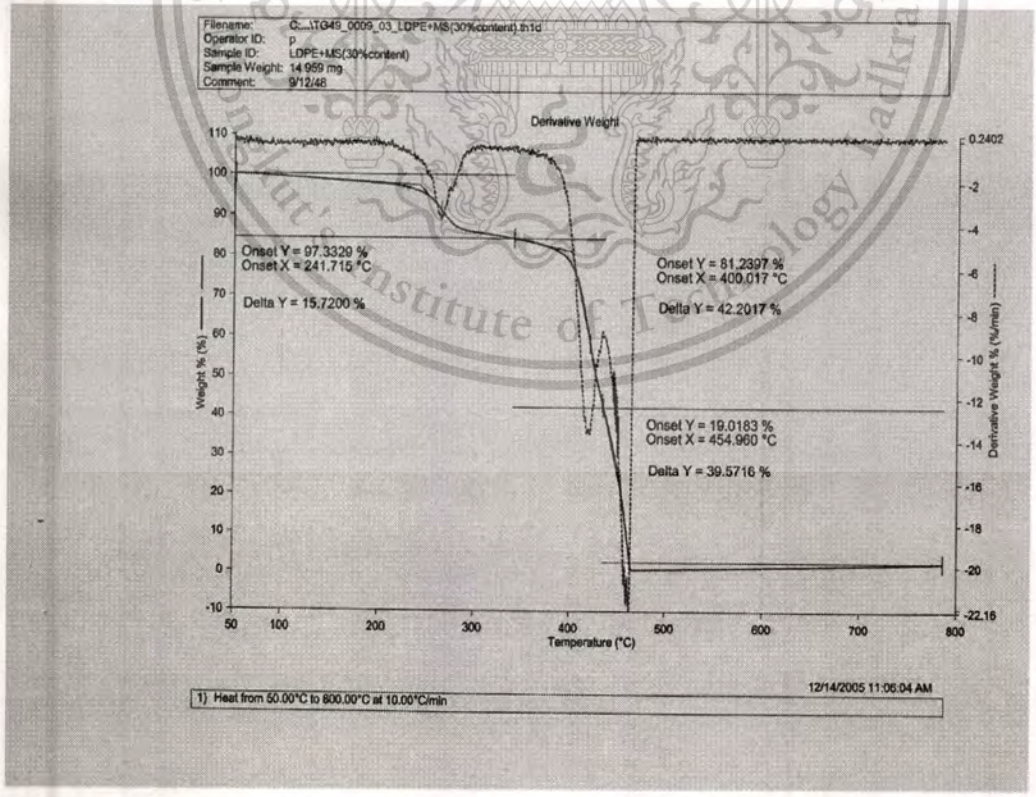

Figure C-4 TGA thermogram of 30%MS filled LDPE