MICROCELLULAR BIODEGRADABLE PLASTIC FOAM FROM TAPIOCA STARCH

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Abstract

This special project aim is to study a foam forming technique of biodegradable plastic produced from tapioca starch. Biodegradable plastic was obtained from styrene butyl acrylate graft tapioca starch compounding with polystyrene in difference ratio and vary amount of diethylene glycol. The biodegradable plastic was compounded by single screw extruder which the optimum condition temperature was the nozzle, zone1, zone2, zone3 were 170, 160, 150, 140 degree celcious, respectively and the rotor speed was 10 L/min. The biodegradable plastic sheet was produced compress by hot compression machine at 170 degree celcious for 2 minutes, repress 3 times and cooled down at 5 degree celcious for 1 minute. After that the microcellular foam was produced by foam forming machine at pressure 2200, 3000 and 3600 psi, the temperature was 100 degree celcious for 3 hours. The foam morphology was performed by scaning electron microscope.

From the experiment found that the suitable condition to produce microcellular biodegradable plastic foam was styrene butyl acrylate graft tapioca starch and polystyrene ratio equal 10:90 using 5% DEG at temperature 100 °C and pressure 3000 psi for 3 hours.

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Piyachay Srijan

Pattarika Methakul

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Abbreviations

SS : sago starch
Bu : butyl acrylate
CAN : ceric ammonium nitrate
CMS-g-AM : carboxymethyl starch graft acrylamide
CO_2 : carbondioxide
EPS : expandable polystyrene
FTIR : x-ray spectroscopy
GPPS : general purpose polystyrene
HIPS : high-impact polystyrene
H_2SO_4 : sulfuric acid
$K_2S_2O_8$: potassium persulphate
MA : methyl acrylate
rpm : round per minute
SEM : scanning electron microscope
SDS : sodium lauryl ether sulfate
St : styrene monomer
St-Bu-g-starch : styrene butyl acrylate graft tapioca starch
TGA : thermogravimetric analysis
UV : ultraviolets
XPS : extruded polystyrene
n : number of cells per cm^3
n_b : number of cells per unit $\ell \times \ell$
ℓ : length of side quadrate in mm
φ : expansion ratio
ρ_p : density of polymer before foaming (g/cm^3)
ρ_f : density of polymer foam (g/cm^3)
°C : degree celcious
%wt : percent by weight

Chapter 1

Introduction

Now a day, plastic products are criticized in the bad way that they can not be decomposed by biodegradation in short time period, so they are accused to be the pollution cause to the environment.

They solution discovery as follow:

Recycle, but there is a limit which is the dirty determination. So recycle plastics can not be used to contain food or drinking water it can be only used as bin, and there is also problems between production process because plastic has been heated in the initial process of the production. These could be cause the burning of the plastic easily in the next production.

Anyway tapioca is one kind of economics plant of Thailand which is very famous growing in many regions of the country, especially in the east and north east. The most tapioca product exported to sell in Europe. In the present agricultures grow tapioca encounter the fluctuated problems in the marketing. These cause of the European countries have limit the import quota and control the product quality. These make the product prices has the decreasing trend because of the product processing and the marketing of tapioca are not accordingly.

So the research about the application of tapioca is very important to increase the product value. From this reason there is an important essencial to research and develop the uses of tapioca for producing the plastic product that can be decomposed by biodegradation for using instead of the plastic produced from petroleum.

1.1 Objective

1.1.1 To produce biodegradable plastic which could be environmental friendly.

1.1.2 To produce microcellular biodegradable plastic foam.

1.1.3 To study the processing of the biodegradable plastic foam.

1.1.4 To study the properties of microcellular biodegradable plastic foam.

1.2 Scope of this work

1.2.1 To produce styrene butyl acrylate graft tapioca starch.

1.2.2 To produce the biodegradable plastic from chemical modification tapioca starch and to find the ratio of the modification tapioca starch blended with polystyrene plastic.

1.2.3 To produce microcellular biodegradable plastic foam.

1.2.4 To measure the physical and morphological properties of biodegradable plastic foam.

1.3 Expect results

1.3.1 To produce microcellular biodegradable plastic foam from tapioca starch.

1.3.2 To find the suitable condition to produce microcellular biodegradable plastic foam.

Chapter 2

Theory and Literature Review

2.1 Literature Review

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 maize starch and chloroacetic acid in sodium hydroxide methanol media. Then, 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 water addition capacity of carboxymethyl starch graft acrylamide is 350 g/g and the corresponding substitute degree is 0.74.

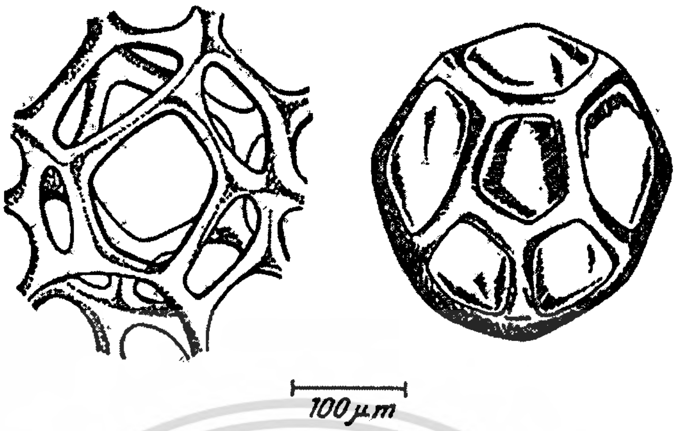
Lahman, et al. (2000) carried out the graft copolymerization by methyl acrylate with sago starch in which ceric ammonium nitrate was used as an initiator based on a free radical reaction. The effect of concentration of ceric ammonium nitrate (CAN), concentration of methyl acrylate (MA), sago starch (SS). 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 8.77×10^{-3}, 0.803, 0.135 and 0.175 mol L^{-1}, respectively. The rate of graft copolymers were characterized by FTIR spectroscopy, TGA and DSC analysis showed that confirmation of the occurrence of methyl acrylate polymer onto sago starch.

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/polyurethanes showed two, indicating phase separation. The solubility parameter from the swelling data of starch and polyurethane blends was discussed about a correlation with thermomechanical properties, and the potential for biodegradation.

2.2 Foam

Cellular plastic or plastic foam also referred to expanded or sponge plastics. In normally that contains at least of solid polymer and gases occurred from blowing agent. Solid polymer contained of one polymer or more such as mixed two types of polymer foam may be soft or strength depends on temperature that like glass state (glass transition temperature : Tg) have range low or higher than room temperature.

Foams consist of two characteristics that is close cell (B) which is pore or cell disconnected. It is suitable for made insulation normally are solid. The other one is open cell (A), which is pore of cell are connected together. The structure of cell depend on the process to produce foam and type of chemical to make a bubble plastic foam.



(A) (B)

Figure 2.1 Open cells(A) and Close cells foam(B)

To produce foam :

1. Degradation when receive heat from blowing agent will be occur nitrogen, carbondioxide or both of them used heat outside or heat from polymerization reaction.
2. Process produce bubble gas in polymer system by exothermic reaction.
3. Vaporization of solution that have low boiling point such as fluorocarbon or methylene chloride in reaction.
4. Vaporization due to heat between occurs the polymerization to be bubble gas such as the reaction between isocyanate and water to carbondioxide will be occur in the system.
5. Expansion of gas in polymer that depend on pressure of system.
6. Cluster together of bubble gas which disperse in polymer

To produce foam that have two ways are :

1. Physical method is expression by gas or mix chemical that gas insert in polymer when use polymer compression by used heat the gas will be expand and expand to be foam example expandable polystyrene.
2. Chemical method is the reaction between two types of chemicals to produced foam, raw material usually are two liquid or more. First one is liquid polymer and another are mixed of crystallization material or harden solution and chemical that have reaction with melting polymer to produce gas such as polyurethane foam.

Apparatus occur foam.

Foam occur from new forming associate with physical and chemical when consider physical property, the new forming call nucleation. It can be occur from changing structure inside of them or disperse of other solution in coming. The basic of synthesis foam associate with occur bubble nucleation and bubble growth for foam product.

Method that important is molecules of gas disperse in polymer. It must have enough power to crush pressure at outside for expandable size that can see foam like a foam increase volume if thermodynamic instability occur more. It will be activate a nucleation produce a lot of molecules gas in short time. The ways to occur of thermodynamic instability that enough have two ways are reduce pressure and increase temperature. The polymer thermoplastics have non-conductor and degrade at high temperature. Popular way is reduce pressure more than increase temperature.

Foaming consists of basic 3 steps: such as

1. Bubble initiation or nucleation is process start a lot of small gases disperse in polymer.
2. Bubble growth is process that increasing of gases expands of size. They come from disperse of gases from sample to the bubble gas when increase temperature or reduce pressure and coalescence of two bubble gas or more.
3. Stabilization of foam are the last process of foaming. It have stable and not changing size.

2.3 Starch

Starch is a combination of amylose, which is a linear polymer and amylopectin. Both are polysaccharides composed of 1,4-alpha-D-glucopyranosyl units $(C_6H_{10}O_5)_x$. Native starch granules swell when they absorb water through hydrogen bonding with their free hydroxyl groups, but they still retain their order and crystallinity. However, when these swollen starch granules are heated, hydrogen bonding between adjacent glucose units is disrupted. The crystallinity is progressively destroyed. This process is called gelatinization, processing with water in a heated extruder is an efficient way to obtain gelatinized starch. High shear can be generated in the extruder to disrupt the starch granules. The pressure generated raises the boiling point of water so that high temperature is attainable for rapid and complete disruption of the granular structure.

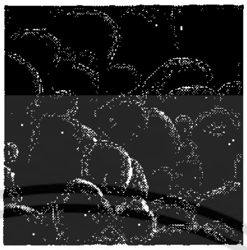


Figure2.2 Tapioca starch granules

2.3.1 Source

Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules, each typically containing several million amylopectin molecules accompanied by a much larger number of smaller amylose molecules. By far the largest source of starch in corn (maize) with other commonly used sources being wheat, potato, tapioca and rice. Amylopectin (without amylose) can be isolated from "waxy" maize starch whereas amylose (without amylopectin) is best isolated after specifically hydrolyzing the amylopectin with pullulanase. Genetic modification of starch crops has recently led to the development of starched with improved and targeted functionality.

Table 2.1 Starch content of various seeds and the characteristics of the starch granules

Botanical origin	Starch(%dry basis)	Shape	Diameter(μm)(mean in parentheses)	Amylose(% dry starch)
Wheat	67.2-68.4	Lenticular, polyhedric	2-38	26-28
Maize	71.0-74.0	polyhedric	5-25	28.0
Smooth pea	43.0-48.0	Reniform (simple)	5-10	33.2-35
Wrinkled pea	32.0-37.0	Rosette (compound)	30-40	62.8-75.4
Sweet potato	69.2-72.0	polyhedric	10-25	-
potato	65.0-85.0	Ellipsoidal	15-100	23

2.3.2 Structural unit

Starch consists of two types of the molecule, amylose (normally 20-30%) and amylopectin (normally 70-80%). Both consist polymer of α–D-glucose units in the conformation. In amylose these are α–(1-4)-links, with the ring oxygen atoms all on the same side, whereas in amylopecin about one residue in every twenty or so also α–(1-6)-links forming branch points. The relative proportions of amylose to amylopectin and α–(1-6)-links branch-points both depend in the source of the starch, e.g. amylomaizes contain over 50% amylose whereas "waxy" maize has almost none (~3%).

Amylose

Amylose is a linear polymer of glucose linked with α(1→4) bonds. It can be made of several thousands glucose units. Most starched contain about 18 to 28% amylose. The digestive enzyme amylase works on the ends of the starch molecule, breaking it down into sugars. Amylose is one of the two components of starch, the other being amylopectin.

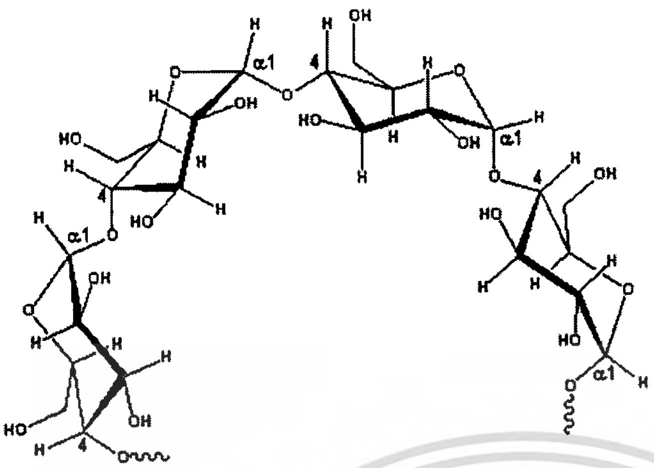


Figure 2.3 Representative structure of amylose

Amylopectin

Amylopectin is a highly branched polymer of glucose found in plants. It is one of the two components of starch, the other being amylose. Glucose units are linked in a linear way with α(1→4) bonds. Branching takes place with α(1→6) bonds occurring every 24 to 30 glucose units.Its counterpart in animals is glycogen which has the same composition and structure, but with more extensive branching that occurs every 8 to12 glucose units.

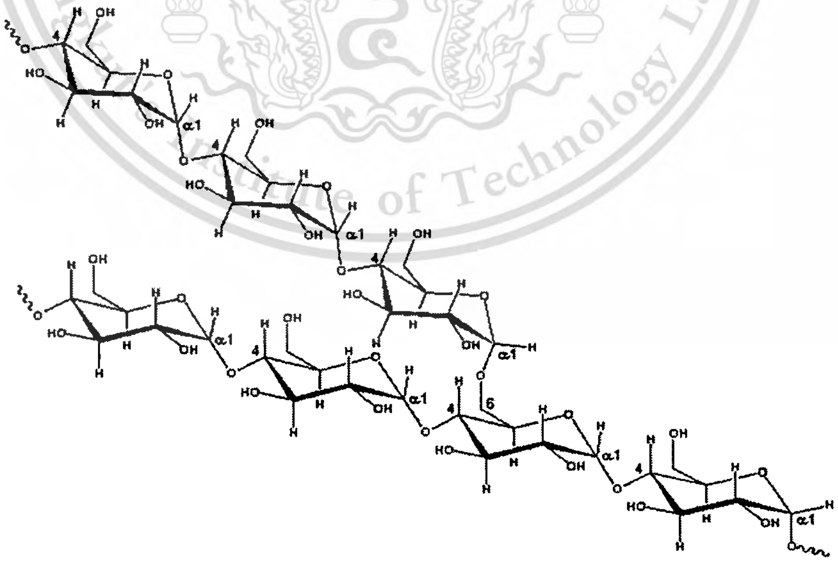


Figure 2.4 Representative structure of amylopectin

3. Polystyrene

Polystyrene belongs to the group of standard thermoplastics that also includes polyethylene, polypropylene, and poly (vinyl choride). Because of its special properties, polystyrene can be used in an extremely wide range of applications.

Polystyrene molding materials are hard, transparent materials with a high gloss. They are most commonly described as general purpose polystyrene(GPPS) but terms such as standard polystyrene, normal polystyrene, clear polystyrene, or styrene homopolymer are also in use.

In this article the definition polystyrene(PS) molding material is used according to ISO 1622-2.

Below 100°C polystyrene molding materials solidify to give a glasslike material with adequate mechanical strength, good dielectric properties and resistance toward a large number of chemicals for many areas of application.

Above its softening point clear polystyrene occures as a melt which can be readily processed by techniques such as injection molding or extrusion. Small quantities of lubricants can be used internally or externally as processing aids. The addition of antistatic agents, UV stabilizers, glass fibers, or colorants is also common.

The mechanical properties of the relatively brittle PS molding materials can be considerably improved by adding rubbers, generally polybutadiene. Styrene-butadiene molding materials are generally referred to as high-impact polystyrene (HIPS).

Styrene copolymers

Styrene can be copolymerized with many other monomers.Styrene-acrylonitrile molding materials in particular have achieved great economic importance in transparent and rubber-modified forms. Compared with the pure styrene polymers they have advantages with regard to hardness, strength, and resistance to heat distortion and environmental stress cracking. However, these advantanges are offset by a higher price and more difficult processing.

Copolymers of styrene and maleic anhydride have softening point that is up to 30°C higher than that of PS molding material. These products are used in form of foams in the automotive industry.

Polystyrene foams

Expandable polystyrene (EPS) is the starting material for PS hard foam materials. It is produced from polystyrene by the addition of ca.6% of low-boiling hydrocarbon as the foaming agent. Extruded polystyrene (XPS) foams are produced from polystyrene and halogenated hydrocarbon as blowing agents.

For more than 50 years, the effectiveness of EPS has been proven in numerous packaging applications used by a wide variety of industries, consumer product manufacturers and catalogue and shipping companies. Lightweight EPS is ideal for these packaging applications due to its physical properties, in particular its cushioning characteristics, dimensional stability and its thermal and moisture resistance.

4. Physical properties of polystyrene foam

Table 2.2 Typical strength characteristics - EPS thermal insulation board

Property	Units	ASTM Test	ASTM C 578 Type			
			I	VIII	II	IX
Density range	pcf	C303	0.90-1.14	1.15-1.34	1.35-1.79	1.80-2.19
Flexural strength	psi	C203	25-30	32-38	40-50	55-75
Compressive resistance-at yield	psi	C165 orD1621	10-14	13-18	15-17	25-33

Reasons why polystyrene foam is bad for the environment and human health.

1. Toxic chemicals leach out of these products into the food that they contain. These chemicals threaten human health and reproductive systems.

2. These products are made with petroleum, a non-sustainable, heavily polluting and disappearing commodity.

3. The product does not biodegrade. It crumbles into fragments that have no expiration date.

3. A certain percentage of product will be dumped in the environment, persisting on land indefinitely as litter and breaking up into pieces that choke and clog animal digestive systems in waterways.

4. The product takes up more space in landfills than does paper and eventually will reenter the environment when landfills are breach by water or mechanical forces.

5. Foam recycling is a public relations stunt, promoted by the chemical industries that manufacture it. This is done in highly centralized, distant facilities using complex chemical processes and expends far more energy than is ever saved by recycling the material.

2.4 Properties of polystyrene

2.4.1 Physical properties

Table 2.3 Physical properties of polystyrene

Density	0.0376-0.0387 lb/in^3
Water absorption	0-0.1 %
Moisture absorption at equilibrium	0.04-0.1 %
Water absorption at saturation	0.1 %
Linear mold shrinkage	0.004-0.006 in/in
Melt flow	1.2-28 g/10 min

2.4.2 Mechanical properties

Table 2.4 Mechanical properties of polystyrene

Hardness, Rockwell M	70-74
Hardness, Rockwell R	104-120
Tensile strength, ultimate	2600-10200 psi
Tensile strength, yield	3630-10000 psi
Elongation @ break	1-45 %
Elongation @ yield	1.5-2.2 %
Tensile modulus	260-490 ksi
Flexural modulus	390-479 ksi
Flexural yield strength	7830-15000 psi
Compressive yield strength	13100 psi
Poisson's ratio	0.33
Izod impact, notched	0.2- 2.38 ft-lb/in
Izod impact, unnotched	2.06 ft-lb/in
Izod impact, notched low temperature	1.31 ft-lb/in
Charpy impact, unnotched	3.81-13.3 ft-lb/in^2
Charpy impact, notched low temperature	0.476-0.952 ft-lb/in^2
Charpy impact, unnotched low temperature	4.28-4.76 ft-lb/in^2
Charpy impact, notched	0.952-1.9 ft-lb/in^2
Gardner impact	4.43 ft-lb
Tensile creep modulus, 1 hour	334000-479000 psi
Tensile creep modulus, 1000 hours	319000-377000 psi

2.4.3 Electrical properties

Table 2.5 Electrical properties of polystyrene

Electrical resistivity	1E+15-1E+17 ohm-cm
Dielectric constant	2-2.8
Dielectric constant, low frequency	2-2.8
Dielectric strength	500-3430 kV/in
Dissipation factor	0.00005-0.0004
Dissipatin factor, low frequency	0.00009-0.0004
Surface resistance	1E+13-1E+15 ohm
Arc resistance	100-180 sec
Comparative tracking index	350-600 V
Hot wire ignition, HWI	15 sec
High amp arc ignition, HAI	120 arcs
High voltage arc-tracking rate, HVTR	4.72-11.8 in/min

2.4.4 Thermal properties

Table 2.6 Thermal properties of polystyrene

CTE, linear 20°C	27.8-69.4 μ in/in-°F
CTE, linear 20°C transverse to flow	38.9-50 μ in/in-°F
Heat capacity	0.287-0.502 BTU/lb-°F
Thermal conductivity	0.833-1.34 BTU-in/hr-ft^2-°F
Melting point	374-500°F
Maximum service temperature, air	156-196°F
Deflection temperature at 0.46 MPa	172-217°F
Deflection temperature at 1.8 MPa	156-210°F
Vicat softening point	33.9-230°F
Glass temperature	181-212°F
Flammability, UL94	HB
Oxygen index	18-19%

2.4.5 Optical properties

Table 2.7 Optical Properties of polystyrene

Haze	0.65-1%
Transmission, visible	80-90%
Processing temperature	392-424°F

2.5 Property of foam

2.5.1 Number of cells

Normally, plastic foam consist a lot of cells depend on process. The number of cells (n) , it use for explain estimate homogeneous of sample or quality of process where n is function of wall thickness, density of plastic foam and number of cells per unit at equation (1).

$$n = \left({n_b}/{\ell^2} \right)^{3/2} \times 10^3 \times \varphi \qquad (1)$$

Where n is number of cells per cm^3
n_b is number of cells per unit $\ell \times \ell$
ℓ is length of side quadrate in mm
φ is expansion ratio

$$\varphi = \frac{\rho_p}{\rho_f} \qquad (2)$$

Where ρ_p is density of polymer before foaming (g/cm^3)
ρ_f is density of polymer foam (g/cm^3)

1.5.2 Wall thickness

The density and number of cells have causality with wall thickness (δ) which it have relationship with average diameter of cells at equation (3).

$$\delta = d\left(\frac{1}{\sqrt{1-\rho/\rho_p}} - 1\right) \quad (3)$$

Where ρ_p is density of polymer before foaming (kg/m^3)
ρ is density of polymer foam (kg/m^3)

Chapter 3

Experiment 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 Styrene monomer (commercial grade)
3.1.1.3 Butyl acrylate monomer (commercial grade)

3.1.2 Initiator

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

3.1.3 Emulsifier

3.1.3.1 Sodium lauryl ether sulfate (commercial grade)

3.1.4 Other Chemicals

3.1.3.1 Diethylene glycol (commercial grade)
3.1.3.2 Polystyrene (general purpose, commercial grade)

3.2 Instruments

The instrument used in this study are listed below:

3.2.1 Four necked 2 L glass reactor with paddle type agitator and vary speed motor
3.2.1 Hot air oven
3.2.3 Granulator (BOSCO)
3.2.4 Single screw extruder D-76227 Thermo Haake Polydrive Germany
3.2.5 Compression machine
3.2.6 Electronic densimeter MD-2000S
3.2.7 Electronic weight
3.2.8 Foam forming machine
3.2.9 Scanning electron microscope(SEM)
3.2.10 Thermogravimetric analyzer(TGA)

3.3 Synthesis of styrene butyl acrylate graft tapioca starch

Figure 3.1 Four necked 2 L glass reactor with paddle type agitator and vary speed motor

In graft copolymerization reaction, tapioca starch 150 g in 1700 mL of distilled water was gelatinized for 1 hour at the temperature 90 °C, in 2 L four necked glass reactor. A rotor speed was 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 450 rpm for 15 minutes then 150 mL of initiator solution was added. The reaction was allowed to stir continuously for 3 hrs at 60 °C. After completion of the reaction, the solution was dried in hot air oven at temperature between 55-60 °C until its weight constant.

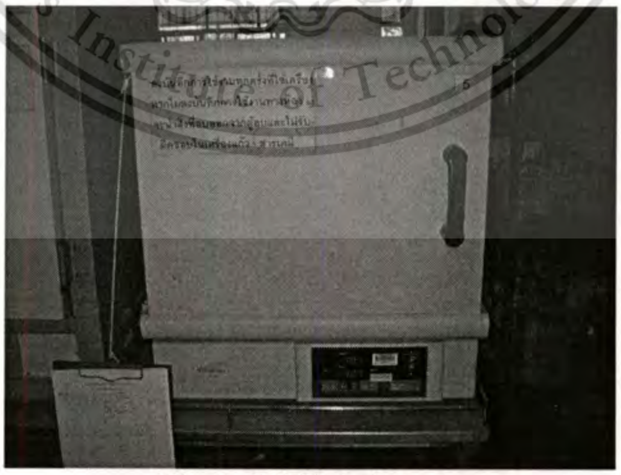


Figure 3.2 Hot air oven

The dried styrene butyl acrylate graft tapioca starch was obtained from the hot air oven at 55-60 °C until its constant weight. The dried tapioca starch graft copolymer was crush by using BOSCO granulator.

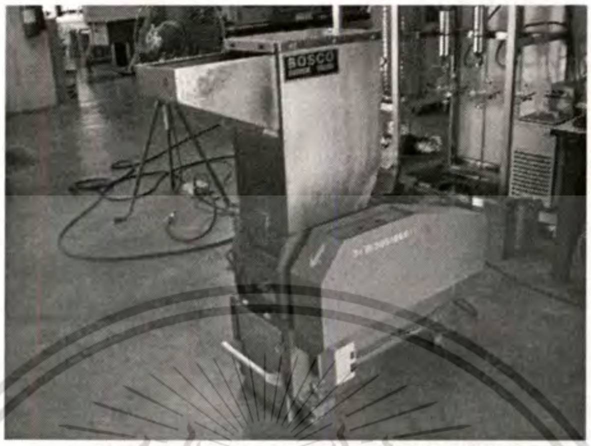


Figure 3.3 Granulator (BOSCO)

Figure 3.4 The styrene butyl acrylate graft tapioca starch after crush by BOSCO granulator

3.4 Compounding

Sample preparation

1. Samples preparation of 5 conditions followed in the table 3.1.

Table 3.1 Samples preparation by vary percent of styrene butyl acrylate graft tapioca starch and polystyrene which this case without diethylene glycol.

Compound	Condition					
	reference	10:90	20:80	30:70	40:60	50:50
styrene butyl acrylate graft tapioca starch	0	10	20	30	40	50
Polystyrene	100	90	80	70	60	50
Diethylene glycol	-	-	-	-	-	-

Table 3.2 Samples preparation by vary percent of diethylene glycol using styrene butyl acrylate graft tapioca starch and polystyrene ratio equal 10:90.

Compounds	Condition		
	3% DEG	4% DEG	5% DEG
styrene butyl acrylate graft tapioca starch	10	10	10
Polystyrene	90	90	90
Diethylene glycol	3	4	5

2. Preparation in plastic bag. Single screw extruder machine integrated into homogenous samples.

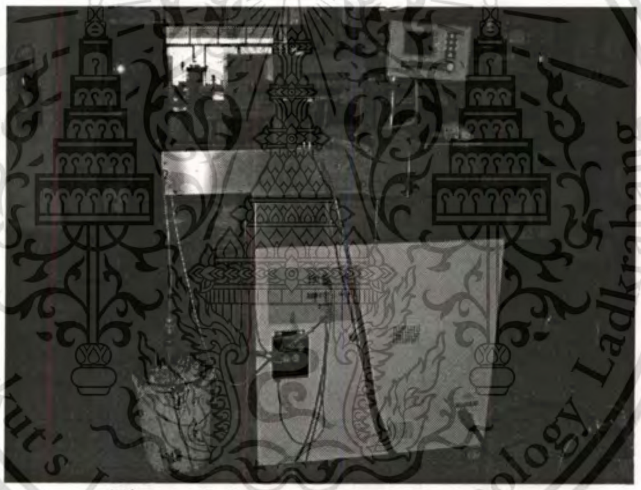


Figure 3.5 Single screw extruder

Single screw extruder machine was set the temperature as follow in table 3.3.

Table 3.3 The temperature in difference zones of single screw extruder.

Single screw extruder temperature (^{o}C)				Screw speed for extrusion (L/min)
Nozzle	Zone 1	Zone 2	Zone 3	
180	170	160	150	10
170	160	150	140	10

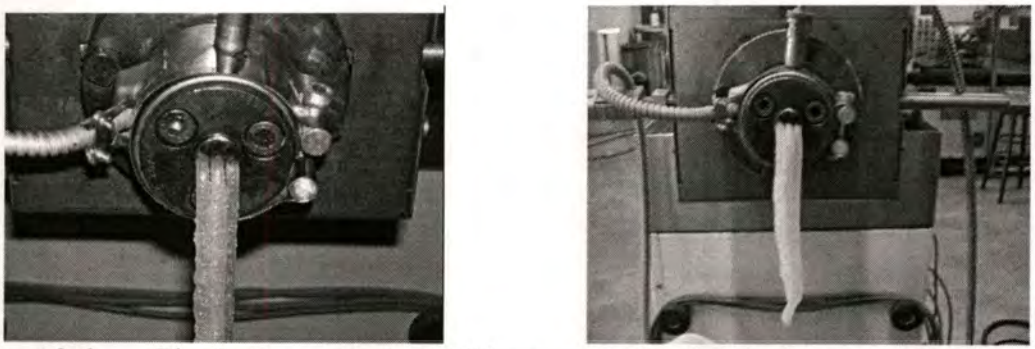


Figure 3.6 The St-Bu-g-starch and PS compounding by single screw extruder.

Figure 3.7 Extruded of St-Bu-g-starch and PS compounding by single screw extruder.

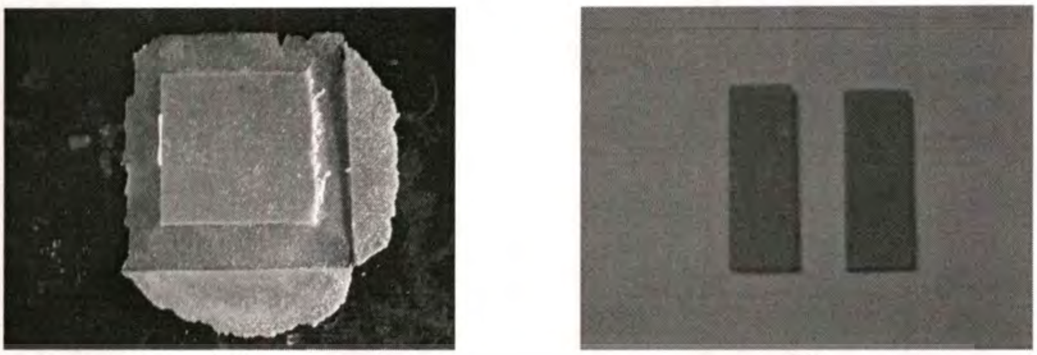
3. The products from single screw extruder were granulated into small particle by using granulator (BOSCO) and kept in vacuum desicator to prevent the moisture absorbtion.

3.5 Compression molding

The plastic was compressed by compression machine. The temperature was set in top and under samples zone were 170 °C. Preheat 1 minute for melt the plastic and repressed 3 times to removed the bubble. After that the machine was recompressed for 1 minute. The sample was rectangular which width, long and thickness were 10×10×0.2 cm. The sample was cut and polished by sand paper number 300 was 3×1×0.2 cm by width, long and thickness.

(A) (B)

Figure 3.8 Compression machine(A) and mold of sample(B)



(A) (B)

Figure 3.9 The product from compression machine(A) and samples for foam forming(B).

3.6 Foam forming

Foam forming machine produced foam which it has pore diameter on micrometer level. The machine used super critical technique by high pressure CO_2 at glass transition temperature (Tg). The product from this process was foam which has high strength at low density.

Figure 3.10 Foam forming machine

In this machine, started by put samples in the chamber and close it. Removed air in the chamber by feed CO_2 gas, waited a few minute and removed air out 2-3 times. After that feed CO_2 into the chamber and controlled pressure at 2000, 3000 and 4000 psi, respectively. The machine was operated for 3 hour at 100 °C.

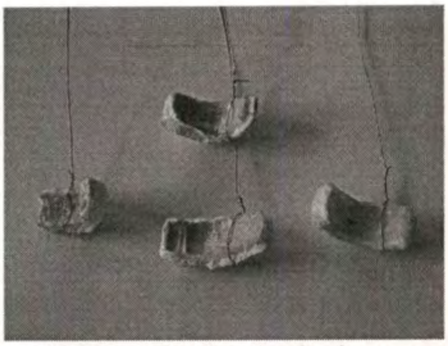


Figure 3.11 Microcellular biodegradable plastic foam produced from styrene butyl acrylate graft tapioca starch and polystyrene plastic.

The samples were cracked at low temperature by dipped in liquid nitrogen for 1 hour before cracked it.

Figure 3.12 Microcellular biodegradable plastic foam after cracked at low temperature.

3.7 Characterizations.

3.7.1 Density of foam

Figure 3.13 Electronic densimeter MD-2000S

To determine density of polymers, the electronic densimeter MD-2000S used Archimedes laws which determine density and controlled density of water is 1g/cm^3 at temperature 4°C to be reference. Its can determine density of solids and liquid materials except powder and high viscosity liquid. In this experiment the examples are foam polymer. Before operate machine should be warmed up the machine about 10 minutes for controlled water temperature equal to 25°C.

1. Set monitor to zero.
2. Weight sample in air and save the result.
3. Weight sample in water and save the result (if sample has air bubble or agglomerate on sample surface could remove it before save the result.)
4. The machine shows density value at monitor.
5. Remove sample from machine.

3.7.2 Foam morphology by scanning electron microscope(SEM)

Figure 3.14 Scanning electron microscope(SEM)

SEM used to study morphology of material. The problem was product that produced from polymer are soft and flexible. So the samples were dipped in liquid nitrogen for 1 hour before cracked it. The cracked sample was produced the best result by scanning electron microscope.

1. Coated gold on surface area
2. Scan the surface of foam by scanning electron microscope

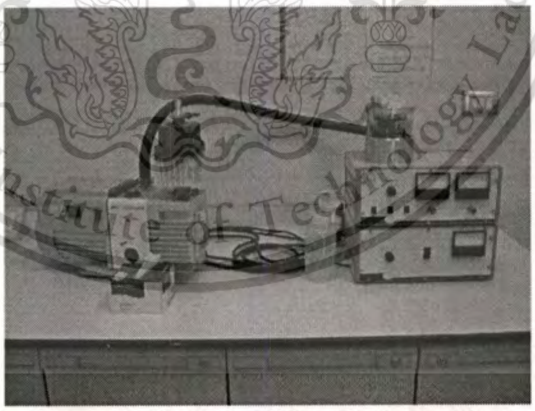


Figure 3.15 The gold coated machine

3.7.3 Thermal property of biodegradable plastic by thermogravimetric analysis(TGA)

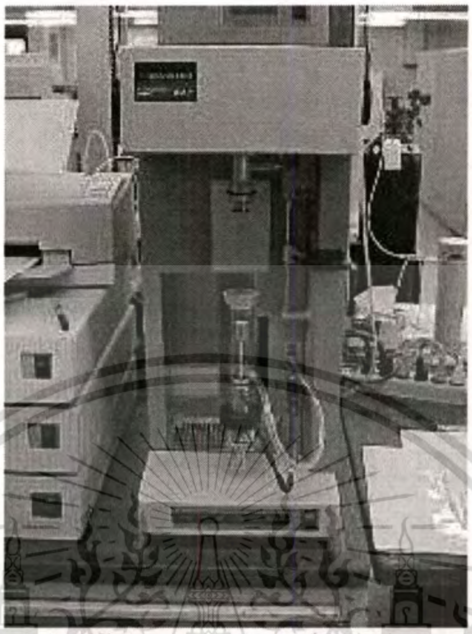


Figure 3.16 Thermogravimetric analyzer (TGA)

Thermogravimetry is one of thermal analysis technique which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time. The mass change characteristics of a material are strongly dependent on the experimental conditions used.

Chapter 4

Results and Discussions

In this study involved processing of tapioca starch graft copolymer foam production from tapioca starch and characterization of foam properties.

4.1 Density of foam

The microcellular biodegradable plastic foams produced from St-Bu-g-starch and PS plastic with vary ratio without DEG at condition 3600 psi and 100 °C. When the ratio of St-Bu-g-starch and PS plastic was increased, density of foam increased which showed in figure 4.1. When the microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary ratio of DEG at condition 2200, 3000 and 3600 psi. The optimum condition of microcellular biodegradable plastic foam produced from styrene butyl acrylate graft tapioca starch and polystyrene equal 10:90 and using 5% of DEG at 100 °C, 3000 psi showed in figure 4.2 and 4.3.

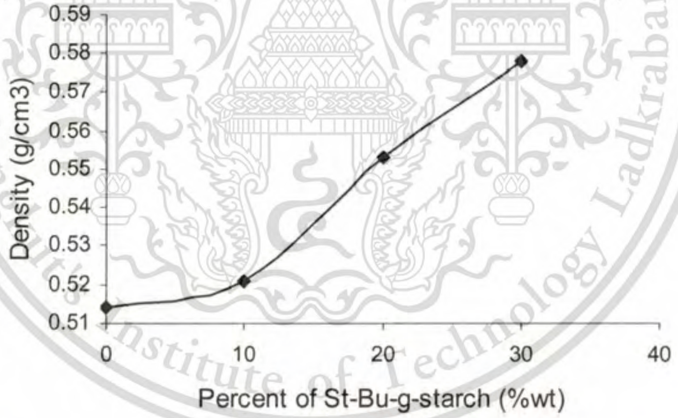


Figure 4.1 The density of microcellular biodegradable plastic foams produced from St-Bu-g-starch and PS plastic with vary ratio and without DEG at condition 3600 psi, 100 °C.

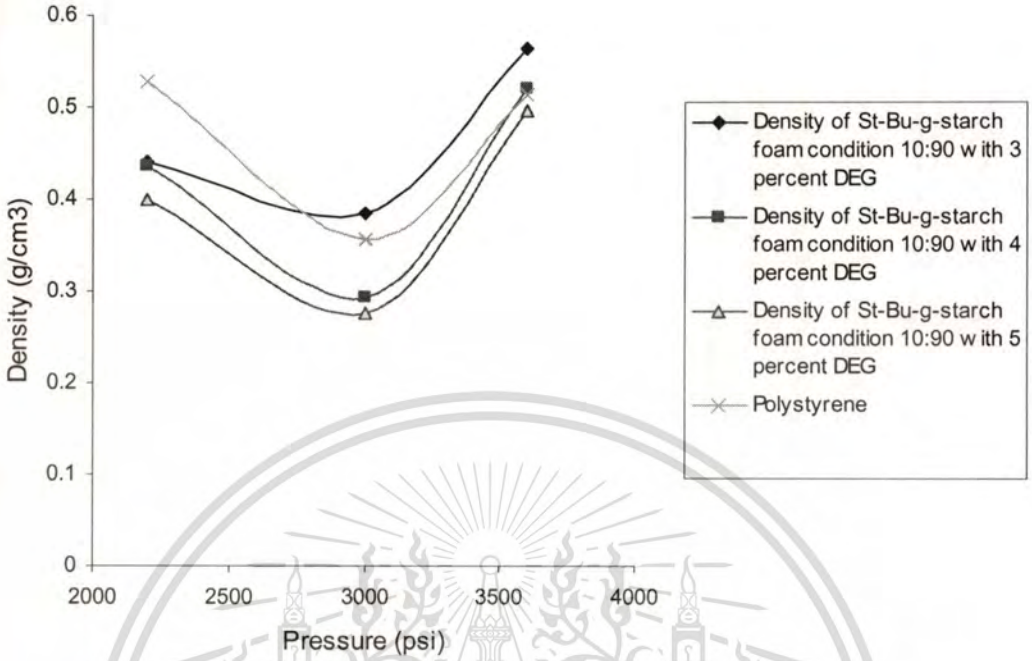


Figure 4.2 The density of microcellular biodegradable plastic foam produced from 10% of St-Bu-g-starch and 90% of PS plastic with difference percent of DEG at 100 °C by vary pressure condition.

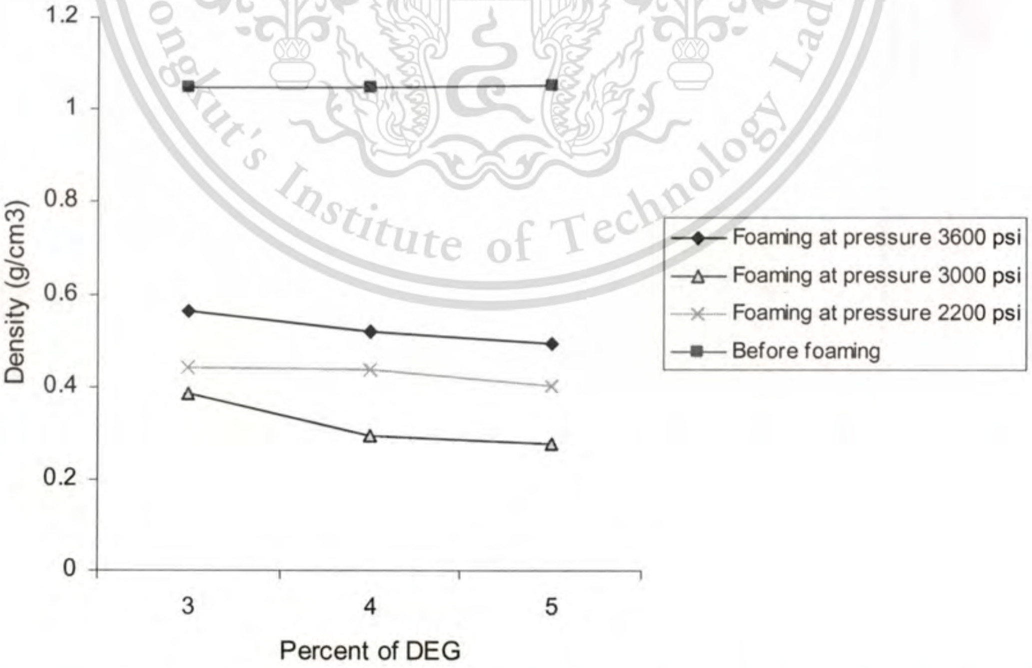
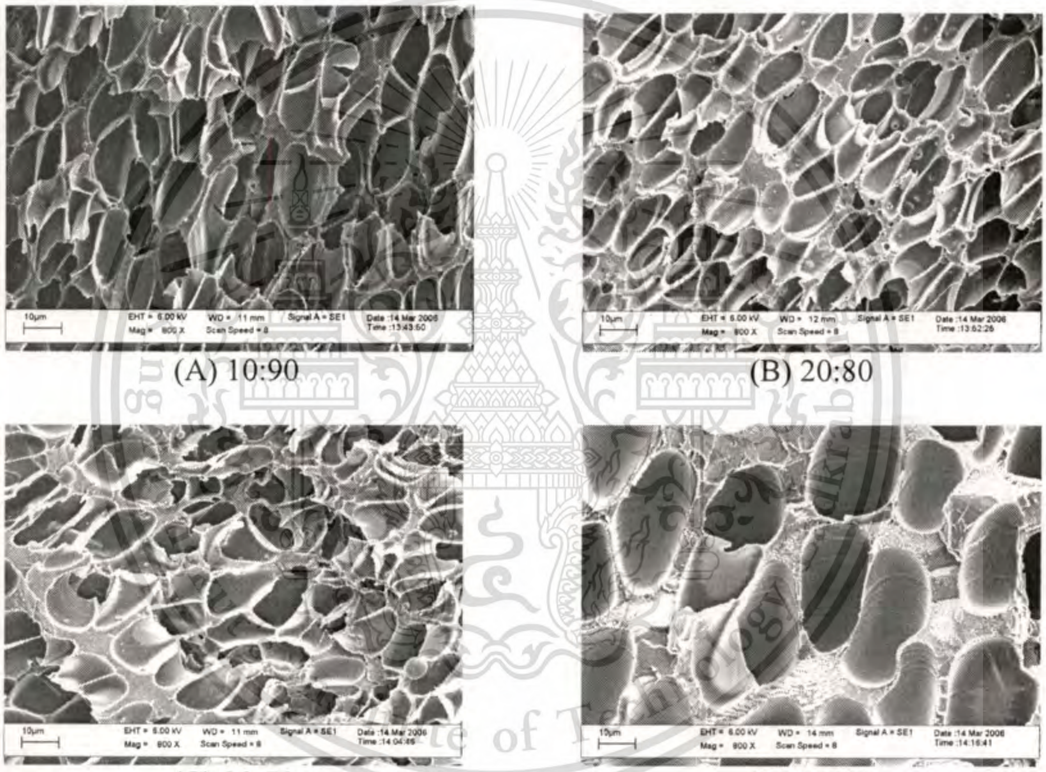


Figure 4.3 The density of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at 100 °C in difference pressure condition.

4.2 Foam morphology by scanning electron microscope

4.2.1 Effect of St-Bu-g-starch/PS ratio

The microcellular biodegradable plastic foams produced from various ratio of St-Bu-g-starch and PS plastic without DEG at condition 3600 psi, 100 °C and 800 magnifications. When the ratio of St-Bu-g-starch and PS plastic was changed, the morphology of microcellular biodegradable plastic foams showed at figure 4.4 (A), (B), (C) and (D) changed, respectively. They had pore size and alignment of cells correspond at every point which had density about 0.5-0.57 g/cm^3 (see figure 4.1), the pore diameter about 10-14 μm (see figure 4.5) and the number of cells about 2.00-3.32 $\times 10^9$ cells/cm^3 (see figure 4.6), respectively.



(A) 10:90 (B) 20:80

(C) 30:70 (D) 0:100

Figure 4.4 SEM images of microcellular biodegradable plastic foams produced from various ratio of St-Bu-g-starch and PS plastic without DEG at condition 3600 psi, 100 °C and 800 magnifications.

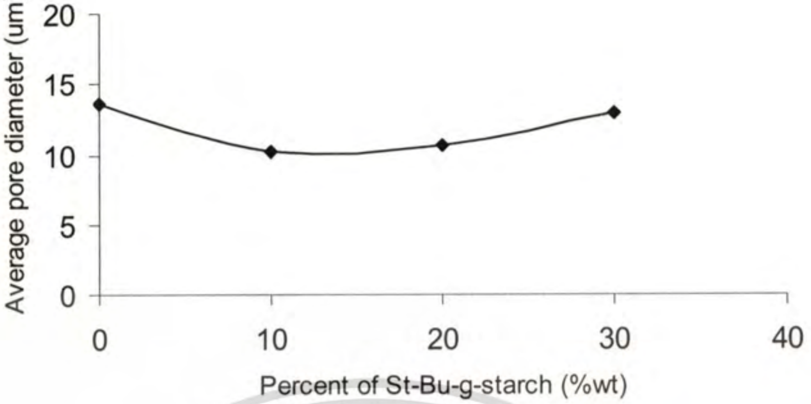


Figure 4.5 The average pore diameter of microcellular biodegradable plastic foams produced from various ratio of St-Bu-g-starch and PS plastic without DEG at condition 3600 psi and 100 °C.

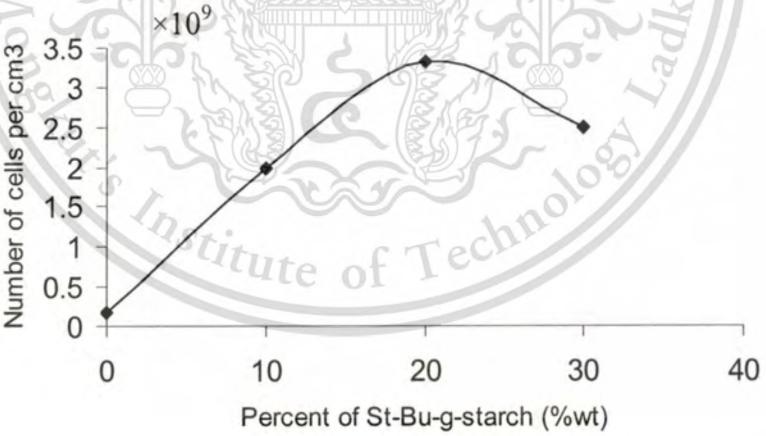
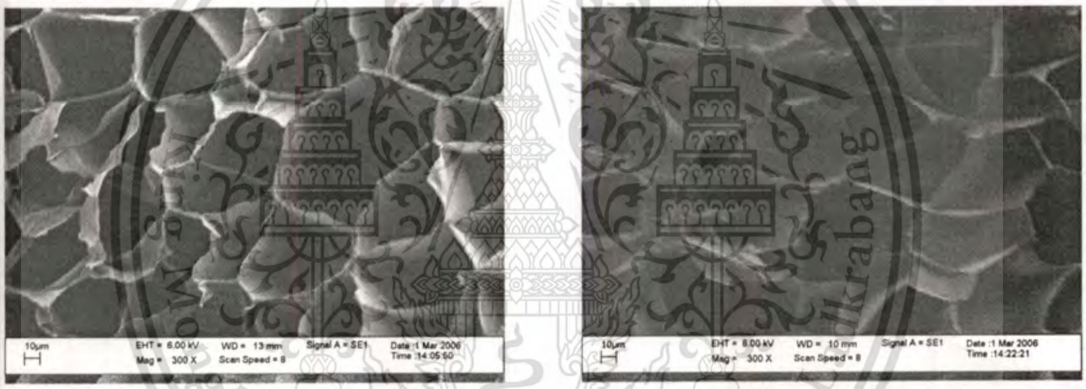


Figure 4.6 The number of cells of microcellular biodegradable plastic foams produced from various ratio of St-Bu-g-starch and PS plastic without DEG at condition 3600 psi and 100 °C.

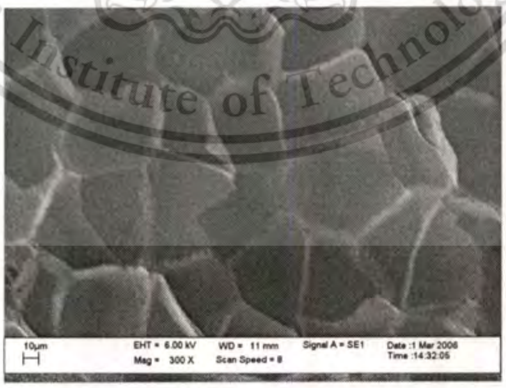
4.2.2 Effect of DEG.

a) At pressure 2200 psi

The microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with ratio of DEG at condition 2200 psi, 100 °C and 300 magnifications. When the amount of DEG was changed, the morphology of microcellular biodegradable plastic foams showed at figure 4.7 (A), (B) and (C), respectively. All of them were good microcellular biodegradable plastic foam because they had pore diameter at micrometer level, pore size and alignment of cells correspond at every point, pore diameter has bigger size when compare with high pressure conditions. They had pore diameter about 56-73 μm (see figure 4.8), the expansion ratio about 2.37-2.62 (see figure 4.9), the number of cells about 0.38-3.52×10^8 cells/cm^3 (see figure 4.10), the wall thickness about 0.004-0.006 μm (see figure 4.11) and density about 0.40-0.44 g/cm^3 (see figure 4.2), respectively.



(A) 3% DEG (B) 4% DEG



(C)5%DEG

Figure 4.7 SEM images of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 2200 psi, 100 °C and 300 magnification.

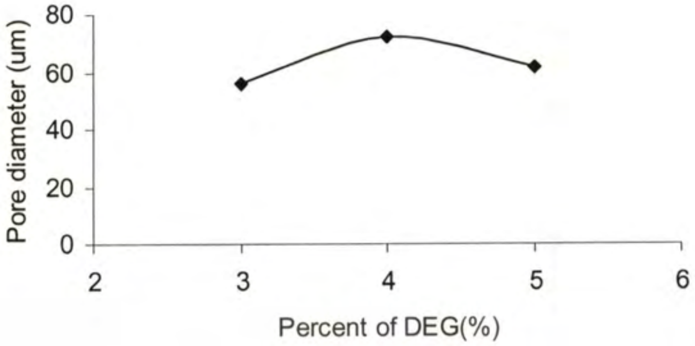


Figure 4.8 The average pore diameter of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 2200 psi and 100 °C.

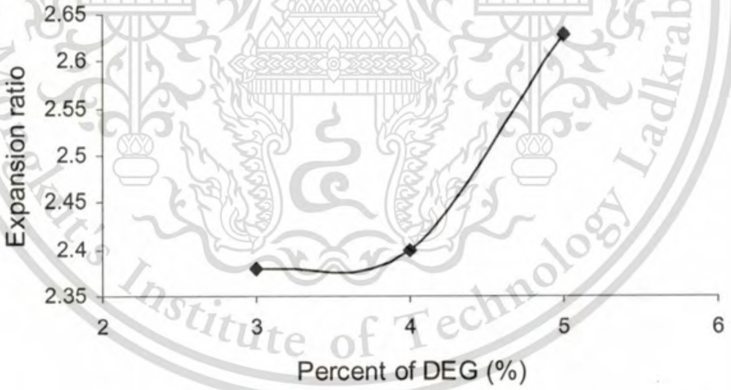


Figure 4.9 The expansion ratio of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 2200 psi and 100 °C.

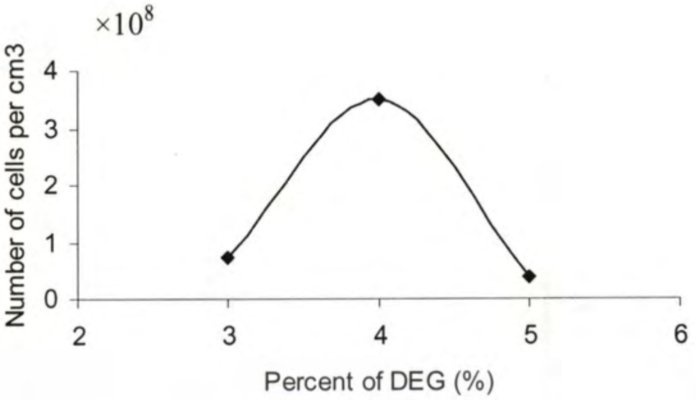


Figure 4.10 The number cells of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 2200 psi and 100 °C.

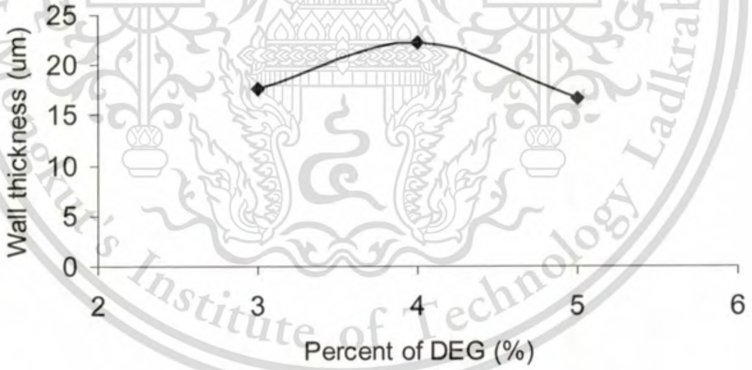
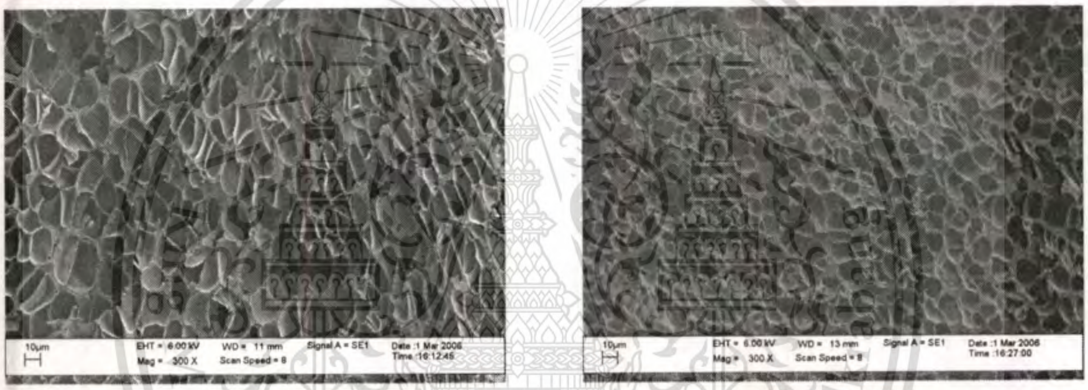


Figure 4.11 The wall thickness of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 2200 psi and 100 °C.

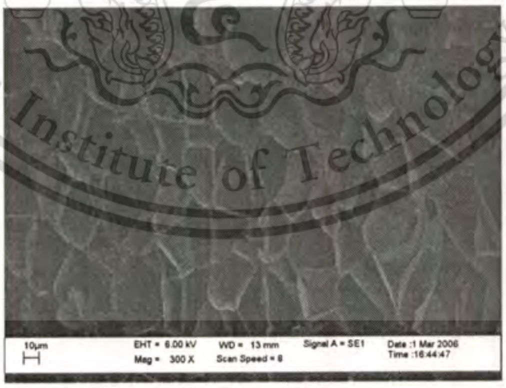
b) At pressure 3000 psi

The microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary ratio of DEG at condition 3000 psi, 100 °C and 300 magnifications. When the amount of DEG was changed, the morphology of microcellular biodegradable plastic foams showed at figure 4.12 (A), (B) and (C) respectively. All of them were good microcellular biodegradable plastic foam because they had pore diameter at micrometer level, pore size and alignment of cells correspond at every point, pore diameter was very small. They had pore diameter about 9.4-25.8 μm (see figure 4.13), the expansion ratio about 2.73-3.81 (see figure 4.14), the number of cells about $1.02\text{-}3.29\times10^9$ cells/cm^3 (see figure 4.15), the wall thickness about 0.006-0.022 μm (see figure 4.16) and density of about 0.27-0.39 g/cm^3 (see figure 4.2), respectively.



(A) 3% DEG

(B) 4% DEG



(C) 5%DEG

Figure 4.12 SEM images of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3000 psi, 100 °C and 300 magnification.

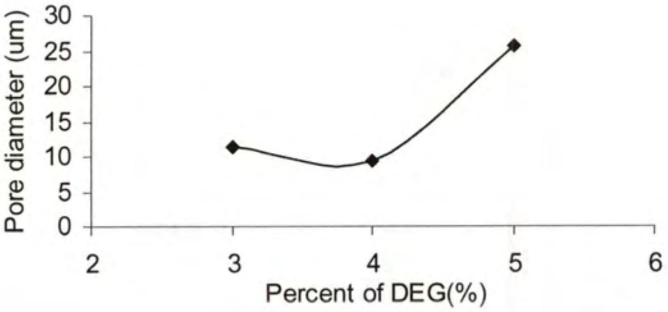


Figure 4.13 The average pore diameter of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3000 psi and 100 °C.

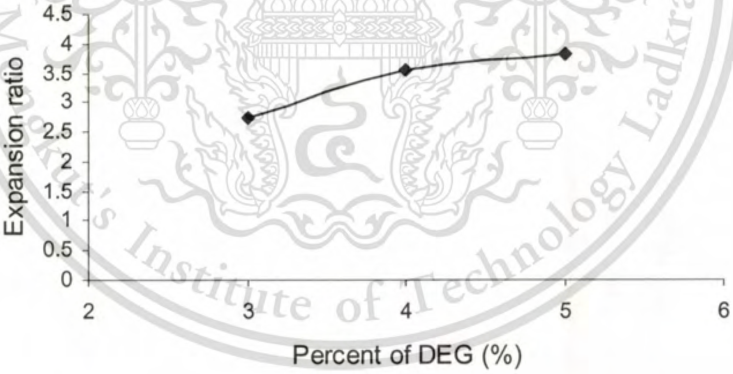


Figure 4.14 The expansion ratio of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3000 psi and 100 °C.

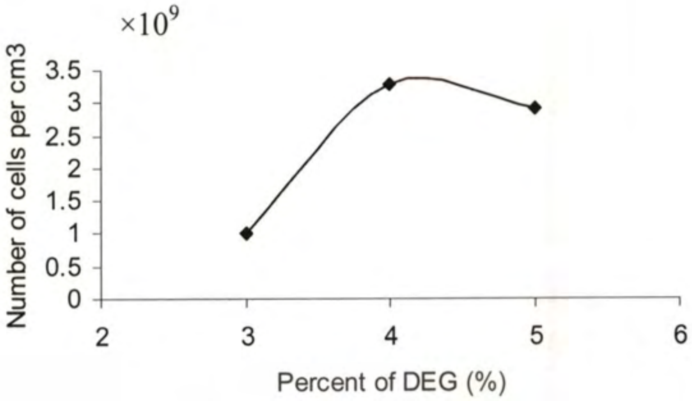


Figure 4.15 The number cells of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3000 psi and 100 °C.

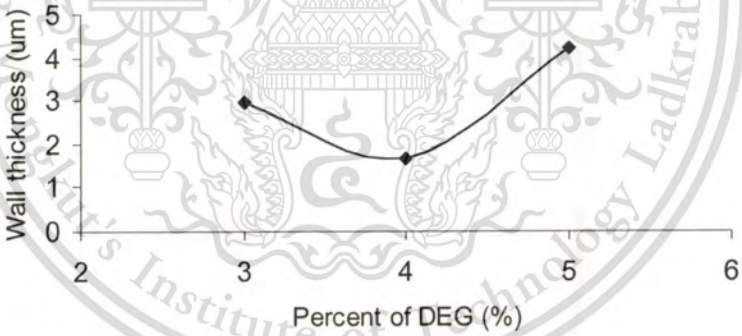
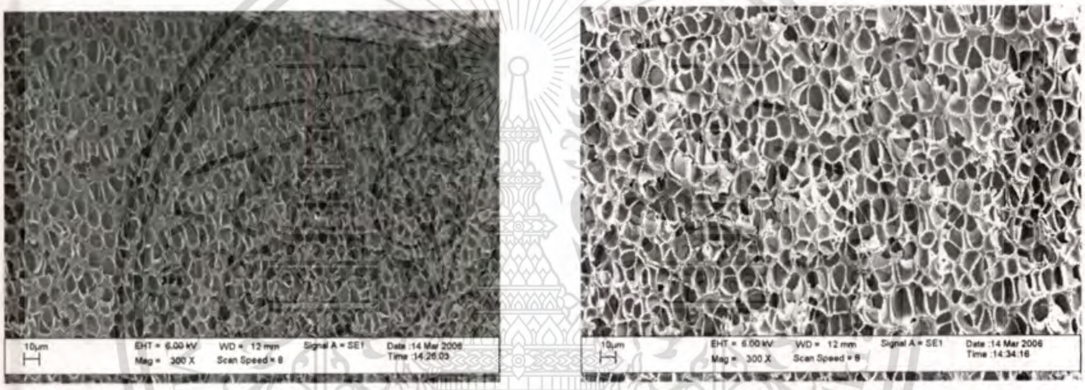


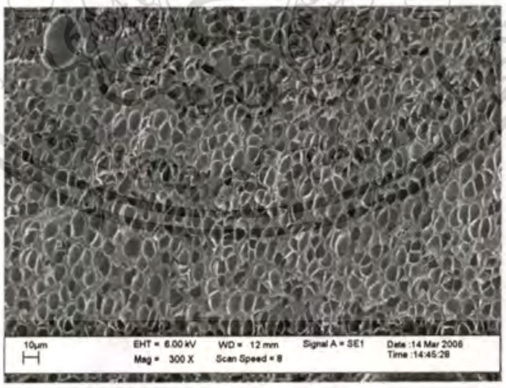
Figure 4.16 The wall thickness of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3000 psi and 100 °C.

c) At pressure 3600 psi

The microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary ratio of DEG at condition 3600 psi, 100 °C and 300 magnifications. When the amount of DEG was changed, the morphology of microcellular biodegradable plastic foams showed at figure 4.17 (A), (B) and (C), respectively. All of them were good microcellular biodegradable plastic foam because they had pore diameter at micrometer level, pore size and alignment of cells correspond at every point, pore diameter was very small. They had pore diameter about 7-10 μm (see figure 4.18), the expansion ratio about 1.86-2.12 (see figure 4.19), the number of cells about $2.54\text{-}3.99\times10^9$ cells/cm^3 (see figure 4.20), the wall thickness about 0.04-0.07 μm (see figure 4.21) and density of about 0.5-0.57 g/cm^3 (see figure 4.2), respectively.



(A) 3% DEG (B) 4% DEG



(C) 5%DEG

Figure 4.17 SEM images of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3600 psi, 100 °C and 300 magnification.

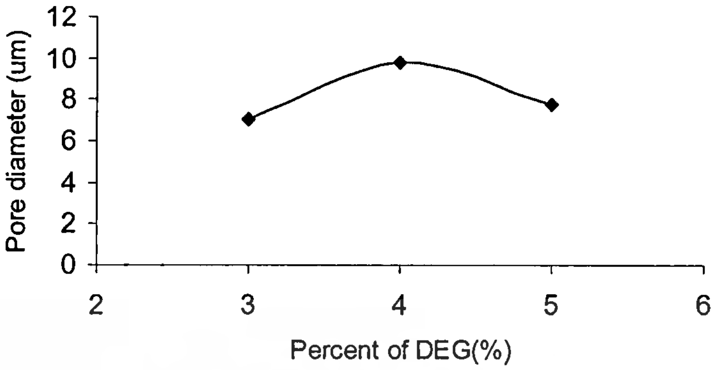


Figure 4.18 The average pore diameter of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3600 psi and 100 °C.

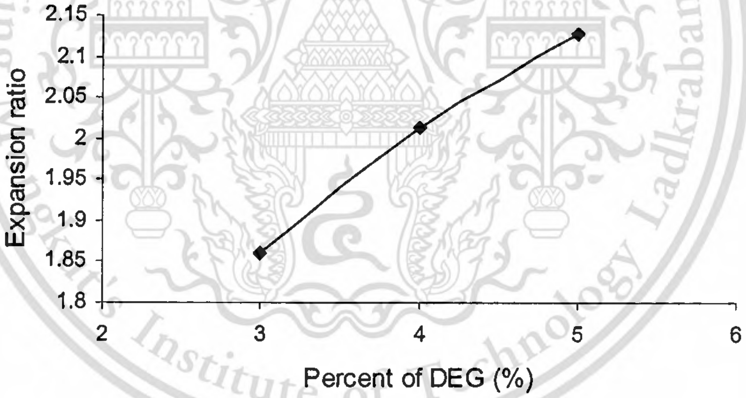


Figure 4.19 The expansion ratio of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3600 psi and 100 °C.

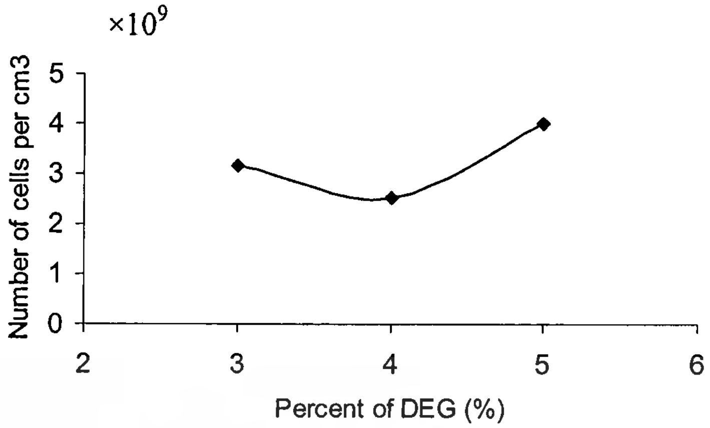


Figure 4.20 The number cells of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3600 psi and 100 °C.

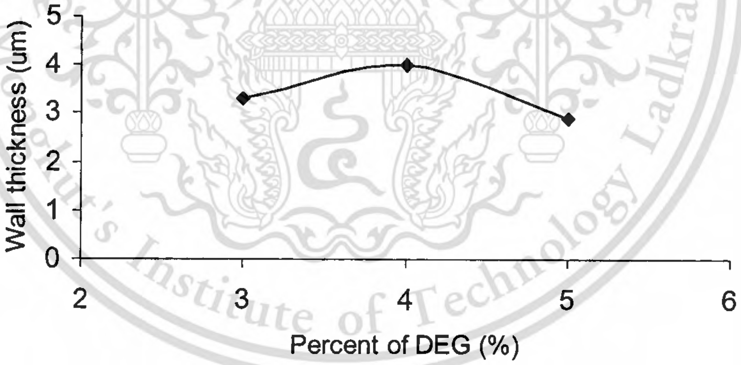
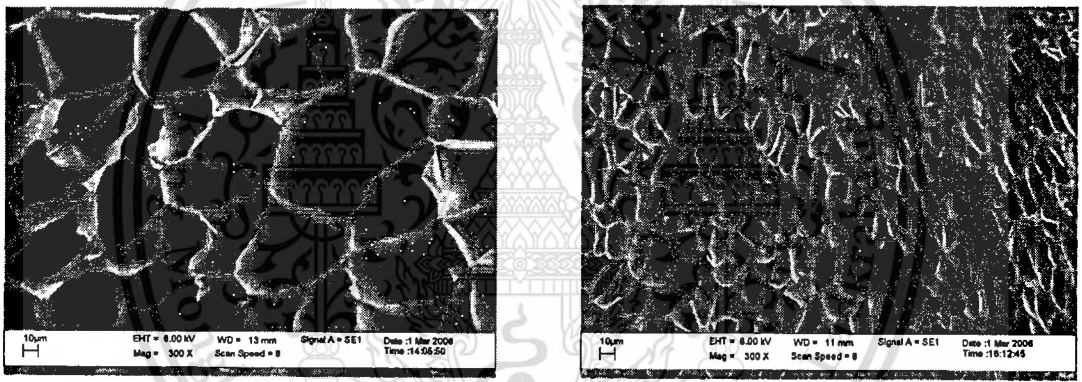


Figure 4.21 The wall thickness of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with vary percent of DEG at condition 3600 psi and 100 °C.

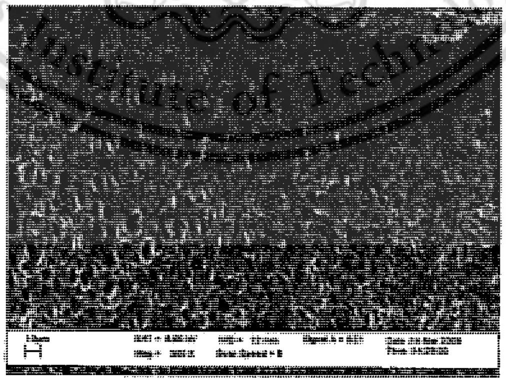
4.2.3 Effect of pressure.

a) At 3% DEG

The microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 3% of DEG at 100 °C by vary pressure condition at 300 magnifications. When the pressure changed, the morphology of microcellular biodegradable plastic foam showed at figure 4.22 (A), (B) and (C), respectively. The morphology of microcellular biodegradable plastic foams were difference. The figure 4.22 (A) showed microcellular biodegradable plastic foam has bigger pore size about 56 μm (see figure 4.23), the expansion ratio about 1.7-2.6 (see figure 4.24) the number of cells about 7.52×10^7 cells/cm^3 (see figure 4.25) and density is 0.441 g/cm^3 when the pressure increased, the pore size decreased, the wall thickness and number of cells were increased. The figure 4.22 (C), the pore diameter about 7 μm (see figure 4.23) the number of cells about 3.18×10^9 cells/cm^3 (see figure 4.25) and density was 0.564 g/cm^3.



(A) 2200 psi (B) 3000 psi



(C) 3600 psi

Figure 4.22 SEM images of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 3% of DEG at 100 °C by vary pressure condition at 300 magnifications.

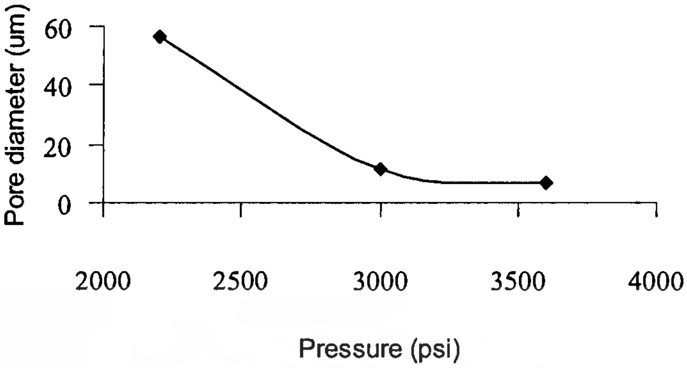


Figure 4.23 The average pore diameter of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% ofPS plastic with 3% of DEG at 100 °C by vary pressure condition.

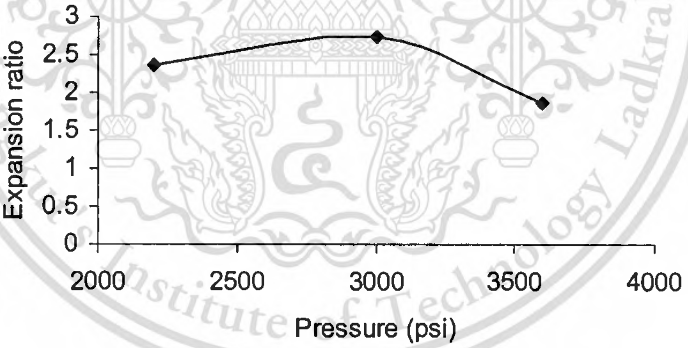


Figure 4.24 The expansion ratio of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 3% of DEG at 100 °C by vary pressure condition.

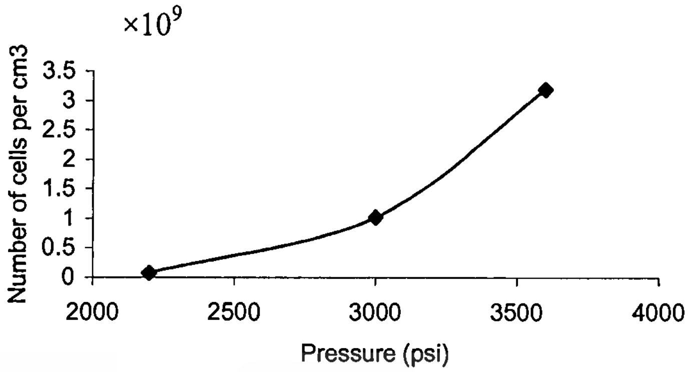


Figure 4.25 The number cells of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 3% of DEG at 100 °C by vary pressure condition.

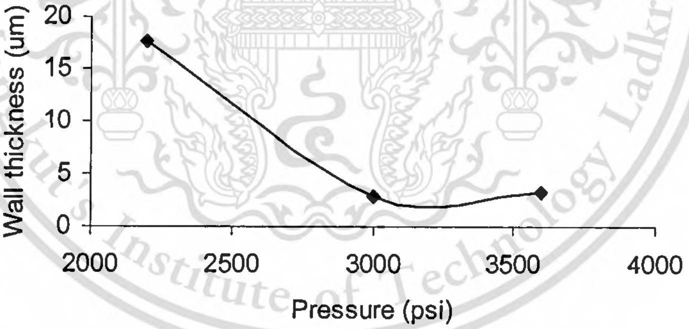
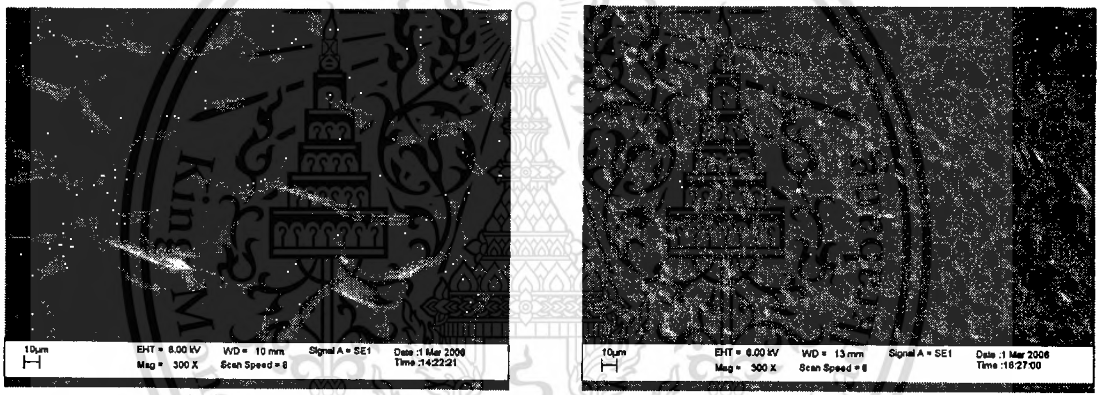


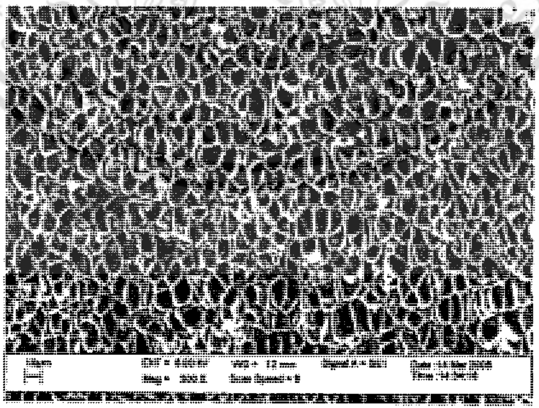
Figure 4.26 The wall thickness of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 3% of DEG at 100 °C by vary pressure condition.

b) At 4% DEG

The microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 4% of DEG at 100 °C by vary pressure condition at 300 magnifications. When the pressure changed, the morphology of microcellular biodegradable plastic foams showed at figure 4.27 (A), (B) and (C), respectively. The morphology of microcellular biodegradable plastic foams were difference.
The figure 4.27 (A) showed microcellular biodegradable plastic foam has bigger pore size about 72 μm (see figure 4.28), the expansion ratio about 2-3.5 (see figure 4.29), the number of cells about 3.52×10^8 cells/cm^3 (see figure 4.30) and density is 0.437 g/cm^3 when the pressure increased, the pore size decreased, the wall thickness and the number of cells were increased. The figure 4.27 (C) the pore diameter about 9.8 μm (see figure 4.28) the number of cells about 2.55×10^9 cells/cm^3 (see figure 4.30) and density was 0.520 g/cm^3.



(A) 2200 psi (B) 3000 psi



(C) 3600 psi

Figure 4.27 SEM images of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 4% of DEG at 100 °C by vary pressure condition at 300 magnifications.

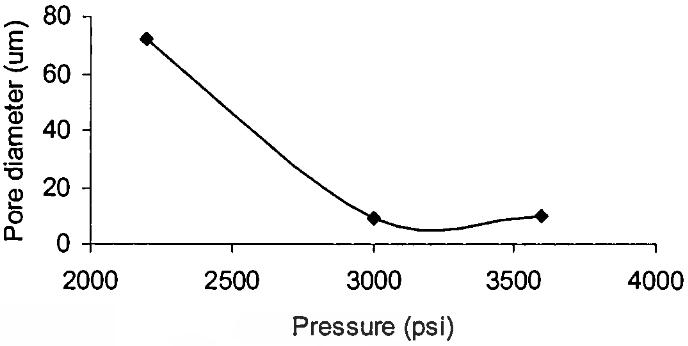


Figure 4.28 The average pore diameter of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 4% of DEG at 100 °C by vary pressure condition.

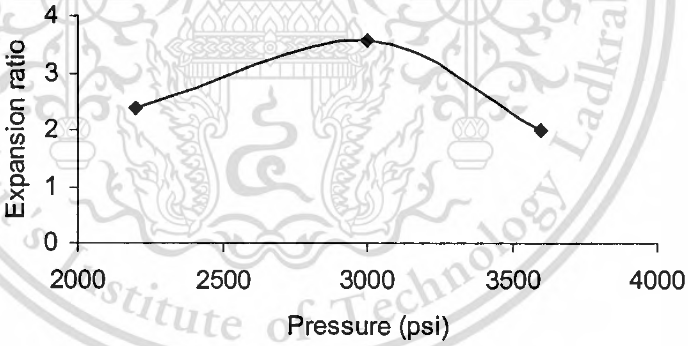


Figure 4.29 The expansion ratio of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 4% of DEG at 100 °C by vary pressure condition.

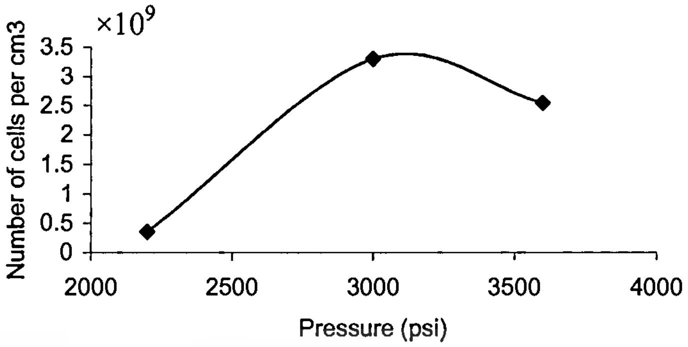


Figure 4.30 The number cells of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 4% of DEG at 100 °C by vary pressure condition.

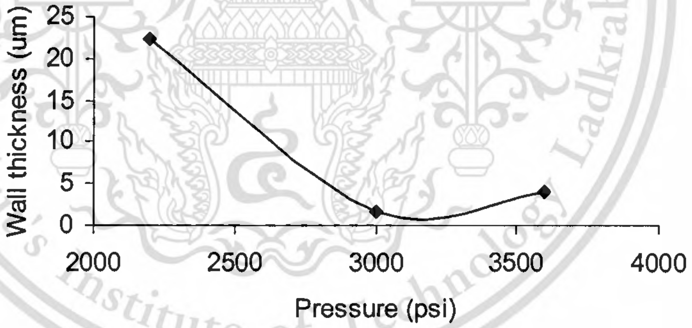
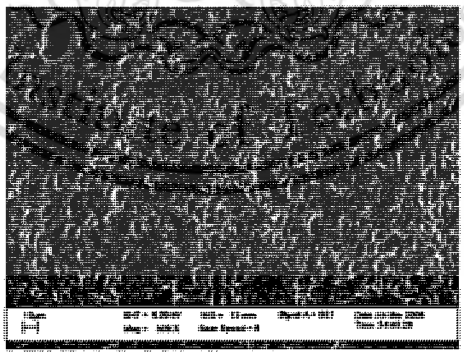


Figure 4.31 The wall thickness of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 4% of DEG at 100 °C by vary pressure condition.

c) At 5% DEG

The microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 5% of DEG at 100 °C by vary pressure condition at 300 magnifications. When the pressure changed, the morphology of microcellular biodegradable plastic foam showed at figure 4.32 (A), (B) and (C), respectively. The morphology of microcellular biodegradable plastic foams were difference. The figure 4.32 (A) showed microcellular biodegradable plastic foam has bigger pore size about 62 μm (see figure 4.33), the expansion ratio about 2-3.7 (see figure 4.34) the number of cells about 3.86×10^7 cells/cm^3 (see figure 4.35) and density is 0.401 g/cm^3 the pressure increased, the pore size decreased, thickness wall and number of cells were increased. The figure (4.32 C), the pore diameter about 7.8 μm (see figure 4.33), the number of cells about 3.99×10^9 cells/cm^3 (see figure 4.35) and density was 0.495 g/cm^3.

(A) 2200 psi (B) 3000 psi



(C) 3600 psi

Figure 4.32 SEM images of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 5% of DEG at 100 °C by vary pressure condition at 300 magnifications.

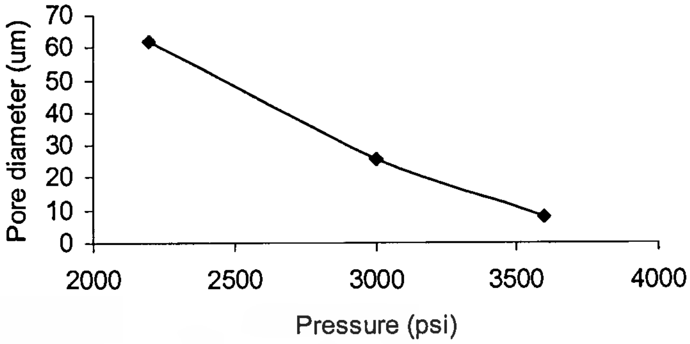


Figure 4.33 The average pore diameter of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 5% of DEG at 100 °C by vary pressure condition.

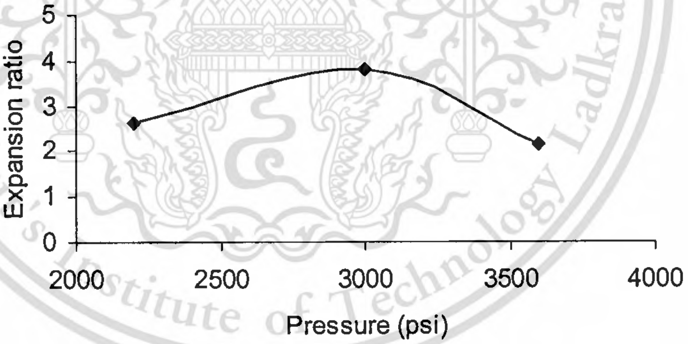


Figure 4.34 The expansion ratio of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 5% of DEG at 100 °C by vary pressure condition.

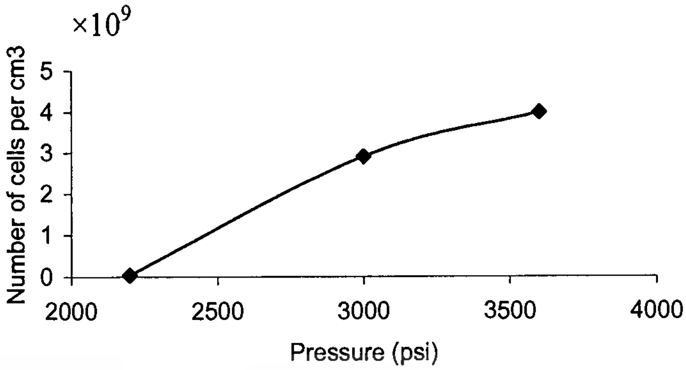


Figure 4.35 The number cells of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 5% of DEG at 100 °C by vary pressure condition.

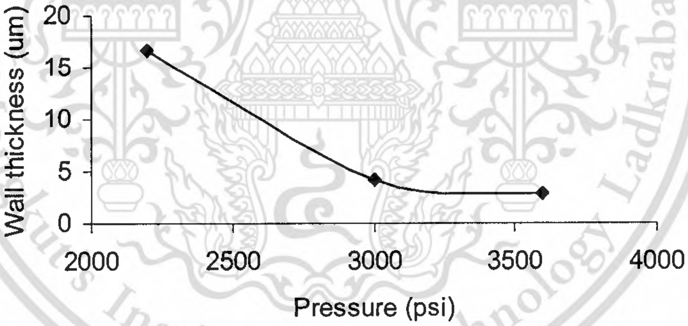


Figure 4.36 The wall thickness of microcellular biodegradable plastic foams produced from 10% of St-Bu-g-starch and 90% of PS plastic with 5% of DEG at 100 °C by vary pressure condition.

4.3 Thermal property of biodegradable plastic by thermogravimetric analysis(TGA)

4.2.1 Effect of ratio of St-Bu-g-starch and PS

The determination of thermal at decomposition of biodegradable plastic was carried out by TGA, the decomposition temperature of PS was 366.67 °C but when increased amount of St-Bu-g-starch in the biodegradable plastic the decomposition temperature decreased (see table 4.1)

Table 4.1 Decomposition temperature at 50% weight loss of St-Bu-g-starch and PS by vary ratio and without DEG

Ratio of St-Bu-g-starch : PS	Decomposition temperature at 50% weight loss (°C)
0:100	366.67
10:90	373.43
30:70	355.56
100:0	340.63

4.2.2 Effect of DEG

Decomposition temperature of St-Bu-g-starch and PS at the ratio 10:90 decreased, when increased amount of DEG (see table 4.2)

Table 4.2 Decomposition temperature at 50% weight loss of St-Bu-g-starch and PS at the ratio 10:90 by vary ratio of DEG

Amount of DEG (%wt)	Decomposition temperature at 50% weight loss (°C)
3	347.60
4	343.75
5	342.20

Chapter 5

Conclusion

1. The compounding of styrene butyl acrylate graft tapioca starch copolymer with polystyrene plastic could produce microcellular biodegradable plastic foam. When the St-Bu-g-starch increased, the decomposition temperature decreased

2. The biodegradable plastic foam produced from tapioca starch had less pore size than polystyrene foam and lower cell wall thickness.

3. The suitable condition to produce microcellular biodegradable plastic foam was using the styrene butyl acrylate graft tapioca starch and polystyrene equal 10:90 and 5% of DEG at 100 °C, 3000 psi, which produced lowest density of microcellular biodegradable plastic foam.

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Appendices

Appendix A
Data of TGA

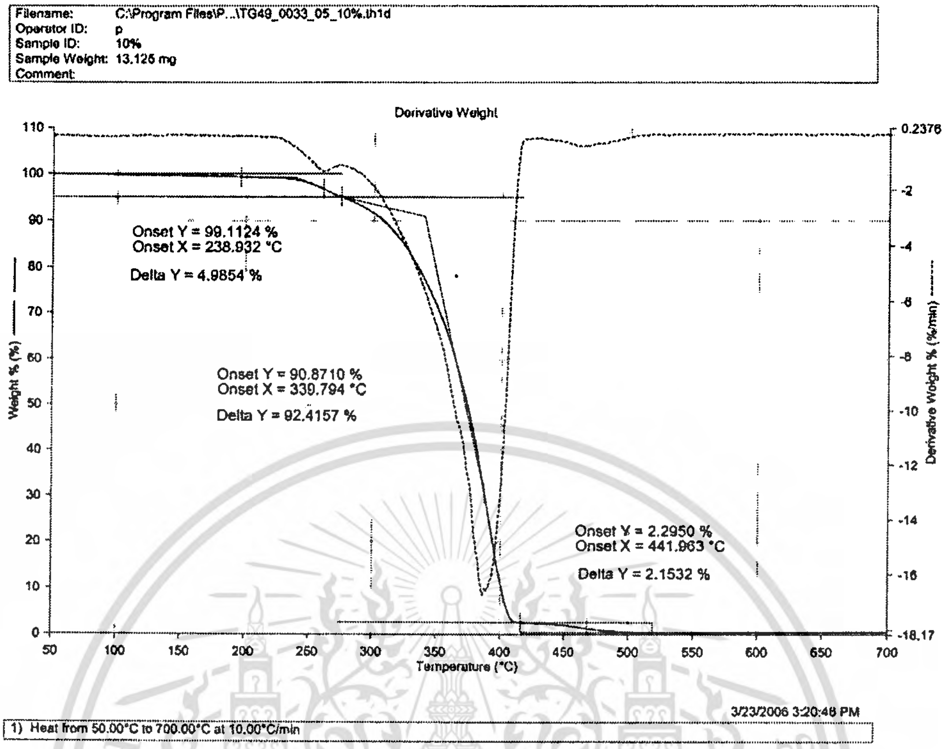


Figure A-1 Thermogram of 10% of St-Bu-g-starch percent by weight without DEG

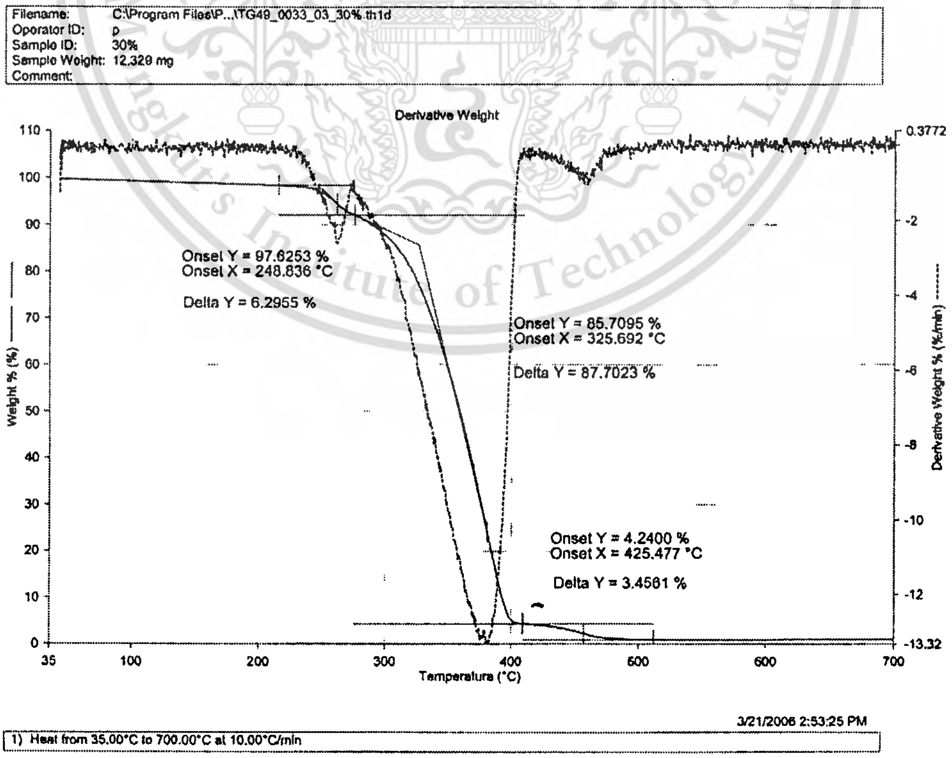


Figure A-2 Thermogram of 30% St-Bu-g-starch percent by weight without DEG

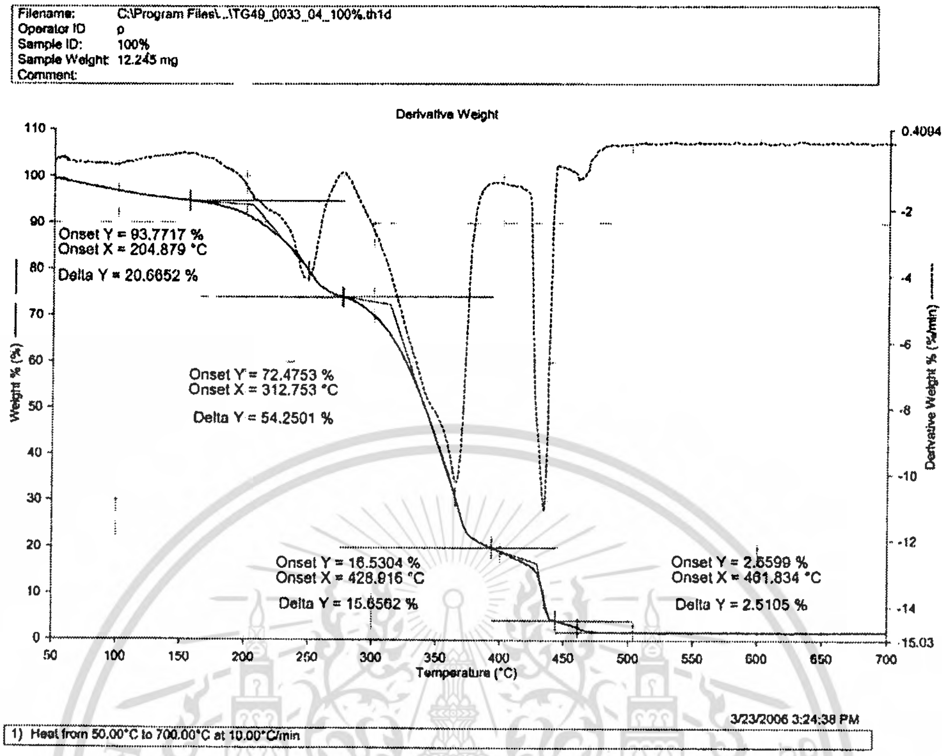


Figure A-3 Thermogram of 100% of St-Bu-g-starch percent by weight without DEG

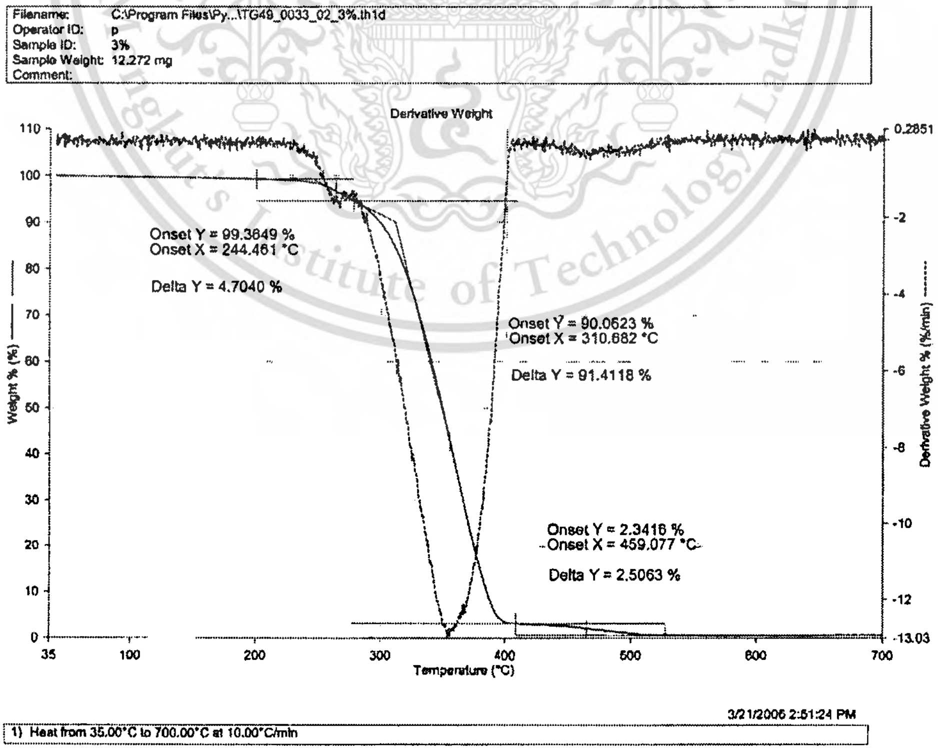


Figure A-4 Thermogram of 10% of St-Bu-g-starch percent by weight with 3% of DEG

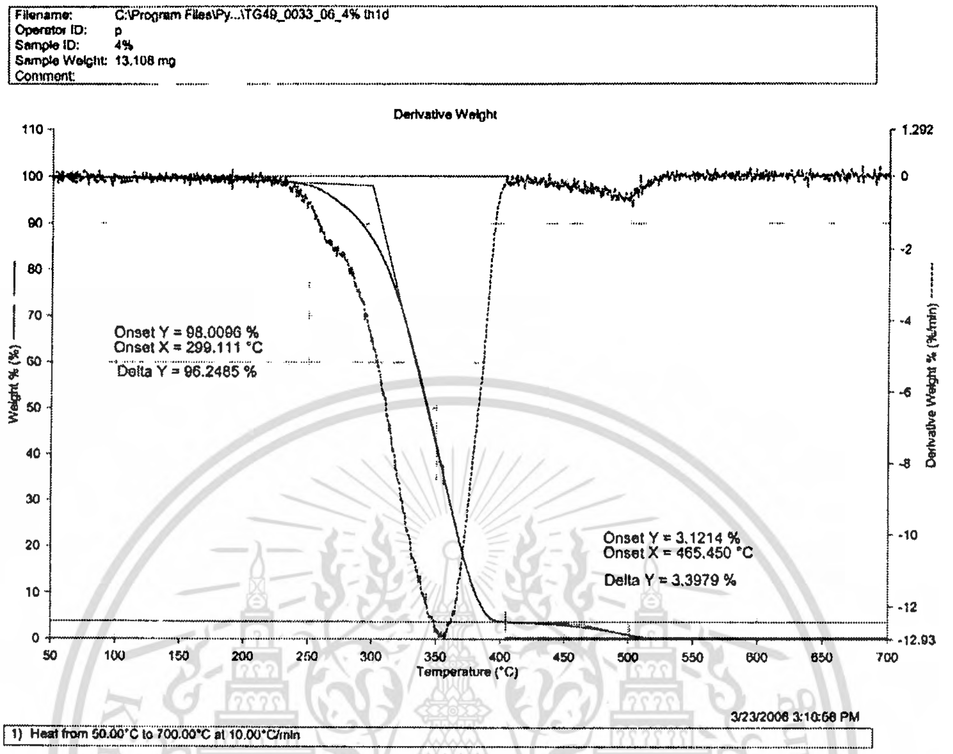


Figure A-5 Thermogram of 10% of St-Bu-g-starch percent by weight with 4% of DEG

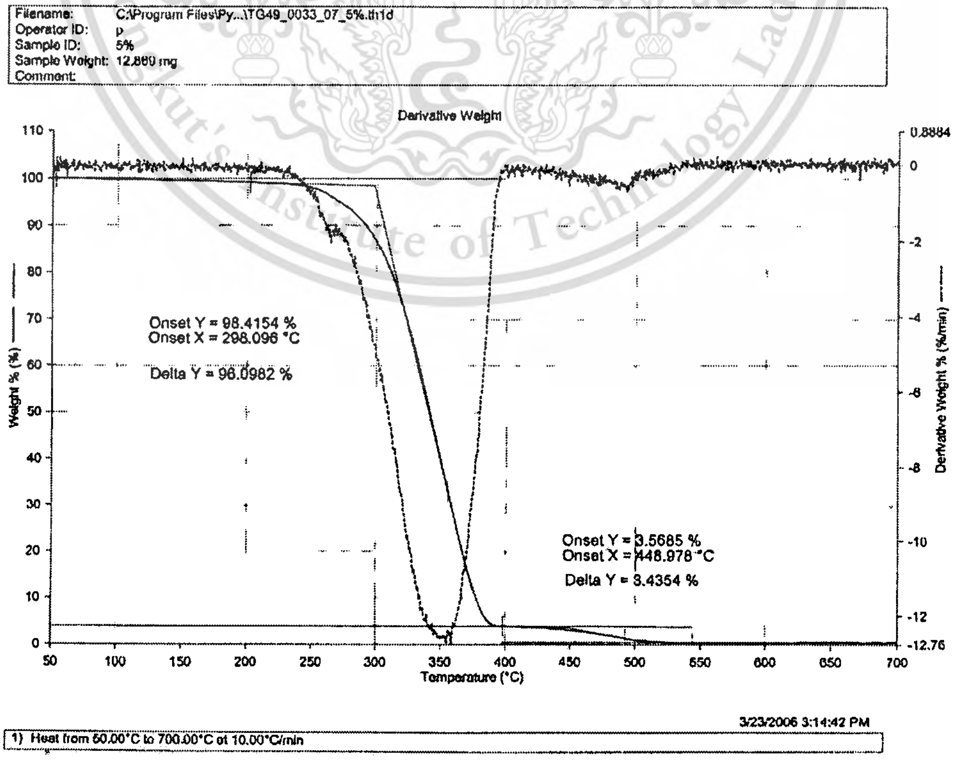
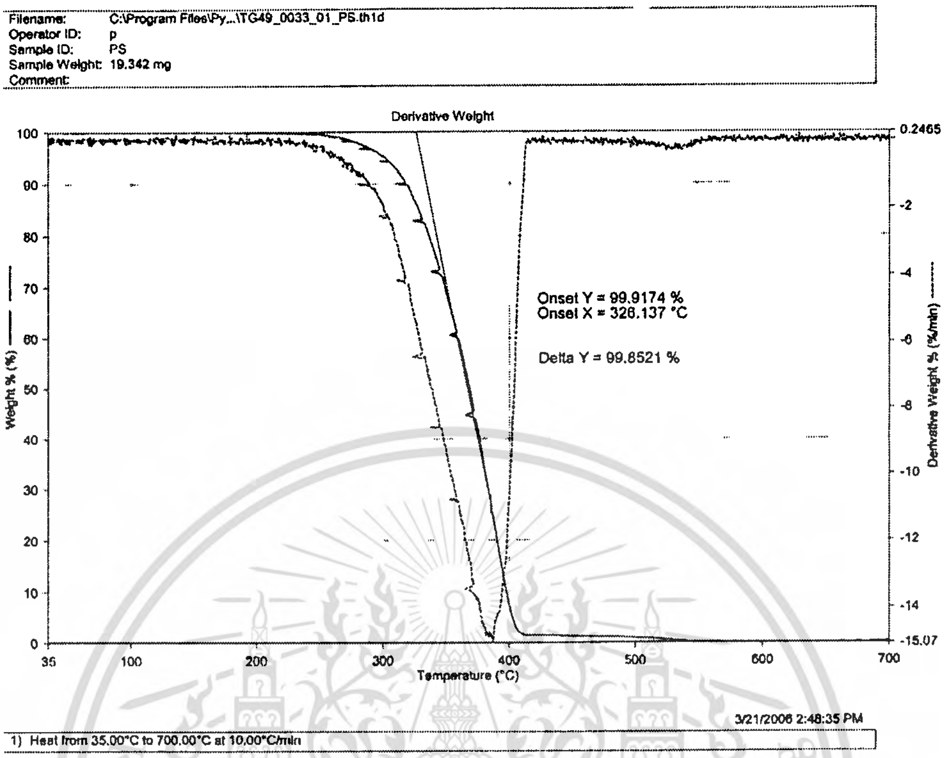


Figure A-6 Thermogram of 10% of St-Bu-g-starch percent by weight with 5% of DEG



Filename: C:\Program Files\Py...\TG49_0033_01_PS.th1d
Operator ID: p
Sample ID: PS
Sample Weight: 19.342 mg
Comment:

Onset Y = 99.9174 %
Onset X = 328.137 °C

Delta Y = 99.8521 %

3/21/2006 2:48:35 PM

1) Heat from 35.00°C to 700.00°C at 10.00°C/min

Figure A-6 Thermogram of polystyrene

Appendix B

Appendix B
The pore size of microcellular biodegradable plastic foam

Table B-1 Average pore size of biodegradable plastic foams produced from various ratio of St-Bu-g-starch/PS and without DEG at 3600 psi.

Amount of St-Bu-g-starch (%wt)	Amount of PS (%wt)	Average cells diameter (μm)	Expansion ratio	Number of cells per cm^3
0	100	13.56	2.030	1.8×10^8
10	90	10.24	2.063	2.0×10^9
20	80	10.59	1.922	3.3×10^9
30	70	12.93	1.829	2.5×10^9

Table B-2 Average pore size of biodegradable plastic foams produced from St-Bu-g-starch/PS equal 10:90 and vary amount of DEG at 2200 psi.

Amount of DEG (%wt)	Average cells diameter(μm)	Expansion ratio	Number of cells per cm^3	Thickness cell wall (μm)
3	56.44	2.380	7.5×10^7	17.687
4	72.03	2.399	3.5×10^8	22.287
5	61.76	2.628	3.8×10^7	16.705

Table B-3 Average pore size of biodegradable plastic foams produced from St-Bu-g-starch/PS equal 10:90 and vary amount of DEG at 3000 psi.

Amount of DEG (%wt)	Average cells diameter(μm)	Expansion ratio	Number of cells per cm^3	Thickness cell wall (μm)
3	11.50	2.733	7.0×10^9	2.943
4	9.40	3.563	3.3×10^9	1.684
5	25.82	3.819	2.9×10^9	4.235

Table B-4 Average pore size of biodegradable plastic foams produced from St-Bu-g-starch/PS equal 10:90 and vary amount of DEG at 3600 psi.

Amount of DEG (%wt)	Average cells diameter(μm)	Expansion ratio	Number of cells per cm^3	Thickness cell wall (μm)
3	7.056	1.861	3.2×10^9	3.319
4	9.82	2.014	2.5×10^9	4.019
5	7.76	2.129	4.0×10^9	2.895