BIODEGRADABLE PLASTIC PROCESSING FROM TAPIOCA STARCH

MR. SAROACH PATTAMAGATE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE
MASTER OF SCIENCE PROGRAMME IN APPLIED CHEMISTRY
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หัวข้อวิทยานิพนธ์	กระบวนการแปรรูปพลาสติกที่สามารถย่อยสลายได้ทางชีวภาพจากแป้งมันสำปะหลัง
นักศึกษา	นายสาโรช ปัทมเกตุ
อาจารย์ผู้ควบคุมวิทยานิพนธ์	ผศ.ดร. นิพนธ์ วงศ์วิเศษสิริกุล
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ภาควิชา	เคมี คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
พ.ศ.	2539

บทคัดย่อ

การศึกษาการต่อกิ่งสายโซ่พอลิเมอร์ของมอนอเมอร์อะคริลิกเอสเทอร์ชนิดต่างๆลงบนโมเลกุลของแป้งมันสำปะหลัง โดยใช้สารโพแทสเซียมเปอร์ซัลเฟตเป็นตัวริเริ่มปฏิกิริยา พบว่า ปริมาณของการต่อกิ่ง(Grafting yield) ขึ้นกับ ความเข้มข้นของมอนอเมอร์ อัตราส่วนของมอนอเมอร์ที่ใช้ (กรณีที่ใช้มอนอเมอร์ผสมสองตัว) ปริมาณสารลดแรงตึงผิว(สบู่) ปริมาณความเข้มข้นของตัวริเริ่มและอุณหภูมิที่ใช้ในการทำปฏิกิริยา ผลการศึกษาทางด้านความร้อนและสมบัติการไหลของแป้งกราฟท์พอลิอะคริลิกเอสเทอร์โคพอลิเมอร์ พบว่ากระบวนการแปรรูปที่เหมาะสมเพื่อให้ได้สมบัติของผลิตภัณฑ์ที่ดี คือกระบวนการแปรรูปที่มีอัตราการเฉือนต่ำๆได้แก่ การอัดขึ้นรูป (Compression molding)และการขึ้นรูปร้อน(Thermo forming) ในกรณีของการอัดขึ้นรูป ปริมาณความชื้นและอุณหภูมิที่เหมาะสมจะอยู่ในช่วง 4-8% และ 140-170 °C ตามลำดับ ผลการศึกษาสมบัติทางกายภาพและสมบัติเชิงกลของแป้งกราฟท์โคพอลิเมอร์ชนิดต่างๆพบว่า มีสมบัติแตกต่างกันมาก ทั้งที่มีลักษณะยืดหยุ่นคล้ายยางไปจนถึงที่มีลักษณะเป็นพลาสติกแข็ง

ส่วนดีของแป้งกราฟท์โคพอลิเมอร์ที่ผลิตได้คือ เป็นวัสดุที่สามารถย่อยสลายได้ง่ายโดยทางชีวภาพ

Thesis Title	Biodegradable Plastic Processing From Tapioca Starch
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Level of Study	Master of Science Programmed in Applied Chemistry
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ABSTRACT

The grafting of various acrylic ester monomers onto tapioca starch were examined using potassium persulphate ($K_2S_2O_8$) as the initiator. The gravimetric analysis showed that the grafting yield depends on monomer concentration, monomer ratio, initiator concentration, emulsifier (soap) concentration and reaction temperature. The thermal and rheological properties of starch graft poly(acrylic ester) were examined. It was found that suitable processes properties are low shear rate processes, such as compression molding and thermo forming. In the case of compression molding, the starch graft copolymer can be processed at a moisture content of 4-8% and temperatures from 140 to 170 $^{\circ}$C. The physical and mechanical properties of the material can be varied in a wide range from elastomeric material to rigid plastic. The advantage of the produced materials is its fast biodegradability.

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CHAPTER 1

INTRODUCTION

Problem Statement

Tapioca is a kind of economic plant in Thailand which grows widely in the eastern and northeastern regions. Mainly tapioca product has been exported to European Union. Nowadays the agriculturist has encountered problem of uncertain marketing. Especially European Union has limited the quota of import and standardized the quality of product. Furthermore the structural of production and marketing of tapioca product are not balanced. Consequently the tendency of price decrease occurs. In order to increase the value of agricultural product especially tapioca starch, the research on the usage of tapioca starch in our country is very important and necessary. Besides in the present the plastic waste effect the environment and cause great problems to the world.

New trends to solve plastic waste problem

The increasing production of plastic means ever increasing problems with disposal of plastic waste. The most counties of the world have recognized the need to reduce the amount of plastic waste. Although the plastic process scrape is largely recycled by feed back into the process and improved efforts to recycle discarded plastic would help accomplish this goal, but so far for plastic in domestic waste because it's highly disperse so recycling in this case is too high cost.

Incineration is one of the most effective method but they is not popular in many countries because of safety and unsatifatory economics when energy lost. Although plastic in domestic waste have been used as fuel or converted to electric power in incineration plants.

Landfill is the same effective method because it's low cost. However in the future shortage of landfill space will be occurs.

According to demands for environmentally friendly material, extensive research programs to develop biodegradable plastic are interesting. The challenge in replacing conventional plastic with biodegradable materials is to design materials that exhibit structural and function stability during storage and use, yet are susceptible by microorganism attack and environmental degradation upon disposal, without any adverse environmental impact.

In recent year, scientists use grafting as a technique for modifying the chemical and physical properties of starch and other natural polymer such as cellulose, lignin and so on. It was assumed that synthesis polymer on to natural macromolecules. The yield of compounds have the combination properties of both materials, leading to increased mechanical stability and they can susceptible by microorganism.

In our research, a free radical chain initiation system with the potassium persulphate($K_2S_2O_8$) has been used to initiate the graft copolymerization of various acrylic ester monomer,both single monomer and binary monomer mixtures on to tapioca starch at controlled reaction condition. The grafting yields,physical and chemical properties have been determined.

We study the grafting of two different monomers to see what's the result of products both at any different monomer ratio and percent of mole of monomer per mole of starch. Afterthat the products were evaluated the different physicochemical

properties and estimated which one of whole products was suitable to process to be the packaging material.

Objective

1. To study the starch graft copolymer production from tapioca starch.
2. To study the process of converting starch graft copolymer to packaging material.
3. To study the properties of starch graft copolymer such as mechanical properties, thermal properties and rheological properties, etc.

CHAPTER 2

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

Starch

Starch is semi-crystalline polysaccharide. It is composed of repeating 1,4 D-glucopyranosyl unit(anhydroglucose unit [AGU]), in plants it exist in two main forms. The linear component (amylose) has a molecular weight of several hundred thousand, whereas the molecular weight of branched amylopectin is on the order of several million, which vary in amount in reserve granules of different plants.

Starch occurs in living plants in the form of discrete granules ranging form about 5-40 microns in diameter. Tapioca starch has granule size about 5-15 microns depending on the plant source. Most cereal and tuber starches contain approximately 30% amylose, although genetic modifications of corn through agricultural breeding have produced starch with virtually no amylose, call "waxy maize", or with up to 70% amylose (high-amylose). Starch is a potentially useful polymer for thermoplastic biodegradable material because of its low cost when compared with the other biodegradable materials as show in Table 1, availability and production from annually renewable resources.

Table 1 Approximate costs for the polymer (as of January 1994) and their production levels in 1993.[a]

Polymer	Costs ($ per lb)	Production level[b] (lb per year)	Principal mode of production
Starch	0.15-0.8	>230 billion	Plant biomass
Cellulose acetate	1.70	2.3-2.4 billion	Chemical conversion, plant biomass
Poly(hydroxybutryate *co*-valerate)	6.00-8.00	660 000	Bacterial fermentation
Poly(vinyl alcohol)	1.50-2.50	150-200 million	Chemical synthesis
Polycaprolactone	2.70	<10 million	Chemical synthesis
Poly(lactic acid)	1.00-3.00	10 million	Chemical polymerization

[a]Additional information from personal communications with companies.

[b]Represents total production level, not all of which is going into biodegradable materials.

Dissolving properties of starch

Starch does not dissolve in cold water. To dissolve native starch, it has to be added to cold water, whilst stirring, the resultant suspension is heated whilst stirring continuously. As the temperature rises, the viscosity in initial time is shows increasing because the hydrogen bond between starch molecules are broken and granule swell and lose their birefringence. The highest viscosity is achieved when the granules are swollen to their maximum diameter, this point is called "The gelatinization point"(for tapioca starch it is reached at temperature of about 49-65 ^{o}C). After this the granules burst open and fall into pieces of irregular conglomerate of starch molecules, now the granules remain large undissolved which are dispersed

more and more as the temperature true rises and stirring continued. When the molecules dispersed completely, a homogeneous solution is obtained with rather low and constant viscosity. Starch solution can be readily prepared by passing starch - water slurries through a steam jet cooker.

Molecular structure.

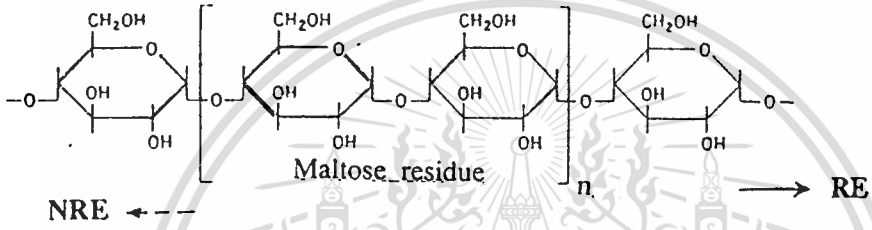

Figure 1 Amylose structure (Haworth projection).

Amylose structure consists of more than 250 D-glucose units liked linearly by the glycosidic bond α(1→4)linked, as show in figure 1. A partial rotation of all glycoside bond result in a helical structure,The interior of which traps iodine,fatty acid,or monoglycerides. Amylose gives a blue color when complexed which iodine in water.

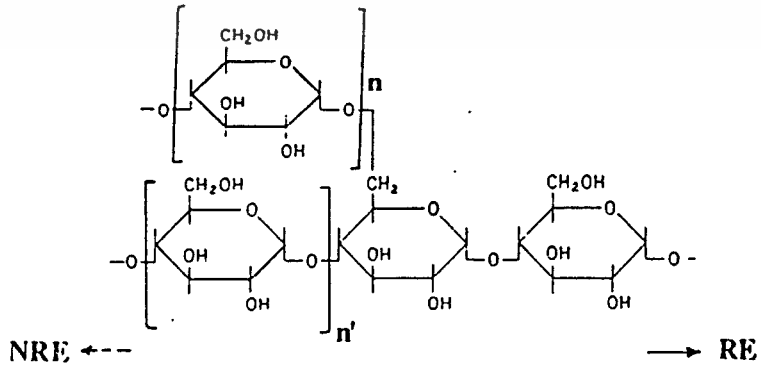

Figure 2. Amylopectin structure (Haworth projection).

An *amylopectin* is a highly branched polysaccharide made of glucose unit,whose branching point are α (1$\rightarrow$ 6) linkages and whose linear branches are made of α (1$\rightarrow$4) linked D-glucose units (similar to amylose), as show in figure 2 Amylopectins have between 10^5 and 10^6 glucose unit and corresponding molecular weight between 1.6×10^7 and 1.6×10^8. Amylopectins give purple color with iodine in water.

Amylose and amylopectin are major components of starch granules.Upon standing, amylopectin can form gel (retrogradation) by weak intermolecular association such as hydrogen bonding. The retrograded amylopectin fraction is redispersed by heating above 50 $^{\circ}$C, whereas the retrograded amylose will not redisperse. In the case of amylose, these association are more numerous and stronger hydrogen bonds are formed between the amylose molecules.The gelatinized starches have tendency to orient themselves and approach each other closely enough to permit hydrogen bonding between hydroxyls on adjacent polymer. This phenomenon is called retrogradation. The rapid increase in the viscosity of gelatinized starch after cooling down and leaving it to stand for some time was cased by their retrogradation which it effected to their viscosity stability.

Table 2 Comparative properties of some commercial starch.

	Starch (%)	Water (%)	Protein (%)	pH	Amylose (%)	Amylopectin(%)	Granule size (μm)	GTR[a] (°C)
Corn								
Normal	88	11	0.35	5	28	72	9.2	62-72
Waxy	88	11	0.28	5	0	100	-	63-72
Sorghum	88	11	0.37	5	28	72	15	68-75
Tapioca	-	12	-	6.3-6.5	16	84	5-15	49-65
Arrowroot	-	-	-	-	21	79	15-70	-
Sago	-	-	-	-	26	74	20-60	-
Potato	~80	17-18	Trace	-	20	80	15-100	50-68
Wheat	–	-	-	-	30	70	2-38	58-64
Rice								
Normal	–	12	0.37	-	20-30	70-80	3-9	58-79
Waxy	–	12	0.13	-	0	100	-	58-79

[a]GTR, Gelatinzation temperature range.

Table 3 Starch properties during cooking in water (5% starch concentration)

Starch property during cooking	Corn	Waxy corn and sorghum	Potato	Tapioca	Rice	Wheat
Rate of granular swelling (on set of thickening)	Slower	Fast	Fast	Fast	Slower	Slower
Extent of granule swelling and solubility (viscosity during cooking)	Moderate	High	Very high	Moderate	Moderate	Low
Swollen granule fragility (cooked starch susceptibility to shear)	Moderate	High	High	Moderate	Moderate	Very low
Retrogradation of linear polymers (gel viscosity)	Very high	Very low	Low	Low	Low	Moderate

Tapioca starch

Tapioca starch is obtained from the large tuberous roots of the cassava plants which grows in many equatorial regions.Cassava roots may either "sweet"containing less than 50 mg of potential hydrogen cyanide per kg of fresh root or "bitter" containing 250 mg or more hydrogen cyanide per kg of fresh root. Sweet root varieties are grown for food purposes and bitter varieties for other industrial uses. In either case, the hydrogen cyanide is lowered to acceptable level during processing.Tropical roots contain 70% water, 24% starch, 2% fibers, 1% protein and 3% fat, minerals and sugars. Tubers should be processed with in 48 h. and sulphur dioxide (0.05%) is added to water used in the starch process to prevent microbial growth.[16]

Modified starch.

Today, with and economics situation in which renewable raw materials are taking on a primary important and the ideas cost are pushing revision of formulations, the native starch and more particularly, the modified starch, are finding the opportunity of participating in the more from synthetic compounds toward more conventional formulas.

The definition of modified starch is any starch whose hydroxyl group has been altered by a chemical reaction such as esterification, etherification, oxidation or grafting technics or disturbance of the initial structure. Such methods can be changed in a chemical or physical properties of native starch.

Chemical modification

Rheological modification

Setting the viscosity and more generally the rheology of a starch is the first step performed by the technologist in developing a modified product viscosity level, dry solids and rheology evolution determine the nature of the chemical treatment. Two categories of modification are involved the depolymerizations and the crosslinking reactions.

1.1 *Depolymerization.* Depolymerizing a starch reduce its viscosity and consequently, allows its use at a higher level of dry solids.There are various ways to do this such as dextrinification, acid conversion, alkaline conversion or oxidation, thermochemical liquefaction and enzyme produced liquefaction.

1.2 *Cross-linking.* Cross-linking or bridging the molecular chains, lead to a more rigid macromolecular network inside the granule. The cross-linking occurs when starch granules are reacted with difunctional reagent that react with hydroxyl group on to reference molecules within the granule. Crosslinks reinforce the granule and reduce both the rate and the degree of granule swelling and subsequent disintegration i.e. reduce sensitivity to processing to conditions (high temperature), extended cooking times, low pH, high shear during mixing, milling, homogenization and /or pumping.

Modification by stabilization

The stabilization of starch reduces the hydroxyl number and decreases the reassociation of the molecules. Consequently, retrogradation in slowed down and starch stability increases particularly at low temperatures.

Specific modification

Special and original property can be introduced by specific reactions. For example, cationization, carboxymethylation, grafting and periodic acid oxidation, generate well-defined products that do not really fall under the heading of stabilized starch, although some of them may be quite stable.

Oxidize and acid modified starch

By treating starch with an oxidizing agent or an acid the chain of the starch molecules are shortened, the long chain are split up into shorter fragments. Since the viscosity of starch solution depends on the length of the chain of molecules, (or : the degree of polymerization, DP) a lower viscosity can be obtained in this way. The resulting type of product is called " thin boiling starch".

Starch ether and starch esters

The gelforming (or insubficient stability) of the native starch is caused by close approach of parts of the starch molecules, so that physical-chemical bond are formed, either directly or with the aid of water molecules. This phenomenon can be prevented by means of attaching side group (this means chemical group) attached perpendicular to the direction of the chain molecules) to the molecule, a "close approach" is then no longer possible, and product giving solutions with an excellent stability can be obtained.

In the described chemical formulas, the formula for starch is simplified in such way that only the reactive OH group have been sketched.

An Anhydroglucose unit (AGU) have 3 OH groups. In principle each of them can react with an etherifying agent, so that on the reaction spot a side group is attached. If this has taken place with only 1 OH group per AGU, the "degree of substitution"(= DS) = 1; if 3 OH group have been introduced per 100 AGU, the DS = 0.03

Starch graft copolymer

A number of researchers have studied the new starch transformation technology, grafting is certain original in that it allows one to associate a synthetic structure with a natural macromolecule. Grafting is performed either in heterogeneous phase (suspension) or in homogeneous phase, depending on the monomer considered (hydrophilic monomer or hydrophobic monomer).

Peroxides give rise to free radical (hydrogen peroxide and persulphate), sometime alone, but generally associated with an activator to form a redox pair (H_2O_2/Fe^{2+}, $K_2S_2O_8/NaHSO_3$) or oxidants, such as Ce^{4+} or Mn^{3+} .

Ceric ion a strong oxidant rapidly complexed with starch and oxidized the polysaccharide, in a slower secondary reaction, to yield free radical on the starch back bone. The advantage of ceric initiation is that it forms considerably less homopolymer than the redox initiation which is not specific, infact, the ceric ions produce a free radical directly on starch but redox pair H_2O_2/Fe^{2+} generate an HO radical, an initiator of free radical on both starch and monomer.

In the presence of monomer, the free radical on the starch backbone act as macroradical with initiate polymerization. Both granular and gelatinized starch have been used as substrates for graft polymerization.

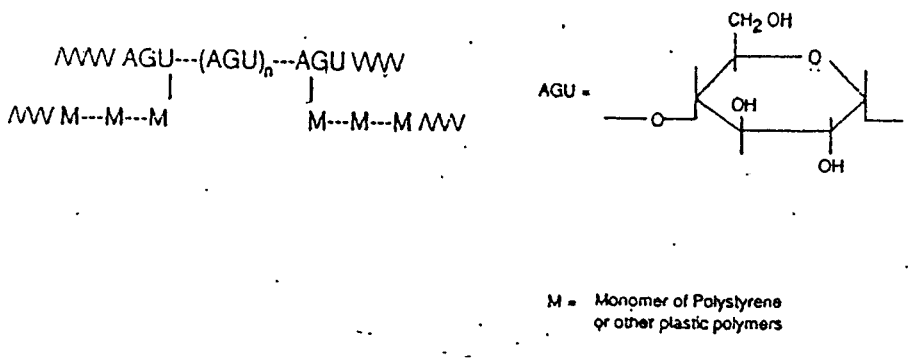

Figure .3 The starch graft copolymer structure.[6]

The starch graft copolymer structure is show in figure 3, the AGU represents a glucopyranosyl (or anhydroglucose) unit and M is the repeating unit of monomer used in grafting reaction. The starch graft copolymer or random polymer are prepared by first generating free radicals on starch and then allowing it to serve as a macroinitiator for other synthetic polymer such as vinyl or acrylic polymer like polystyrene and polyethylene(see Figure 4) generally, these free radical initiated graft copolymers have high molecular weight branches that in frequently found alone the starch backbone.

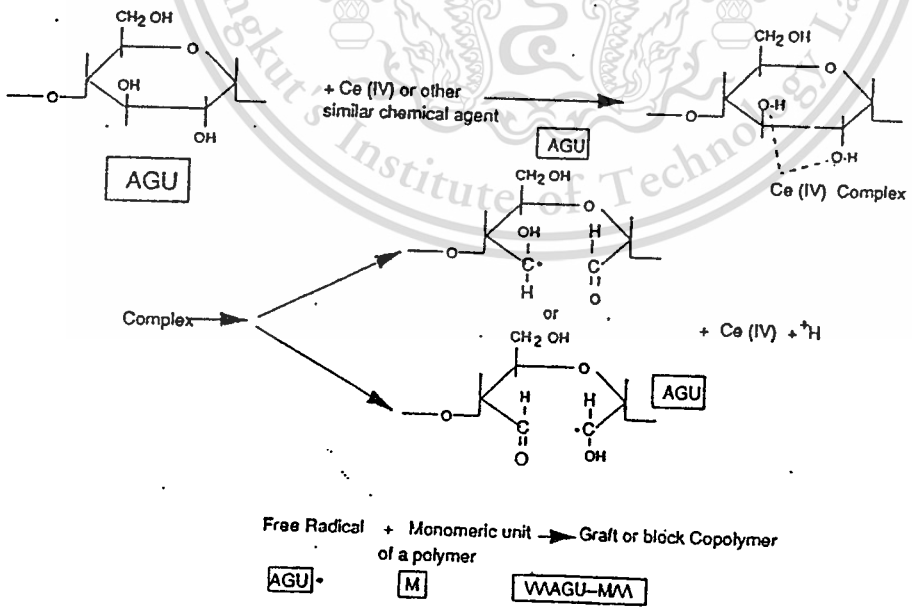

Figure 4 Mechanism of free radical initiated starch graft polymerization.[6]

In free radical polymerization, the average number of glucopyranosyl unit per high molecular weight graft (grafting frequency) will range thousand and therefore, each molecule will have only a very few grafted branches. A number of free radicals initiating system have been suggested the preparation of starch graft copolymer and these are classified as chemical initiation, irradiation initiation and mastication. The choice of method depends on type of polymers used for grafting as well as desired functional properties of the product. The macroradicals formed from the mastication technique have been used to prepare a limited number of starch block copolymer[6].

polyacrylic ester polymer

polyacrylate

Polyacrylates are produced by free radical initiated polymerization of acrylics acid esters the property of acrylic ester polymer depend to a large extent on the type of alcohol from which the acrylate is prepared. Solubility in oils and hydrocarbon such as acetone, as expected with increase in the length of side chain. Polyacrylate with short chain are relatively soluble in polar solvent. Because of their low glass transition temperature, polyacrylate are permanent plasticizers. To optimize properties of polyacrylate, copolymer often produced.

The relative case of free radical induced copolymerization of a 1:1 mixture of and an acrylate ester with other comonomer as show by reactivity ratio is given in table 4 the lower values indicate that comonomer lower reactivities than acrylate ester.[33]

Poly(methyl acrylate) and poly(ethyl acrylate) are produced from methyl acrylate monomer and ethyl acrylate monomer by free radical chain polymerization,

light, and peroxides. The pure monomer can be stored below 10 °C without incurring polymerization. Both of them are transparent, elastic substance. Practically no odor, little adhesive power, resists the usual solvent.

Table 4 Relative ease of copolymer formation for 1:1 ratio of acrylates and other comonomer $(R_1/R_2)X100$.

Comonomer	Methyl acrylate	Ethyl acrylate	Butyl acrylate
Acrylonitrile	53	46	77
Butadiene	66	4.7	8.1
Methyl methacrylate	50.3	30.6	14.6
Styrene	21	16	26
Vinyl chloride	2.7	2.1	1.6
Vinyllidine chloride	100	52	55
Vinyl acetate	1.1	0.7	0.6

Table from Ulich, H. :1993,p 91

Using the methyl acrylate monomer in manufacture leather finish resin, textile paper coatings, and plastic film. Produce the hardest resin of the acrylic ester resin.

Using the ethyl acrylate monomer in the manufacture of water emulsion paint vehicles, textile, paper coating, leather finish resins and adhesives, impart flexibility to hard film.

Caution, both of monomers are highly irritating to eyes, skin mucous membranes. Lethargy and convulsions may occur if vapors of monomer are in haled in high concentration.

Poly(butyl acrylate) and *poly(2-ethylhexyl acrylate)* are elastic, tacky substance. Brittle temperature are -44 °C and -34 °C. The monomers are used in the manufacture of polymers and resin for textile, leather finishes, paints formulations, and adhesivee.

Poly(methyl methacrylate), PMMA

Poly(methyl methacrylate) is produced by free radical chains initiated polymerization. It has crystal clear transparency, good chemical resistance and useful combination of stiffness, density and moderate toughness but unexcelled weatheability. The glass transition temperature of PMMA is 105 °C and heat defection temperature range from 74 to 100 °C.

Poly(methyl methacrylate) can be modified by copolymerization of methyl methacrylate with other monomer, such as acrylate, acrylonitrile, styrene. and butadiene. Major uses of PMMA are safety glazing fixtures, windows, skylight and PMMA molding compound are use in the automotive industry for taillights.

The structure and molecule formula of acrylic ester monomer are show in table 5. Physical properties of monomers are show in table 6. Rate and heat of polymerization of monomers are shows in table 7 and some physical properties of acrylic ester polymer are show in table 8.

Table 5 Structure and molecular of monomer.

Monomer	Formula	Structure
Methyl acrylate	$C_4H_6O_2$	$CH_2=CHCOOCH_3$
Ethyl acrylate	$C_5H_8O_2$	$CH_2=CHCOOC_2H_5$
Butyl acrylate	$C_7H_{12}O_2$	$CH_2=CHCOOC_4H_9$
2-Ethylhexyl acrylate	$C_{11}H_{20}O_2$	$CH_2=CHCOOCH_2CH(C_2H_5)C_4H_9$
Methyl methacrylate	$C_5H_8O_2$	$CH_2=C(CH_3)COOCH_3$

Table 6 Physical properties of acrylate monomer and methacrylate monomer.

Physical properties	Methyl acrylate	Ethyl acrylate	Butyl acrylate	2-Ethylhexyl acrylate	Methyl methacrylate
boiling range (°C)	bp_{608} 70	98-100	145-149	130	100-101
density (g/cm^3)	d_4^{20} 0.9561	0.917	0.894	0.881	0.939
n_D^{25}	n_D^{20} 1.401	1.4037	1.4106	1.4332	1.4119
flash point (°F)	-	50a	120a	195b	55a
solubility at 25 °C					
- in water, part/100	6[c]	1.5	0.2	0.01	0.015
-part/100 monomer	1.8	1.5	0.7	0.15	-
heat of vaporization (cal/g)	95	83	46	61	86
specific heat (cal/g °C)	0.444	0.47	0.46	0.46	0.45

a = Tagliabue open cup b = Cleveland open cup c = at 20 °C

Table 7 Rate and heat of polymerization.

Monomer	$Kp/Kt^{-1/2}$		Ka		ΔH
	44.1 (°C)	60(°C)	44.1(°C)	60(°C)	K.cal/mole
Methyl acrylate	0.982b	1.93b	250b	1480b	18.8
Ethyl acrylate	123[b]	2.27[b]	313[b]	1730[a]	18.6
Butyl acrylate	-	-	-	-	18.5
2-Ethylhexyl acrylate	-	-	-	-	14.5
Methyl methacrylate	0.105[a]	1.161[a]	27[a]	123[a]	13.8

a = Measured in the bulk

b = Measured in the solution

Table 8 Physical properties of polymer.

Polymer	Density(25°C) (g/cm^3)	Tg (°C)	Brittle point (°C)	Softening point (°C)
Methyl acrylate	-	6	-	-
Ethyl acrylate	1.095	-22	-24	-17
Butyl acrylate	-	-54	-44	-
2-Ethylhexyl acrylate	-	-55	-34	-
Methyl methacrylate	1.190	105	92	113

Packaging

The basic function of all packaging is to identify the product and carry it safely through the distribution system to the final user. The packaging must protect the product from mechanical and limited hazard of environment countered during distribution. All retail packages must communicate, convenience and use. They must also assist in selling and the quality and cost effectiveness must be ensure for success in marketing.

The principal material in packaging today are paper, glass, steel, aluminum and plastics. The vast range of products available in packed form requires sophisticated materials capable of containing, protecting, transporting, preserving and dispensing each product according to its particular characteristics and purpose.

Plastic packaging

Plastic are exhibit such properties as transparency, flexibility, high tensile and impact strength. To provide an even greater range of properties, plastic are often combined either paper or aluminum foil or with other plastic materials to form a laminate, the major plastic materials used in packaging application are polyethylene, poly(vinyl chloride)(PVC), polystyrene, polypropylene and poly(ethylene terepthalate)(PET)[22].

Biodegradable packaging

The one way of solving the plastic waste problem to reduce packing. Many applications are expected from biodegradable plastic. The starch- synthetic polymer blend, low density polyethylene(LDPE) mixed with starch has been market. These

plastic break down through a combination of biodegradation, photodegradation and oxidation of the LDPE. The various aliphatic polyester can be completely degraded by microorganisms, there are hydrolyzed by lipase, a digestive enzyme, and break down into smaller molecules to be assimilated by microorganism. Copolyesters of aliphatic polyesters are biodegradable, but low melting points, poor heat resistance, low mechanical strength and other factor. Copolyesters made by alternating aromatic polyester afford different characteristics and better performance.

Biodegradable packaging from starch

There have been a number of patent involving biodegradable packing. The various techniques have been used to produce biodegradable polymer. Thermoplastic materials with starch as the major component, although additives, including water as a plasticizer are necessary to obtain the desired processability and properties. These materials are readily degraded in hydrolytic enviroments and susceptible by microorganism, yet have properties comparable to commercial plastic, the other biodegradable materials produced by any company are listed in table 9.

Plastic processing

The term plastic processing is technology of converting raw polymer, or compounding polymer to articles of a desired shape.

Table 9 Biodegradable materials producers.

Company	Base polymer	Feedstock	Cost ($/lb)	Capacity (MM Lb/yr)
Cargill, Minneapolis, MN	Polylactide (PLA)	Renewable resources, Corn	1.00-3.00	10 ('94 scale up); 250 (mid-1996)
Ecochem, Wilmington, DE	Polylactide copolymers	Renewable resources, Cheese whey, corn	<2.00 proj'd	0.15 ('94 scale up)
Flexel, Atlanta GA	Cellophane (Regenerated cellulose)	Renewable resources	2.15	100
Zeneca (business unit of ICI)	Poly (hydroxybutyrate-co-hydroxyvalerate), PHBV	Renewable resources, Carbohydrates (glucose), organic acids	8.00-10.00; 4.00 proj'd	0.66, additional capacity slated for '96 is 11-22
Novamont, Montedison, Italy	Starch-synthetic polymer blend containing approx. 60% starch	Renewable resources Petrochemical	1.60-2.50	50, in Turni, Italy
Novon Products (Warner-Lambert), Morris Plains, NJ*	Thermoplastic starch polymer compounded with 5-25% additives	Renewable resources, Starch	2.00-3.00	100
Union Carbide, Danbury, CT	Polycaprolactone (Tone polymer)	Petrochemical	2.70	<10
Air Products & Chemicals, Allentown, PA	Polyvinyl alcohol (PVOH) & Thermoplastic PVOH alloys (VINEX)	Petrochemical	1.0-1.25 (PVOH); 2.50-3.00 (VINEX)	150-200 (water sol. PVOH); 5 (VINEX)
National Starch & Chemicals, Bridgewater, NJ	Low ds starch ester	Renewable resources, Starch	2.00-3.00	Not available
MI Biotech Inst./GRT-Japan Corn Starch John Venture, MI	Water repellant, thermoplastic modified starches	Renewable Resources, Starch	1.0-1.50	0.1 (pilot scale); 150 slated for early '96
Planet Packaging Technologies, San Diego, CA	Polyethylene oxide blends (Enviroplastic)	Petrochemical	3.00	10
Showa Highpolymer Co., Ltd.	condensation polymer of glycols with aliphatic dicarboxylic acids (BIONELLE)	Petrochemical	approx. 3.00	0.2 (pilot); 7 (semi-commercial, end '94)

* Warner-Lambert has recently announced the closing of its Novon Products Division.

Injection molding

Injection mold is the most common mean of fabricating thermoplastic articles. The molding compound usually in the form of pellets is fed from hopper and they are conveyed forward through the barrel by rotating screw. The material is melted as its goes by combination of heat from the barrel and the shearing of the screw. The molten polymers were injected through a nozzle into the water-cooled mold where it travels in turn through a sprue, runner and gate into the mold cavity by hydraulically driven plunger. When the parts have cooled sufficiently, the mold opens and where then the cooled parts are ejected from mold, the mold closes and the screw is pushed forward hydraulically, injecting a new shot into the mold.

Compression molding

Thermosetting compounds are traditionally compression molded. The molds are mounted in hydraulic presses on the steam, electric, oil-heated platens. The molding compound is fed to the heated mold which closes, maintaining the material under pressure until cured. The part is then ejected from mold. Molding compound in the form of granules or powder may be fed to the mold in weighted shot or as preformed tablets. The charge is often preheat by cold pressing to reduce heating time.

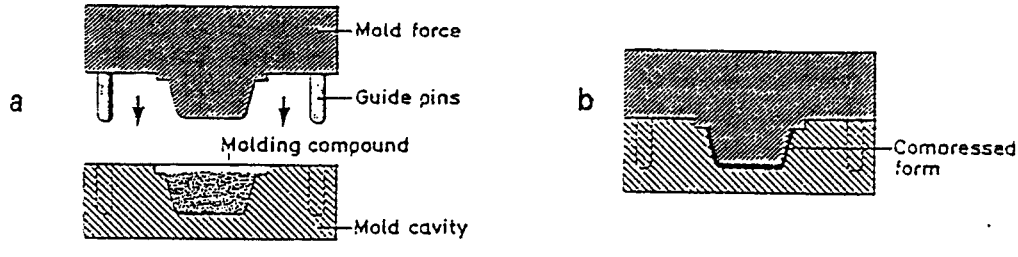

Figure 5 compression molding (a) mold open (b) mold closed .

Thermoforming (Sheet forming)

Thermoplastic sheet is converted to wide variety of finished articles by process. These processes all involve heating the sheet above its softening point and forcing it to conform to cooled mold. In vacuum forming, the heat- plasticized sheet either directly from an extruder or preheated in oven, is drawn against the mold surface by the application of vacuum from preheat the surface. Similarly, a positive pressure may be used to force the sheet against the mold surface and very deep draws are required, mechanical assists plug forming are used.

From a material standpoint, polymers used for thermoforming should have high "melt strength" that is high melt viscosity so that they do not drawn or thin out excessively or perhaps even tear in the forming operation. Thus, high molecular weight resins are preferred. One of the great advantages of thermoforming is that relatively in expensive molds are required since no high pressure are involved. Epoxy mold are often used because they can be easily cast to shape from a hand-made pattern.

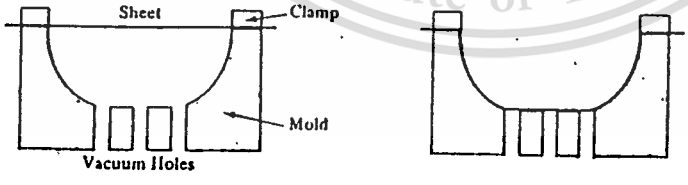

Figure 6 Sheet forming process.[27]

Copolymerization

We can think of copolymerization as an extension of free radical addition polymerization but using two monomer feedstock instead of the single monomer feedstock. The composition of random copolymer can influence many of its important properties, including solubility, degree of crystalinity, Tg and Tm, the control of copolymer composition is therefore of great practical importance.

The copolymer composition equation

A quantitative treatment of copolymerization is base on the assumption.

1. The reactivity of the growing chain free radical is independent of its length (same as for homopolymerization).
2. The reactivity of the growing chain is determined only by the terminal unit, i.e. the last type of monomer added.
3. During copolymerization a steady state is established, i.e. there is a constant number of free radicals of both monomer type in the reaction mixture.

Considering a reaction mixture consisting of two different types of monomer, monomer type1 and monomer type2 and polymerization is taking place.

There will be four different types of propagation reactions , i.e.

Reaction		Rate equation	
$P_1 + M_1 \xrightarrow{K11} P_1$	=	$K_{11}[P_1][M_1]$	2.1
$P_1 + M_2 \xrightarrow{k12} P_2$	=	$K_{12}[P_1][M_2]$	2.2
$P_2 + M_2 \xrightarrow{K22} P_2$	=	$K_{22}[P_2][M_2]$	2.3

$$P_2 + M_1 \xrightarrow{K21} P_1 \qquad = K_{21}[P_2][M_1] \qquad 2.4$$

where P_1 and P_2 refer to the growing chain of any length with terminal unit of each monomer and M_1 and M_2 refer to monomer types. Rate of disappearance of monomer type M_1 will be;

$$-d[M_1]/dt = K_{11}[P_1][M_1] + K_{21}[P_2][M_1]$$
$$= [M_1](K_{11}[P_1] + K_{21}[P_2]) \qquad 2.5$$

And rate of disappearance of M_2 will be;

$$-d[M_2]/dt = K_{12}[P_1][M_2] + K_{22}[P_2][M_2]$$
$$= [M_2](K_{12}[P_1] + K_{22}[P_2]) \qquad 2.6$$

The first subscript on the rate constants designates the nature of chain end and the second identifies of the monomer being added to the chain.

divided 2.5 by 2.6

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](K_{11}[P_1] + K_{21}[P_2])}{[M_2](K_{12}[P_1] + K_{22}[P_2])} \qquad 2.7$$

Application of the stead - state assumption to P_1 and P_2 requires that they be generated and consumed at equal rate. P_1 are generated in reaction 2.4 and consumed in reaction 2.2. Note that 2.1 just converts one P_1 into another one, with no net change in their number. Therefore;

$$K_{12}[P_1]\,[M_2] = K_{21}\,[P_2]\,[M_1] \qquad 2.8$$

From which

$$\frac{[P_1]}{[P_2]} = \frac{K_{21}[M1]}{K_{12}[M_2]}$$

Substitution of this expression for $\frac{[P_1]}{[P_2]}$ in 2.7 followed by divided through the resultant by K_{21} lead to;

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \qquad 2.9$$

This expression is known as the copolymer equation r_1 and r_2 are the monomer reactivity ratios.

$r_1 = \frac{K_{12}}{K_{11}}$; which represents the rate constant for radical P_1 adding its own monomer M_1 to the rate constant for its adding the other monomer M_2.

Similarly

$r_2 = \frac{K_{22}}{K_{21}}$; represent the rate constant for radical P_2 adding its own monomer M_2 to the rate constant for its adding monomer type M_1.

Reactivity ratios are experimentally determined or may be estimated. In organic free- radical copolymerization, for a given monomer pair they are pretty much independent of initiator and solvent, and are only weakly temperature dependent. In ionic copolymerization,however, they depend strongly on the gegen ion and solvent.

This relation may be put in a more convenient from by defining.

f_1 = mole fraction of monomer 1 in the reaction mixture at any instant.

F_1 = mole fraction of monomer 1 in the copolymer formed.

$$F_1 = (1-F_2) = \frac{dM_1}{d(M_1+M_2)} \qquad 2.10$$

$$f_1 = (1-f_2) = \frac{M_1}{M_1 + M_2} \qquad 2.11$$

Combination of 2.9 - 2.11 gives

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} = \frac{(r_1-1)f_1^2 + f_1}{(r_1+r_2-2)f_1^2 + 2(1-r_2)f_1 + r_2} \qquad 2.12$$

$$F_1 = F_1(r_1, r_2, f_1)$$

Significance of reactivity ratio

To gain an appreciation for physical significance of 2.12, let look at some case study of reactivity ratio.

Case 1; $r_1 = r_2 = 0$, here neither type of chain end can add its own monomer, so a perfectly alternating copolymer results, $F_1 = 0.5$ regardless of f_1, unit one of the monomer is used up ,at which point, polymerization stops.

Case 2; $r_1 = r_2 = \infty$, here, P_1 can add only M_1 monomer and P_2 only M_2 , so the polymer formed will be a physical mixture of homopolymer 1 and homopolymer 2 chain ("self polymerization").

Case 3; $r_1 = r_2 = 1$, under these conditions, the growing chain find the monomer equally attractive, so the addition depends only on the ratio of monomers in the vicinity of the chain ends $F_1 = f_1$.

Case 4; $r_1 r_2 = 1$, this is the so - called ideal copolymerization, where each chain displays the same preference for one of the monomers over the other.

$K_{11}/K_{12} = k_{21}/K_{22}$, so it doesn't matter what's on the end of chain. In this case, 2.12 reduces to;

$$F_1 = \frac{r_1 f_1}{(r_1 - 1)f_1 + 1} \qquad 2.13$$

Case 5 ; $r_1 < 1$, $r_2 < 1$, this common situation corresponds to an azeotrope in vapor-liquid equilibrium. At the azeotrope;

$$F_{1az} = f_{1az} = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \qquad 2.14$$

System for which $r_1 > 1$, $r_2 > 1$, also from azeotrope, but have been reported only rarely. At this point there will be no drift in monomer ratios and composition of copolymer and feed will remain constants during polymerization.

Variation of composition with conversion.

If $F_1 \neq f_1$, where one monomer is very much more reactivity than the other, the first polymer formed contains mostly the more reactive monomer. Later in the polymerization this monomer is used up and last polymer formed consists mainly of the less reactive monomer.

Because of the wide difference in the reactivity ratio of many monomer mixture, considerable heterogeneity in the composition of the chains and in the distribution of monomer unit along the chain may be developed to give the wide range of properties. Controlling the heterogeneity of copolymer involve either programmed addition of the more reaction monomer or " short stopping" of the reaction at the proper conversion. Computer methods for predicting heterogeneity and the planning of monomer charging schedules have been developed base on the copolymer composition equation.

The literature of the preparation of acrylic ester copolymer is very extensive. Although any process may in principle be used, commercial production is confine largely to solution and emulsion process. The choice and proportions of comonomer are usually determined by the product. Many of the more important physical properties bear a relationship to the glass transition temperature (Tg).

The effect of copolymerization on Tg

The glass transition temperature of many copolymer vary as monotonically with composition between those of the homopolymer. They can be approximated fairly well from a knowledge of Tg values of homopolymers, Tg_1 ,Tg_2 and Tg_n with the empirical relation.

$$\frac{1}{Tg_1} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} \cdots \frac{W_n}{Tg_n} \qquad 2.15$$

Where the W's are weight fractions of monomer in the copolymer.

Literature Review

C.C. Nguyen et al., U.S. Pat. No. 5,003,022. (1990) disclosed a stable aqueous polymeric dispersion comprising a graft copolymer of thinned, gelatinized starch and one or more vinyl monomers utilizing potassium persulfate initiator, the vinyl monomers including at least 10% by weight 1,3-butadiene is disclosed. This patent teaches the preparation of graft copolymer of gelatinized starch which

provides a high grafting efficiency. The polymeric dispersion used in paper coating applications.

A. M. Henderson and A. Rudin (1982) reported the successful grafting of styrene and methyl acrylate onto wheat starch by gamma radiation and chemical initiation. The respective percent add on value were 46 and 45, 68% of the polystyrene formed was grafted to starch, and the corresponding proportion of poly (methyl acrylate) was 41%. The molecular weight distribution of the homopolymer and graft portions were characterized and extrusion condition were established for production of ribbon samples of starch-g-PS and starch-g-PMA. Both copolymer type were considerably weaken by soaking in water and this effect was more immediate and drastic for starch-g-poly(methyl acrylate). Both graft copolymer regained their original tensile strength on drying, but the poly(methyl acrylate) specimens did not recover their original unswollen dimensions and retained high breaking elongations characteristic of soaked specimens. Tensile and dynamic mechanical properties of extruded and molded sample of both graft polymers are reported and the plasticizing of water are summarised.

J.S. Shukla and G.K. Sharma (1987) described efforts using ceric ammonium nitrate(CAN)/thioglycolic acid(TGA) redox couple system to graft methyl methacrylate(MMA) onto wool at 55 $\pm$ 2°C under atmospheric oxygen. Graft copolymer was characterized by IR spectroscopy, scanning electron micrographs and thermogravimetric analysis. Effect of amines, acid, alkali, oxidizing, and reducing agents were determined experimentally. The molecular weights of graft poly(methyl methacrylate) and homopolymer were also evaluated.

C.E. Brockway(1964) has been studies the factor which influence the efficiency of extraction of homopolymer of methyl methacrylate from its graft copolymer with granular corn starch. The moisture content and various solvent for the homopolymer are evaluated, about 25% moisture seems optimum for many samples. For the starch/PMMA system, chloroform and dichloroethane are about equally efficient and either is superior to benzene which in turn is better than toluene, methyl ethyl ketone or acetone.

R. Chinaswamy and M.A. Hana(1991) presented the review outlines the rationale behind starch polymer based thermoplastic resin product using reactive extrusion processing techniques, as well as characterization of these polymer. They are also reported reactive extrusion processing technique for starch grafting onto polystyrene. The mixtures of starch, polystyrene, sodium bicarbonate, citric acid and water were extrusion processed at temperatures of 100 to 200 ^{o}C, a combination of molecular mechanism produced a starch graft onto polystyrene and/ or copolymer. This product contained about 60% starch on dry weight basis.

G.M. Gurruchaga, J. Sanroman, M. Valero and G.M. Guzman(1993) have been studied the simultaneous grafting of ethyl acrylate with methyl methacrylate onto amylose with redox method with the Ce(IV) ammonium nitrate initiated the graft copolymerization. Grafting yields obtained using gravimatric and ^{13}C n.m.r. spectroscopic methods. A study of microstructure of grafted products obtained involving either the quantitative determination of the grafted copolymer composition or qualitative study of sequence distribution and the stereochemical. Configuration of grafted copolymer sequences has been carried out. The α - methyl group carbon, the quaternary carbon and the carbonyl group carbon have

found to be sensitive to relative stereochemical configuration .of the chain segments.

D. Patil and G.F. Fanta (1993) characterized starch graft poly(methyl acrylate) copolymer containing 55-60% PMA which prepared from corn starch with ceric ammonium initiation. Graft copolymers were characterized grafting yield, grafting frequency, the molecular weight and molecular weight distribution of PMA grafts. Variables investigated in graft copolymerization reaction were nitric acid concentration , ceric ion-to-starch ratio, reaction time, gelatinization of the starch, and reactant concentration in water. At high reactant concentrations, high conversion of methyl acrylate to grafted PMA could be obtained in less than 0.5 hour at 25 ^{o}C.

D. Trimnell, C.L. Swanson, R.I. Shogen. and G.F. Fanta(1993) studied the extrusion processing of granular starch graft poly(methyl acrylate) and the effect of extrusion condition on morphology and properties. starch-g-poly(methyl acrylate) copolymer containing various percent PMA by weight, were prepared by ceric ammonium nitrate initiated polymerization. Graft copolymer were extrusion processed through a strand die with water content of 10 and 30% (base on starch) and at temperature of 140 and 180 ^{o}C. Properties of ribbons prepared from extrusion process depended on the combined effect of processing temperature, PMA level in the graft copolymer and water content during extrusion. The value of ultimate tensile strength(UTS), % elongation at break(%E) and DSC data were evaluated.

M. Liu, R. Cheng, J. Wu and C. Ma (1993) disclosed a study of the copolymerization of the ceric ammonium nitrate(CAN) initiated graft copolymerization of methyl acrylate(MA) onto potato starch. The variables effecting the graft were investigated such as concentration of MA ,CAN nitric acid, reaction time and reaction temperature. The molecular weight of grafted poly(methyl acrylate) has been determined. The mechanism of grafting has been explored, a new kinetic equation of graft copolymerization is established.

D.R. Patil, M.N. Crookston and G.F. Fanta (1994) reported the preparation of starch graft poly(methyl acrylate) containing 40-65 % PMA using ceric ammonium nitrate(CAN) initiation in a 2-gallon reactor. CAN initiator was added either in one portion or portionwise. Graft copolymers were characterized with respect to % homopolymer, PMA content of the graft copolymer, molecular weight of grafts. Conversion of monomer to polymer was nearly quantitative. Continuous plastic ribbons for tensile testing were prepare by extrusion processing. Tensile properties varied with the preparation method used for addition of CAN initiator (i.e., single portion vs. portionwise) and depended on the particular starch variety used in the polymerization reaction. Since water acted as a plasticizer for starch. Sample extruded at high moisture content exhibit higher %elongation(%E) values than the same polymer extruded at low moisture content. Value for %E also increased with higher percentages of PMA in the graft copolymer.

CHAPTER 3

EXPERIMENT

Apparatus

Characterization and identification of a graft copolymer

Extraction of graft copolymers was used by soxhlet extraction apparatus, the dimension was 30x100 mm and using 28x100 mm of cellulose extraction timber. The reflux was heated with model MR 3001 Heidolph heater.

Infrared spectra were obtained with IR-810 Jasco spectrophotometer. Thermogravimetric analysis was performed on TGA 51 Dupont thermogravimetric analyzer. DSC data were obtained with the DSC 50 Shimadzu differential scanning calorimeter. Molecular weight of grafted polymer and ungraft freepolymer were determined with a Water GPC system, model 150 C consisting of The Styragel column(10^6), a pump and autosampler in combination with RI detector.

Physical and mechanical properties testing

Graft copolymer sample was processed without acetone extraction of freepolymer. The casting sheet of graft copolymer pelletized by Cosmo crusher was then masticated to form sheet by two rolls mill (10" diameter) from Lab Tech Engineering Co, Ltd., model LRM 110. The testing specimens were prepared by hot compression molding of masticated sheet using LP20 hot compression machine,

Lab Tech Engineering Co, Ltd. Tensile strength, % elongation and flexural modulus were tested with LR 30, Lloyd instrument materials testing machine, Lloyd instruments Co.,Ltd. Impact strength data was determined with impact tester, model 258-PC, Yasuda Seiki Seisakusho Co., Ltd. Hardness testing were operated by Shore A and D type hardness tester. Rheological properties were characterized by Rosand Precision Advanced Capillary Rheometer. Rosand Co, Ltd.

Material

Tapioca starch (13% moisture content) was obtained from Tai wah Co., Ltd. Methyl methacrylate(MMA), Methyl acrylate(MA), Ethyl acrylate(EA), Buthyl acrylate (BA) and 2- Ethylhexyl acrylate(2-EHA) were commercial graded monomers from Mitsubishi Rayon Co.,Ltd, DIA Acrylate Co., Ltd, Inter Chem Co., Ltd. and Forhosa Plastics Co., Ltd. respectively. All of the monomers were used without futher purification. Potassium persulphate($K_2S_2O_8$) was AR graded purchased from Famitalia Calo Erba Co., Ltd. The initiator solution was prepared by dissloving 27.00 g. of $K_2S_2O_8$ in 1000 ml. of 1 N nitric acid(HNO_3). Disodium ethylenetetraacetic acid solution (Na_2EDTA) was prepared by dissolving 40 g of Na_2EDTA in 1000 ml of distillated water. Commercial gread Nonyl phenol ethoxylate (40 mole ethoxylate group, NP-40) was used as emulsifier. Commercial gread Propylene glycol was used as a chain transfer agent and all others were analytical grad.

Graft copolymerization

The graft copolymerization reaction was carried out under nitrogen atmosphere in four- necked 2L glass reactor equipped by a stirrer with a paddle type designed in our laboratory and a variable rotor speed control, a thermometer, a reflux condenser and a gas inlet tube (see figure 7).

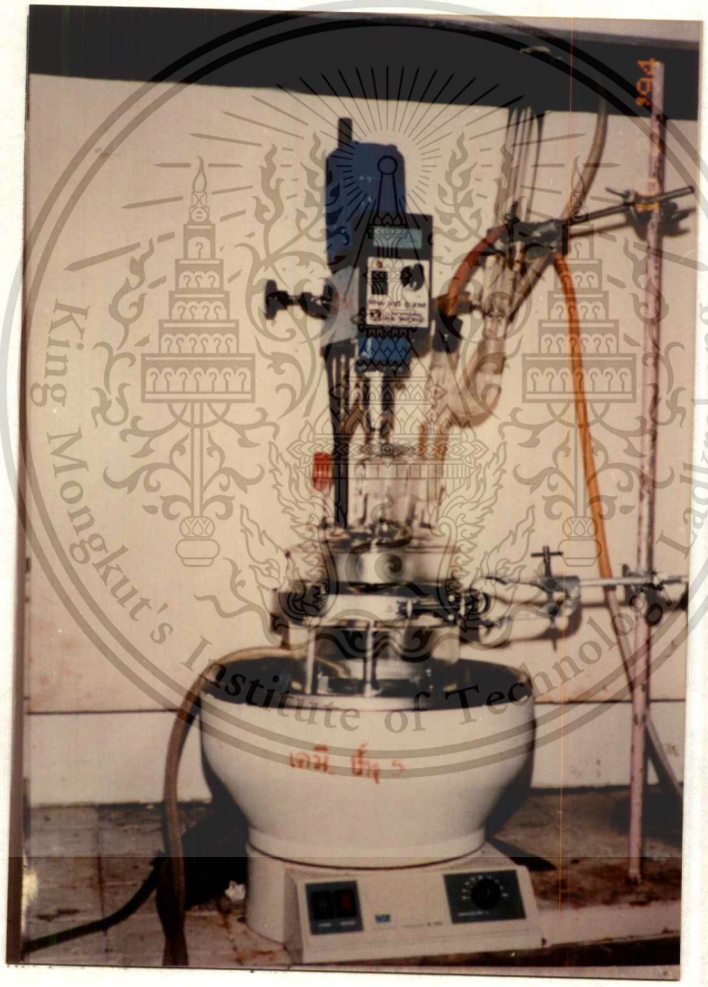

Figure 7 The 2 L reactor for preparation of a starch graft copolymer.

Hundred grams of starch in 1200 ml of distillated water were gelatinized for 1 hour at the temperature 90 °C, rotor speed at 500 rpm and then cooled down to the desired reaction temperature, NP-40 was added and stirred until it became homogeneous solution, followed by the required amount of monomers. The mixture was stirred at the rotor speed 700 rpm for 10 min and then initiator solution was added. The reaction was allowed to continue for a specific period of time, whist stirring continuously at 500 rpm. After completion of the reaction, the resultant was neutralized with 1 N NaOH, excess methanol was added to quench the reaction and to coaggurate the product. The crude product was isolated by filtration and throughly washed with water and methanol and dried in thermal oven at 50-55 °C until its weight constant .

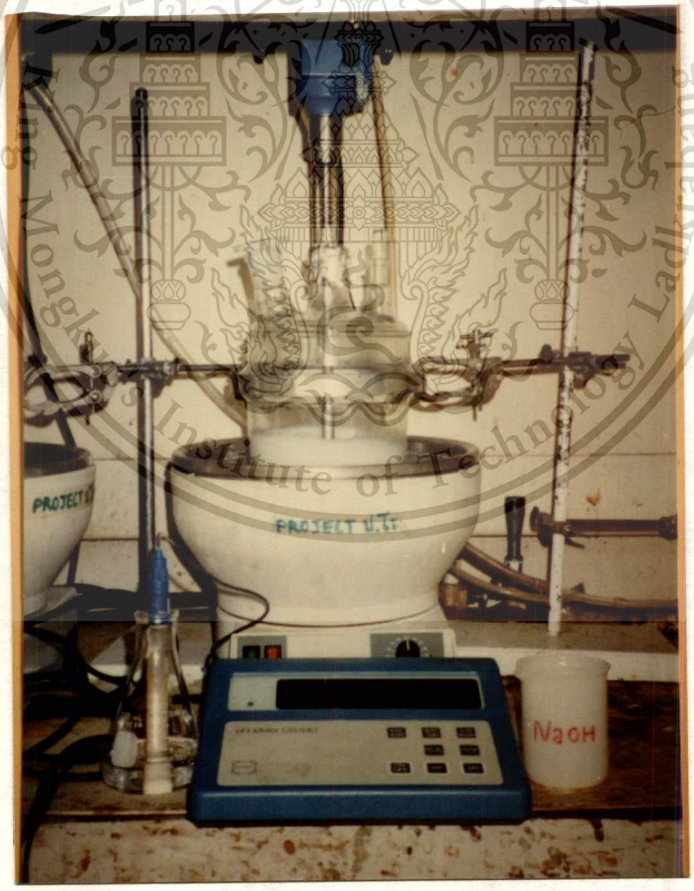

Figure 8 Neutralization of latex product of starch graft copolymer.

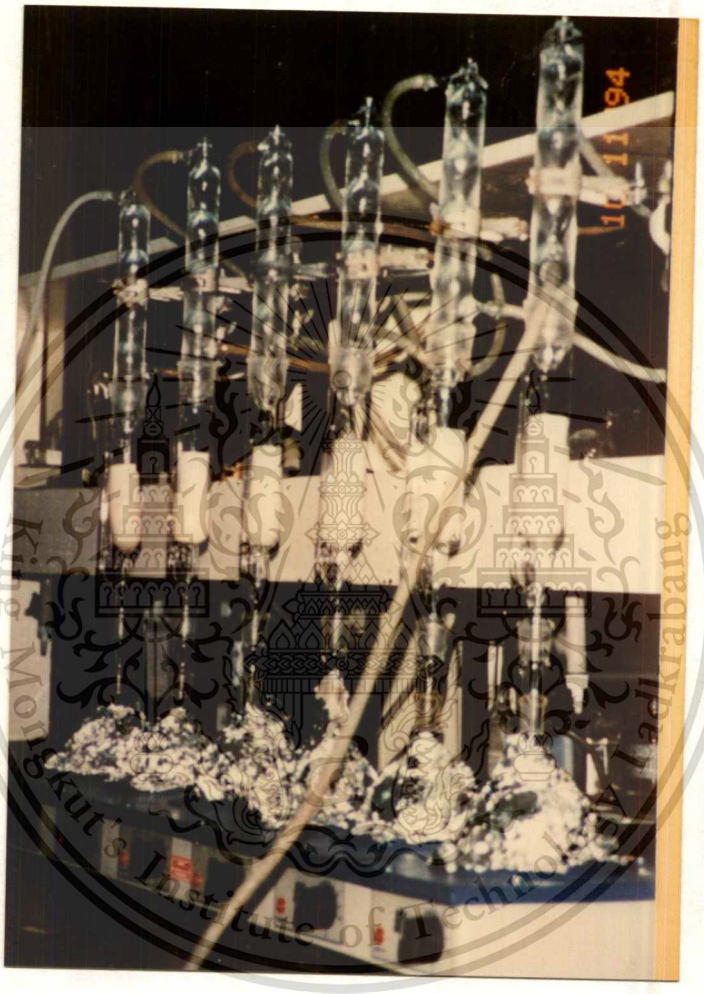

Figure 9 The soxhlet extraction apparatus for the separation a free polymer from a starch graft copolymer.

Free acrylic polymer separation

To remove free acrylic polymers, about 2 g of dried sample were weighed accurately and extracted in soxhlet extractor with acetone for 72 hours. The residues was then dried and weighed. This fraction was used to calculate the percentage of free polymers in the graft copolymers. The Figure 9 shows the apparatus for the separation of a freepolymer from a starch graft copolymers.

Side chain separation

In order to obtain acrylic copolymer chains(grafted) free from starch, 1 g of starch grafted copolymer was weighed accurately and added to 100 ml glacial acetic acid. The mixture was stirred for 1 hour at temperature about 90-100 ^{o}C to swelling the graft copolymer, followed by hydrolysis proceeded by adding dropwise 2 ml of perchloric acid(60%), within 1-2 min, the mixture became clear solution. The product was immediately poured into water to precipitate the side chain copolymer. The precipitate was thoroughly washed to neutral and dried until a constant weight was obtained.

Molecular weight determination

Molecular weight of grafted polymer and ungrafted free polymer were determined with a Water GPC system, model 150 C consisting of a pump and autosampler in combination with RI detector. The styragel column(10^{6}) was calibrated with polystyrene standard. The mobile phase was HPLC-grade tetrahydrofuran (THF), and flow rate of the mobile phase was 1ml/ min. Grafted

poly (acrylic ester) and ungrafted poly (acrylic ester) (~15 mg) were stirried with 10 ml of THF for 3 days at room temperature. Insoluble material was separated by centrifugation and solution was through a 0.46 μm nylon filter before injection.

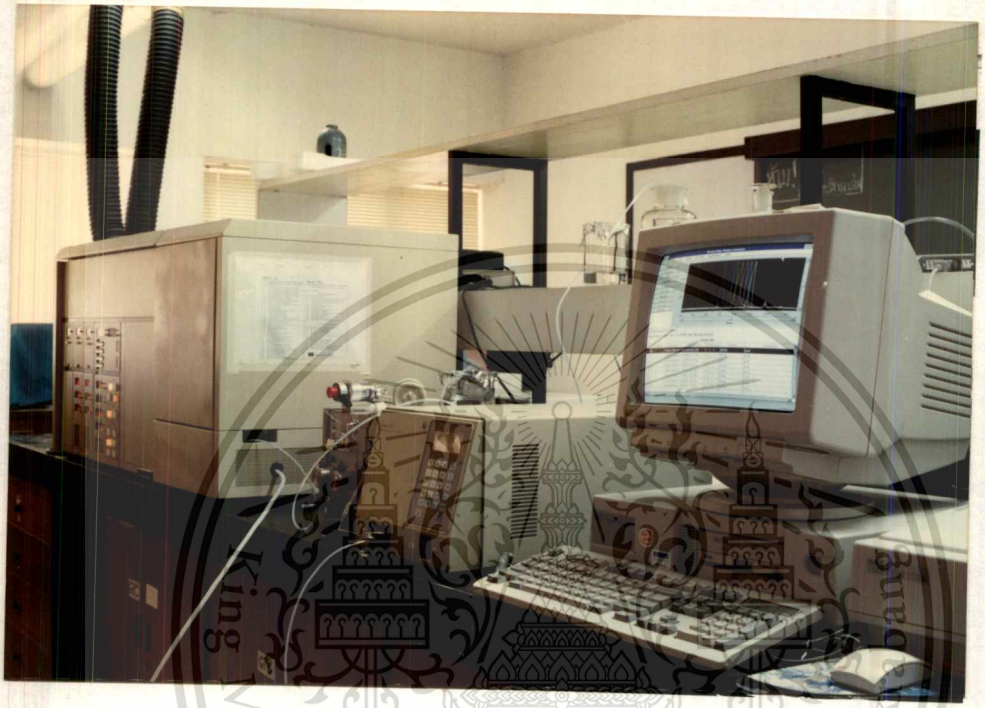

figure 10 Gel permeation chromatography apparatus, Water GPC system model 150C.

Gravimetric characterization

Grafting yield parameter such as the percentage of grafting(G), grafting efficiency(GE) and grafting frequency (AGU/chain) were determined by the following formulas[14]:

$$\%G = \frac{W_1 - W_o}{W_1} \times 100$$

$$\%GE = \frac{W_3}{W_3 + W_2} \times 100$$

$$\text{AGU chain} = \frac{W_o / 162}{W_3 / Mw}$$

where W_o, W_1, W_2 and W_3 were weighed of starch, starch graft copolymer, the free polymer and grafted polymer respectively.

%Free polymer = weight of acetone extractable polymer in 100 g of starch graft copolymer

Total solid content and conversion

The total solid content of starch graft copolymer was determined by weighing 2 g of sample, then putting wide-spread into a dish. After drying dried the sample in vent air oven at 110 ^{o}C for 2 hours, the sample was cooled down to room temperature in desiccator and weight accurately. Drying until the sample was proceeded its weight constant.

The percent total solid content(%TSC) percent conversion were calculated by the following formulas[25]:

$$\%TSC = \frac{(C-A) \times 100}{(B-A)}$$

where, A= weight of dish, g unit.

B = weight of dish contained sample before dried, g unit

C = weight of disch contained sample after dried, g unit.

$$\% \text{ Conversion} = \frac{X \times 100}{Y}$$

where, X = TSC from the experiment

Y = TSC from the theory

Identification of grafting

Infrared spectroscopy, IR spectra were obtained with Jasco IR 810 spectrophotometer. KBr pellets were prepared for measurements of tapioca starch, starch graft copolymer and side chain polymer.

Thermal properties determination

Differential scanning calorimeter(DSC)

A shimadzu DSC 50 was used to determine glass transition temperature of starch graft copolymer. The thermal block was set at 30 °C and purged with nitrogen prior to DSC analysis, starch graft copolymers were purified by soxhlet extraction, and grinded by vibration grinder in liquid nitrogen. At last the fined powder was obtained. Approximately 10 mg of each sample was sealed inside aluminum DSC pan and the sample was heated in the DSC from 30 to 250 °C at heating rate 10 °C /min.

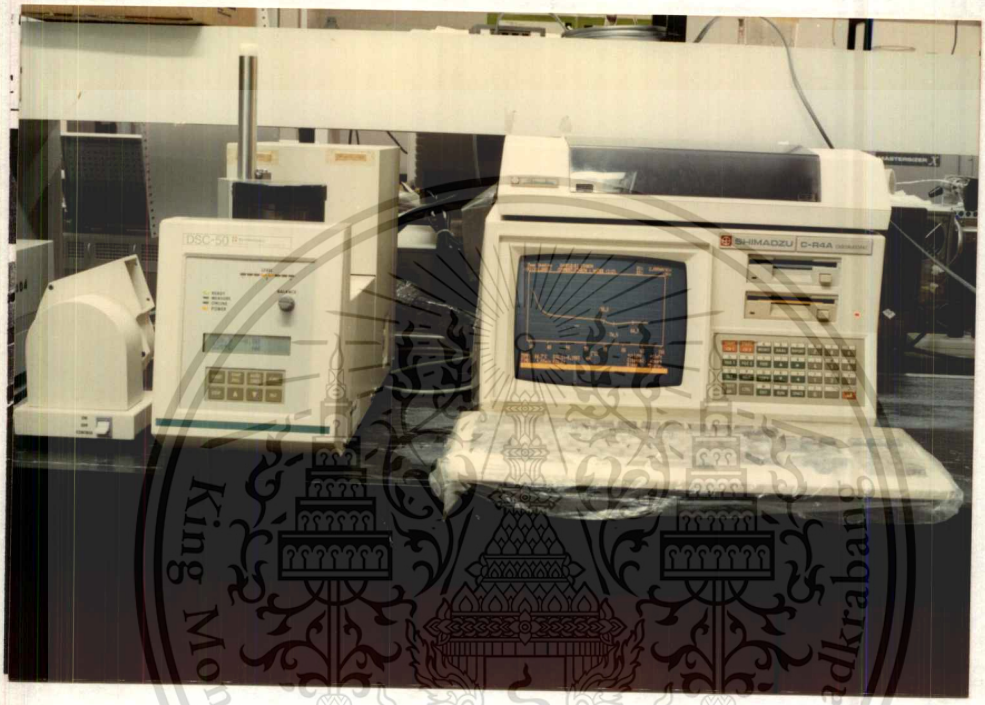

Figure 11 Differrential scanning calorimeter.

Thermogravimetric analysis

The thermogravimetric diagrams of starch and starch graft copolymer were measured by a Dupont TGA 51 equipped with recorder and purged with nitrogen, the heating rate was 20 ^{o}C/min from the room temperature to 900 ^{o}C.

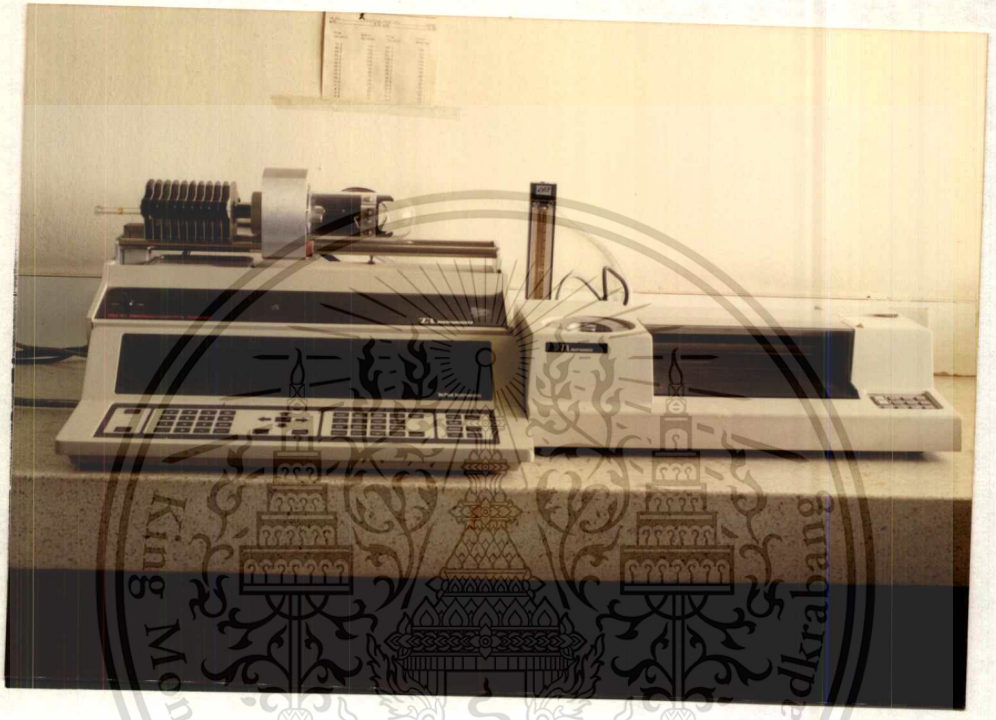

Figure 12 The thermogravimetric analyzer.

Physical and mechanical properties testing

The graft copolymer samples for mechanical properties testing were used in solid form without acetone extraction. The solid sheet was obtained by casting the emulsion product on the aluminum tray which has been covered with polypropylene film and were then dried in vent oven at 50-60 ^{o}C. The casting sheet was grinded to pellets form by a crusher and the pellets then were masticated in to

homogeneous sheet by two- rolls mill. The test specimens was obtained by placed masticated sheet on compression mold which having been designed refering to ASTM standard. The heating temperature of compression molds was set between glass transition temperature(Tg) and decomposition temperature (Td, about 150 ^{o}C). The compression condition was with 85 kg/cm^{2} of pressure for 5 mim.

Table 10 Mechanical properties test method.

Mechanical properties	Test method	unit
Tensile strength	ASTM D 638	N/mm^{2}
Elongation	ASTM D 638	%
Modulus of elastic	ASTM D 638	N/mm^{2}
Flexural modulus	ASTM D 790	N/mm^{2}
Impact strength	ASTM D 256	kJ/m^{2}
Hardness	Shore A,D	

Tensile properties testing

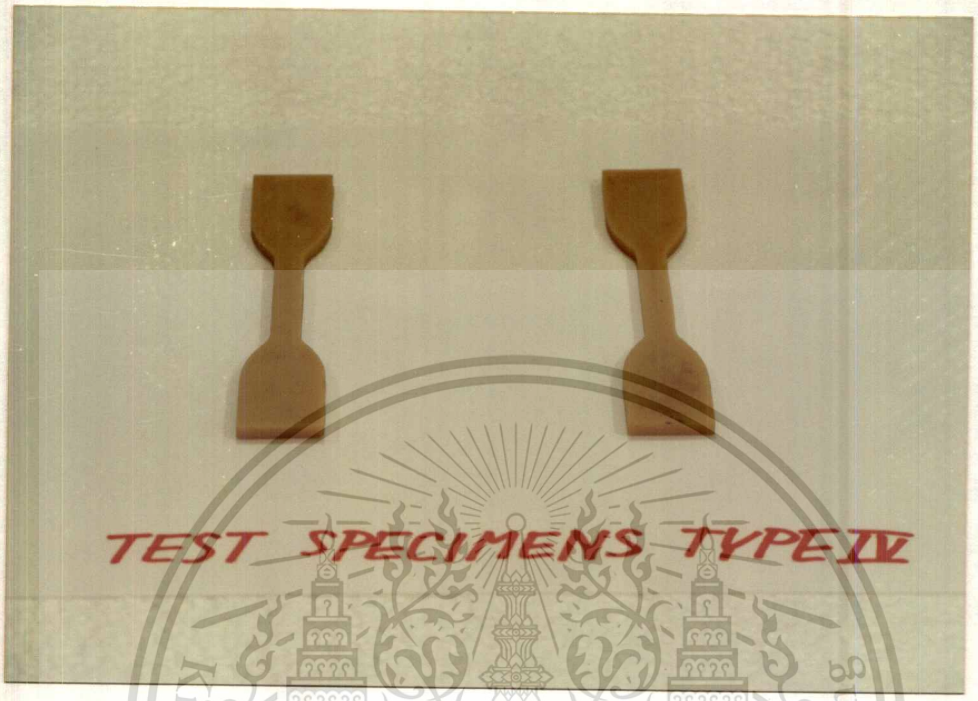

Figure 13 The molded starch graft copolymer specimens (ASTM D-638 type(Ⅳ).

ASTM D-638 type IV tensile test specimens were compression molded from masticated starch graft copolymer (including free polymer). Tensile properties such as tensile strength, %elongation at break, and modulus of elastic were measured with Lloyd instrument material testing machine model LR30, equipped with a laser strain detector and operated with "Windap" software programming. The test specimens was holded with grips, control speed with respect to stationary grip(in range of 10 to 50 mm/min) and 1 kN load cell detector was used. Breaking elongation was detected using a laser-strain detector to measured the progressive separation of gauge line marked on the sample, the initial gauge length was 4 cm. The testing value was analyzed by "Windap" computer software programming.

Figure 14 The instrument material testing machine for tensile properties testing.

Tensile strength

The tensile strength (σ) was calculated as:

$$\sigma = \frac{F}{A}$$

where σ = tensile strength , N/mm^2

F = load at break,N

A = cross sectional area of gauge length section, mm^2

Elongation at break

The elongation at break was calculated as followed :

$$E\ (\%) = \frac{L - L_o}{L_o}$$

where, E = elongation at break, (%)

L = stretched length at break

L_o = original length of gauge

Modulus

The modulus of elasticity(Young's modulus) was calculated by extending the initial linear portion of load-extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by corresponding strain. For a straight forward tension test the formula is simply:

$$\text{Modulus} = \frac{\text{stress } (N/mm^2)}{\text{strain } (mm/mm)}$$

In fact, all elastic modulus value can be computed using the average initial cross-sectional area of test specimens in calculation, and the result is in pounds-force per a square inch.

Impact properties testing

ASTM D-256 v - notch type Izod impact test specimens were compressive molded from masticated product. Impact strength were tested with Yazuda impact tester model 258-PC,linked with computer, and the testing results were analyzed by software programming.

Hardness testing

Shore D-type hardness tester was used in measuring rigid sample and shore A type for elastic sample. The sample was laid down on the pan and where then pressed under 5 kg of load for 1 or 10 second, read the resultant in 0 to 100 scale range.

Rheological properties testing

Starch graft copolymer(including freepolymer) was used in testing. Extrusion were carried out with Rosand Precision Capillary Rheometer, with a long die length 24 mm, long die diameter 1.5 mm. Drive was provided by hydraulic piston at programming speed 1 to 500 mm/min. The extruder barrel has two temperature controlled zone, bottom zone(die zone) was controlled and pressure transducer mounted in barrel.

Water absorption

The masticated sheet sample accurately weight was immersed in 10 ml. of distillated water and allowed to stand at 25 $^{\circ}$C for 18 hour. After that removed the water which adhering on surface of sample and weight. Water absorption was calculated as follows:

$$\%\text{Water absorption} = \frac{\text{wet weight of sample - starting weight of sample} \times 100}{\text{starting weight of sample}}$$

Density

The density of sample was determined by liquid displacement of sample in pycnometer. Methanol was used as immerse liquid. Density test formula is[25]:

$$\text{Density}(g/cm^3) = \frac{[(C-A)xd_k]}{[(B-A)-(D-A)]}$$

where, A = weight of pycnometer, g

B = weight of pycnometer filled with methanol, g

C = weight of pycnometer contained the specimens,g

D = weight of pycnometer contained the specimens and filled with methanol,g

d_k = density of methanol, (0.79 g/cm^3)

Moisture content

The 1g of starch graft copolymer sample(isolated free polymer) was accurately weighed on glass dish and then dried in an oven at 105 °C for 2 hours. The sample was cooled down to room temperature in desicator and weighed accurately. Moisture content was calculated as followed[1]:

$$\%\text{Moisture content} = \frac{[(F+T)_1 - (F+T)_2] \times 100}{F}$$

where; F = initial weight of sample

$(F+T)_1$ = weight of dish contained with sample

$(F+T)_2$ = weight of dish contained with sample after dried.

Figure 15 Impact tester

Figure 16 Hardness tester.

Figure 17 The Extrusion capillary rheometer.

CHAPTER 4

RESULT AND DISCUSSION

An examination of reaction variable

Effect of monomer ratio

The percentage of total conversion of the starch graft poly(MMA,EA) polymerization was initialy rise sharply when monomer ratio of MMA/EA were 100/0, 80/20, 50/50 to 45/55 and later decline. This could be explained by the assumption of a strong gel effect and solubility of polymers in the monomer phase (Figure 18). The value of the grafting parameter was obtained from various monomer ratio variation on starch graft poly(MMA,EA) polymerization. In the comparison of %G and %GE values obtained from mixture monomer and single monomer usage, both values of mixture monomer were higher than the later, except for MMA/EA = 80/20. Nevertheless the maximum value of %GE is 39.42 for MMA/EA =45/55, the same behavior observed the percentage of grafting (%G) with a maximum value of 32.02 for MMA/EA 45/55. Whereby under this reaction condition, the present of another monomer lead to the increasing in the propagation rate of graft copolymerization.

The percentage of total conversion of the starch graft poly(MMA,BA) polymerization at various monomer ratio, at first increase and later it is constant in tendency. When the amount of BA monomer in the polymerization was higher the percentage of total conversion is higher than those obtained from single MMA monomer usage. Therefore the present of BA into MMA lead to an increase in

over all propagation rate of polymerization. Also the result achieved from any monomer ratio of MMA/BA did not effect to the percentage of total conversion (Figure 4.3). The same behavior can be observed for starch graft poly(MMA,2-EHA) showed in figure 4.4

Table 11 Effect of monomer MMA/EA ratio on graft copolymerization[a].

Monomer ratio MMA/EA	% Solid content	%Total conversion	% free polymer	% G	% GE	Mw[c]	grafting frequence (AGU/chain)
100/0	12.2	78.69	33.38	23.45	31.88	484968	9771.09
80/20	13.69	88.33	38.29	19.86	24.25	683522	17024.32
50/50	12.57	81.1	32.27	27.32	36.45	546427	8579.39
45/55	15.3	98.73	32.98	32.02	39.42	540468	7083.25
40/60	10.99	70.94	33.08	23.98	32.66	855348	16742.4
0/100	9.92	63.97	39.99	19.19	19.19	895110	29406.09
100%mole (45/55)[b]	5.97	49.67	14.50	3.56	17.37	-	-
200% mole (45/55)[b]	15.30	98.73	32.98	32.02	39.42	540468	7083.25
300% mole (45/55)[b]	18.67	99.78	45.44	5.53	10.33	-	-

[a]Reaction carried out with starch 150 g,1.5 g propylene glycol and 18.75g(10.17 by weight monomer)NP-40 in water 1800 ml, 100% starch mole: 200%monomer mole(150 g:185.18 g)

[b]Monomer MMA/EA ratio 45/55 ;% mole monomer compared with % mole starch (weight of starch, g divided by 162 mole/g = 100%mole starch)

[c]Mw of grafted polymer from acid hydrolysis measured by GPC method.

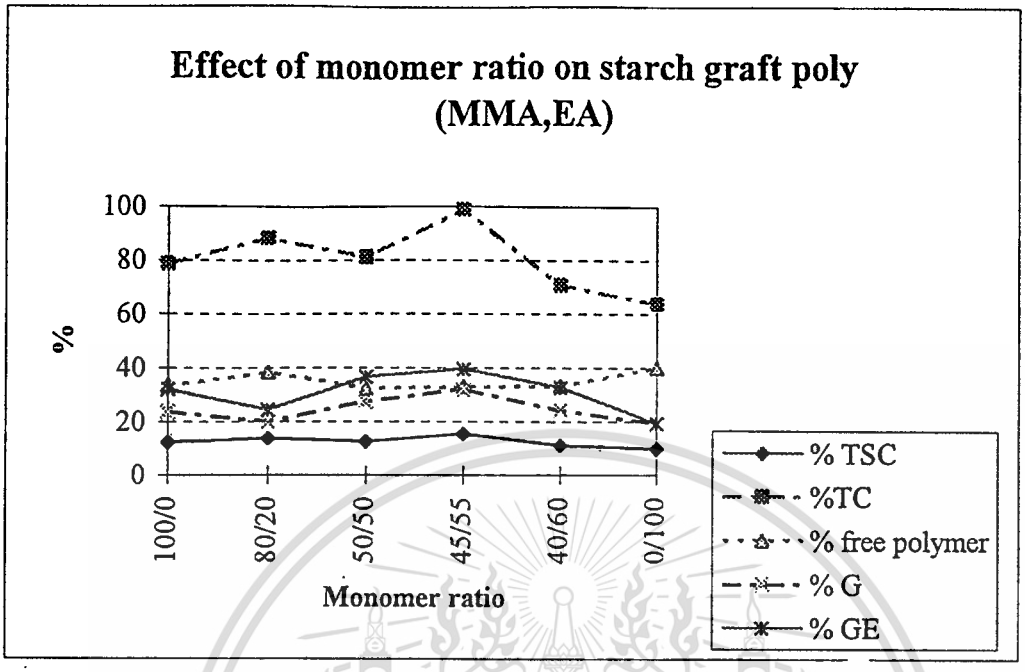

Figure 18 Effect of monomer ratio on starch graft poly(MMA,EA) polymerization, starch/monomer ratio = 1/2 mole.

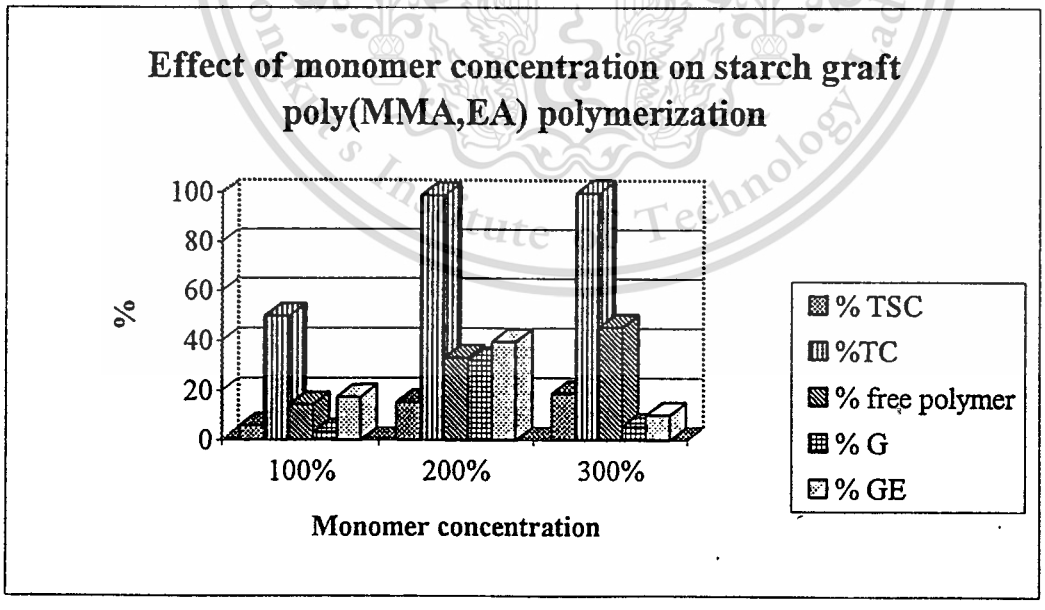

Figure 19 Effect of monomer concentration on starch graft poly(MMA,EA) polymerization, starch/monomer ratio = 1/2 mole, monomer ratio MMA/EA = 45/55.

The percentage of grafting (%G) and grafting efficiency (%GE) increase when the amount of butyl acrylate in monomer mixture was increased. The maximum %G and %GE of starch graft poly(MMA,BA) polymerization were observed when MMA/BA = 0/100 were 49.65 and 65.12 respectively (Figure 20). The same behavior were observed for starch graft poly (MMA,2-EHA), in case the amount of 2-EHA increased the maximum values of %G and %GE were observed for MMA/2-EHA = 0/100 were 51.84 and 74.80 respectively, as shown in figure 21 This could be explained that reaction conditions, using both hydrophobic monomer (BA and 2-EHA) in monomer mixture can accelerate grafting of starch.

In all cases, except for MMA/EA = 80/20 ,%free polymer decrease when used single monomer in the graft polymerization. Thus under these reaction condition the present of another monomer lead to a decrease in propagation rate of free polymer. However , any ratio of monomer mixture except for MMA/EA = 80/20 there were no significant effect on %free polymer.

Figure 20 and 21 show that the percentage of free polymer of monomer mixture used were higher with respect to single monomer used. Thus under these reaction conditions the present of BA or 2-EHA comonomer to MMA lead to an increase in propagation of free polymer, The increasing of the amount of both comonomer in monomer mixture scarcely effected on percentage of free polymer. (a little decreasing).

Polymerization with increased amount of ethyl acrylate showed that higher levels of ethyl acrylate monomer led to higher graft molecular weight except for MMA/EA = 80/20. The highest grafting frequency (AGU/chain) and molecular weight were obtained from a usage of a single monomer. When used ethyl acrylate as single monomer, the grafting frequency and molecular weight were 29406.09, and 895110 respectively.

Table 12 Effect of monomer ratio and monomer concentration on starch graft poly (MMA,BA) polymerization.

Monomer ratio MMA/BA[a]	%Free polymer	%TSC	%TC	%G	%GE
100/0	45.21	11.77	76.47	25.35	35.93
95/5	51.64	15.51	92.34	29.70	36.52
80/20	52.86	15.80	96.88	32.49	38.10
70/30	49.69	16.01	93.88	33.73	40.43
60/40	42.50	16.22	96.06	38.58	47.58
0/100	26.59	17.40	95.74	49.65	65.12
100%mole(70/30)[b]	25.48	11.26	94.78	23.25	47.71
200% mole(70/30)[b]	48.00	18.25	95.61	35.12	42.25
300% mole(70/30)[b]	59.53	24.96	96.50	45.73	43.44
200%mole(65/35)[b]	46.67	18.18	90.37	34.12	42.23
200%mole(65/35)[c]	49.48	14.78	96.29	35.20	41.57
200%mole(60/40)[b]	47.01	18.47	87.18	33.12	41.33

[a]Reaction carried out with 100 g starch, 1g propylene glycol(PG) and 200%mole monomer compared with 100%mole starch, NP-40 =10% by weight monomer in water 1200 ml,25 ml Na_2EDTA, $K_2S_2O_3$ 0.01 mole (100 ml, 0.1N $K_2S_2O_3$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[b]Reaction carried out with 150 g starch, 1.5g propylene glycol(PG) and NP-40 = 10% by weight monomer in water 1500 ml,37.5 ml Na_2EDTA, $K_2S_2O_3$ 0.015 mole(150 ml 0.1N $K_2S_2O_3$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[c]Reaction carried out with 150 g. starch, 1.5g propylene glycol(PG) and 200%mole monomer ,NP-40 = 10% by weight monomer in water 2000 ml, 37.5 ml Na_2EDTA, $K_2S_2O_3$ 0.015 mole (150 ml 0.1N $K_2S_2O_3$ in 1 N HNO_3) 60 °C 3.h 90 °C 1h.

Table 13 Effect of monomer ratio and monomer concentration on starch graft poly (MMA,2-EHA) polymerization .

Monomer ratio[a] MMA/2-EHA	% free polymer	% TSC	%TC	%G	%GE
100/0	45.21	11.77	76.47	25.35	35.93
95/5	53.63	15.71	95.28	31.02	36.64
80/20	52.37	16.62	97.71	36.78	41.26
70/30	46.90	17.21	95.33	40.64	46.42
60/40	39.43	17.81	96.97	46.38	54.05
0/100	17.46	19.23	90.96	51.84	74.80
100%mole(70/30)	43.97	19.71	94.77	50.28	53.35
200% mole(70/30)	46.90	17.21	95.33	40.64	46.42
300% mole(70/30)	57.76	24.19	98.50	64.37	52.71

[a]Reaction carried out with 100 g starch, 1g propylene glycol(PG) and 200%mole monomer compared with 100%mole starch, NP-40 =10% by weight monomer in water 1200 ml, 25 ml Na_2EDTA, $K_2S_2O_8$ 0.01 mole (100 ml, 0.1N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

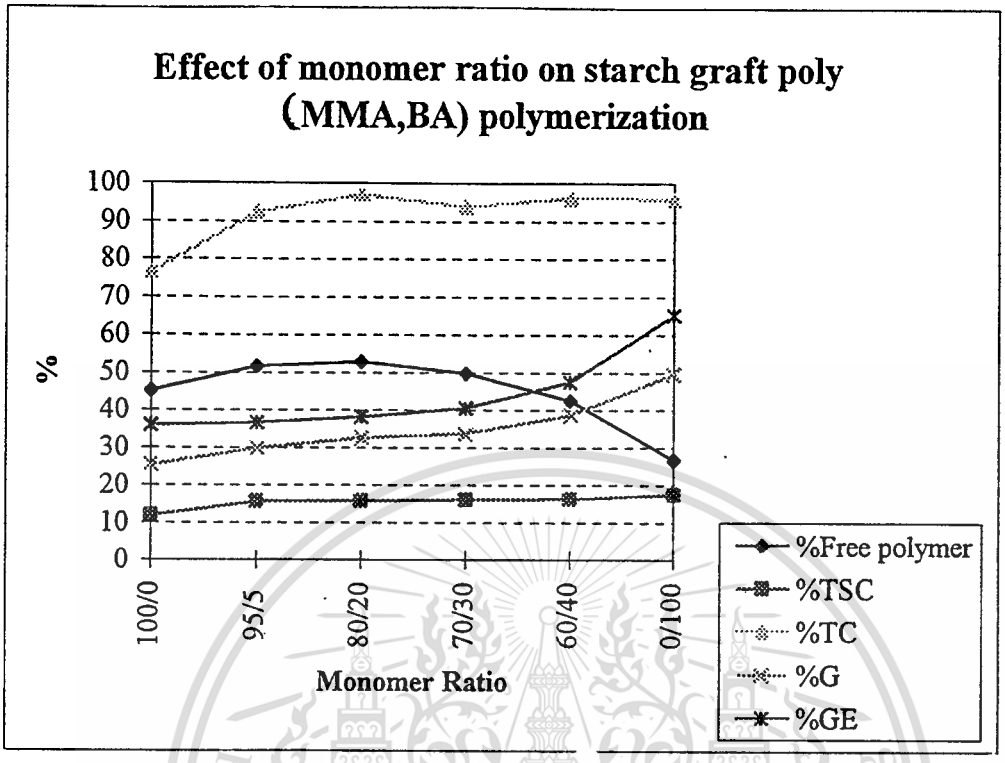

Figure 20 Effect of monomer ratio on starch graft poly(MMA,BA) polymerization, starch/monomer ratio = 1/2 mole.

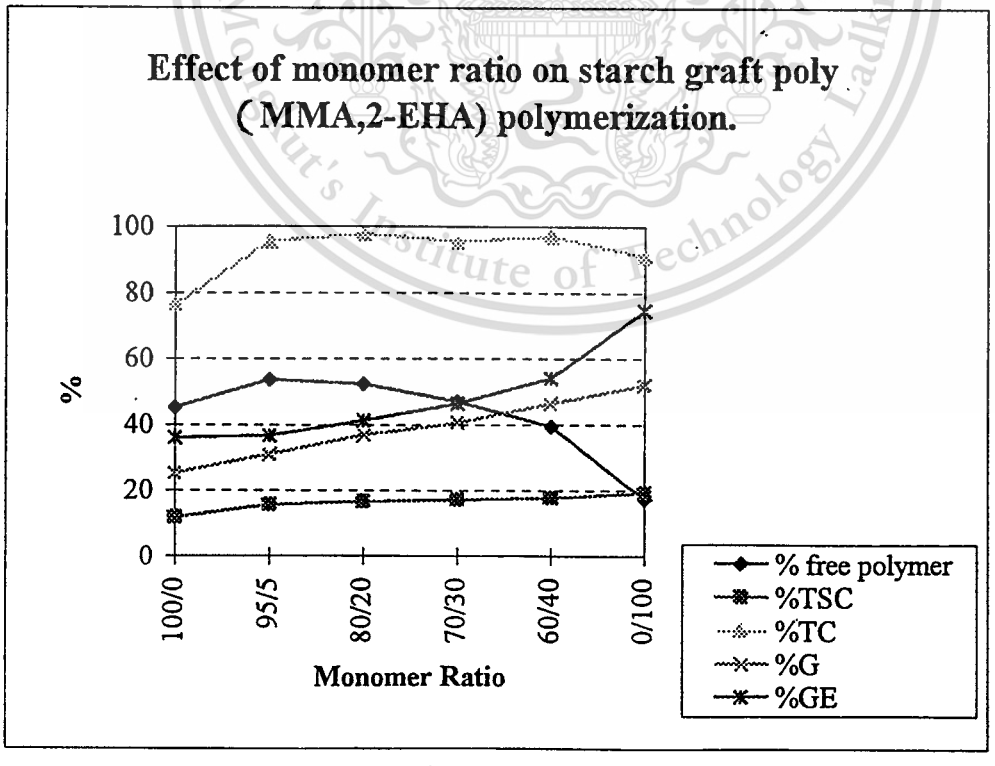

Figure 21 Effect of monomer ratio on starch graft poly(MMA,2-EHA) polymerization, starch/monomer ratio = 1/2 mole.

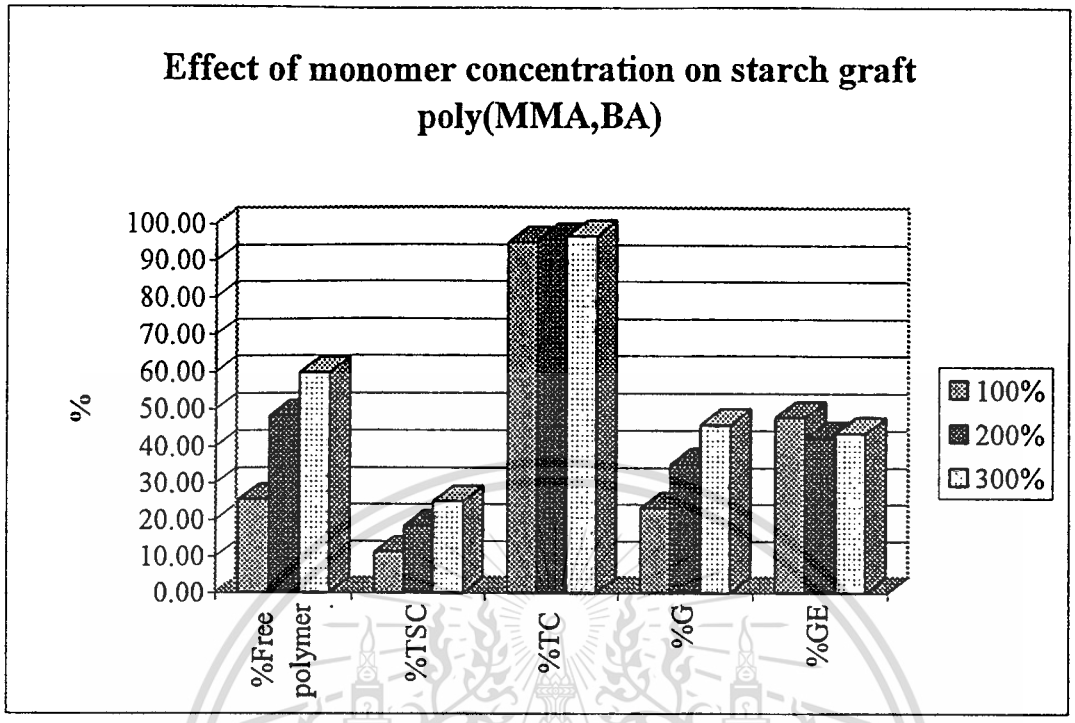

Figure 22 Effect of monomer concentration on starch graft poly(MMA,BA) polymerization, starch/monomer ratio = 1/2 mole, monomer ratio MMA/BA = 70/30.

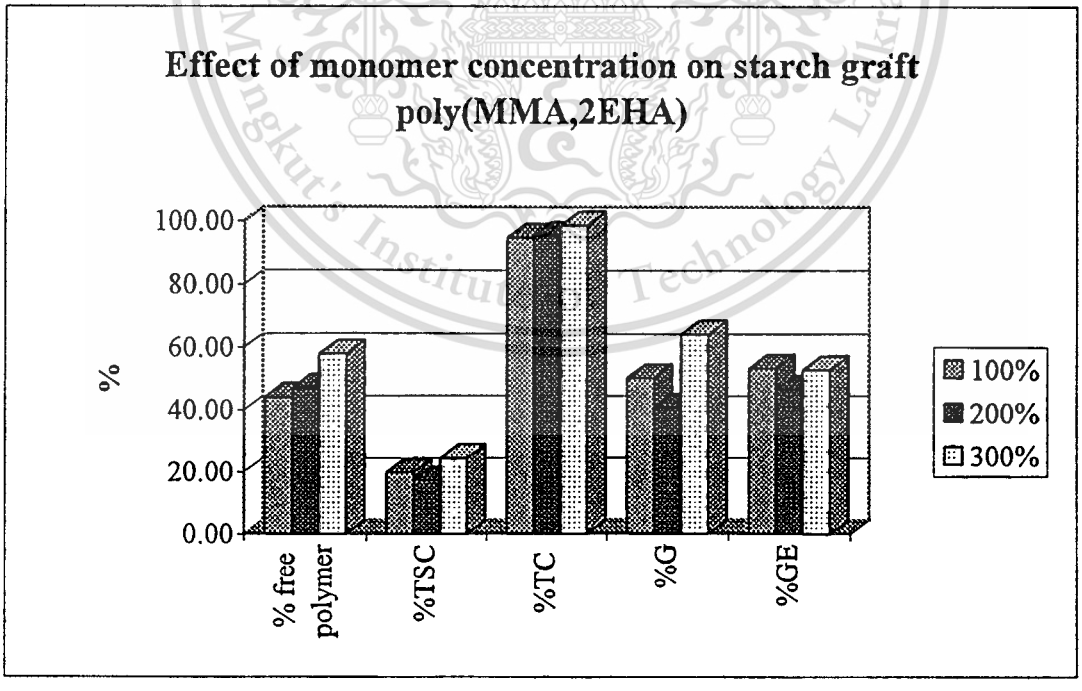

Figure 23 Effect of monomer concentration on starch graft poly(MMA,2-EHA) polymerization, starch/monomer ratio = 1/2 mole, monomer ratio MMA/2-EHA = 70/30.

The effect of monomer concentration

The effect of monomer concentration on percentage of graft(%G) and percentage of grafting efficiency(%GE) of starch graft poly(MMA,EA) were illustrated in figure 19. At the increase in monomer concentration from 100% mole monomer compared with 100% mole starch to 300% mole led to an increase in %graft and % grafting efficiency with maximum %G and %GE were achieved at 200% mole and then decreased rapidly.

The %G and %GE increased because of rising of grafting rate which the accelerating effect of grafting of the monomer mixture MMA:EA(45/55) onto tapioca starch is in agreement with previous studies which described this to gel effect[2,30]. At higher monomer concentration, 300% mole monomer, the decrease in grafting yield might be due to two reason. The first one is the waste of the monomer due to the formation of large amount of free polymer. That is to say, increasing in %free polymer the rate of diffusion is bounded to be progressively effected by formed polymer, which increased rapidly at higher monomer concentration.[30] The second one is the increase of monomer concentration, this causes the chain transfer from starch macroradical to monomer increase, leading to the decreasing of %G.

Effect of soap(NP-40) on graft copolymerization

Table 14 Effect of soap concentration on starch graft poly(MMA,EA) polymerization.

%NP-40[a]	%TSC	%TC	%Free polymer	%G	%GE	Mw[b]	Grafting freequency (AGU/chain)
2.56	9.06	60.35	14.47	10.76	38.88	465279	23361.60
5.06	11.03	72.37	22.63	8.23	21.95	590000	40619.40
6.34	14.94	98.51	46.55	14.96	14.66	717136	25157.00
8.00	15.07	98.08	36.56	14.07	19.63	983627	37062.60
10.12	15.30	98.73	32.98	32.02	39.42	540468	7083.25

[a]Reaction carried out with 150 g,1.5 g propylene glycol and 200%mole monomer (% mole monomer compared with % mole starch (weight of starch,g divided by 162 mole/g = 100% mole starch) which monomer MMA/EA ratio 45:55 in water 1800 ml

[b]Mw of grafted polymer from acid hydrolysis measured by GPC method.

The increase in percentage of total conversion because of the more soap (NP-40) was used, the more micelles were established in the state which the reaction mass at this time consists of a stable number of growing polymer (originally micelle) and monomer droplets, and higher particle per liter of reaction mass (N) or higher growing chain per liter of reaction mass N/2, consider the polymer rate in following equation.[27]

$$r_p = k_p[M]\,[P]$$

where k_p is the usual homogeneous propagation rate constant for polymerization within particle and [M] is the equilibrium monomer concentration within particle,

now, $[P] = \frac{N}{2A}$ mole radical/liter of reaction mass

where A is Avogadro's number(6.02×10^{23} radical/mole radical)

The rate of polymerization is then

$$r_p = \frac{k_p N [P]}{2A}$$

So the increase in the rate with soap concentration because the N value increase with soap concentration.

The percentage of free polymer(%free polymer) was observed to be increased in tendency until the maximum value of 6.34 for %NP-40. After this value the faster termination of free polymer in the polymerization and the reduction of amount of free polymer may be the cause of the increase of percentage of graft (%G).

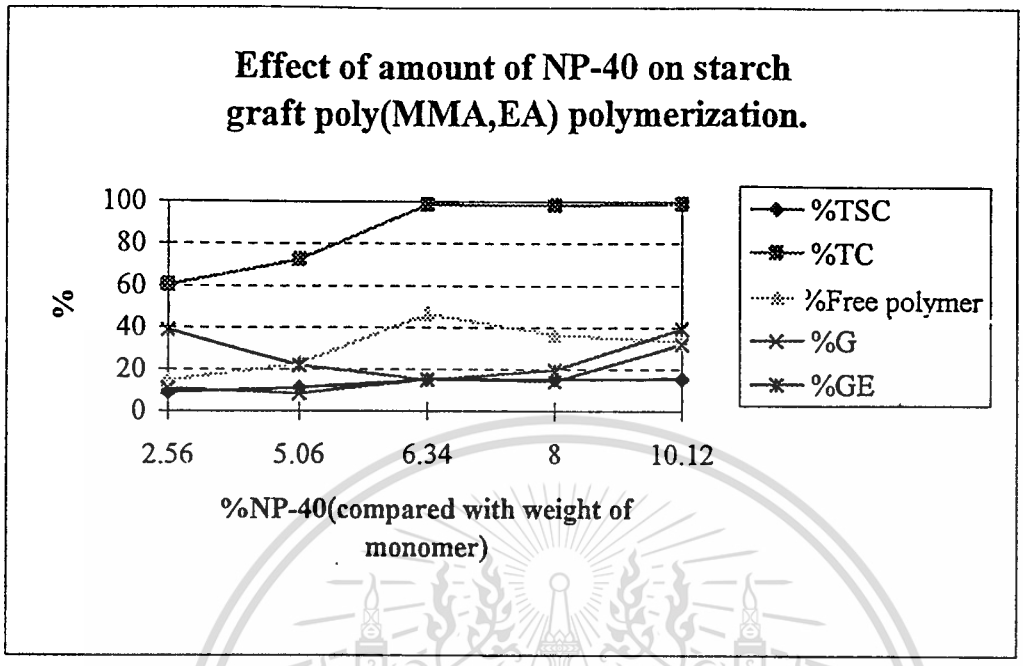

Figure 24 Effect of soap(emulsifier) concentration on starch graft poly(MMA,EA) polymerization, starch/monomer ratio = 1/2 mole, monomer ratio MMA/EA = 45/55.

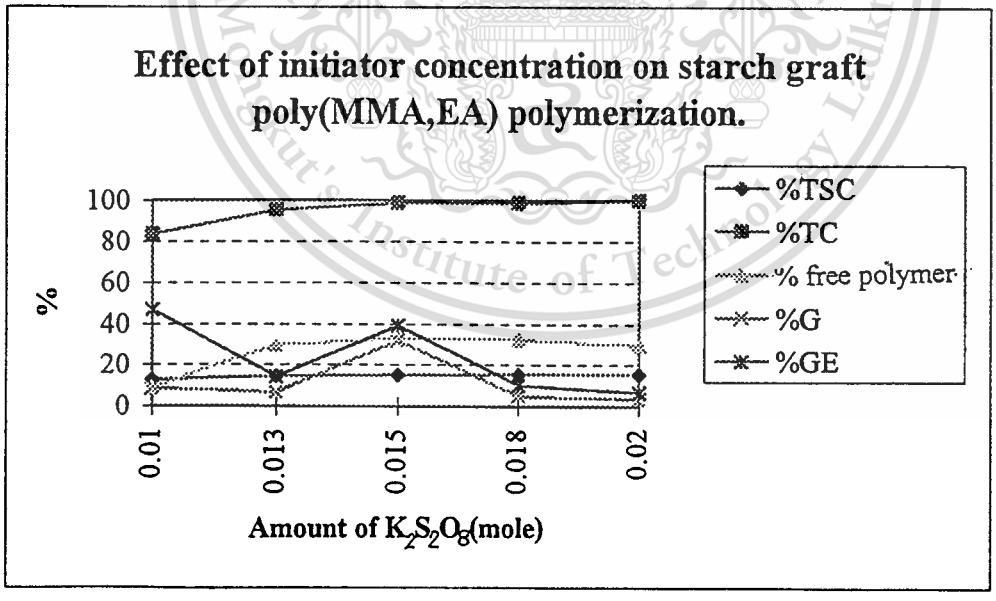

Figure 25 Effect of initiator concentration on starch graft poly(MMA,EA) polymerization, starch/monomer ratio = 1/2 mole, monomer ratio MMA/EA = 45/55

Effect of initiator concentration

Table 15 Effect of initiator concentration on starch graft poly(MMA,EA) polymerization.[a]

Amount of $K_2S_2O_8$ (mole)	%TSC	%TC	%Free p[olymer	%G	%GE	Mw[b]	Grafting freequency (AGU/chain)
0.01	12.83	83.46	8.95	8.77	47.15	754234	48417.86
0.0125	14.54	95.47	29.64	6.95	14.26	-	-
0.015	15.3	98.73	32.98	32.02	39.42	540468	7083.25
0.0175	15.56	98.61	32.44	4.90	10.34	929929	154718.5
0.02	15.62	99.85	29.83	3.57	6.9	915725	109697.7

[a]Reaction carried out with 150 g starch,1.5 g propylene glycol, 18.75g(10.17% by wt of monomer) NP-40 and 200% mole monomer which monomer ratio 45:55 in water 1800 ml, 100% mole:starch 200%mole monomer (150 g:185.18 g) .

[b]Mw of grafted polymer from acid hydrolysis measured by GPC method .

The effect of initiator concentration on the percentage of total conversion (% TC) in figure 25 indicated that the %TC increased at the increasing of the amount of $K_2S_2O_8$ initiator in beginning and then the %TC is constant in tendency with further increasing of $K_2S_2O_8$ initiator over 0.015 mole. Figure 25 shows that a maximum percentage of graft (%G) and percentage of grafting efficiency(%GE) value were observed at the initiator concentration of 0.015 mole, before this concentration both value increased and beyond this critical concentration both percentage of graft (%G) and percentage of grafting efficiency(%GE) decreased. At the increase in $K_2S_2O_8$ initiator, the $\dot{S}O_4^{\bullet}$ and macroradical of starch were also increased by the decomposition of $K_2S_2O_8$ initiator to $\dot{S}O_4^{\bullet}$, these primary free radicals abstract the

hydrogen from the reactive functional group of tapioca starch(C-H bond of starch molecule) and produce macroradical of starch which lead to the formation of graft copolymers. Consequently, graft yield(%G and %GE) were increased. The decrease grafting yield at higher initiator concentration may be due to efficiency of $\dot{SO}_4^-$ to take part in the termination of growing grafted chain and free polymerization. Perhaps this is the result of the increasing in molecular weight of graft copolymer due to the viscosity of reaction system getting higher. It is difficult for monomers to reach the radical site of macroradical. Grafting yield effected much more than %free polymer because of its steric hindrance of macroradical molecule.

Effect of temperature

Table 16 Effect of temperature on graft copolymerization of starch graft poly (MMA,EA).[a]

Temperature (^{o}C)	%TSC	%TC	%Free polymer	%G	%GE	Mwb	Grafting frequency (AGU/chain)
40	7.82	50.23	0.85	-	-	-	-
60	8.17	52.45	0.94	-	-	-	-
40/90	9.74	62.57	7.07	-	-	-	-
60/90	15.3	98.73	32.98	32.02	39.42	540486	7083.25
90	15.55	99.84	40.25	11.45	16.76	673870	32167.32

[a]Reaction carried out with 150 g starch, 1.5 g propylene glycol(PG) and 18.75 g NP-40 (10.12% by weight monomer) in water 1800 ml, 200% mole monomer which monomer ratio 45:55 MMA:EA, 0.015 mole $K_2S_2O_8$ (150 ml 0.1 N $K_2S_2O_8$ in 1 N HNO_3), 4 h reaction time.

[b]Mw of grafted polymer from acid hydrolysis measured by GPC method.

The increase in percentage of total conversion(%TC), percentage of graft(%G) and %free polymer indicated that the polymerization of acrylic ester monomer onto tapioca starch can be speeded up by heat. The decrease in %G, and %GE from reaction temperature from 60/90 °C to 90 °C might be due to the termination of grafted chain free radical and the large amount of free polymer may be the cause of decrease of graft yield. Besides, high temperature may be cause of reducing of monomer concentration in emulsion phase and lead to lowering of grafting rate.

$r_p = k_p[M][P]$; $[M] \downarrow r_p \downarrow$

Effect of monomer type

Table 17 Polymerization of starch graft copolymer with various monomers [a].

Monomer	% free polymer	%TSC	%TC	%G	%GE
MMA	45.21	11.77	76.47	25.35	35.93
EA	39.99	9.92	63.97	19.19	19.19
BA	26.59	17.40	95.74	49.65	65.12
2-EHA	17.46	19.23	90.96	51.84	74.80

[a] Reaction carried out with 100 g starch, 1 g propylene glycol and 200 % mole of monomer, NP-40 = 10% weight monomer in water 1200 ml, 25 ml Na_2EDTA, $K_2S_2O_8$ 0.01 mole (100ml of 0.1 N $K_2S_2O_8$ in 1N HNO_3) 60 °C 3h, 90 °C 1h.

The effect of monomer type on the starch graft polymerization could be compared of yield obtained with each monomer type, the increase in tendency of %G and %GE value when more hydrophobic acrylate monomer (2-EHA> BA> EA) were used. Therefore the starch graft poly(MMA) was produced higher than the starch graft poly(EA) and lower than the starch graft poly(BA) and the starch graft poly(2-EHA). The maximum (%G & %GE) are 51.84 and 74.80 for the starch graft

poly(2-EHA). The percentage of free polymer are observed to convert tendency because of the increasing in grafted polymer formed. Thus, the extent of synthetic polymer reactivity with the tapioca starch was depending on the type of monomer. The order of reactivity is 2-EHA> BA> MMA>EA. Meanly, the percentage of total conversion of MMA/EA used in polymerization are lower than MMA/BA and MMA/2-EHA used because the polymerization rate in present of EA must be lower than the rate that in present of BA or 2-EHA. In fact, the percentage of total conversion are related with colloid behavior of system (reduction of the number of polymerizations centers as a result of flocculation). Thus, BA and 2-EHA have smaller degree of flocculation than EA and the introduction of more hydrophobic monomer resulted in the increase in the value of emulsifier adsorption.

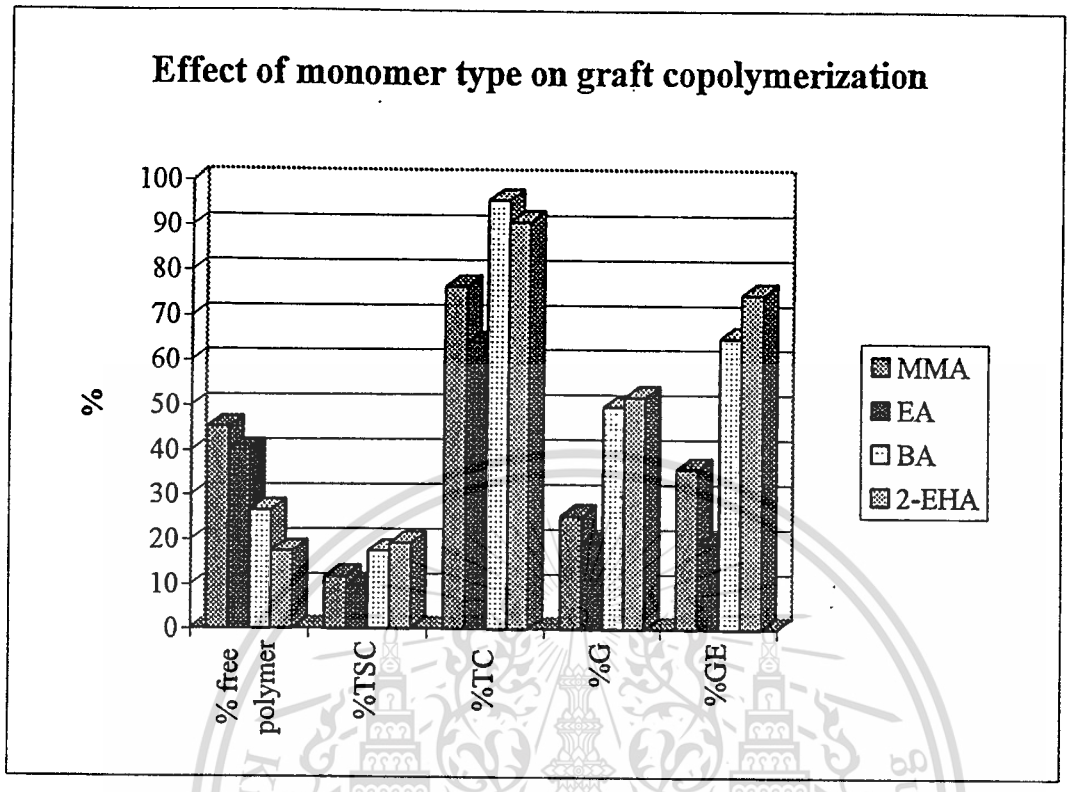

Figure 26 Effect of monomer type on starch graft polymerization.

Identification of grafting

The starch graft poly(acrylic ester) spectra are shown characteristic IR band of C=O of grafted acrylic ester polymer appeared at 1730-1750 cm^{-1}, it indicated an evidence of grafting. (see Appendix A)

Table 18 Infrared spectroscopy characterization.

Absorption Wave Number (cm^{-1})	Assignment
1100-1300	C-O stretching (C-O and C-O-H) of starch and C-O of acrylic ester polymer
1600-1700	multiplete band C=O aldehyde group of starch
1730-1750	C=O stretching of acrylic ester polymer
2900-3000	C-H stretching of hydrocarbon of acrylic ester polymer and C-H group of starch
3200-3600	O-H stretching of starch

Thermal properties of starch graft poly(acrylic ester)

Differential scanning calorimetry(DSC) data

Table 19 Data of starch graft poly(MMA, BA).

Monomer ratio (MMA/BA)	%G	moisture content (%)	T_g of starch component($^{\circ}$C)
100/0	11.77	8.4392	101.50
80/20	15.80	5.9299	128.70
65/35	18.18	4.8191	133.60
0/100	17.40	4.3098	112.10

Table 20 Data of starch graft poly(MMA, 2 - EHA).

Monomer ratio (MMA/BA)	%G	moisture content (%)	T_g of starch component($^{\circ}$C)
100/0	11.77	8.4392	101.50
80/20	16.62	4.9341	121.80
60/40	17.81	4.4298	142.20
0/100	17.46	4.0530	135.20

Starch graft copolymer were examined by DSC to obtained information for processing condition setting. Result of DSC measurements on some starch graft poly(acrylic ester) copolymer(after an extract of the free polymer) are shown in table 19 and 20. Values for glass transition temperature(T_g) of starch component increased with the level of grafting(%G). This evidence suggests that increases in T_g

are the result from absorption of some of the moisture in system by grafted chain at high temperature and their low moisture content. Thus the decreasing in amount of water are available for plasticizing starch. This result is correspond with the previous research, on which extrusion processing of starch graft poly(methylacrylate)[32].

Thermogravimetric analysis(TGA)

Thermogravimetric analysis(TGA) of the starch graft copolymer are shown in table 21 and appendix B. The TGA thermogram give the decomposition temperature (T_d) of which indicates thermal stability of polymer(reported onset temperature). The weight loss(T_d) of ungrafted starch occurred in the range of 310 to 355 ^{o}C. The thermal behavior of starch graft poly(acrylic ester) polymers are composed of two main components. One component is to start the decomposition of starch occurred in the range of 282.6 to 295.6 ^{o}C, the other is to start the decomposition of grafted polyacrylic ester chain, occurred beyond this temperature up to about 400 ^{o}C. These results show that thermal stability of starch was improved with grafting due to the lately decomposition of grafted polymer.

The decrease in thermal satability of starch component from from 310 ^{o}C to 282.6-295.6 ^{o}C can be explained by the result from absorption of some of water in the system by grafted chain at high temperature. Thus by decreasing the amount of water for plasticizing starch, its easier to decompose. These results correspond with the result of D. Trimmell studies with the effect of grafting on T_g and T_m.

Table 21 TGA Data of starch graft poly(acrylic ester).

Polymer	%G	T_d (°C)	
		Starch component	Polymer component
Ungrafted starch	-	310 - 355	-
PMMA (Free polymer)	-	-	300 - 422
poly(MMA/2-EHA) ;80/20 (Free polymer)	-	-	350
Starch graft poly (MMA)	35.93	282.60	408.70
Starch graft poly (MMA/BA) ;65/35	34.21	287.00	400
Starch graft poly (MMA/2-EHA) ;80/20	36.78	284.80	395.60
Starch graft poly(BA)	49.65	295.60	386.95

Rheological properties of starch graft copolymer .

The study of the rheological properties provide the information about the deformation and flow characteristic. The flow curve of starch graft copolymer cover the transition from pseudoplastic to upper Newtonian region. The flow curve of starch graft copolymer in figure 27 shows the relation between shear stress and shear rate.

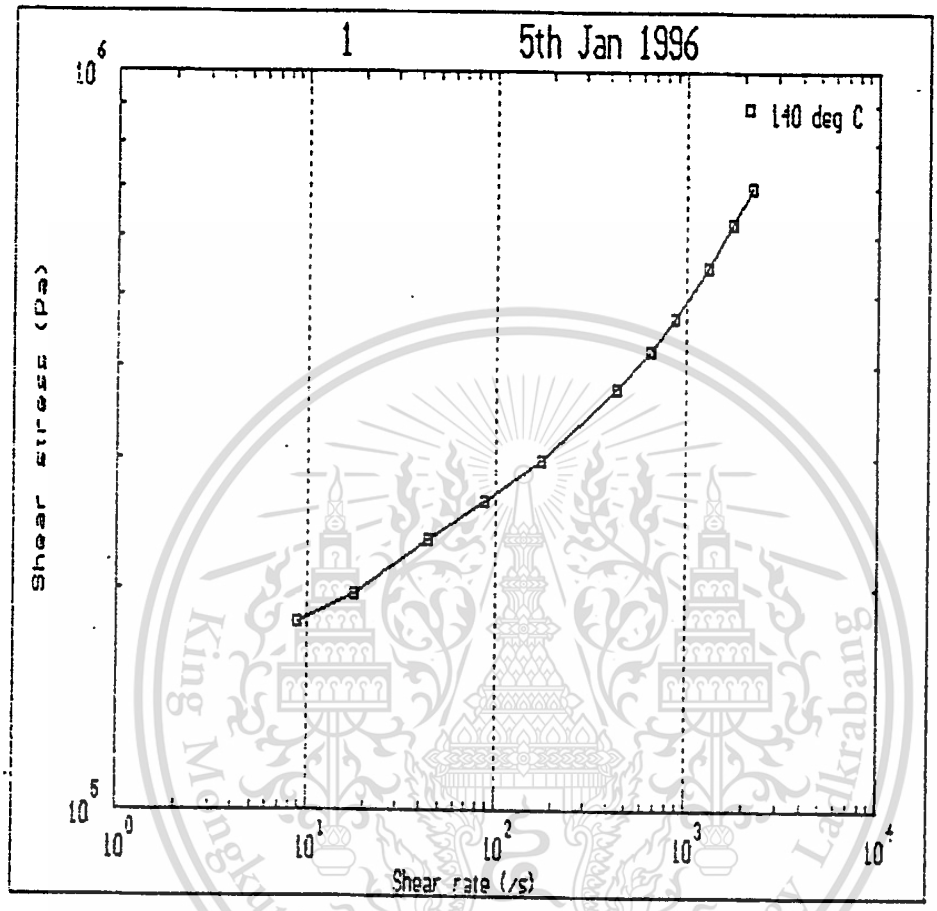

Figure 27 The relation between shear stress and shear rate of starch graft copolymer.

It is not obey Newtonian' s law (the viscosity states that the shear stress is not linearly proportional to shear rate $\tau \neq \eta\gamma$). Dilatant fluid(shear tickening), the flow curve has a slope greater than 1 and pseudoplastic (shear thinning) the flow curve has a slope less than 1. Both behaviors of the fluids were observed at high shear rate (high stress) and low shear rate(low stress) respectively. Pseudoplastic behavior which occurred at high shear rate region shows that the resistance against the flow of starch graft copolymer compound was decreased with intensified shearing and dilatant behavior was reported an increase resistance to flow with intensified shearing .

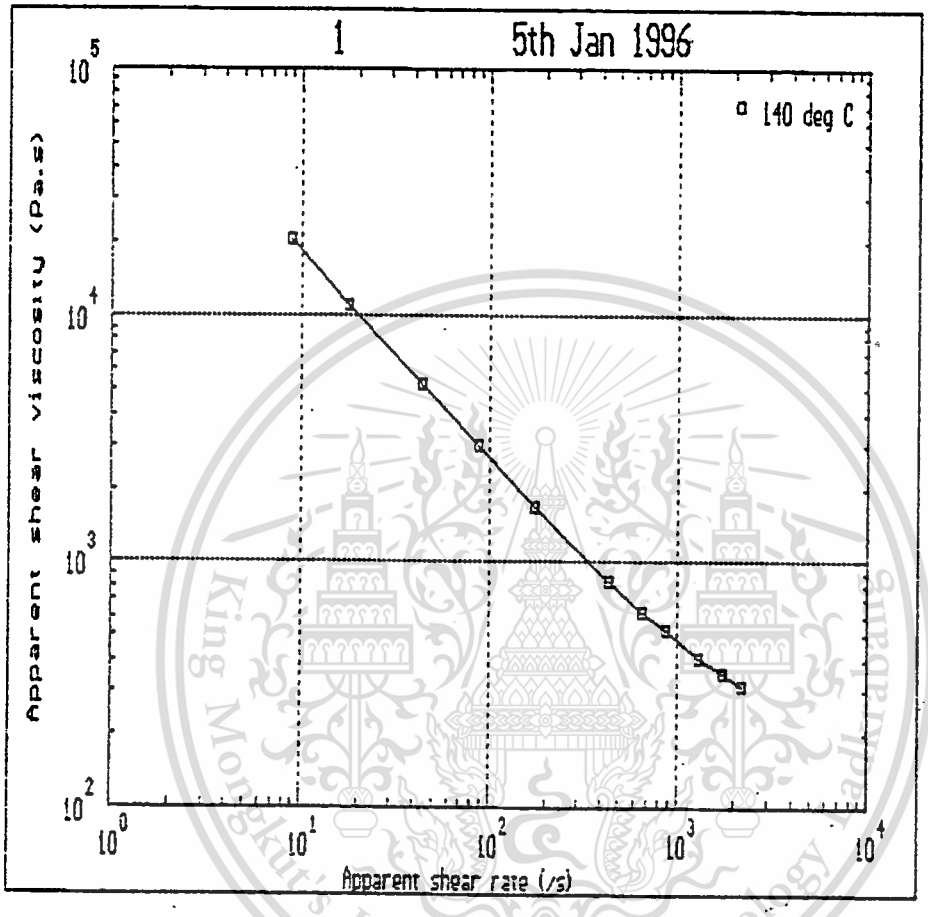

Figure 28 The relation between apparent viscosity and shear rate of starch graft copolymer.

The viscosity of a material express its resistance to flow. The flow curve shows the relation between apparent viscosity and shear rate of starch graft copolymer in figure 28. It has a higher apparent viscosity than many more general purpose thermoplastics at the same shear rate and when the shear rate increased the apparent viscosity reduced. At low shear rate range the material

pseudoplastic behavior and at very high shear rate it has a tendency to be at the region of upper Newtonian behavior(less changed in apparent viscosity when shear rate was increased). The higher apparent melt viscosity than the general thermoplastics due to the high molecular weight of starch graft copolymer(Mw> 1,000,000). It has a strong influence on its melt viscosity, which it derived from molecular weight entanglements which begin to dominate the rate of slippage of molecules. An increasing shear rate lead to reducing in apparent viscosity This behavior has been explained by Stephen L. Rosen in terms of molecular structure[27]. This illustrated schematically in figure 29

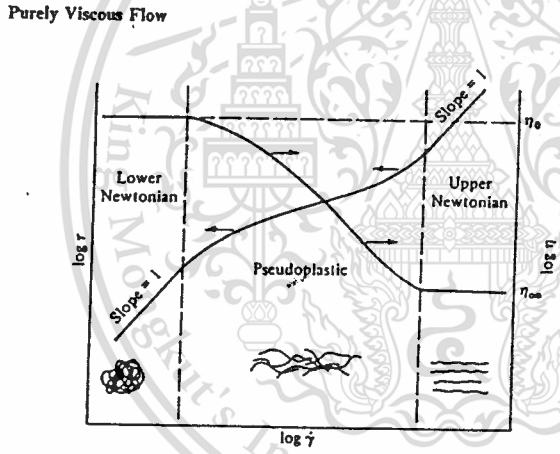

figure 29 Generalized flow properties for polymer melt and solution.

At low shear rate the randomization effect of thermal motion of chain segments overcomes any tendency toward molecular alignment in the shear field. The molecules are thus in their most random and highly entangled state and have their greatest resistance to slippage(flow). As the shear increased the molecules will begin to entangle and align in the shear field, reducing their resistance to slippage past one another. Under severe shearing, they will be pretty much completely unentangled and aligned, to reach a state of minimum resistance to flow[27].

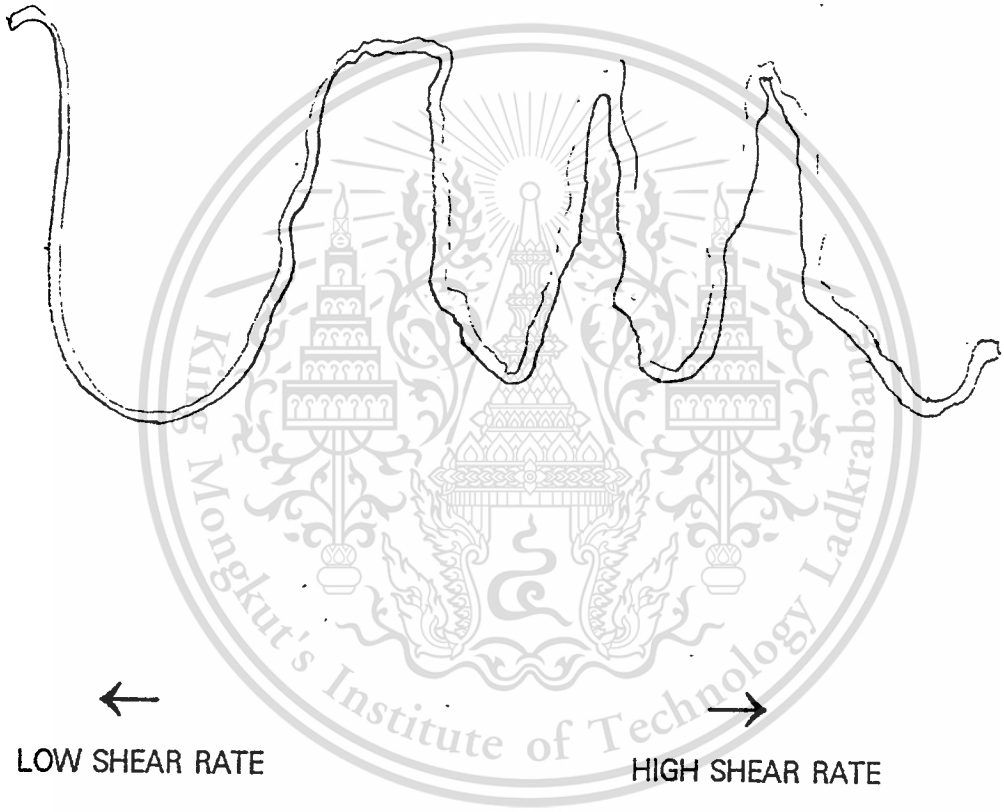

Figure 30 The effect of shear rate (stress) variation on properties of extruded.

Figure 30 shows the effect of shear rate (stress) variation on properties of extruded, die swell and melt fracture were occurred at high level of shear rate due to intense shearing, eventually lead to an extensive breakage of starch graft copolymer bond. In fact, this reaction is mechanical degradation. This will be defined as a deformation process under intense shearing, especially in upper- Newtonian region, with all the applied mechanical energy is not recoverably dissipated as heat in material

through molecular friction, this process is known as viscous energy dissipation. It is difficult to maintain the temperature constant under intense shearing.

Mechanical properties of starch graft poly(acrylic ester).

Figure 31 - 36 illustrate the mechanical properties of molded starch graft (MMA,BA). The values obtained from the mixture of monomer used in graft copolymerization, shows the increasing amount of butyl acrylate monomer(BA) which leads to a decrease in tensile strength, hardness and modulus of elastic and increasing in % elongation and impact strength. The same behavior was observed in molded starch graft poly(MMA,2-EHA). This phenomenon could be explained by the glass transition temperature. Starch graft copolymer is composed of some elastomeric segment in amorphous linear grafted chains. This segment gives a higher mobility in molecular chain. Thus the more proportion of low glass transition temperature segment (BA) lead to the more loses some mechanical properties such as tensile strength, hardness and modulus of elastic, because in its rubbery state it deforms much more easily.

Table 22 Effect of monomer ratio and monomer concentration on mechanical properties of starch graft poly(MMA,BA).

Monomer ratio MMA/BA[a]	Tensile strength (N/mm^2)		%Elongation (%)		Modulus of elasticity (N/mm^2)	Impact strength (KJ/m^2)	Hardness[d]
	at yield	at break	at yield	at break			
100/0	–	–	–	–	–	–	–
95/5	22.86	21.96	2.68	2.87	955.26	20.35	62.89
80/20	14.10	13.89	3.76	3.83	437.43	27.55	84.00
70/30	8.72	9.20	5.65	14.57	198.00	13.80	65.56
60/40	3.34	6.24	9.19	231.06	55.82	Nb	60.56
0/100	–	–	–	–	–	Nb	35.00
100%mole(70/30)[b]	–	–	–	–	–	–	–
200%mole(70/30)[b]	5.68	8.79	6.68	56.13	126.40	24.40	63.33
300%mole(70/30)[b]	6.68	10.8	8.64	151.9	123.79	11.20	60.44
200%mole(65/35)[b]	3.90	9.73	9.73	175.47	62.06	12.90	52.89
200%mole(65/35)[c]	3.45	8.85	8.85	190.05	48.40	13.12	60.33
200%mole(60/40)[b]	2.04	5.46	2.04	333.55	27.64	17.80	65.57

[a] Reaction carried out with 100 g starch, 1g propylene glycol(PG) and 200%mole monomer compared with 100% mole starch, NP-40 =10% by weight monomer in water 1200 ml,25 ml Na_2EDTA, $K_2S_2O_8$ 0.01 mole (100 ml, 0.1 N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[b] Reaction carried out with 150 g starch, 1.5g propylene glycol(PG) and ,NP-40 = 10% by weight monomer in water 1500 ml,37.5 ml Na_2EDTA,$K_2S_2O_8$ 0.015 mole(150 ml 0.1N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[c] Reaction carried out with 150 g. starch, 1.5g propylene glycol(PG) and 200%mole monomer, NP-40 = 10% by weight monomer in water 2000 ml,37.5 ml Na_2EDTA, $K_2S_2O_8$ 0.015 mole (150 ml 0.1N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3.h ,90 °C 1h.

[d] Tested by shore D hardness tester. (_) = could not be prepared the good specimens by compression mold , Nb = Not break.

Table 23 Effect of monomer ratio and monomer concentration on mechanical properties of starch graft poly(MMA,2-EHA)

Monomer ratio MMA/2-EHA[a]	Tensile strength (N/mm^2)		%Elongation (%)		Modulus of elasticity (N/mm^2)	Impact strength (KJ/m^2)	Hardness[b]
	at yield	at break	at yield	at break			
100/0	–	–	–	–	–	–	–
95/5	–	–	–	–	–	–	–
80/20	9.56	11.270	0.59	10.62	270.30	14.00	70.00
70/30	2.28	4.700	12.79	327.20	26.01	28.05	47.89
60/40	1.15	2.040	11.70	677.20	11.09	20.20	35.17
0/100	0.07	0.002	50.55	282.00	0.21	Nb	13.33[c]
100%mole(70/30)[b]	0.13	0.143	64.84	1081.0	0.40	Nb	29.56[c]
200%mole(70/30)[b]	1.90	4.296	1.90	4.30	1.90	84.09	46.83
300%mole(70/30)[b]	2.41	2.405	4.82	5.27	31.47	15.60	48.00

[a] Reaction carried out with 100 g starch, 1g propylene glycol(PG) and 200%mole monomer compared with 100% mole starch

NP-40 =10%weight of monomer in water 1200 ml,25 ml Na_2EDTA, $K_2S_2O_8$ 0.01 mole (100 ml, 0.1N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[b] Tested by shore D hardness tester , [c] Tested by shore A hardness tester.

(_) = could not be prepared the good specimens by compression mold , Nb = Not break ,

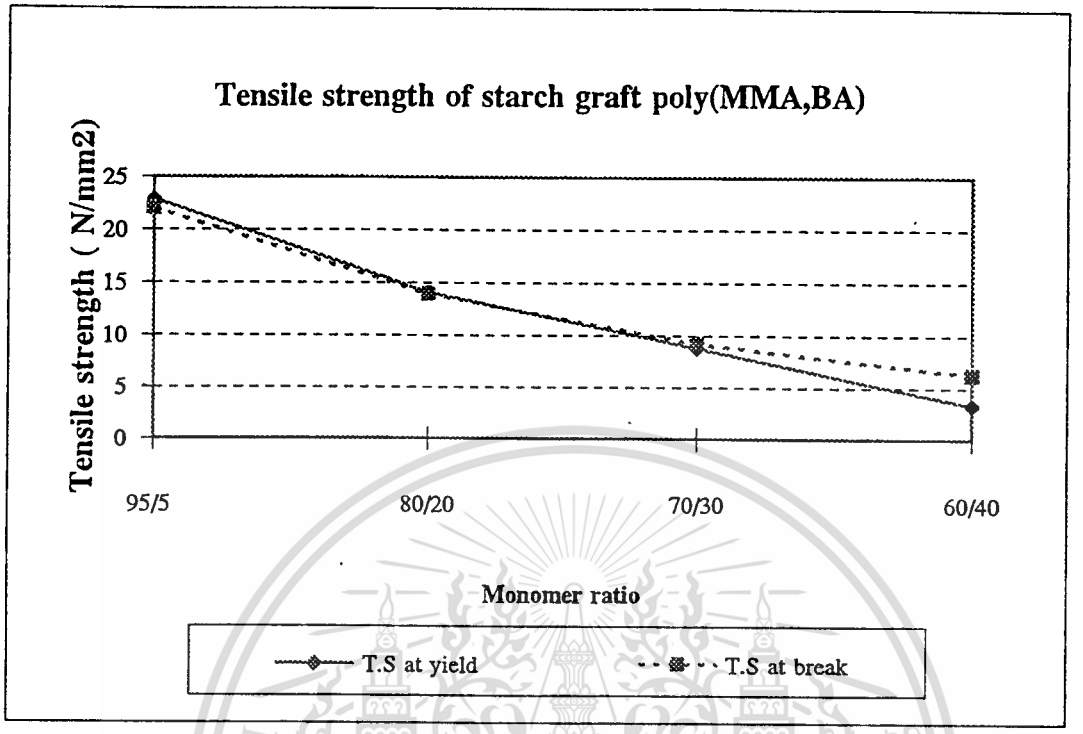

Figure 31 Tensile strength of starch graft poly(MMA,BA).

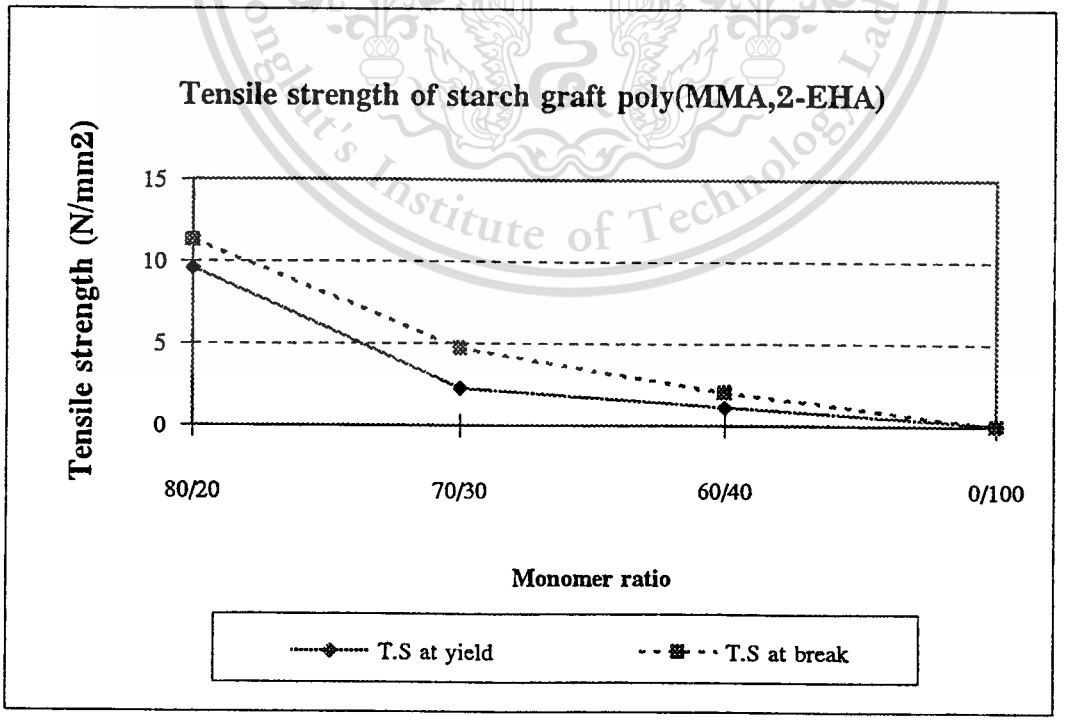

Figure 32 Tensile strength of starch graft poly(MMA,2-EHA).

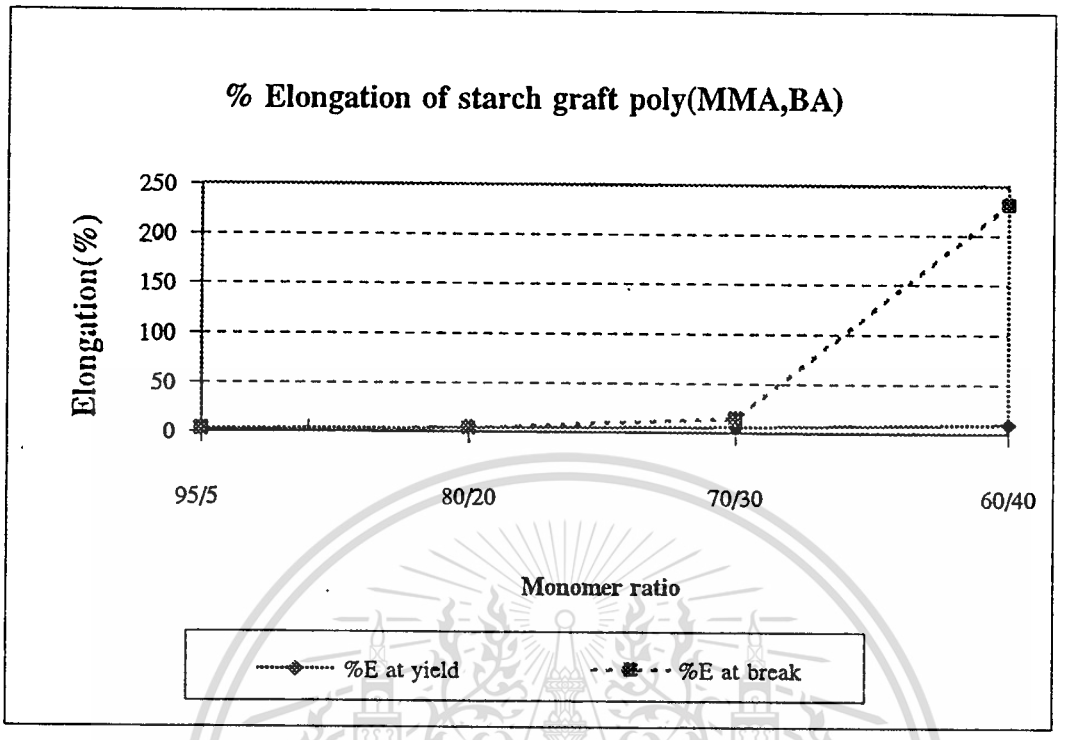

Figure 33 %Elongation of starch graft poly(MMA,BA).

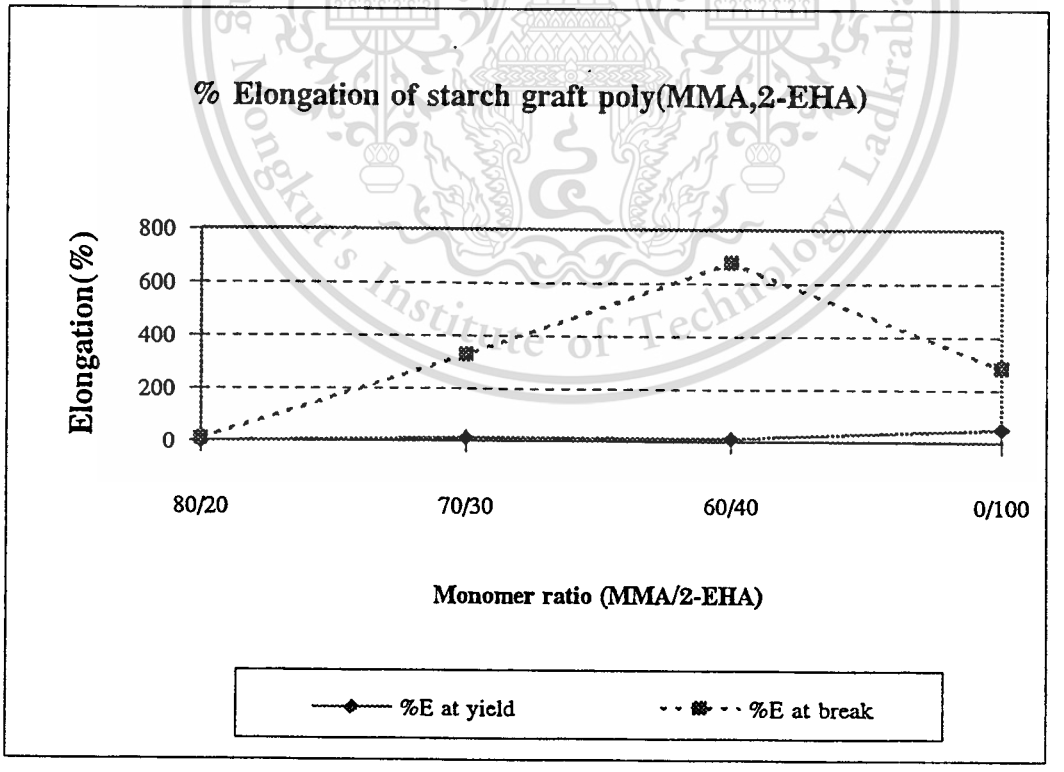

Figure 34 %Elongation of starch graft poly(MMA,2-EHA).

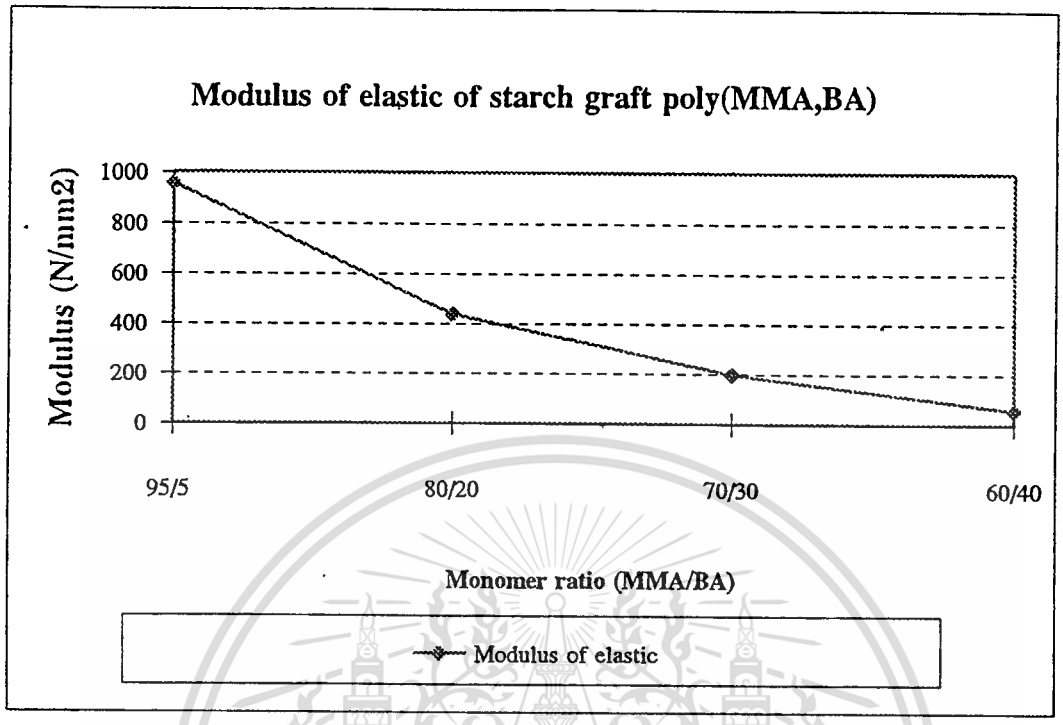

Figure 35 Modulus of elastic of starch graft poly(MMA,BA).

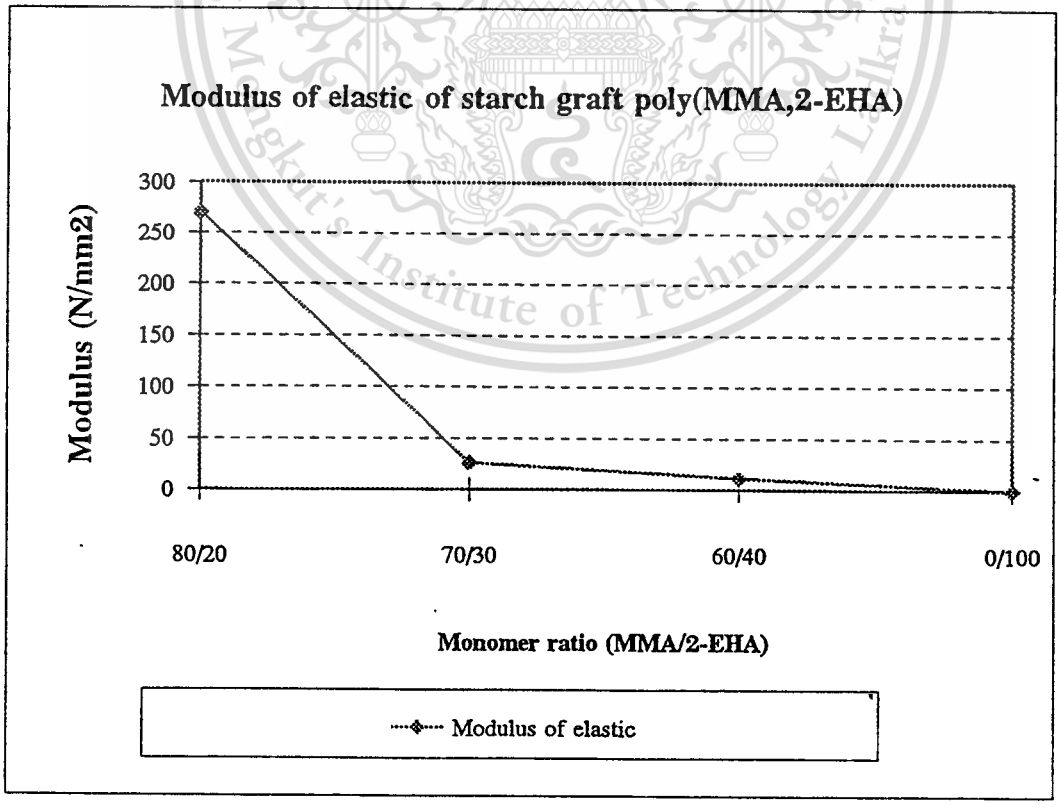

Figure 36 Modulus of elastic of starch graft poly(MMA,2EHA).

The strength of starch graft copolymer provided by domain starch and a high T_g segment of methyl methacrylate(MMA) in grafted chain. The impact strength of starch graft copolymer is related to its ability to absorb energy and the fact that the material of lower T_g is high impact strength. The starch graft copolymer with the more low T_g (more rubbery phase) in the molecule is getting higher impact strength. Thus, its obvious that the rubber phase has better energy dissipation than rigid phase.

Processability and some physical properties of starch graft poly(acrylic ester).

The results of thermal properties are that the processing temperature of starch graft copolymer should be in between T_g and T_d. At this temperature is especially important for processability because upper T_g the starch graft copolymers changed to rubbery state. The significant thermal decomposition of them occurred quite rapidly above T_d and the reason for high apparent melt viscosity of starch graft copolymer which indicate a high melt strength and the deformation of their melt easily occurred at high shear rate. So this could be determined that the suitable processes are compression molding or thermoforming(low shear rate process). In the case of compression molding, the starch graft copolymer could be processed at a moisture content of 4-8% and temperatures from 140 to 170 $^{\circ}$C. Some physical properties of starch graft copolymer are shown in table 24 and 25 . The result of grafting products lead to decrease in moisture content of starch from 13% to 4-8%. The starch graft copolymer can absorbed water from 20% to 120% when immersed in water. The density of graft copolymer were observed higher then the general polymer.

Table 24 Some physical properties of starch graft poly(MMA,BA).

Monomer ratio MMA/BA[a]	%Moisture content	%Water absorption	density[d] (g/ cm^3)
100/0	8.4392	59.19	1.2193
95/5	8.0792	74.99	1.249
80/20	5.9299	19.26	1.3372
70/30	6.025	52.97	1.2515
60/40	4.8603	58.55	1.2036
0/100	4.3098	65.44	1.1508
100%mole(70/30)[b]	5.3679	77.48	1.2451
200%mole(70/30)[b]	5.3265	71.07	1.1882
300%mole(70/30)[b]	3.7221	54.81	1.1764
200%mole(65/35)[b]	4.8191	86.22	1.5956
200%mole(65/35)[c]	4.3000	84.09	1.2756
200%mole(60/40)[b]	6.813	62.87	1.5595

[a]Reaction carried out with 100 g starch, 1g propylene glycol(PG) and 200%mole monomer compared with 100% mole starch, NP-40 =10% by weight monomer in water 1200 ml,25 ml Na_2EDTA, $K_2S_2O_8$ 0.01 mole (100 ml, 0.1 N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[b]Reaction carried out with 150 g starch, 1.5g propylene glycol(PG) and, NP-40 = 10% by weight monomer in water 1500 ml, 37.5 ml Na_2EDTA,$K_2S_2O_8$ 0.015 mole(150 ml 0.1N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[c]Reaction carried out with 150 g. starch, 1.5g propylene glycol(PG) and 200%mole monomer, NP-40 = 10% by weight monomer in water 2000 ml,37.5 ml Na_2EDTA, $K_2S_2O_8$ 0.015 mole (150 ml 0.1N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3.h, 90 °C 1h.

[d]The values were evaluated by liquid (methanol) displacement method in pycnometer.

Table 25 Some physical properties of starch graft poly(MMA,2EHA).

Monomer ratio MMA/ 2-EHA[a]	%Miosture content	%Water absorption	density[d] (g/cm^3)
100/0	8.4392	59.19	1.2193
95/5	4.4925	74.99	1.4355
80/20	4.9341	36.22	1.2770
70/30	5.2110	115.31	1.3819
60/40	4.4298	70.34	1.3693
0/100	4.0530	64.18	1.2472
100%mole(70/30)	4.3098	120.62	1.3229
200% mole(70/30)	5.2110	115.31	1.3693
300% mole(70/30)	4.3254	45.10	1.6093

[a]Reaction carried out with 100 g starch, 1g propylene glycol(PG) and 200%mole monomer compared with 100% mole starch, NP-40 =10%weight of monomer in water 1200 ml,25 ml Na_2EDTA, $K_2S_2O_8$ 0.01 mole (100 ml, 0.1N $K_2S_2O_8$ in 1 N HNO_3) 60 °C 3h, 90 °C 1h.

[d]The values were evaluated by liquid (methanol) displacement method in pycnometer.

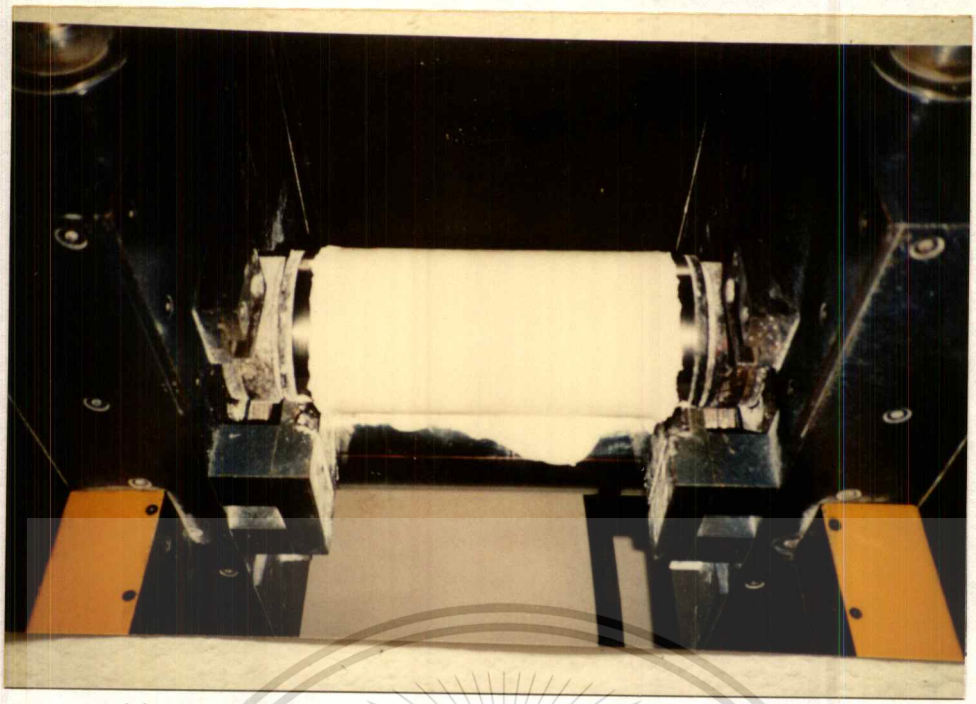

Figure 37 Masticated sheet of starch graft copolymer compound on the two rolls mill.

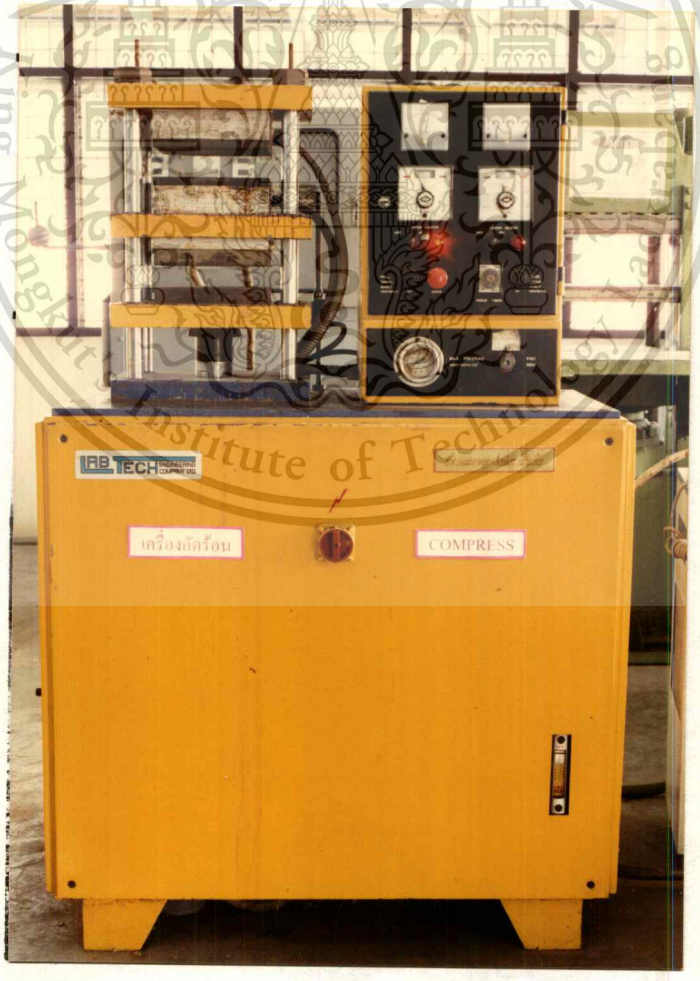

Figure 38 The compression molding machine used to form starch graft copolymer.

Figure 39 Biodegradability of starch graft copolymer in water (After 6 month) .

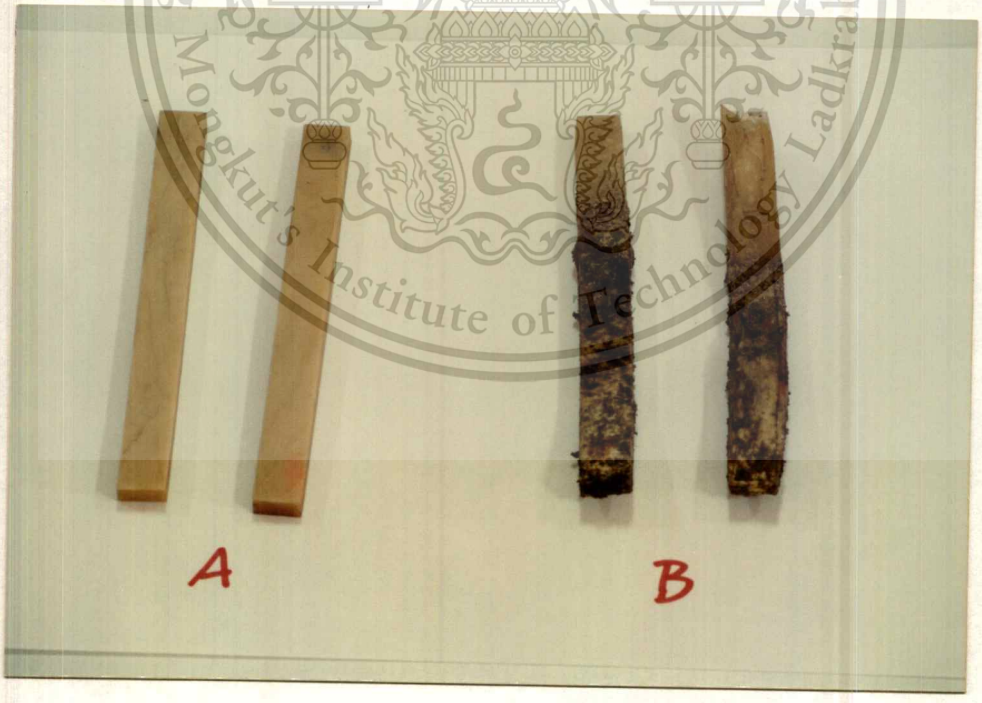

Figure 40 Biodegradability of starch graft copolymers in soil . (a) Before testing (b) After 4 weeks .

CHAPTER 5

CONCLUSION

Starch graft poly(acrylic ester) copolymers containing 23-64 % of grafted polymer by weight were prepared by a free radical chain initiation system. The potassium persulphate($K_2S_2O_8$) has been used to initiate the graft copolymerization of various acrylic ester monomer[methyl methacrylate(MMA)), ethyl acrylate(EA), butyl acrylate(BA) and 2-ethylhexyl acrylate(2-EHA)], both single monomer and binary monomer mixtures were graft copolymerization onto tapioca starch under nitrogen atmosphere. They were found that the percentage of grafted(%G), grafting efficiency (%GE), and percentage of free polymer(%free polymer) were all dependent to some extent, on the monomer concentration, monomer ratio (MMA/EA,BA or 2-EHA), concentration of potassium persulphate($K_2S_2O_8$) initiator and reaction temperature. The suitable condition are concluded as followed.

Variable parameter	suitable condition
Monomer type	depended on required properties
Monomer ratio	depended on required properties
Amount of monomer	200% mole monomer/100% mole starch
Amount of initiator($K_2S_2O_8$,0.1N)	0.015 mole/150 g starch
Soap(NP-40) concentration	10% by weight monomer
Temperature,Time	60 ^{o}C, 3 h followed by 90 ^{o}C, 1h

The evidence of grafting was identified by IR spectroscopy. Thermal and rheological properties were determined by thermogravimetric analyzer(TGA), differential scanning calorimeter(DSC) and capillary rheometer, respectively. The resulted data show that T_d and T_g depended on percentage of grafting. The result of study indicates that the starch graft copolymer has a high shear viscosity (high melt strength) and it should be process at low shear rate range with moisture content 4-8 % (base on starch graft copolymer) and in the range of temperature 140-170 ^{o}C. The suitable processing are compression molding or thermoforming. Both processes can be used to form the starch graft copolymer to be a packaging material. The mechanical properties such as tensile strength,% elongation, modulus of elasticity, impact strength and hardness properties of starch graft poly(MMA,BA) and starch graft poly(MMA,2-EHA) were reported, and the effect of water was summarized by immersing the material in water. The wide range of properties of starch graft copolymer compound were obtained (elastomeric material to rigid plastic). The properties depended on the combined effect of monomer concentration, monomer ratio and type of monomer using in graft copolymerization onto tapioca starch, which lead to increased mechanical stability and they can susceptible by biological attacked.

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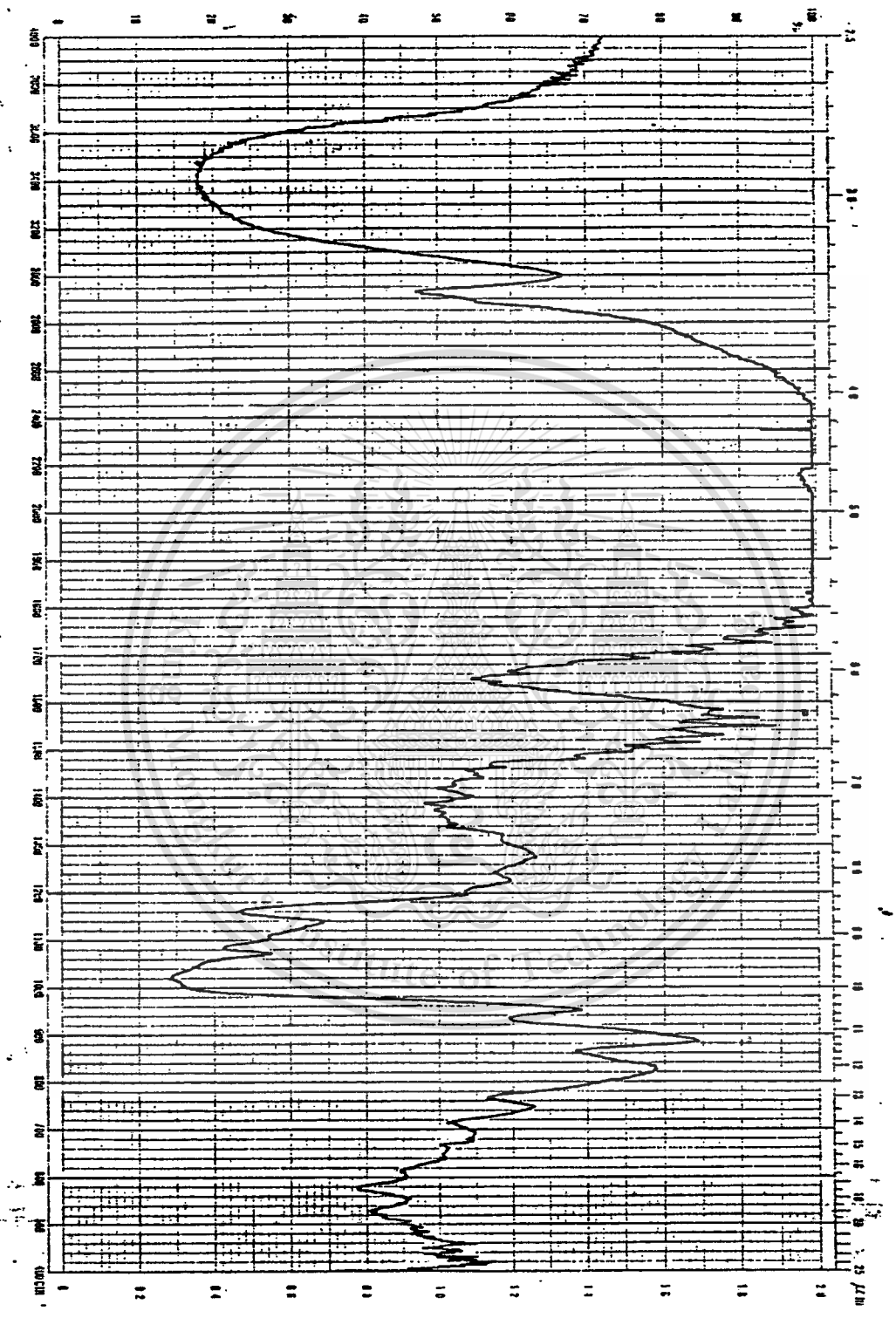
Appendix A. The IR spectra of starch graft copolymers, grafted chains and free polymers.



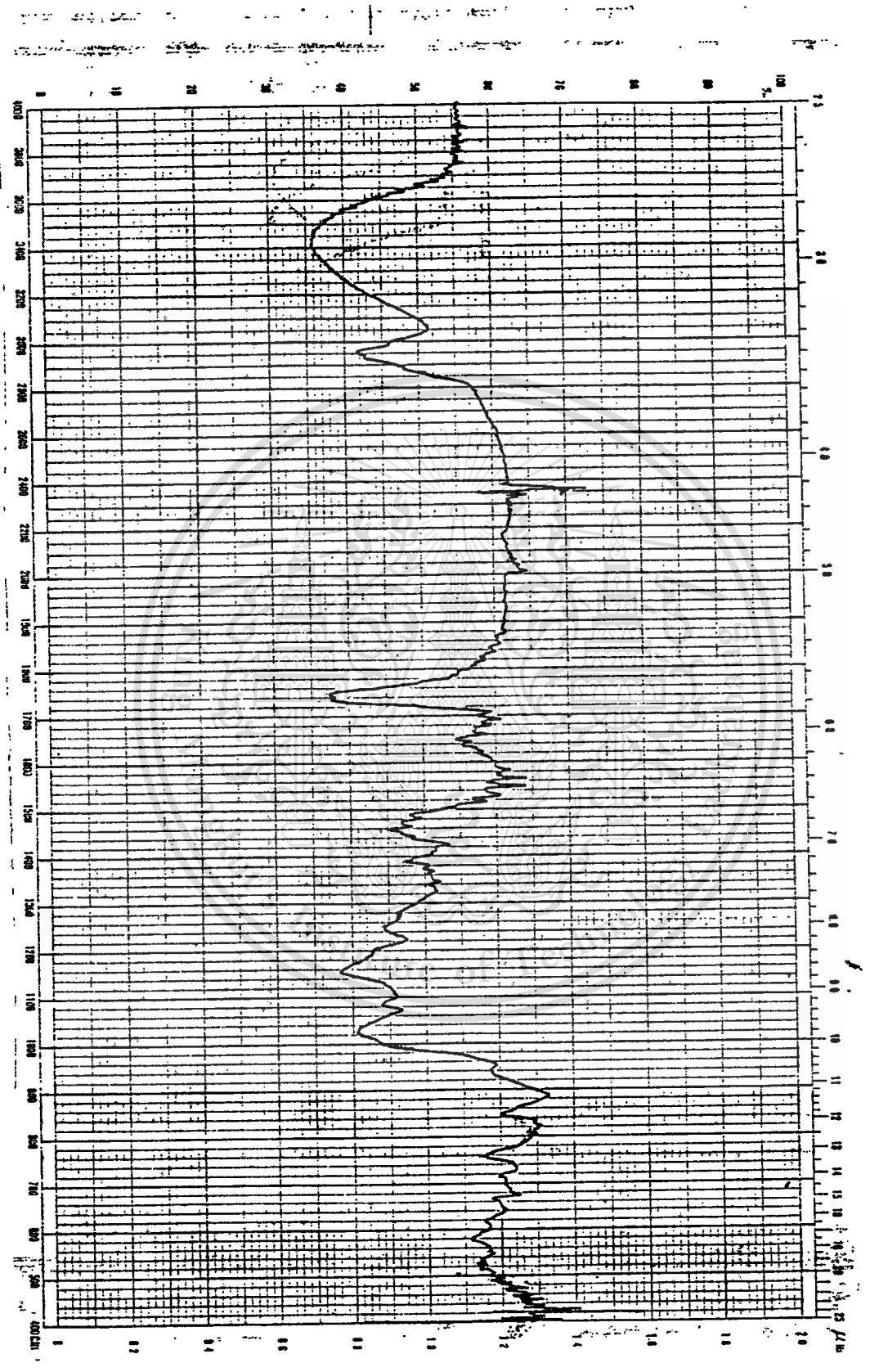


Figure 42 Infrared spectrum of starch graft poly(MMA, BA), monomer ratio MMA/BA = 80/20, Starch/ monomer ratio = 1/2 mole

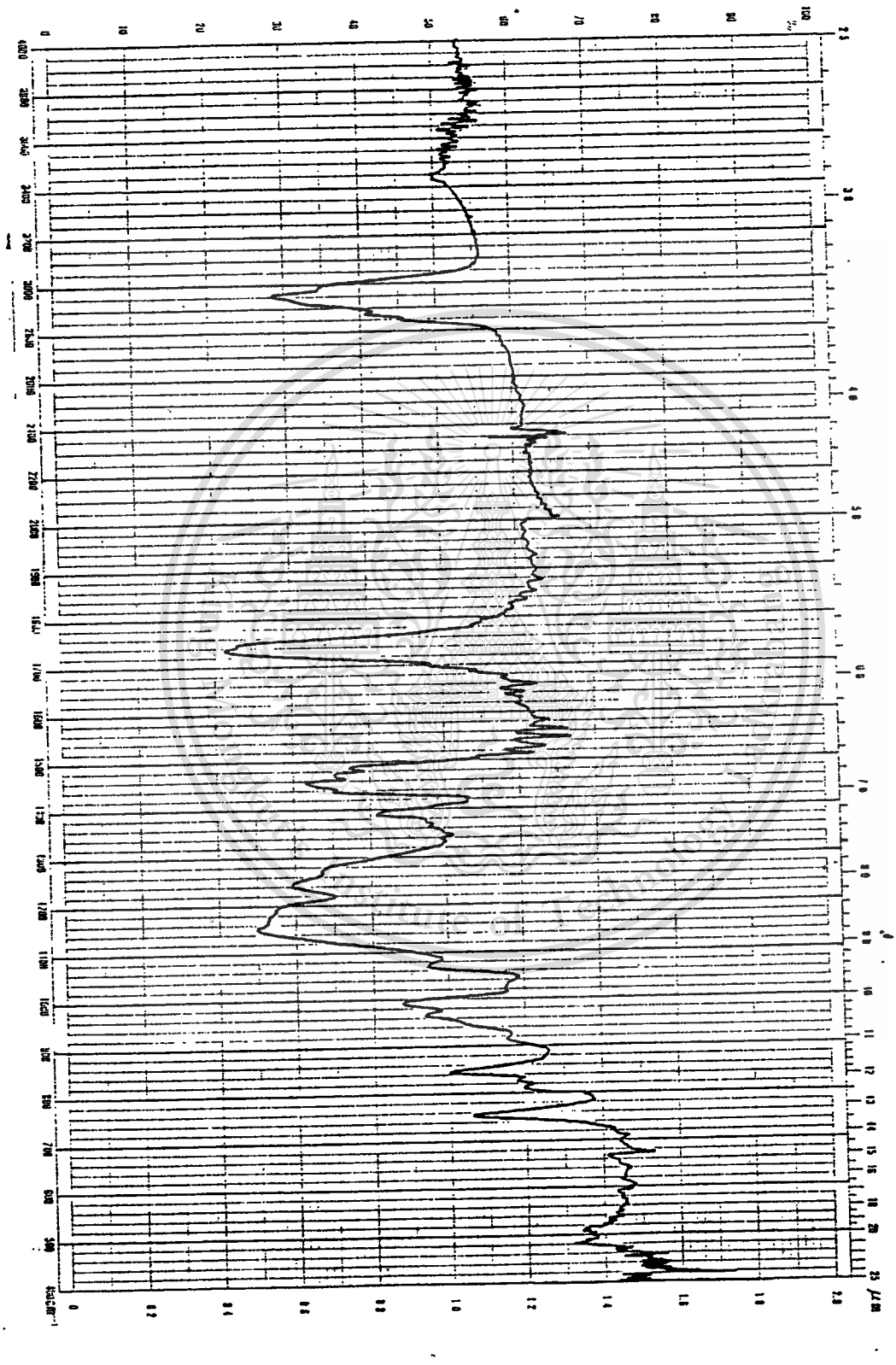


Figure 43 Infrared spectrum of free poly(MMA, BA), monomer ratio MMA/BA = 80/20, Starch/ monomer ratio = 1/2 mole

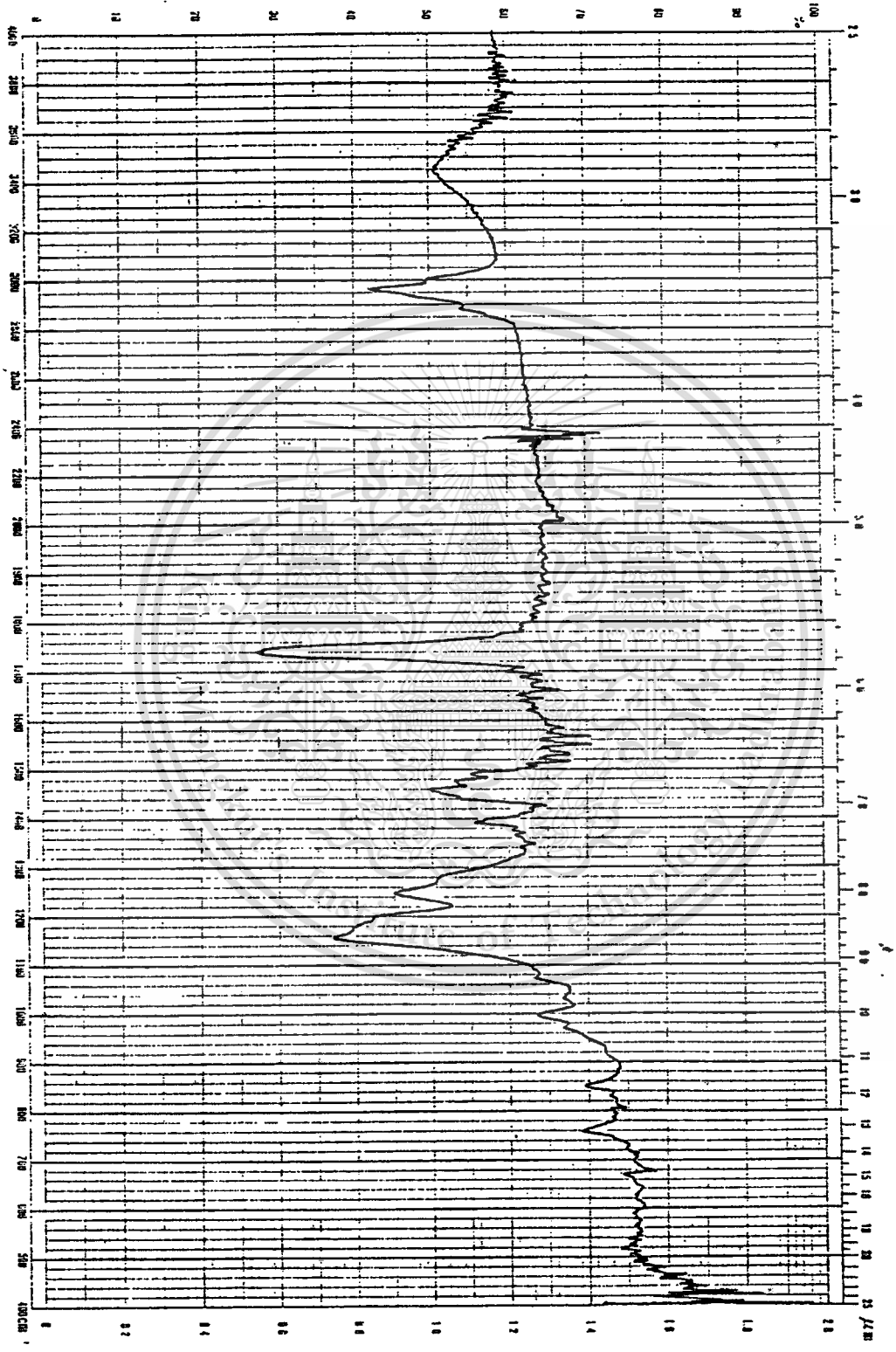


Figure 44 Infrared spectrum of grafted chain poly(MMA, BA), monomer ratio MMA/BA = 80/20, Starch/ monomer ratio = 1/2 mole

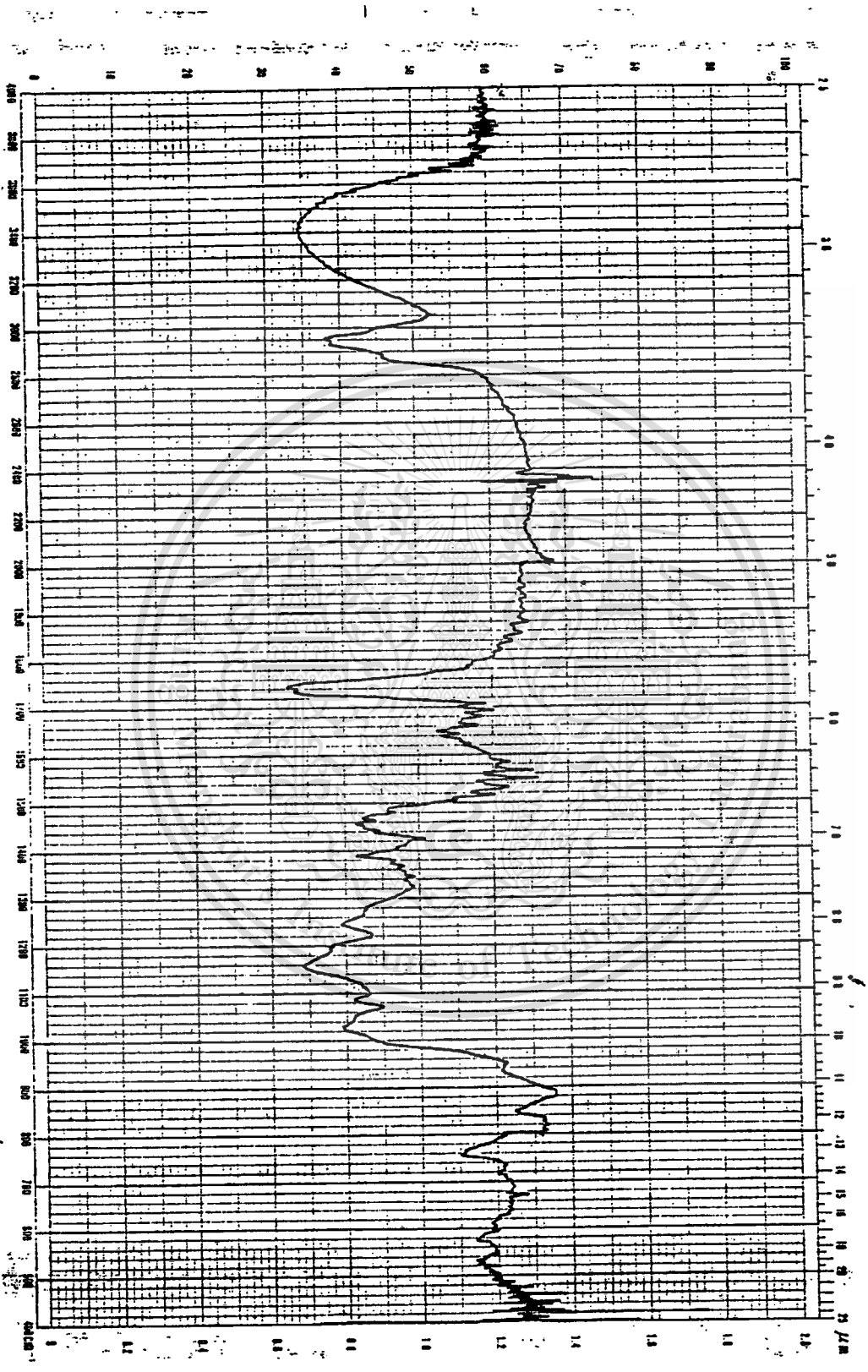


Figure 45 Infrared spectrum of starch graft poly(MMA, 2-EHA), monomer ratio MMA/2-EHA = 80/20, Starch/ monomer ratio = 1/2 mole

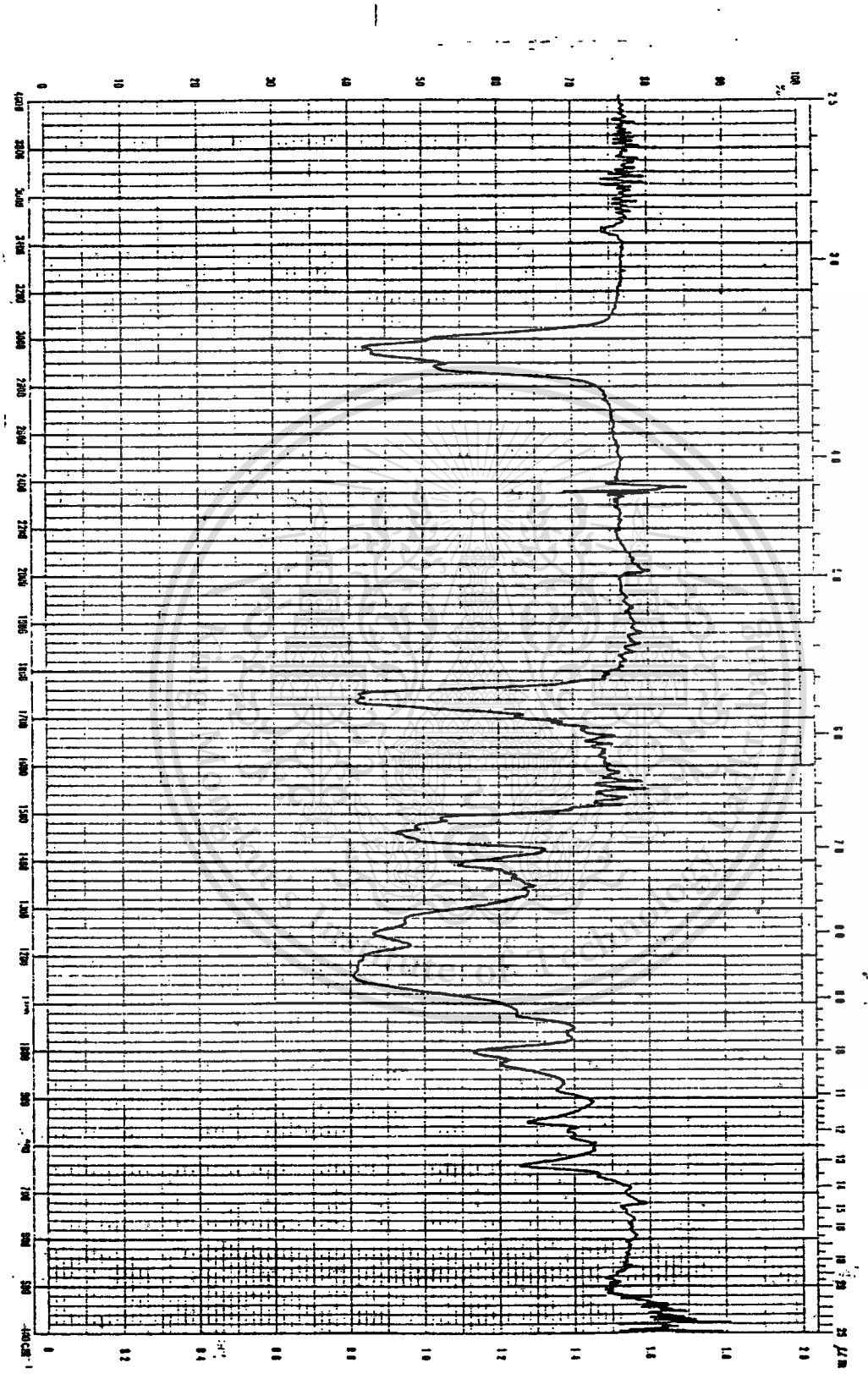


Figure 46 Infrared spectrum of free poly(MMA, 2-EHA), monomer ratio MMA/2-EHA = 80/20, Starch/ monomer ratio = 1/2 mole

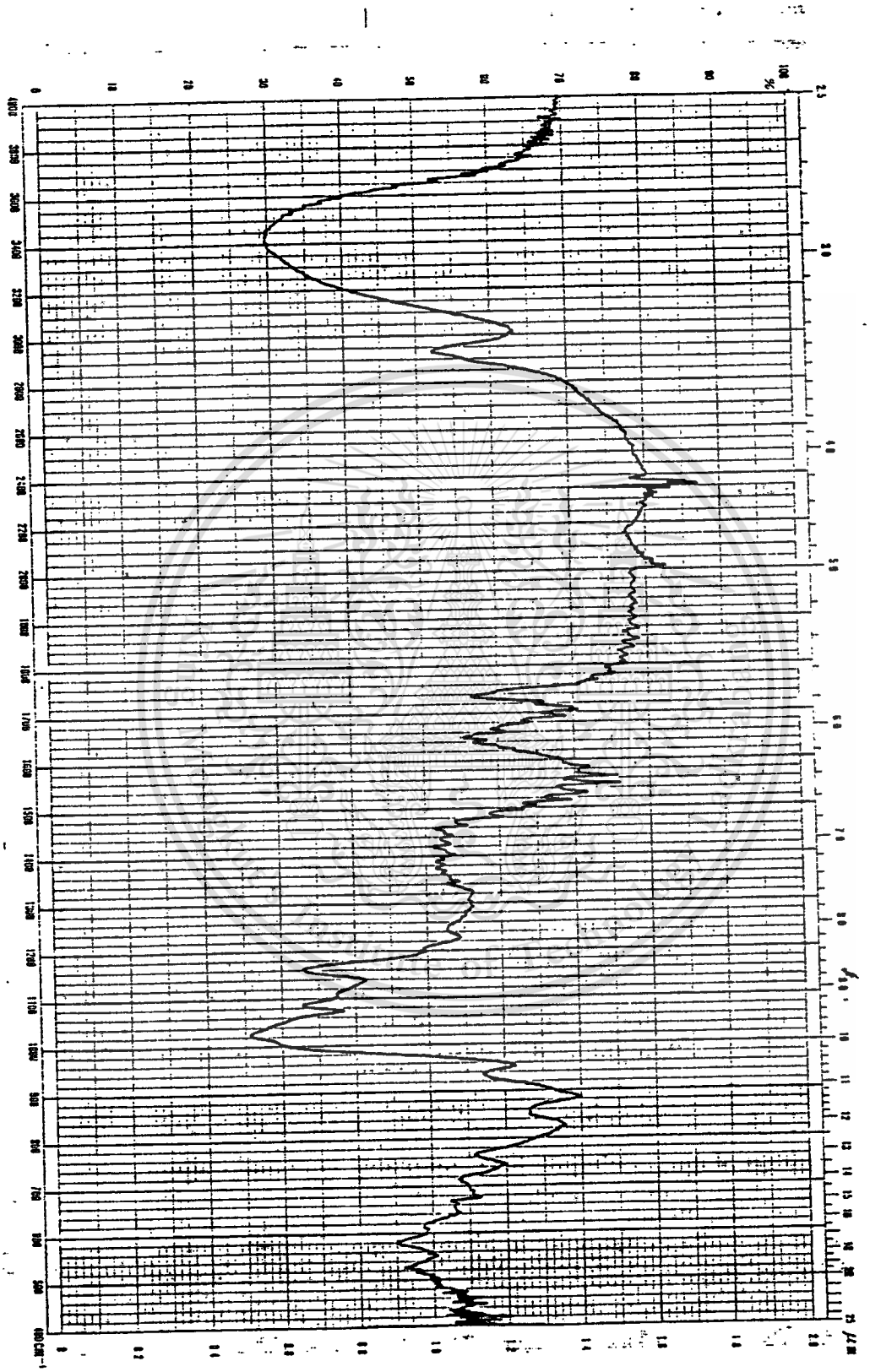


Figure 47 Infrared spectrum of starch graft poly(MMA), Starch/ monomer ratio = 1/2 mole

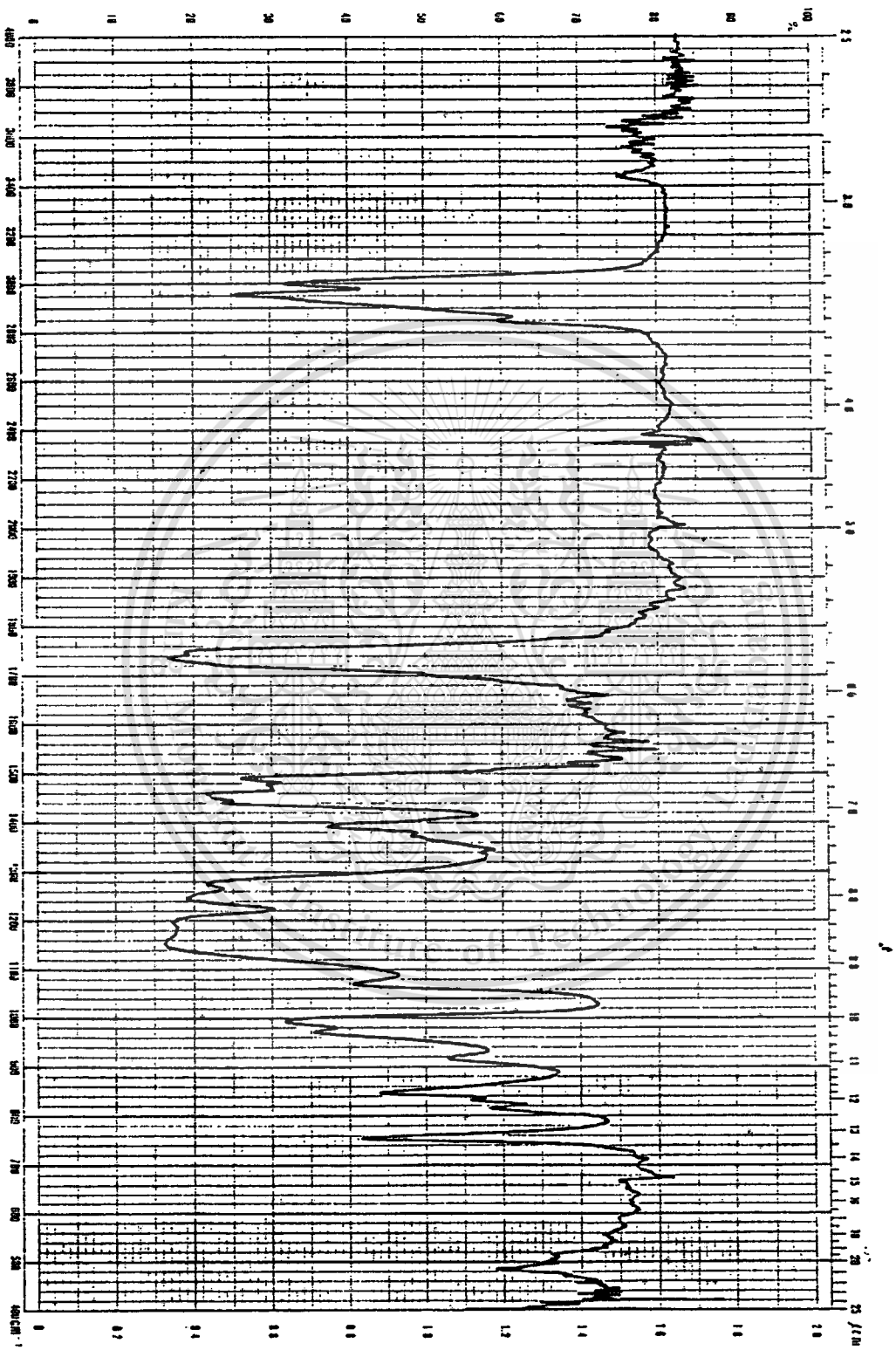


Figure 48 Infrared spectrum of poly(MMA) free polymer , Starch/monomer ratio = 1/2 mole

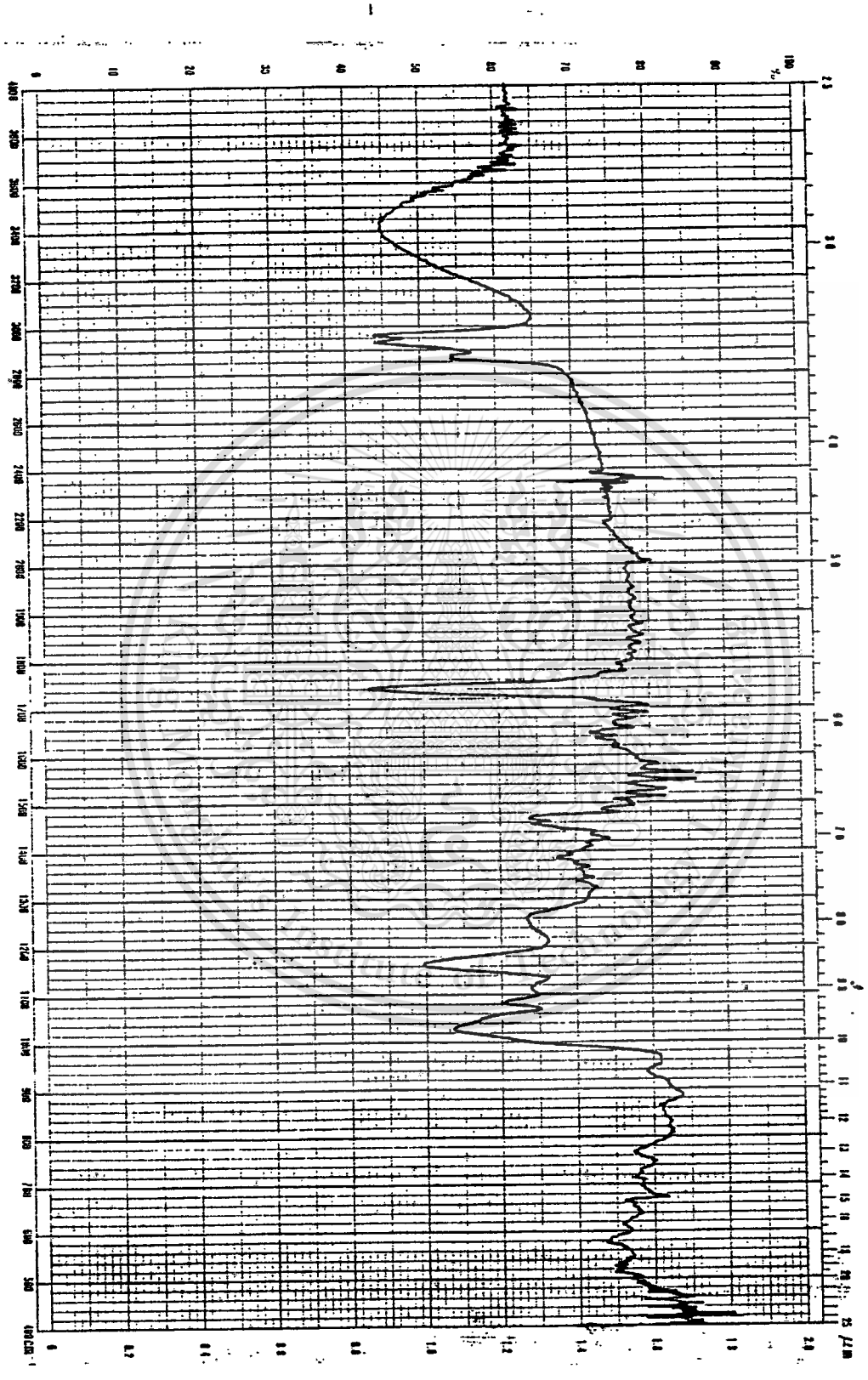


Figure 49 Infrared spectrum of starch graft poly(2-EHA). Starch/ monomer ratio = 1/2 mole

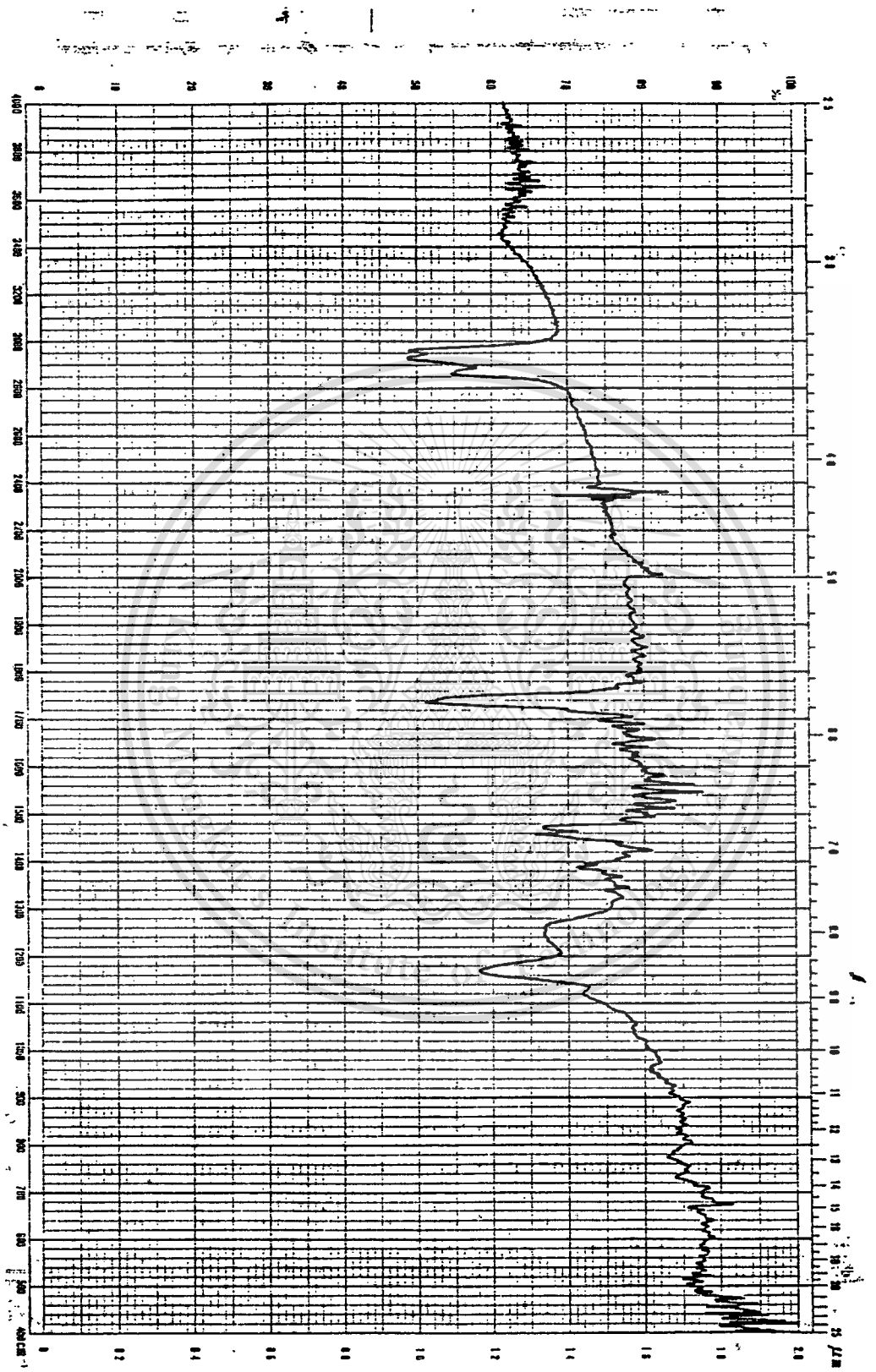


Figure 50 Infrared spectrum of poly(2-EHA) free polymer , Starch/monomer ratio = 1/2 mole

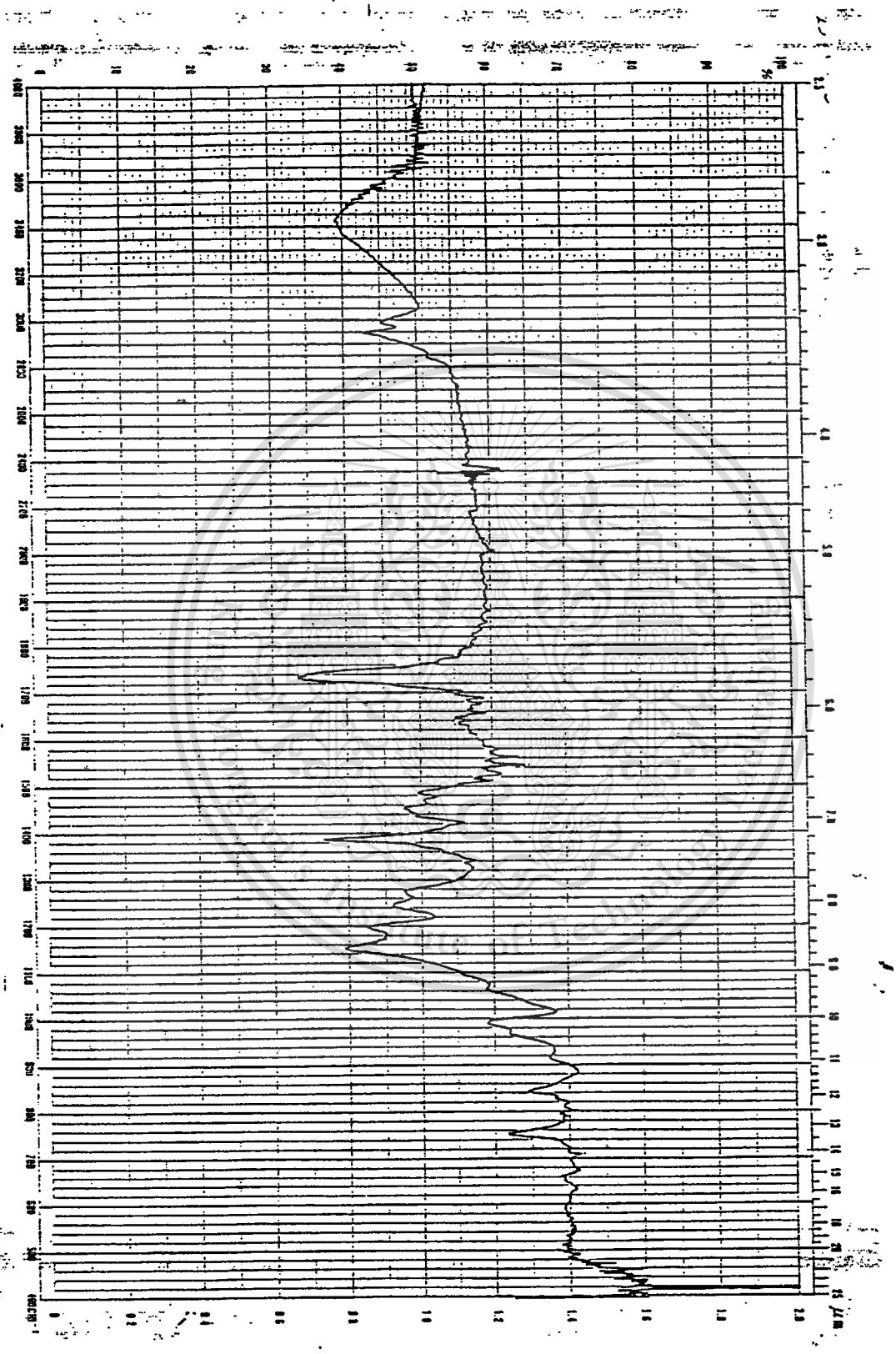


Figure 51 Infrared spectrum of poly(BA) free polymer

Appendix B. Thermogram of starch graft copolymer.

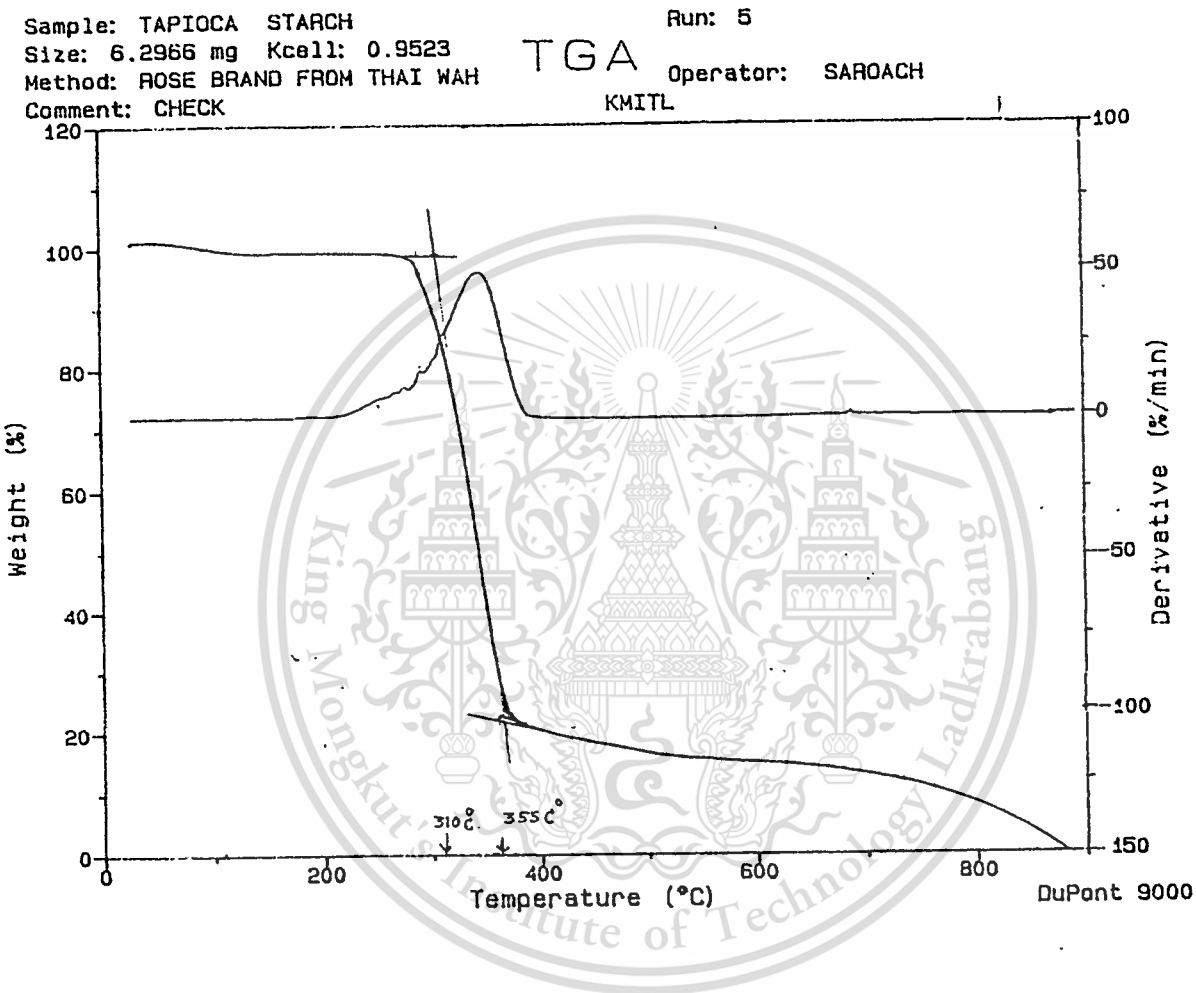


Figure 52 TGA Thermogram of ungraft starch

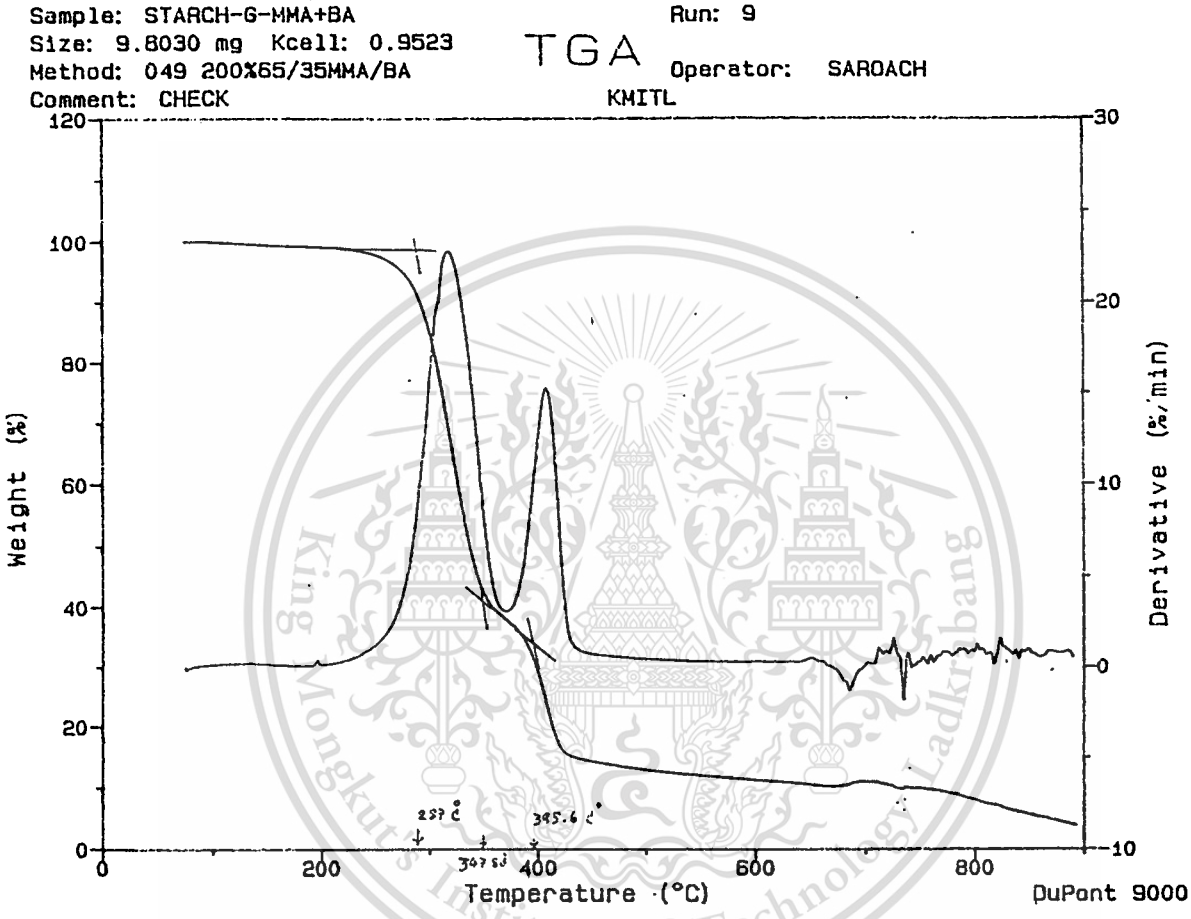


Figure 53 TGA Thermogram of starch graft poly(MMA, BA), monomer ratio MMA/BA = 65/35, Starch/ monomer ratio = 1/2 mole

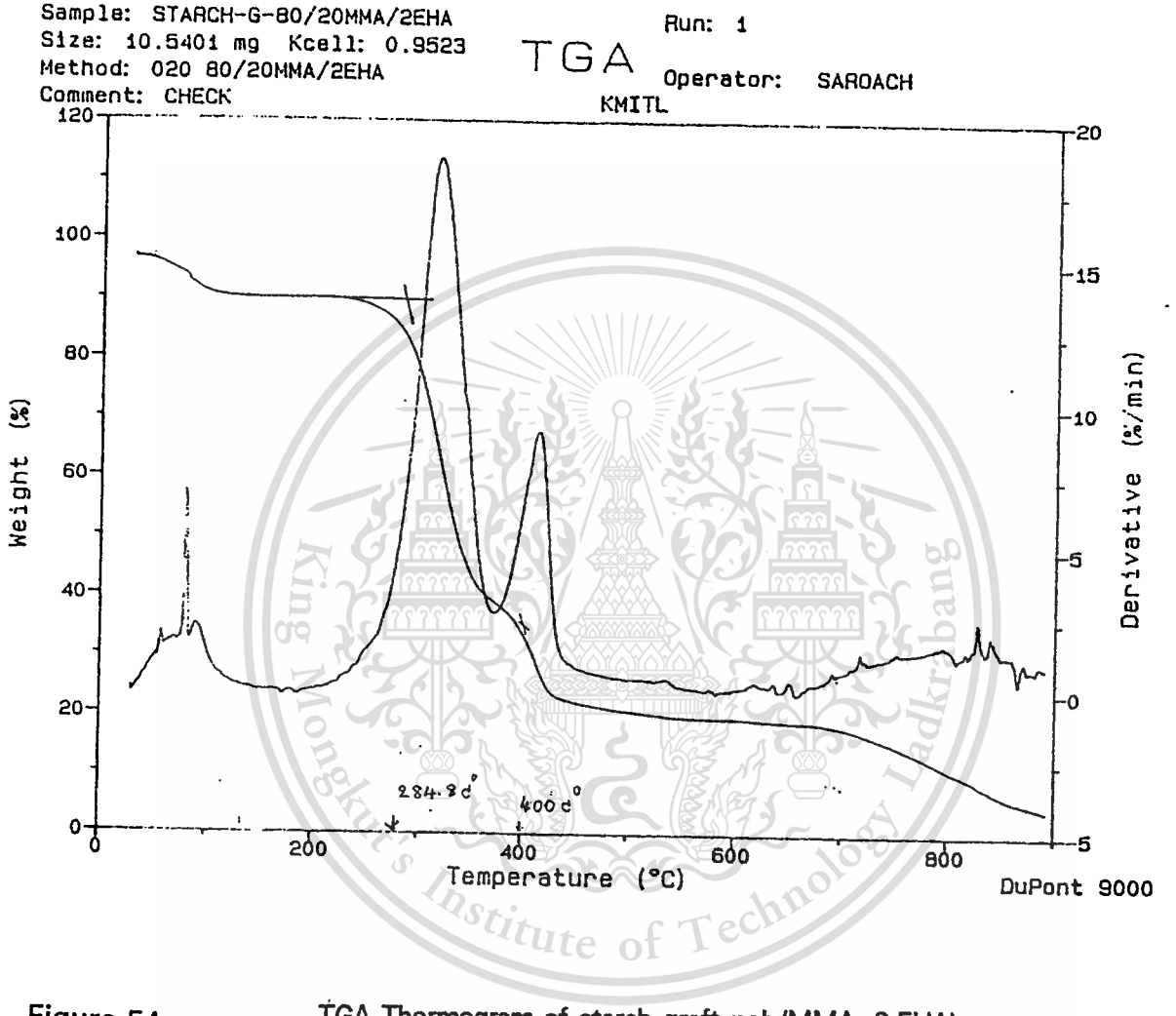


Figure 54 TGA Thermogram of starch graft poly(MMA, 2-EHA), monomer ratio MMA/2-EHA = 80/20, Starch/ monomer ratio = 1/2 mole

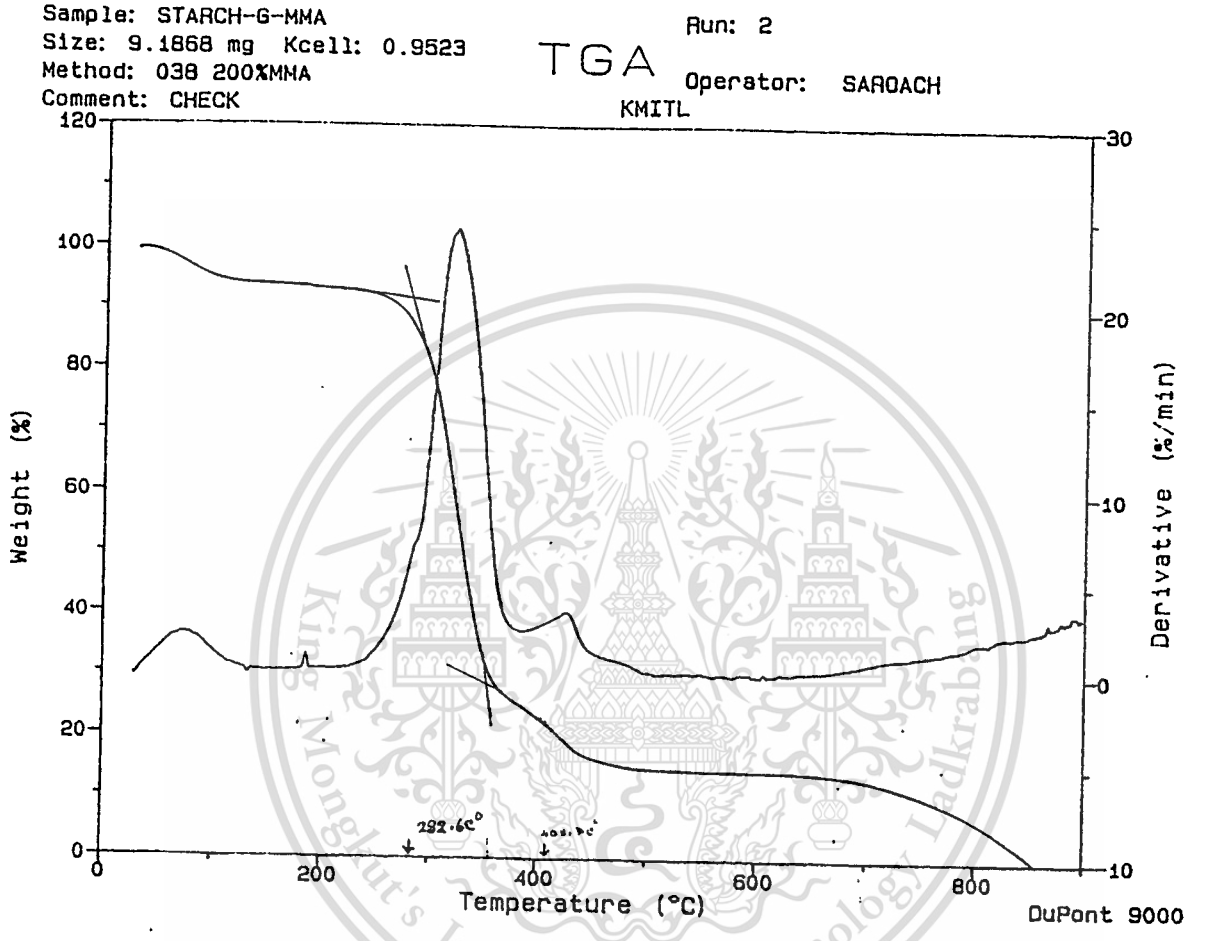


Figure 55 TGA Thermogram of starch graft poly(MMA,), Starch /monomer ratio = 1/2 mole

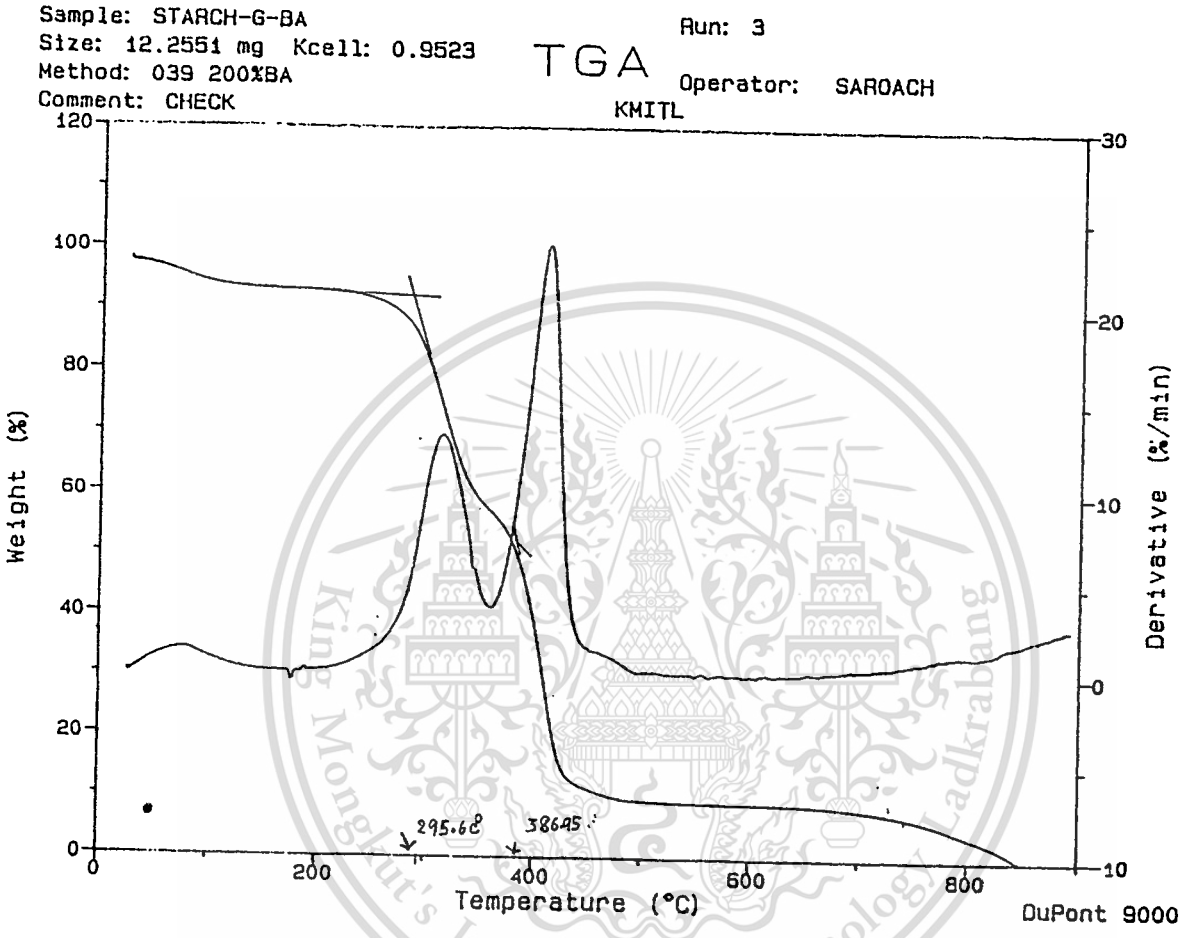


Figure 56 TGA Thermogram of starch graft poly(BA,), Starch / monomer ratio = 1/2 mole

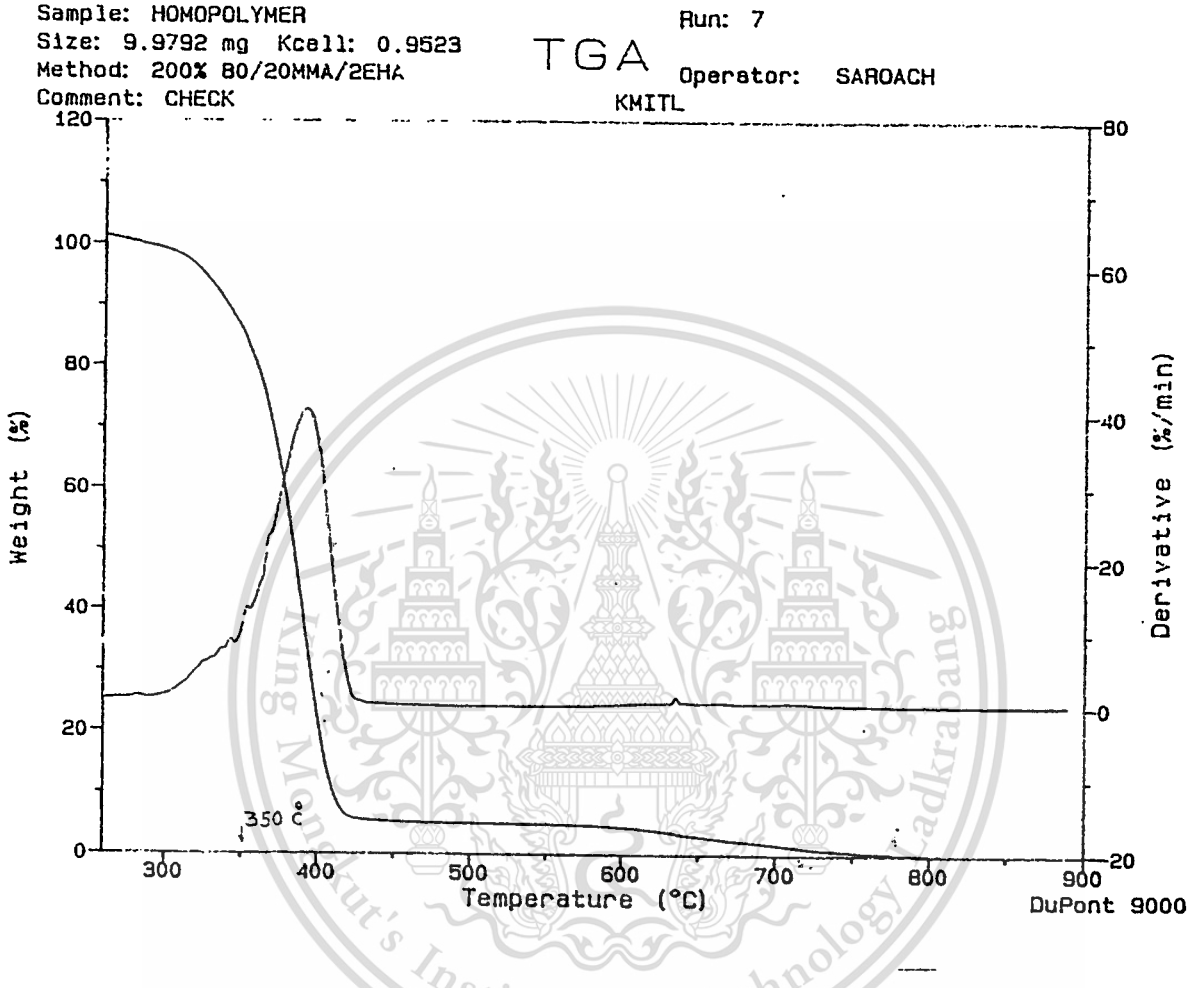


Figure 57 TGA Thermogram of poly(MMA, 2-EHA) free polymer, monomer ratio MMA/2-EHA = 80/20, Starch / monomer ratio = 1/2 mole

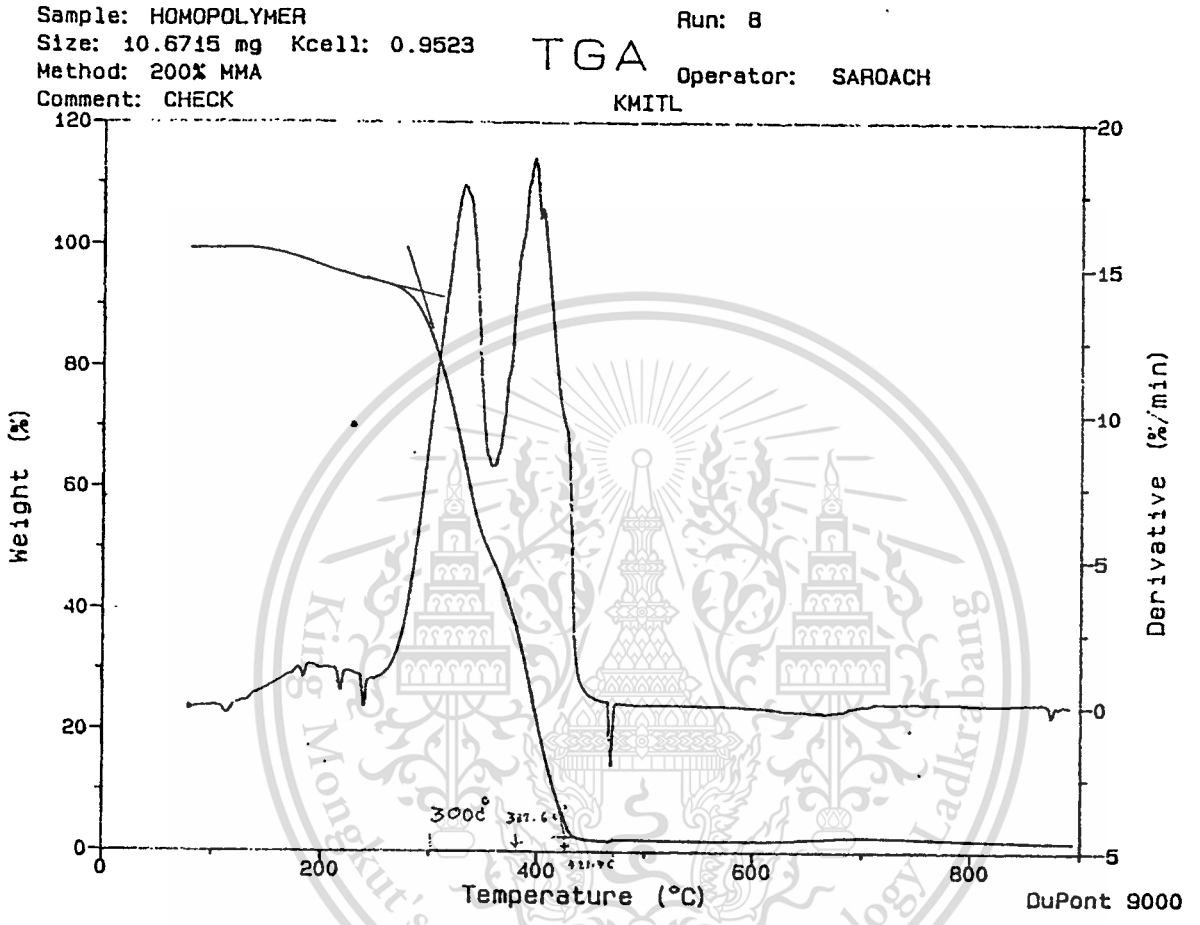


Figure 58 TGA Thermogram of poly(MMA,) freepolymer, Starch / monomer ratio = 1/2 mole

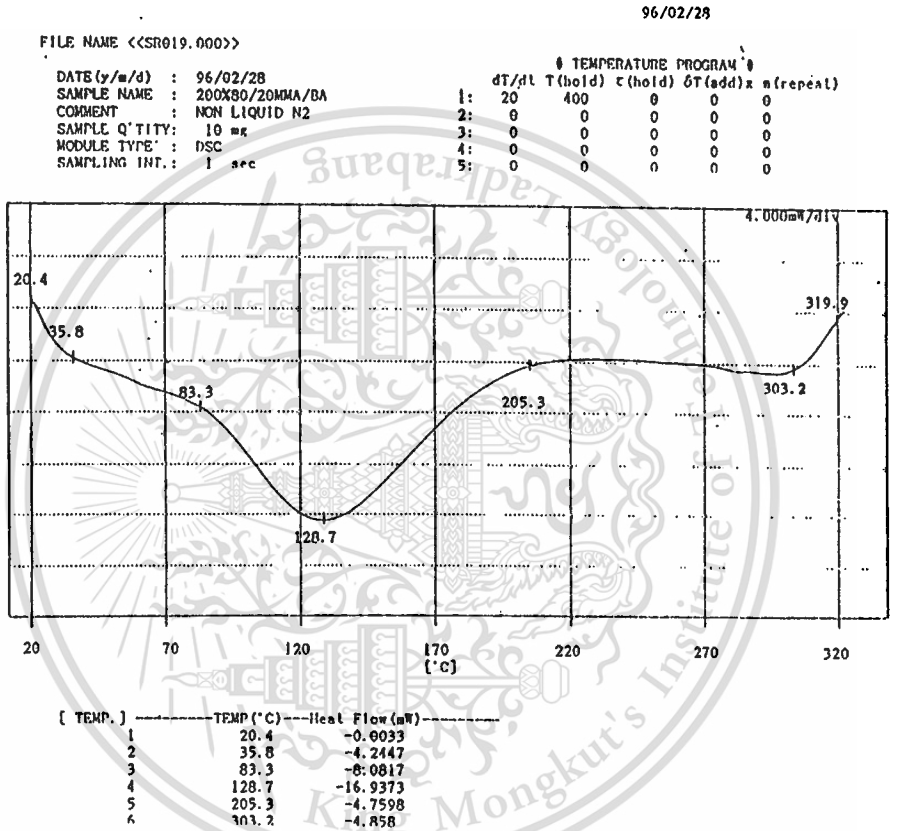


Figure 59 . DSC Thermogram of starch graft poly(MMA, BA), monomer ratio MMA/BA = 80/20, Starch / monomer ratio = 1/2 mole

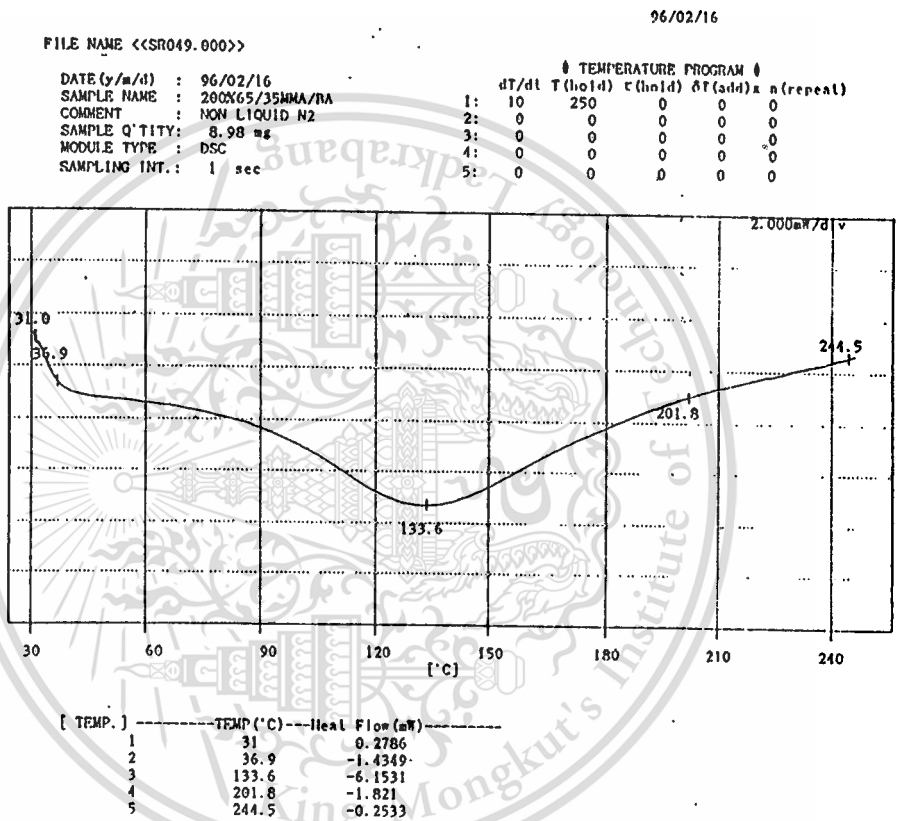


Figure 60 DSC Thermogram of starch graft poly(MMA, BA), monomer ratio MMA/BA = 65/35, Starch / monomer ratio = 1/2 mole

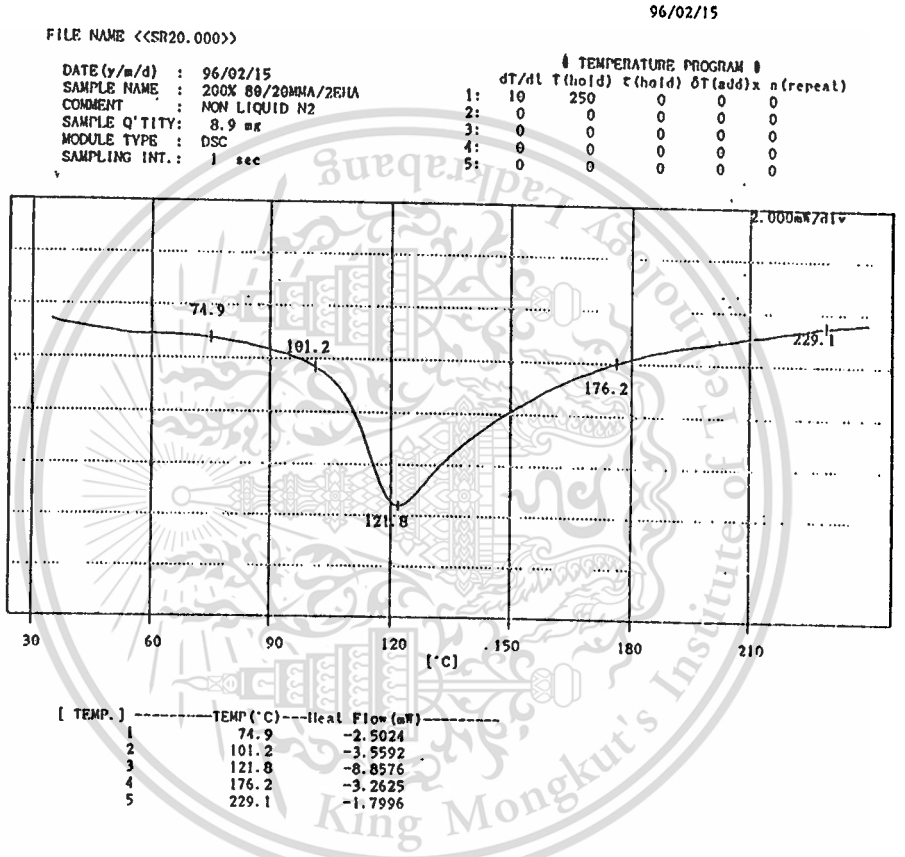


Figure 61 DSC Thermogram of starch graft poly(MMA, 2-EHA), monomer ratio MMA/2-EHA = 80/20, Starch / monomer ratio = 1/2 mole

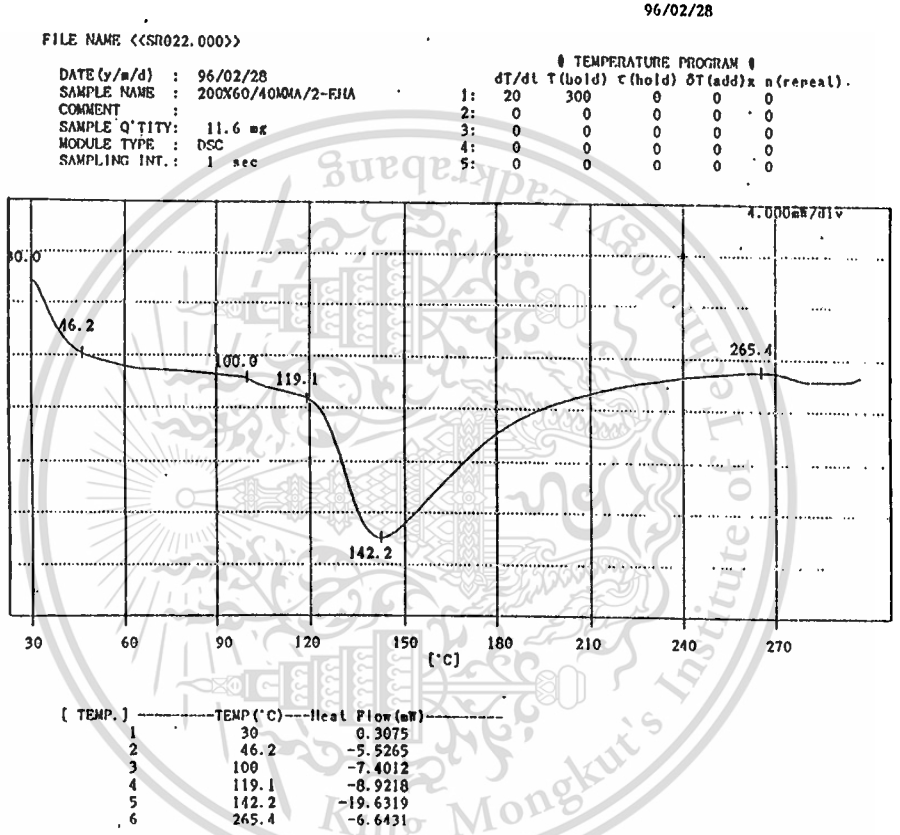


Figure 62 DSC Thermogram of starch graft poly(MMA, 2-EHA), monomer ratio MMA/2-EHA = 60/40, Starch / monomer ratio = 1/2 mole

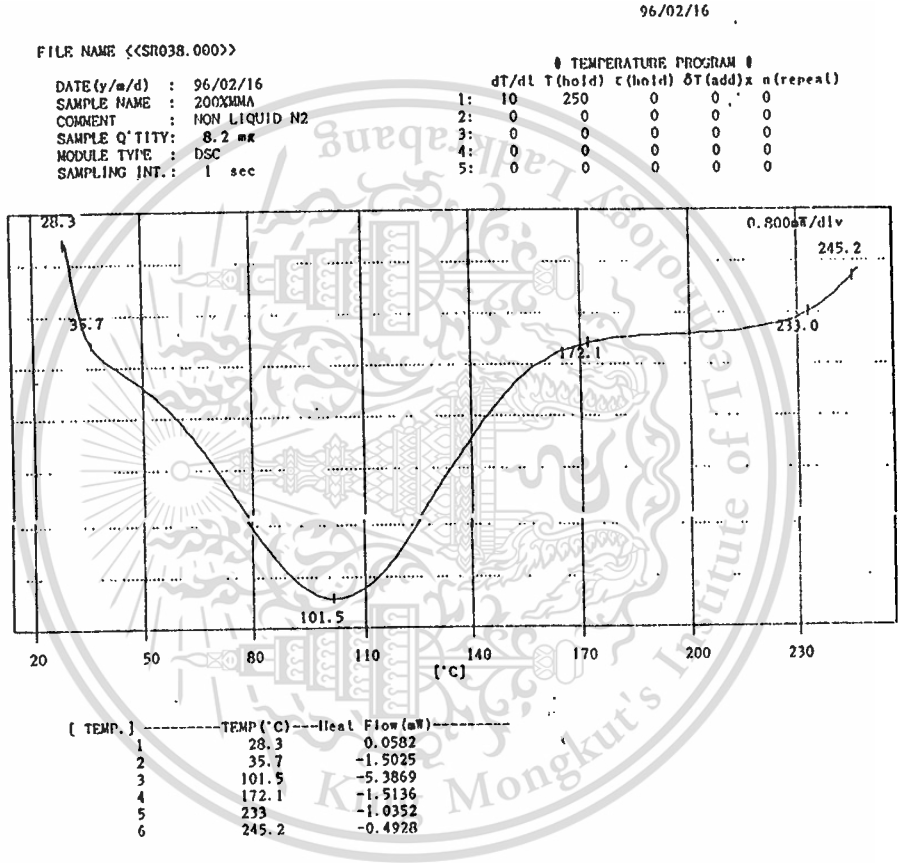


Figure 63 DSC Thermogram of starch graft poly(MMA,), Starch/ monomer ratio = 1/2 mole

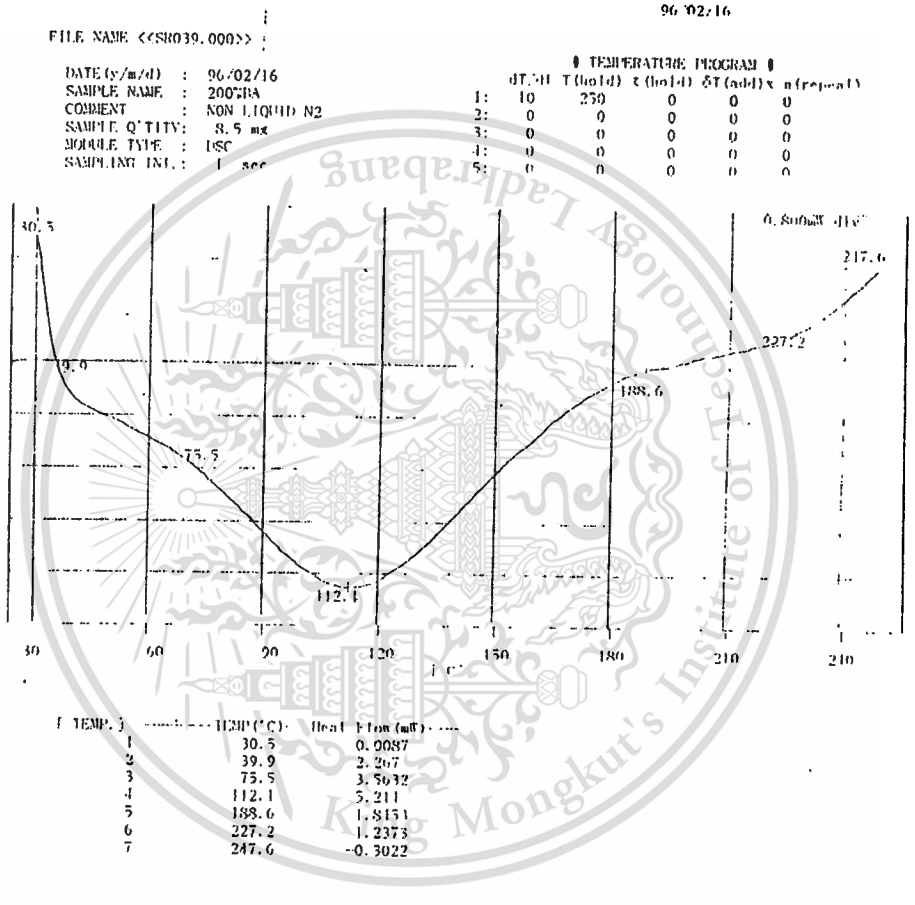


Figure 64 DSC Thermogram of starch graft poly(BA,), Starch/ monomer ratio = 1/2 mole

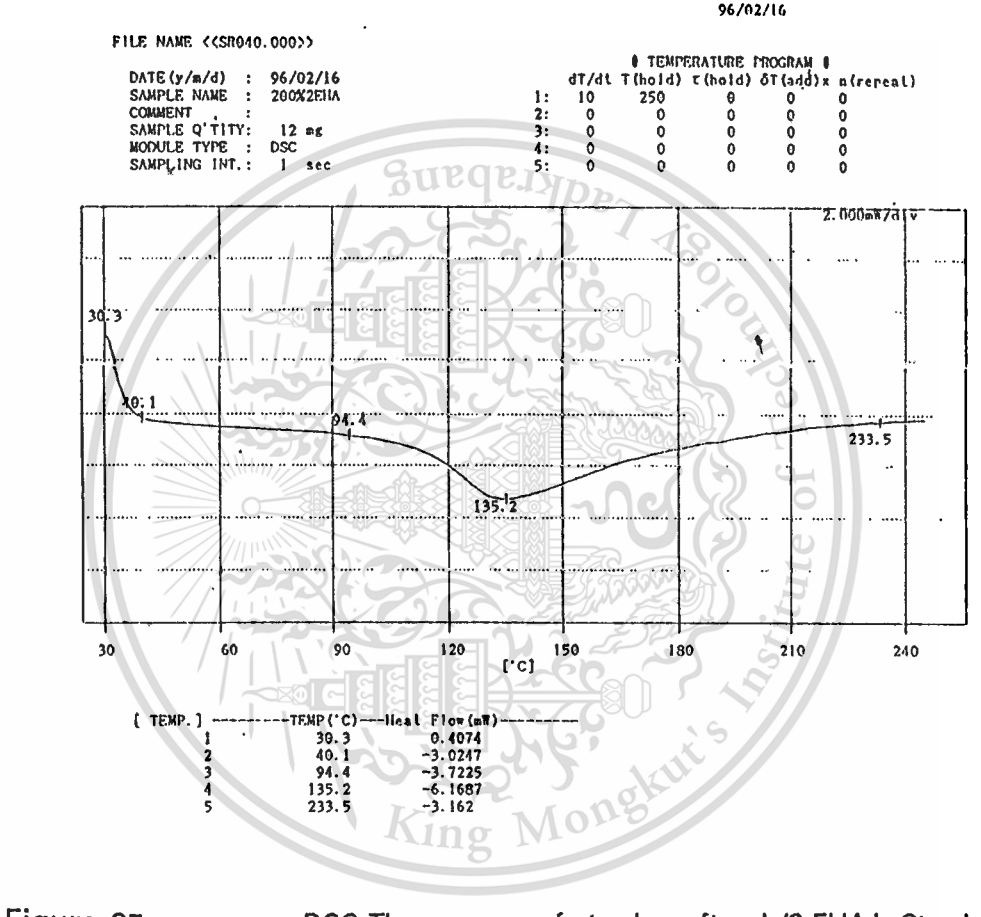


Figure 65 DSC Thermogram of starch graft poly(2-EHA,), Starch/monomer ratio = 1/2 mole

Appendix C. The flow curve of starch graft copolymer.

ROSAND PRECISION CAPILLARY RHEOMETER

5th Jan 1996 3:44am **TEST INFORMATION**

Polymer type..... 049MMA/BA65/35 Starch graft poly(MMA, BA) monomer ratio MMA/BA = 65/35
Trade name.....
Grade.....
Batch number..... 1

Lab code number.....
Molecular weight Mw.....
Filler percentage.....
Filler types.....
Sample origin..... DIE 1.5MMX24 90DEG
Additional information... 200%mole

Operator's initials..... SAROJ
Mw/Mn.....
Drying temperature.....
Drying atmosphere.....
Drying hours.....

TEST TEMPERATURE

Top zone temp (°C)..... 140
Middle zone temp (°C)..... 140
Bottom zone temp (°C)..... 140
Bottom actual temp (°C)... 139.9

TEST GEOMETRY

Long die length (mm).... 24
Long die diameter (mm).. 1.5
Short die length (mm)... 0
Short die diameter (mm). 1
Die entry angle (deg)... 90

RUN SCHEDULE – Piston Speeds mm/min
1, 2, 5, 10, 20, 50, 75, 100, 150, 200, 250, 300

PRESSURE TRANSDUCERS
Transducer at long die...
Max pressure (psi)..... 10000
Information..... 672992(RS)
Transducer at short die..
Max pressure (psi)..... 1500
Information..... 11-22-94672123(DY)

PREHEAT SEQUENCE
Initial pressure long die (MPa).... 0.5
Initial pressure short die (MPa)... 0.5
Time before 2nd compression (min).. 6
Final pressure long die (MPa)..... 0.5
Final pressure short die (MPa)..... 0.5
Preheat time (min)..... 2

CONTROL FACTORS
Variation on standard sample rate.. 1
Max no. of samples at any speed.... 50
Endpoint filter time constant..... 2
Allowable deviation at end point... 0.2
Disc title....
File title.... 9 0

CURRENT TEST RESULTS

	Shear rate /s	Time s	Pl MPa	Ps MPa	Po MPa	Shear Stress kPa	Shear Visc Pa.s	Exten Stress kPa	Elong Visc kPa.s	n
	8.9	115.7	11.52	0	0	180.02	20253	0	0	0.07
	17.8	142.7	12.58	0	0	196.50	11053	0	0	0.11
	44.4	159.2	14.84	0	0	231.90	5218	0	0	0.16
	88.9	169.2	16.72	0	0	261.23	2939	0	0	0.21
	177.8	175.8	19.01	0	0	296.96	1670	0	0	0.25
	444.4	180.8	23.69	0	0	370.14	833	0	0	0.30
	666.7	184.8	26.84	0	0	419.40	629	0	0	0.33
	888.9	188.8	29.77	0	0	465.18	523	0	0	0.34
	1333.3	193.8	34.91	0	0	545.45	409	0	0	0.37
	1777.8	197.8	39.98	0	0	624.67	351	0	0	0.38
	2222.2	201.8	44.56	0	0	696.27	313	0	0	0.40
N	2666.7	209.3	21.70	0	0	339.12	127	0	0	1.00

Figure 66 Test information of extrusion capillary rheometer for starch graft poly(MMA, BA), monomer ratio MMA/BA = 65/35, Starch/ monomer ratio = 1/2 mole.

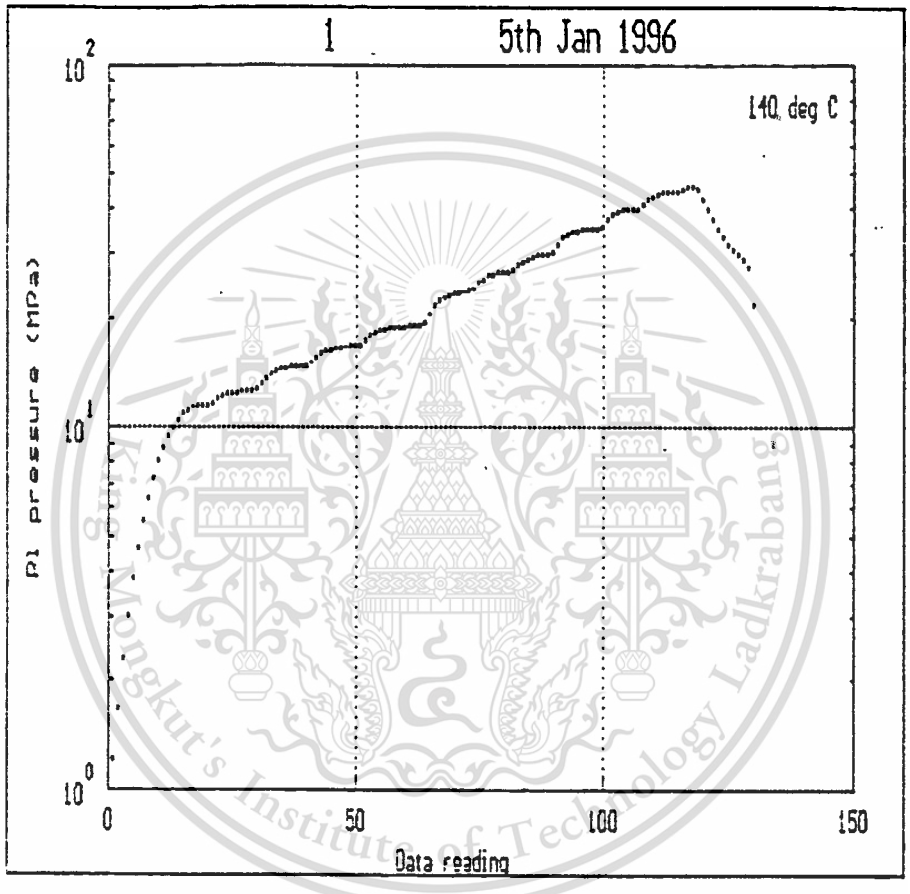


Figure 67 Data from reading rheological of starch graft poly(MMA, BA), monomer ratio MMA/BA = 65/35, Starch/ monomer ratio = 1/2 mole.

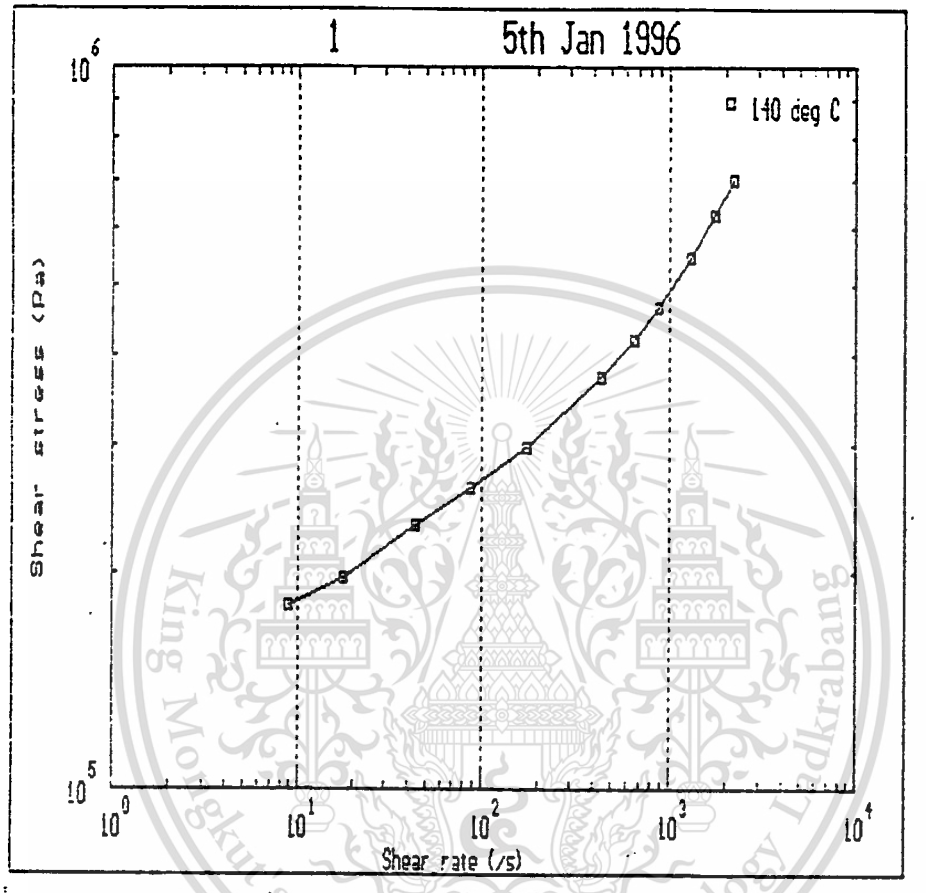


Figure 68 The relation between shear stress and shear rate of starch graft poly(MMA, BA), monomer ratio MMA/BA = 65/35, Starch/ monomer ratio = 1/2 mole.

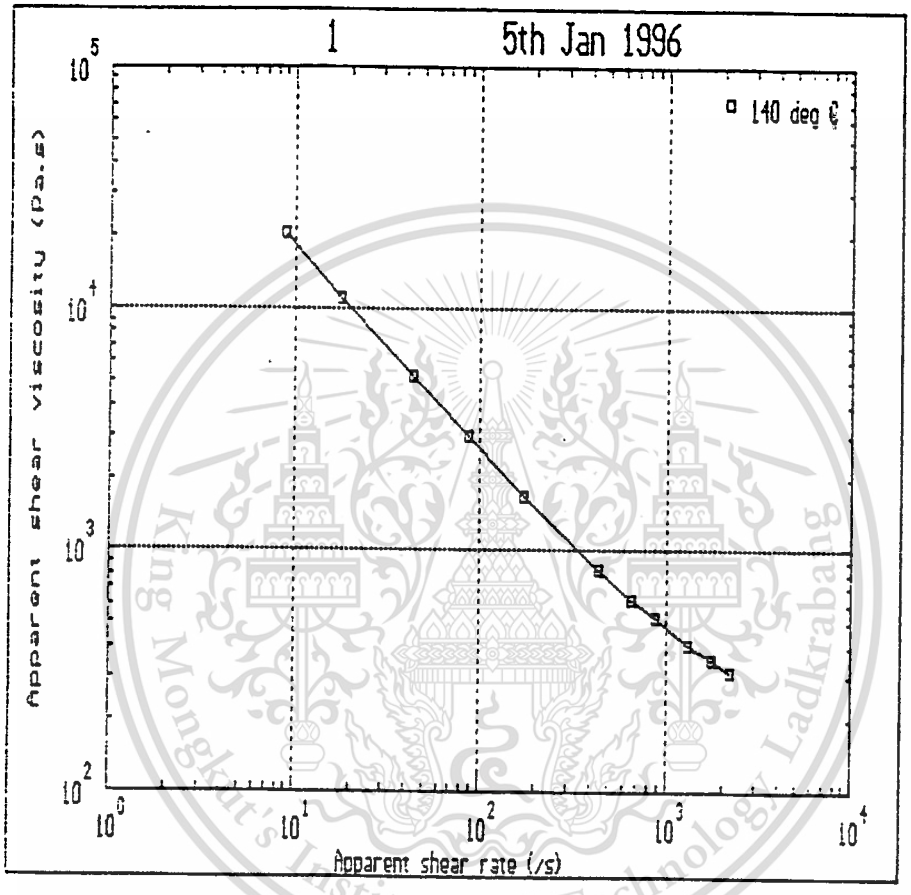


Figure 69 The relation between apparent viscosity and shear rate of starch graft poly(MMA, BA), monomer ratio MMA/BA = 65/35, Starch/ monomer ratio = 1/2 mole .

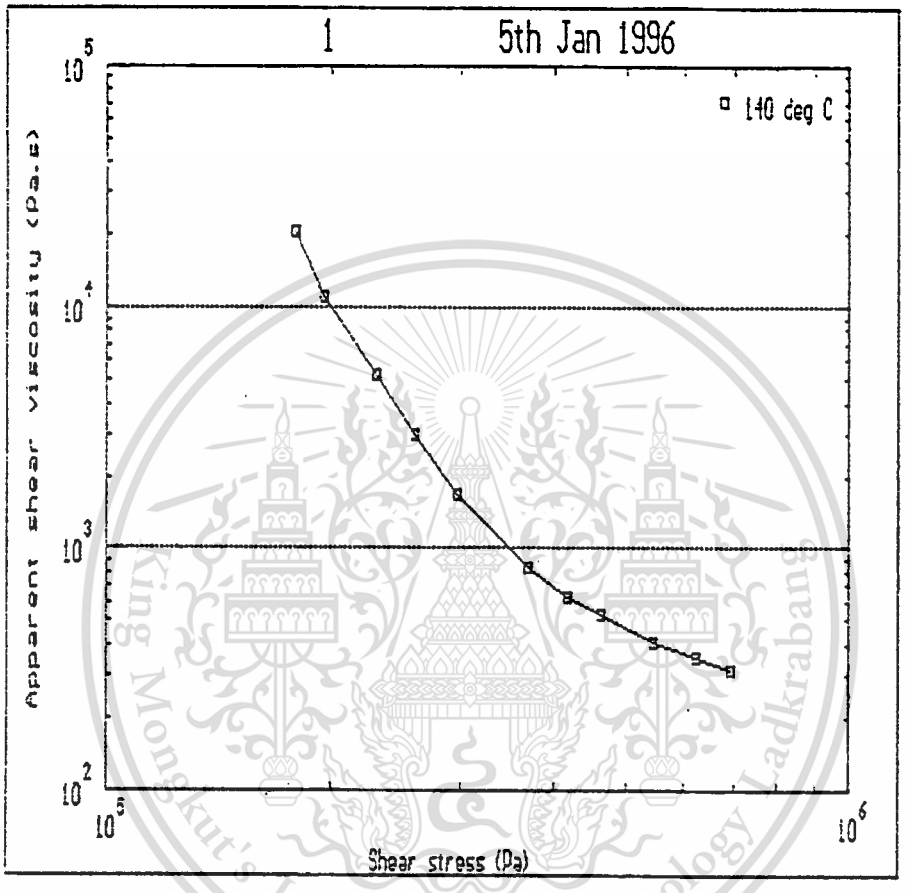


Figure 70 The relation between apparent viscosity and shear stress of starch graft poly(MMA, BA), monomer ratio MMA/BA = 65/35, Starch/ monomer ratio = 1/2 mole .

Apendix D. The specification of tapioca starch

Appendix E. The machanism of emulsion polymerization.

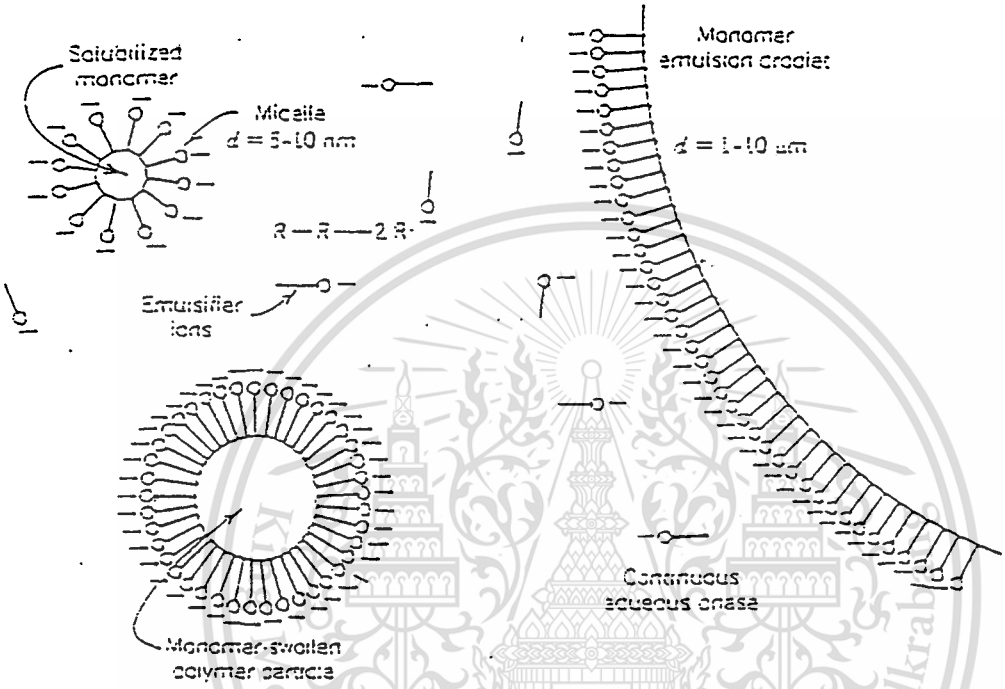


Figure 72 The mechanism of emulsion polymerization

BIOGRAPHY

Saroach Patamagate

I was born in 1970.

I graduated a B.Sc (Chemistry) from Ramkhamhaeng University.

I found work at TOYO INK (Thailand) CO., LTD. in 1993.

I got the scholarship from Nation Science and Technology Development (NSTDA) Agency during master degree study.