

สำนักหอสมุดกลาง พระจอมเกล้าลาดกระบัง

**PLASTIC FROM TAPIOCA STARCH -g- POLY
(STYRENE -co- BUTYL ACRYLATE)**



เลขหมู่.....
เลขทะเบียน..... 41531
วัน, เดือน, ปี.จ.อ.ส.ป. 2547

.b.....
.i.....

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE IN APPLIED CHEMISTRY
SCHOOL OF GRADUATE STUDIES
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG**

2003

ISBN 974-324-675-4

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.



COPYRIGHT 2003

SCHOOL OF GRADUATE STUDIES

KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

หัวข้อวิทยานิพนธ์

พลาสติกจากพอลิเมอร์ร่วมแบบตอกิ่งของแป้งมันสำปะหลัง
พอลิ(สไตรีน – บิวทิลอะคริเลต)

นักศึกษา

นางสาวสุภัตรา เจริญเกษมวิทย์

รหัสประจำตัว

39065105

ปริญญา

วิทยาศาสตร์มหาบัณฑิต

สาขาวิชา

เคมีประยุกต์

พ.ศ.

2546

อาจารย์ผู้ควบคุมวิทยานิพนธ์

ผศ.ดร. นิพนธ์ วงศ์วิเศษสิริกุล

บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาเทคนิคกระบวนการฉีดขึ้นรูปของพลาสติกย่อยสลายได้ทางชีวภาพจากพอลิเมอร์ร่วมแบบตอกิ่งของแป้งมันสำปะหลังกับมอนอเมอร์สไตรีนและบิวทิลอะคริเลต โดยปริมาณอัตราส่วนมอนอเมอร์เป็น 2:1 โดยโมลของแป้งและอัตราส่วนระหว่างสไตรีนกับบิวทิลอะคริเลต เท่ากับ 4:1 โดยโมล พลาสติกจากพอลิเมอร์ร่วมแบบตอกิ่งของแป้งมันสำปะหลังพอลิ (สไตรีนบิวทิลอะคริเลต) เตรียมจากปฏิกิริยาพอลิเมอร์ไรเซชันแบบอิมัลชันและใช้ตัวริเริ่มปฏิกิริยาโฟแทสเซียมเปอร์ซัลเฟต ที่อุณหภูมิ 60-90 องศาเซลเซียส จำนวน 6 สภาวะ สภาวะที่ 1 เตรียมจากปฏิกิริยาดังกล่าวข้างต้น สภาวะที่ 2 เปลี่ยนชนิดของสารลดแรงตึงผิว สภาวะที่ 3 ใช้แป้งที่ไม่ผ่านขั้นตอนการทำให้เป็นเจล สภาวะที่ 4 ใช้ตัวริเริ่มปฏิกิริยาละลายในน้ำ สภาวะที่ 5 และ 6 เพิ่มขั้นตอนการล้างพอลิเมอร์ด้วยน้ำและไอโซโพรพานอล ตามลำดับ พบว่าสภาวะที่เหมาะสมในการฉีดขึ้นรูป คืออุณหภูมิบริเวณหัวฉีด ช่วงที่ 1 ช่วงที่ 2 และช่วงที่ 3 เท่ากับ 150 140 130 และ 120 องศาเซลเซียส ตามลำดับ เวลาในการฉีดขึ้นรูป ระดับที่ 1 ระดับที่ 2 ระดับที่ 3 และเวลาในการหล่อเย็น เท่ากับ 45 40 35 และ 50 วินาที ตามลำดับ ความเร็วในการฉีดขึ้นรูป เท่ากับ 20 มิลลิเมตรต่อวินาที และความดันในการฉีดขึ้นรูปช่วงที่ 1 ช่วงที่ 2 และช่วงที่ 3 เท่ากับ 4.41×10^6 3.92×10^6 และ 3.43×10^6 นิวตันต่อตารางเมตร ตามลำดับ นำชิ้นงานที่ได้มาศึกษาสมบัติต่างๆเปรียบเทียบกับพลาสติกทางการค้า พบว่าสมบัติทางความร้อน ได้แก่ อุณหภูมิเปลี่ยนสถานะคล้ายแก้วและอุณหภูมิเสถียรอยู่ในช่วง 150-170 องศาเซลเซียส และ 51.1-51.8 องศาเซลเซียส ตามลำดับ สมบัติเชิงกลได้แก่ ค่ามอดุลัส ความทนแรงดึง สมบัติการดึงยืด ความทนแรงกระแทก และค่าความแข็ง อยู่ในช่วง 480-1600 นิวตันต่อตารางมิลลิเมตร 10-20 นิวตันต่อตารางมิลลิเมตร ร้อยละ 2.3-5.6 1.3-1.6 กิโลจูลต่อตารางเมตร และ 64-68 ชอริดี ตามลำดับ สมบัติทางกายภาพได้แก่ ปริมาณความชื้นอยู่ในช่วงร้อยละ 3.5-4.0 การดูดซึมน้ำอยู่ในช่วงร้อยละ 14-16 และความหนาแน่นอยู่ในช่วง 1.2-1.3 กรัมต่อลูกบาศก์เซนติเมตร พลาสติกที่ได้ไม่มีสมบัติด้านความปลอดภัยในการนำไปบรรจุอาหารตามประกาศกระทรวงสาธารณสุขฉบับที่ 111 (พ.ศ.2531)den to modify the content, and cite the document when use.

Thesis Title	Plastic from Tapioca Starch –g– Poly(Styrene –co– Butyl Acrylate)
Student	Miss Supattra Charoenkasemwit
Student ID.	39065105
Degree	Master of Science
Programme	Applied Chemistry
Year	2003
Thesis Advisor	Asst. Prof. Dr. Nipon Wongvisetsirikul

ABSTRACT

The research work involves the study of injection molding technique of biodegradable plastic formed from tapioca starch graft copolymers. Tapioca starch graft copolymers were synthesized by reacting a mixture of tapioca starch and styrene with butyl acrylate by emulsion polymerization using potassium persulfate as an initiator. The reaction temperature was between 60 to 90 degree celcius in nitrogen blanket in six different conditions. The monomer was 2:1 by mol of tapioca starch and the ratio of styrene to butyl acrylate was 4:1 by mol. Condition 1 was prepared as mentioned above. Condition 2 was prepared with the same process as condition 1, with changing of surfactant type. Condition 3, the same process as 1, but using tapioca starch flour directly without gel preparation. Condition 4, the same process as 1, but dissolved initiator in water. Condition 5 and 6, using the product from condition 1, which washed with water and isopropanol, respectively. The tapioca starch graft copolymer specimens were produced by an injection machine at difference conditions in order to find the optimum condition. The results showed that the temperatures of the nozzle, zone 1, zone 2 and zone 3 were 150, 140, 130 and 120 degree celcius, respectively. The injection molding time at the first, the second, the third stages and the cooling time were 45, 40, 35 and 50 seconds, respectively. The injection molding speed was 20 mm/second. The injection molding pressure at the first, the second and the third stages were 4.41×10^6 , 3.92×10^6 and 3.43×10^6 N/m², respectively. The finished products were tested to compare with commercial plastics, the glass transition temperature were found at 150-170 degree celcius and the heat distortion temperature at 51.1-51.8 degree celcius. Their mechanical properties were found as(modulus: 480-1600 N/mm², tensile strength:10-20 N/mm², elongation:2.3-5.6%, impact strength: 1.3-1.6 kJ/m², and hardness : 64-68 Shore D). Some physical properties were found as followed moisture content:3.5-4.0%, water absorption:1.2-1.3% and density 1.2-1.3 g/cm³. Furthermore, the test results suggested that the tapioca starch graft copolymers were not safe for food packaging according to the notification of the ministry of public health no.111(B.E.(1988)).

ACKNOWLEDGEMENT

During the time has taken to complete this thesis, many people help me to complete this study. I do appreciate their understanding and helpful advises.

I would like to express my sincere gratitude to my advisor, Asst. Prof. Dr. Nipon Wongvisetsirikul for his valuable guidance and discussion throughout the course of this work. His help has enabled me to carry out my study successfully. I am also grateful to Assoc. Prof. Arunee Kongsakphaisal, Asst. Prof. Dr. Malinee Chaisupakitsin and Asst. Prof. Dr. Preecha Teansomprasong for their helpful suggestions and completion of this thesis.

I would like to thank KMITL for providing the laboratory and other facilities, Thai Wah Public Co.,Ltd. for providing tapioca starch. In addition, my sincere thanks are given to Chemistry Department staff members, my friends and everyone for their kindness helpful.

Finally, I would like to thank Mr. Thawat Nusonthara and my family for their love and helpful encouragement.

Supattra Charoenkasemwit

TABLE OF CONTENTS

	Page
THAI ABSTRACT	I
ENGLISH ABSTRACT	II
ACKNOWLEDGEMENT	III
TABLE OF CONTENTS	IV
LIST OF TABLES	VII
LIST OF FIGURES	VIII
ABBREVIATIONS	XII
CHAPTER 1 INTRODUCTION	1
1.1 Objective.....	3
1.2 Scope of this work.....	3
CHAPTER 2 THEORETICAL CONSIDERATION AND LITERATURE REVIEW	4
2.1 Starch.....	4
2.1.1 Chemical Structure of Starch.....	4
2.1.2 Tapioca Starch.....	6
2.2 Biodegradable Plastic.....	8
2.2.1 Photodegradable Polymer.....	11
2.2.2 Biodegradable Polymer.....	11
2.2.3 Starch based Polymer.....	12
2.3 Graft Copolymerization.....	14
2.3.1 Emulsion Polymerization.....	14
2.3.2 Components and Their Locations.....	15
2.3.3 The Three Intervals in Emulsion Polymerization.....	15
2.4 Plasticization of Polymers.....	16
2.4.1 Mechanism of Plasticization.....	17
2.5 Rheological Properties of Polymer Melts.....	18
2.6 Polymer Processing.....	21
2.6.1 Injection Molding.....	21

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

TABLE OF CONTENTS (continued)

	Page
2.7 Plastic Packaging for Foodstuffs.....	24
2.8 Literature Review.....	26
 CHAPTER 3 EXPERIMENT	 31
3.1 Materials.....	31
3.1.1 Tapioca Starch and Monomers.....	31
3.1.2 Initiator.....	31
3.1.3 Emulsifier.....	31
3.1.4 Other Chemicals.....	31
3.2 Instruments.....	32
3.3 Synthesis of Tapioca Starch Graft Copolymer and Purification	33
3.3.1 Graft Copolymerization.....	33
3.3.2 Ungrafted Polymer Separation.....	34
3.3.3 Side Chain Grafted Polymer Separation.....	34
3.4. Characterizations.....	35
3.4.1 The Particle Size of Tapioca Starch Graft Copolymer....	35
3.4.2 Molecular Weight Determination.....	35
3.4.3 Gravimetric Characterization.....	35
3.4.4 Total Solid Content and Conversion.....	36
3.4.5 Identification of Grafting.....	36
3.4.6 Thermal Properties Determination.....	36
3.4.7 Mechanical Properties Testing.....	37
3.4.8 Physical Properties Testing.....	41
3.5 Food Packaging Properties.....	42
3.5.1 Lead Determination.....	42
3.5.2 Migration Test.....	42
 CHAPTER 4 RESULTS AND DISCUSSIONS	 45
4.1 Synthesis of Tapioca Starch Graft Copolymer and Determination	45
4.1.1 Effect of Monomers Ratio.....	45
4.1.2 Effect of Injection Condition for Preparing Tensile and Impact Specimens.....	46

This material is reserved for educational use only; not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

TABLE OF CONTENTS (continued)

	Page
4.2 Characterization of Tapioca Starch Graft Copolymer.....	52
4.2.1 Rheological Properties.....	53
4.2.2 Identification of Grafting.....	54
4.2.3 Molecular Weight Determination of Side Chain Polymer	56
4.2.4 The Particle Size of Tapioca Starch and Tapioca Starch Graft Copolymer.....	57
4.2.5 Thermal Properties.....	58
4.2.6 Mechanical Properties Testing.....	59
4.2.7 Physical Properties Testing.....	62
4.2.8 Food Packaging Properties.....	64
4.2.9 Biodegradable Properties.....	70
CHAPTER 5 CONCLUSIONS AND SUGGESTIONS	72
REFERENCES	75
APPENDICES	77
APPENDIX A The Tables of Synthetic Data on Tapioca Starch Graft Copolymer and Characterization.....	78
APPENDIX B FT-IR Spectra of Tapioca Starch Graft Copolymers 1-6..	82
APPENDIX C The Particle Size of Tapioca Starch and Tapioca Starch Graft Copolymer.....	86
APPENDIX D DSC Thermograms of Tapioca Starch Graft Copolymers 1-6 and Commercial Plastics.....	94
APPENDIX E Rheological Properties of Tapioca Starch Graft Copolymers 1-6.....	101
APPENDIX F Molecular Weight Determination of Side Chain Polymers..	114
APPENDIX G Notification of The Ministry of Public Health No. 111 (B.E. 2531 (1988)).....	118
APPENDIX H Monthly FOB Price of Tapioca Starch (Unit : Baht / kg)..	123
APPENDIX I Condition of Injection Molding Machine for Preparing Tensile and Impact Specimens	124

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

LIST OF TABLES

Table		Page
2.1	Biodegradable materials cost and producers	12
3.1	The leaching solution used in the residue on evaporation test method	43
4.1	Varying injection molding temperature at nozzle, zone 1, zone 2 and zone 3	47
4.2	Varying injection molding time of 1 st STG INJ, 2 nd STG INJ and 3 rd STG INJ	47
4.3	Varying cooling time of injection molding condition	48
4.4	Plunger speed of injection molding condition	48
4.5	Varying injection pressure 1 st INJ, 2 nd INJ, 3 rd INJ	48
4.6	The optimum condition of injection molding machine for preparing tensile and impact specimens	49
4.7	The tapioca starch graft copolymer was synthesized as reaction conditions 1-6	50
4.8	Infrared spectroscopy characterization	54
4.9	The average molecular weight of side chain polymers 1-6	56
4.10	The particle size of tapioca starch and starch graft copolymers 1-6 ..	57
4.11	Thermal properties determination	58
4.12	Results of testing food packaging properties	69
A-1	The percentage of total solid content (%TSC) of a mixture of St/BA monomers ratio on tapioca starch graft copolymerization at different reaction time	79
A-2	The percentage of total conversion of St/BA monomers ratio on tapioca starch graft copolymerization at different reaction time	79
A-3	Effect of St/BA monomer ratios on tapioca starch graft copolymerization at 3 hours	80
A-4	Polymerization parameters of tapioca starch graft copolymers 1-6 ..	80
A-5	Mechanical properties testing	81
A-6	Physical properties testing	81

This material is for personal use only; not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

LIST OF FIGURES

Figure		Page
2.1	Chemical structure of the components of starch.....	5
2.2	Schematic representation of retrogradation mechanism.....	6
2.3	Tapioca starch granules.....	7
2.4	Shows the “cradle to grave concept“ for material design, role of biodegradable polymers in waste management from agricultural feed stocks.....	9
2.5	Schematic presentation of experimental variations of conversion rate with time in interval I, II and III.....	16
2.6	Schematic diagram of a capillary viscometer.....	18
2.7	Flow curves of idealized fluids.....	20
2.8	Injection molding machine.....	22
2.9	The injection molding cycle.....	23
2.10	Migration process between foodstuff component and packaging materials.....	24
2.11	Migration potential foodstuff component and packaging materials.....	25
3.1	Flow chart of the experiments.....	33
3.2	The 2 L reactor for preparation of tapioca starch graft copolymer..	34
3.3	Dimensions of HDT specimen.....	37
3.4	Dimensions of the tensile specimen.....	37
3.5	Tensile testing machine. (LLOYD; 30 kN).....	38
3.6	Impact tester.....	39
3.7	Shore D hardness tester.....	40
3.8	Analytical balance for density determination.....	42
4.1	The percentage of total conversion of a mixture of St/BA ratios on tapioca starch graft copolymerization at different reaction time	45
4.2	Effect of styrene and butyl acrylate monomers on tapioca starch graft copolymerization.....	46
4.3	%Total solid content of tapioca starch graft copolymers 1-6	51
4.4	%Conversion of tapioca starch graft copolymers 1-6.....	51

This material is prepared for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

LIST OF FIGURES (continued)

Figure		Page
4.5	%free polymer, %G and % GE of tapioca starch graft copolymers 1-6.....	52
4.6	Relation of shear stress and shear rate of tapioca starch graft copolymers 1-6.....	53
4.7	Relation of shear rate and shear viscosity of tapioca starch graft copolymers 1-6.....	54
4.8	FT-IR spectrum of tapioca starch.....	55
4.9	FT-IR spectra of tapioca starch graft copolymers 1-6.....	55
4.10	Heat distortion temperature (°C) of tapioca starch graft copolymers 1-6 and commercial plastics.....	59
4.11	Young's modulus of tapioca starch graft copolymers 1-6 and commercial plastics.....	59
4.12	Tensile Strength of tapioca starch graft copolymers 1-6 and commercial plastics.....	60
4.13	Elongation at break of tapioca starch graft copolymers 1-6 and commercial plastics.....	60
4.14	Hardness of tapioca starch graft copolymers 1-6 and commercial plastics.....	61
4.15	Impact strength of tapioca starch graft copolymers 1-6 and commercial plastics.....	62
4.16	Density of tapioca starch graft copolymers 1-6.....	62
4.17	Moisture content of tapioca starch graft copolymers 1-6.....	63
4.18	Water absorption of tapioca starch graft copolymers 1-6.....	64
4.19	Residue volatile in distill water of tapioca starch graft copolymers 1-6.....	65
4.20	Residue volatile in 4% acetic acid of tapioca starch graft copolymers 1-6.....	66
4.21	Residue volatile in 20% ethanol of tapioca starch graft copolymers 1-6.....	66

This material is reserved for educational use only; not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

LIST OF FIGURES (continued)

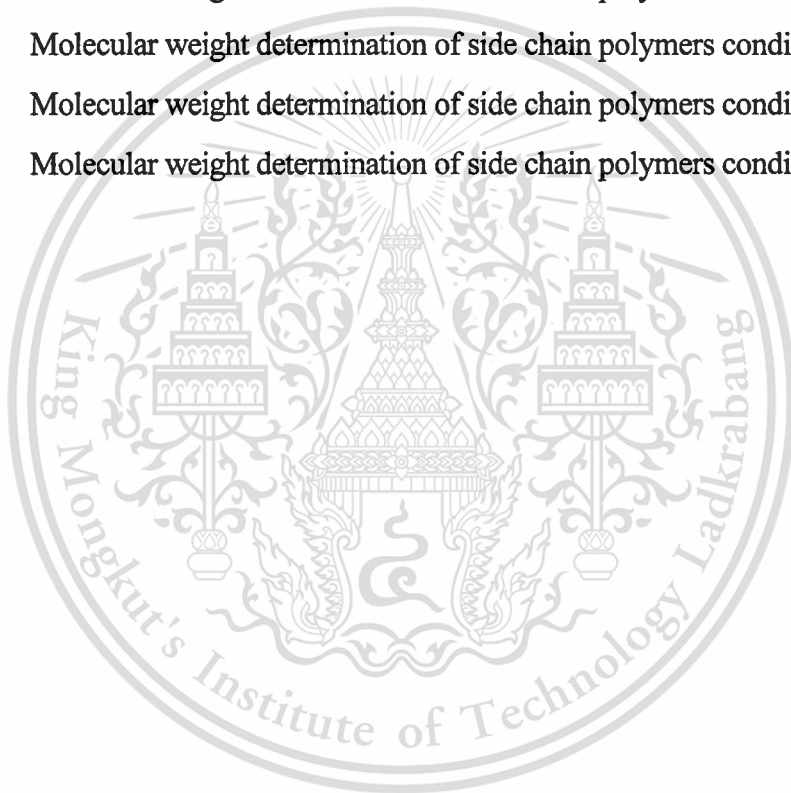
Figure		Page
4.22	Residue volatile in heptane of tapioca starch graft copolymers 1-6.....	66
4.23	Potassium permanganate used for making chemical reaction of tapioca starch graft copolymers 1-6	68
4.24	Biodegradability of tapioca starch graft copolymers by buried in soil.	70
4.25	Biodegradability of tapioca starch graft copolymers by immersed in water.....	71
B-1	FT-IR spectrum of tapioca starch graft copolymer 1.....	83
B-2	FT-IR spectrum of tapioca starch graft copolymer 2.....	83
B-3	FT-IR spectrum of tapioca starch graft copolymer 3.....	84
B-4	FT-IR spectrum of tapioca starch graft copolymer 4.....	84
B-5	FT-IR spectrum of tapioca starch graft copolymer 5.....	85
B-6	FT-IR spectrum of tapioca starch graft copolymer 6.....	85
C-1	Size and distribution of tapioca starch.....	87
C-2	Size and distribution of tapioca starch graft copolymer 1.....	88
C-3	Size and distribution of tapioca starch graft copolymer 2.....	89
C-4	Size and distribution of tapioca starch graft copolymer 3.....	90
C-5	Size and distribution of tapioca starch graft copolymer 4.....	91
C-6	Size and distribution of tapioca starch graft copolymer 5.....	92
C-7	Size and distribution of tapioca starch graft copolymer 6.....	93
D-1	DSC thermogram of tapioca starch graft copolymer 1.....	95
D-2	DSC thermogram of tapioca starch graft copolymer 2.....	95
D-3	DSC thermogram of tapioca starch graft copolymer 3.....	96
D-4	DSC thermogram of tapioca starch graft copolymer 4.....	96
D-5	DSC thermogram of tapioca starch graft copolymer 5.....	97
D-6	DSC thermogram of tapioca starch graft copolymer 6.....	97
D-7	DSC thermogram of tapioca starch	98
D-8	DSC thermogram of PS.....	98
D-9	DSC thermogram of PP.....	99

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

LIST OF FIGURES (continued)

Figure		Page
D-10	DSC thermogram of HDPE.....	99
D-11	DSC thermogram of LDPE.....	100
D-12	DSC thermogram of LLDPE.....	100
F-1	Molecular weight determination of side chain polymers condition 1	115
F-2	Molecular weight determination of side chain polymers condition 2	115
F-3	Molecular weight determination of side chain polymers condition 3	116
F-4	Molecular weight determination of side chain polymers condition 4	116
F-5	Molecular weight determination of side chain polymers condition 5	117
F-6	Molecular weight determination of side chain polymers condition 6	117



ABBREVIATIONS

AA	:	acrylic acid
AGU	:	anhydroglucose unit
BA	:	butyl acrylate
%C	:	percentage of conversion
CAN	:	ceric ammonium nitrate
CMC	:	critical micelle concentration
DSC	:	differential scanning calorimetry
EB	:	elongation at break
FT-IR	:	fourier transform infrared
%G	:	% grafting
%GE	:	% graft efficiency
GPC	:	gel permeation chromatography
HDT	:	heat distortion temperature
IR	:	infrared
MA	:	methyl acrylate
MAA	:	methylacrylic acid
MMA	:	methyl methacrylate
SEM	:	scanning electron microscope
St	:	styrene
T _g	:	glass-transition temperature
TGA	:	thermal gravimetric analysis
THF	:	tetrahydrofuran
UTS	:	ultimate tensile strength
XRD	:	x-ray diffraction

CHAPTER 1

INTRODUCTION

For many years, there have been scientific research relating to plastics concentrated on increasing their durability and stability. Now, plastics have gained a unique position in materials technology for a number of quite different reasons. Initially they were used as replacements for paper, glass, metal and wood in many products, particularly in the area of packaging. Because of their better physical properties (e.g. strength, durability, light weight) and this led to a revolution in the packaging and distribution of consumer products. Plastics have also achieved a dominant position in agriculture which has the new description 'plasticulture' to describe the use of plastics in greenhouses, in protective covers for crops (mulching films), etc. The increasing use of plastics means ever increasing disposal problems of plastic waste. Although the amount of plastic waste in the waste stream is small, but it is increased accumulately. Because of its inability to degradable. In terms of weight, they only make up 8 % of solid waste stream, but in volume terms their proportion comes to about 30 % [4]. This is due to the relatively low bulk density of polymers in comparison to the other materials. At present possible role to solve the problem of waste are as followed :

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

Incineration of plastic waste via clean and controlled combustion for energy generation is another way but the disadvantage are as followed :

- creation of permanent environmental contamination.
- the cost for construction a large plant would be high.
- prevention of emission from waste incineration plants is difficult.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

- incineration has no ecological advantages.

Recycle is simple and widely used today. In general, there are two possible recycling methods for this type of waste. The first one emphasizes on the process of cleaning and separation, so that the end result of the processing is a re-granulate which is close to the pure material in all its properties. The second recycling method gets round the high costs associated with cleaning and separation. The result is a raw material for the manufacture of mixed plastic products. The advantage of this process is low cost of the technological operation. But the disadvantage is the fact that a recycled plastic is of lower quality. Even if it is possible to produce short lived objects from this kind of recycled materials, which will soon be waste again. That means we still have to face the problem of what the final method for the recycling of the waste should be [8] .

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

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

Starch is the second largest biopolymer (cellulose is the most) and starch dominant, especially from tapioca starch is carbohydrate purity more than 97 % , cheap and adequate quality. Because tapioca is one of economic plants in Thailand which grows widely in several areas. Nowadays the agriculturist has encountered problem of uncertain marketing and price decreasing. The research on the usage of tapioca starch in our country is very necessary and important to increase the value of tapioca starch. Besides the incorporation of these natural polymers into plastic not only reduces our dependence on petrochemical-derived monomers, but the natural

polymer will also biodegrade, causing the finished plastic to lose its stability and be reduced to particles to cause minimal environmental damage.

1.1 Objective

- 1.1.1 To study the processing technique of tapioca starch graft copolymer.
- 1.1.2 To study the injection processing of converting tapioca starch graft copolymer to biodegradable packaging material.
- 1.1.3 To study the properties of tapioca starch graft copolymer such as mechanical and thermal properties, etc.

1.2 Scope of This Work

Synthesis the tapioca starch graft copolymer, then study the processing technique of converting tapioca starch graft copolymer to packaging material. Besides studying the effect of processing condition on mechanical, its physical and thermal properties were studied and to compare with commercial plastics, also study the suitability of using the tapioca starch graft copolymer as the food packaging material.

CHAPTER 2

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Starch [17]

Starch is semi-crystalline polysaccharide of repeating glucose units. It originates on the fleshy parts of plants, especially the seeds, tubers or roots of plants. Starch is extracted from plant sources as discrete granules that range in diameter from about 5 to 40 micrometer. Starch granules are insoluble in water at room temperature. They vary in size and shape depending on the plant source.

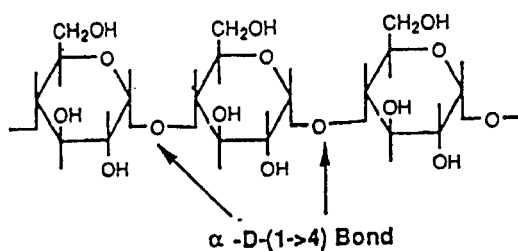
Various type of processes are used in the manufacture of starch depending on the plant source. In general they involve freeing starch granules from the other constituents such as the fiber, protein and purify by screening washing, separation by centrifuge and then dewatering and drying.

2.1.1 Chemical Structure of Starch

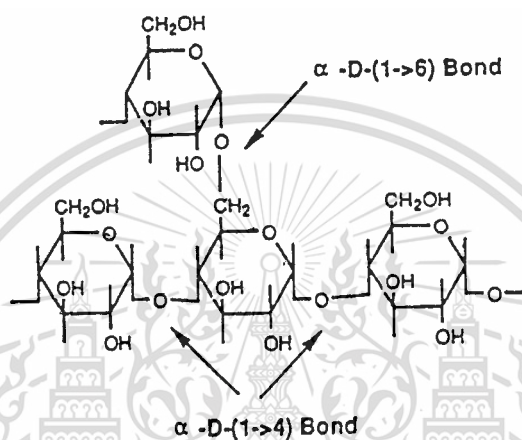
The simplest form of these substances contain only carbon, hydrogen and oxygen and has the structural formula as $(C_6H_{10}O_5)_n$ indicating a polymer of glucose. Starch is a mixture of linear and branched polymers of 1,4- α -D-glucopyranosyl (anhydroglucose [AGU]) units as shown in Figure 2.1

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

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



AMYLOSE – LINEAR POLYMER



AMYOPECTIN – Branched Polymer

Figure 2.1 Chemical structure of the components of starch.

The abundant hydroxyl groups on the starch molecules impart the characteristic hydrophilic properties, giving it an affinity for moisture and dispersibility in water. However because of their linearity mobility and hydroxyl groups, amylose polymers have a tendency to orient themselves in a parallel and approach each other closely enough to permit hydrogen bonding between hydroxyls on adjacent polymers. This is known as “set back” or retrogradation (Figure 2.2). The self-attraction and crystallization tendencies are most readily apparent for the amylose or straight chain component. The association of the polymer chains results in the formation of an intermolecular network that traps waters. At sufficient starch concentrations, gel are produced whereas in dilute solutions the associated forms may precipitate. Precipitation is particularly evident for amylose. Amylopectin association is interrupted because of its highly branched character.

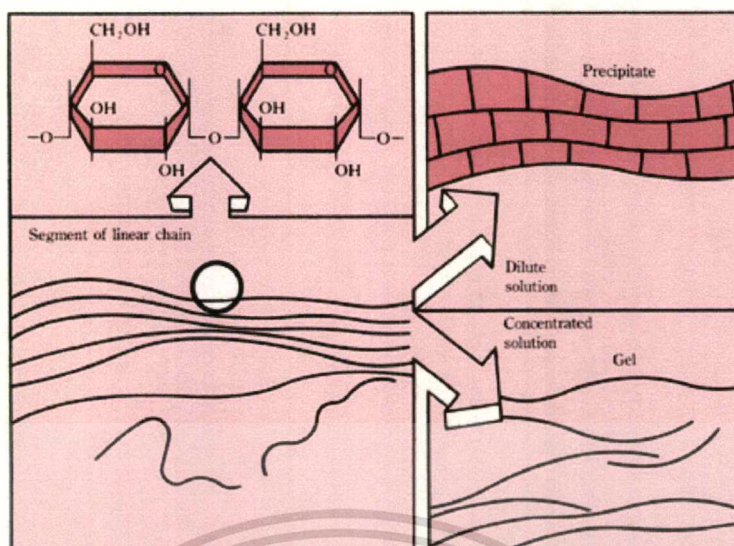


Figure 2.2 Schematic representation of retrogradation mechanism [25]

The linear segments of the amylopectin or amylose molecules run closely parallel, hydrogen bonding between adjacent segments may occur forming micellar crystalline which are responsible for the granule integrity and for imparting birefringence properties. Birefringence is defined as the difference between the refractive index in two orthogonal directions, a loss of birefringence can be observed using polarized light microscopy.

2.1.2 Tapioca Starch

Tapioca starch is manufactured from the large tuberous roots of the cassava or manioc plants which is one of the most important starchy tubers in tropical zones, with 167 million tons of fresh tuber and roots produced annually all over the world. Cassava roots contain 70% water, 24% starch, 2% fibers, 1% protein and 3% fat, minerals and sugars [26]. Tapioca starch granules usually have rounded shapes which are truncated at one end. They average about 20 μm in diameter but may range from 5 to 35 μm in diameter. Tapioca starch contain about 17% amylose and 83% amylopectin.

Tapioca (*Manihot esculents*), or cassava as it is often known, is the third most important crop in Thailand. About 18 to 20 million tons of cassava root are produced

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

each year from over 1 million hectares (2.5 million acres) of planting area. Cassava is widely grown in Thailand because of its drought resistant properties and it can be planted on almost any type of land. In addition to being economically important, cassava is the cheapest raw material for starch production

Tapioca provides a major source of calories for poor families because of its high starch content. With minimum maintenance, the farmers can dig up the starchy root of the cassava and eat it six months to three year after planting. For this reason, people cultivate cassava during times of war or natural disaster when no other food is available.

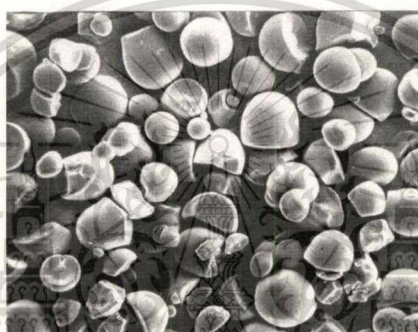


Figure 2.3 Tapioca starch granules

How to prepare tapioca starch.

1. Wash and peel cassava tubers.
2. Grate the cassava to a fine mash.
3. Mix the grated cassava with a high volume of clean water (about 10 times the mash volume).
4. Remove fibers in the mash by sieving the watery mash through a fine muslin cloth or other fine mesh.
5. Allow the fine particles of starch to settle in water.
6. Decant water from the settled starch.
7. If required wash the starch again with water to get white, odorless and tasteless starch.
8. Place the decanted starch on a tray or the drying floor in an oven.
9. Once dry, sieve the starch again to remove any foreign material.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

10. Store the dry starch in an airtight container.

2.2 Biodegradable Plastics [6, 22]

Although the term biodegradable is sometimes used to refer to all degradable plastics, it actually only applies to materials degraded by microorganisms as by the enzymes in bacteria and fungi.

Biodegradable plastics are defined by the International Standards Organization (ISO) as plastics in which degradation results from the action of micro-organisms such as bacteria, fungi, and algae. This process includes direct modification of the plastic materials and the changes that increase the rates of physical and chemical degradation. The speed at which these processes occur depends on a number of factors such as the polymer type, the concentration of active components in the polymers, as well as temperature, moisture content, biological activity and other environmental conditions.

As plastics have been developed to increase their stability, plastic refuse has become a major environmental concern. Stabilized plastics are non-biodegradable and often unsinkable when disposed of at sea. This led to research interest in the 1960s into biodegradable plastics. However with the oil crisis of 1973 much of the research into biodegradable plastics was discontinued on view of plastic recycling efforts designed to reduce dependence on petroleum-based products. In the late 1980s, interest again in plastic disposal. This time interest was due to the cost of municipal solid waste disposal. This leads us to the concept of designing and engineering new biodegradable materials. Materials that have the needed performance characteristics of plastic but after use can be disposed in a manner that is compatible with the environment.

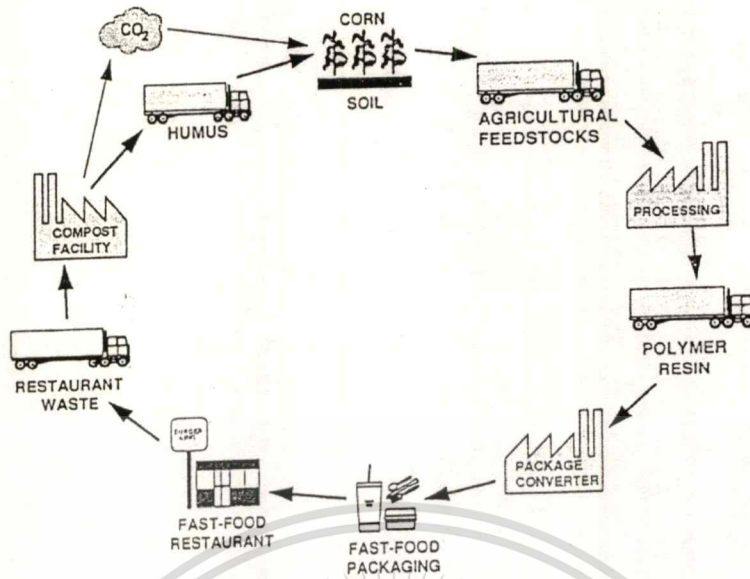


Figure 2.4 Shows the “cradle to grave concept” for material design, role of biodegradable polymers in waste management from agricultural feed stocks.

Biodegradable polymers from renewable resources have gained an increasing interest from industry as well as from research groups the last few years. The advantages of biodegradable plastics are the natural new materials that can be derived, such as starch, proteins, fatty acids, glucose, cellulose, etc. Furthermore, the plastics can be broken down by nature and are therefore environmentally sound. However, the total production of biodegradable plastics is still limited to a worldwide yearly production of 40,000 ton. There are several reasons for the small scale of production:

1. The process of natural resources is higher than the resources for normal plastic. The cheapest biodegradable plastic costs USD 2/kg. Which is 2 times more expensive than the minimum costs for normal plastic.
2. Not all chemical and physical properties of biodegradable plastics are yet known.
3. There is no full knowledge on the processing of biodegradable plastics.
4. From an environmental point of view it is not clear whether a net environmental profits can be achieved.
5. Industries are not familiar with these new products and processes.

The advantages of plastics made of starch:

1. They are easy to process with the conventional techniques, such as injection molding and extrusion.
2. They have sufficient elasticity when breaking.
3. They are biodegradable and can be processed into compost or even cattle feed.
4. They are edible, and not dangerous to health, which can be of use when packaging food.
5. They are soluble in water.
6. They have anti-static characteristics, Which makes them suitable for the packaging of electronic equipment.
7. Because of the polarity, starch based plastics form a barrier against oxygen, which makes it suitable for the packaging of (fresh) foods.
8. The plastic is easy to colour with biodegradable pigments.

Biodegradable plastics are defined by the International Standards Organization (ISO) as plastics in which degradation results from the action of micro-organisms such as bacteria, fungi, and algae. This process includes direct modification of the plastic materials and the changes that increase the rates of physical and chemical degradation. The speed at which these processes occur depends on a number of factors such as the polymer type, the concentration of active components in the polymers, as well as temperature, moisture content, biological activity and other environmental conditions.

In order to make plastics degradable, it is necessary first to break them down into very small particles with large surface area, and second to reduce their molecular weight. Biodegradable products accomplish this differently from those that are photodegradable. Not only do the mechanisms differ, but so do the processing requirements and environmental conditions for degradation.

Biodegradation is the process whereby living organisms (such as fungi or bacteria) secrete enzymes that chemically break down the material into small pieces that can be digested by the microorganism. Plastics can be made biodegradable in two ways:

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

1. By making the polymer itself susceptible to enzyme attack (biopolymer).
2. By incorporating biodegradable additives into the resin, which doesn't necessarily make the polymer biodegradable but leaves a porous plastic article that may disintegrate (additive based polymer).

Biodegradation of both types depends greatly on several factors:

- Environmental conditions such as moisture, temperature, oxygen, pH level.
- Presence and type of microorganisms that secrete enzymes and digest polymer molecules.
- Molecular weight of the polymer (biodegradability increases as molecular weight decreases).
- Relative proportions of polymer and active ingredients.
- Polymer type surface area and thickness of plastic.

The development of biodegradable plastics can be divided into photodegradable, biodegradable and starch based polymer.

2.2.1 Photodegradable Polymer

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

2.2.2 Biodegradable Polymer

A different approach is the production of new polymers from microbiology derived materials by fermentation that demonstrate high degradation rates.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

2.2.3 Starch Based Polymer

The mixture of polymer with natural polymer known to be readily biodegradable such as starch, improve the biodegradation of the copolymer as a whole. These natural polymer is available in great supply and may therefore be competitively priced as compared to oil derived component plastics. However the level of natural biodegradable polymer required to achieve biodegradation of the copolymer and pollution control has been estimated at 30-50%. At these high natural polymer addition rates, the copolymer is difficult to process and loss of physical properties. So this research is try to improve this material can be process easily. The other biodegradable materials produced by any company are listed in table 2.1

Table 2.1 Biodegradable materials cost and producers.

Company	Base Polymer	Feedstock	Cost (\$/lb)	Capacity (MM lb/yr)
Cargill, Minneapolis, MN	Poly lactide (PLA)	Renewable resources, Corn	1.00-3.00	10('94 scale up);250(mid-1996)
Ecochem, Wilmington, DE	Poly lactide Copolymers	Renewable resources, Cheese Whey, Corn	<2.00	0.15 ('94 scale up)
Flexel, Atlanta GA	Cellophane (Regenerated cellulose)	Renewable resources	2.15	100
Zeneca (business unit of ICI)	Poly (hydroxy butyrate-co-hydroxyvalerate), PHBV	Renewable resources, Carbohydrates (glucose), organic acids	8.00-10.00	0.66, additional capacity slated for '96 is 11-22
Union Carbide, Danbury, CT	Polycarprolactone (Tone polymer)	Petrochemical	2.70	<10

Table 2.1 (continued).

Company	Base Polymer	Feedstock	Cost (\$/lb)	Capacity (MM lb/yr)
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
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 repellent, 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 (Environ plastic)	Petrochemical	3.00	10

2.3 Graft Copolymerization

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

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

2.3.1 Emulsion Polymerization [20]

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

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

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

1. the physical state of the emulsion system makes it easy to control the process. Reduced thermal and viscosity problems of the process by using water as the dispersing medium.
2. The product of an emulsion polymerization is synthetic latex can in many instances be used directly without further separations. Such applications as coatings or paints.
3. Possibility of conduction the polymerization at a high rate while at the same time obtaining a polymer of high molecular weight.

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

1. Necessity of introducing an additional operation for separation of the polymer.
2. Unavoidable contamination of the polymer with residues of the emulsifying agent and other components of the system.

2.3.2 Components and Their Locations

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

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

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

Emulsifier is partly dissolved in the continuous phase. If concentration is exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate together to form micelles: and some is absorbed on monomer droplets to stabilized them.

Initiator is dissolved in the continuous phase known as water-soluble initiators are usually used.

2.3.3 The Three Intervals in Emulsion Polymerization

Before the reaction starts, the reactor charge contains two phase, monomer and water. The monomer is located at two sites: in very small micelles and larger monomer droplets. In the early stages of the reaction, during Interval I shown in Figure 2.5, latex particles are being formed and the initial two-phase system becomes one containing three phases : water, monomer free from polymer and latex particles containing

polymer swollen with monomer. The particle number increases initially in this three-phase system; subsequently particle number becomes constant. As the reaction proceeds further during Interval I, the volume of the monomer-swollen polymer phase increases while that of the polymer-free monomer phase decreases. During Interval II, at the end of the reaction, the monomer phase disappears and all unreacted monomer is in the latex particles.

The three intervals of emulsion polymerization are defined in terms of particle number (the concentration of polymer particles in units of number of particles per milliliter) and the separate monomer phase. During Interval I there is a separate monomer phase; during Interval II and III, the particle number remains constant. In Figure 2.5 shown that during Interval I the conversion rate increases rapidly, during Interval II it remains constant or increases slightly and it starts to decrease during Interval III.

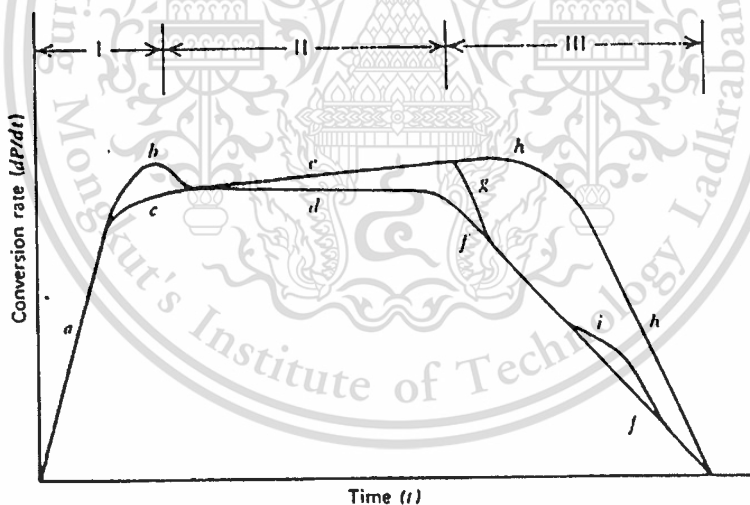


Figure 2.5 Schematic presentation of experimental variations of conversion rate with time in interval I, II and III.

2.4 Plasticization of Polymers

The most graft copolymerization of styrene onto tapioca starch may have a T_g too high for such purposes. The addition of low molecular weight materials to a polymer to make it more flexible is known as plasticization and the diluent is called a plasticizer. American Standard Test Method (ASTM-D-883) adapted the following

definition, a plasticizer is a material incorporated in a plastic to increase its workability and flexibility or distensibility. The major function of the plasticizer is to impart flexibility and workability; it also has a major effect on cost and other properties. The addition of a plasticizer may lower the melt viscosity, hardness, modulus and glass transition temperature of a plastic and higher elongation friction and abrasion loss. All of which pointed to a mechanism which involved penetration tack tensile elongation and tearing as steps on the process of friction and wear.

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

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

2.4.1 Mechanism of Plasticization [12]

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

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

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

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

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

2.5 Rheological Properties of Polymer Melts

Rheological is the studied of deformation and flow of materials emphasis the relationships between stress, strain and time. The flow of polymeric materials is of interest because most processing techniques involve direct flow of polymer melts, many mechanical properties are affected by the relatively small amount of flow. Thorough understanding of the rheological properties of materials help in :

1. correcting processing faults and obtaining a good production rate ; and
2. knowing how to choose the best polymer or polymer combination for use under given process conditions to achieve the desired mechanical properties in the final product.

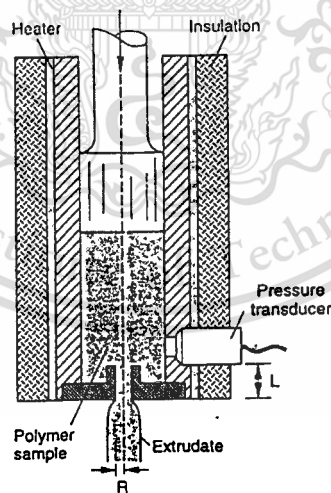


Figure 2.6 Schematic diagram of a capillary viscometer.

A great variety of instruments has been used to measure the viscosity and other rheological properties of liquid and molten polymers. Most of these instruments are capable of measuring the rheological properties as a function of temperature and

rate of shear. A very popular type of instrument for studying the rheological behavior of molten polymers is the capillary viscometer. As shown in Figure 2.6, a molten polymer is forced by a piston or by pressure from a reservoir through a capillary die. The quantity of polymer coming from the capillary per unit of time at a given pressure drop is the basic measurement used to calculate the viscosity.

The capillary rheometer has a number of advantages.

1. The instrument is relatively easy to fill. This is an important consideration since most polymer melts are too viscous to pour readily even at high temperatures.
2. The test temperature and rate of shear are varied readily.
3. The shear rates and flow geometry are similar to the conditions actually found in extrusion and in injection molding.
4. In addition to the viscosity some indication of polymer elasticity is found from the die swell of the extrudate.
5. Finally, factors affecting the surface texture of the extrudate and the phenomenon of melt fracture can be studied.

The main disadvantage of the capillary viscometer is as follows,

1. The rate of shear is not constant but varies across the capillary.
2. The necessity of making a number of corrections in order to get accurate viscosity values.
3. Problems with viscoelastic characterization.
4. Unreliable at high shear rates (temperature effects).

Viscous Flow Behavior [3]

Viscosity is a fundamental rheological parameter of fluids. It is defined as the ratio of shear stress and shear rate.

$$\text{Viscosity } (\eta) = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\sigma}{\dot{\gamma}}$$

The SI units of viscosity are Nsm^{-2} .

Fluids can divide by viscosity depending on shear rate as follow. (see Figure

2.6)

1. Newtonian fluid. This fluids in which the viscosity is a single valued function of the shear rate. Example of this class is water and most organic liquids.
2. Non-Newtonian fluid. This fluids in which the viscosity depends on the shear rate. The shear stress-shear rate behavior of this fluids is not constant.

2.1 Pseudoplastic or Shear thinning. For this class of fluids viscosity decreases as shear rate increases. This is the most common response for polymer melts.

2.2 Dilatancy or shear thickening. This behavior of a melt means that the viscosity increase with increasing shear rate. Example of this class is honey.

2.3 Bingham body or liquid with yield point. Material of this class will not deform if the applied shear stress is less than the yield stress of the material. Above the yield stress the model behaves as a simple newtonian fluid. Mud and greased are examples of materials which can be described as Bingham bodies.

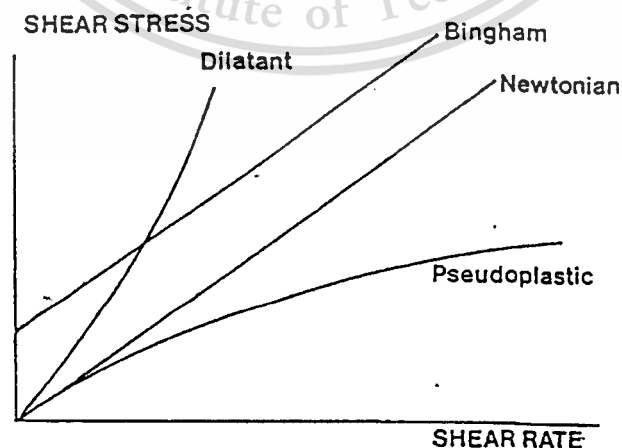


Figure 2.7 Flow curves of idealized fluids.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

Fluids can divide by viscosity depending on time.

1. Thixotropy. A reduction in viscosity during an experiment.
2. Rheopexy or Anti-thixotropy. The viscosity increase with time under a given shear stress.

The manufacturing processes for polymers usually involve considerable shear rates. At these large shear rates the behavior of polymer melts is largely determined by their elastic properties. The aim of the measurement is to show how they relate to process.

2.6 Polymer Processing

Polymer processing is an engineering specially concerned with the operation carried out on polymer to increase their utility.

A plastic material is seldom chosen for a particular application because its mechanical properties are ideal for that usage. The consideration is that material can be processed into the required article easily and economically. The most widely used method for polymer processing is injection molding and therefore the reason is most effective in this study.

2.6.1 Injection Molding [15,16]

The injection molding process is greatly preferred by designers because the manufacture of parts of complex shape and three-dimensions can be more accurately controlled and predicted with injection molding than with other processes. Products can made from granules or powders of thermoplastics, rubbers and thermosets.

The basic principle of injection molding is to inject molten polymer into a closed , cooled mold where it solidifies to give the product. The molding is recovered by opening the mold to release it. Figure 2.8 shows the injection molding machine.

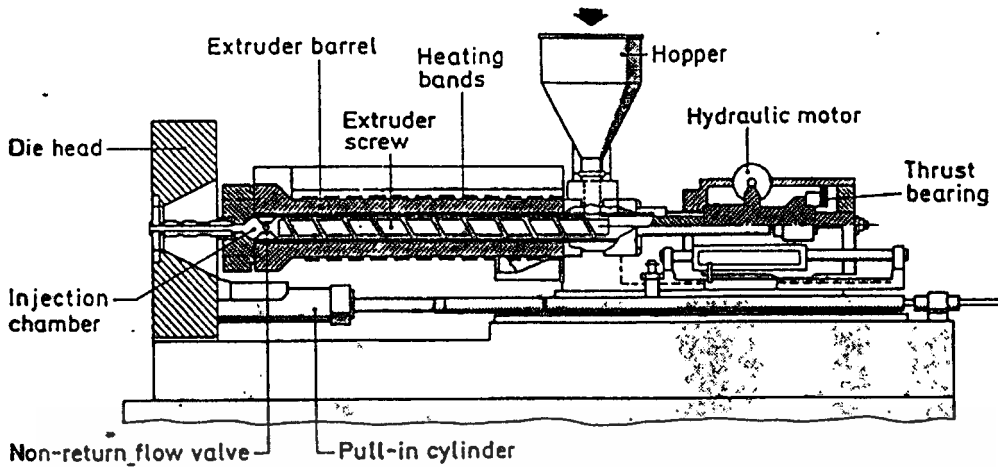


Figure 2.8 Injection molding machine.

As the screw rotates granules or powders from the hopper are melted by heat conducted from the barrel and by viscous heating from the screw. The check valve opens and melt is pushed into the space between the screw and the nozzle. As the screw continues to rotate the pressure developed in the melt by the nozzle pushes the screw backwards towards the hopper. The exact volume of material to fill the mold is melted ahead of the screw is a limit switch. When the backward movement of the rotating screw trips the limit switch, the back-flow check valve closes and the screw stops to rotate. The cycle of operations for the production of injection molding (Figure 2.9) is as follows ;

1. The mold is closed. At this stage it is of course empty. A shot of melt is ready in the injection unit.
2. Injection occurs. The screw stops rotating and moves along the barrel, acting as a plunger force the melt through the nozzle into the mold.
3. The hold-on stage when the screw remains in the forward position maintaining pressure long enough for the melt in the gate region to solidify.
4. While the rest of the molding cools in the mold, the screw rotation starts, This draws in new melt ahead of the screw which causes the screw to move backwards to accumulate a fresh shot melt in front. The rotation stops.
5. The mold opens to eject the product.
6. The mold closes again and the cycle repeats.

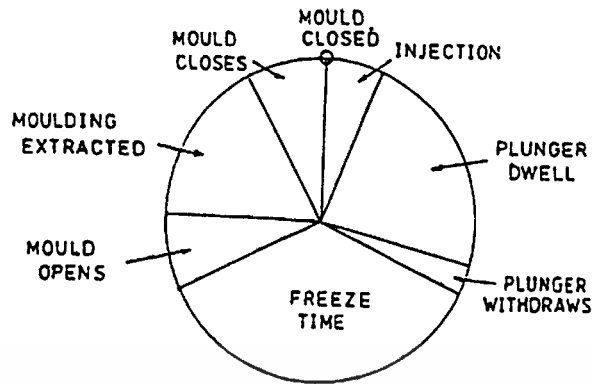


Figure 2.9 The injection molding cycle.

Figure 2.9 shows a typical injection molding cycle. We can see that a large proportion of the total cycle time is taken by cooling the product so that it will not deform on being ejected from the mold, including of course the hold-on time. As a consequence cooling rates are an important concern in the economics of injection molding.

The advantages of injection molding as a process are :

1. Molding are produced completely finished.
2. The process is accurately repeatable.
3. Metal inserts , threads and holes can be molded in.
4. High output rates can be achieved with automatic operation and multi-cavity molds.
5. Relatively low labor cost per unit is obtainable.

The disadvantages are :

1. The capital cost of the injection molding machine is high compared with that of other molding machinery.
2. Tool costs are also similarly high.
3. Unless foaming the material , it is difficult to mold parts with large variation in wall thickness.

2.7 Plastic Packaging for Foodstuffs

It is well known that foodstuffs, once they have been produced, must be protected in such a way that they are reaching the market in high quality. Nowadays food markets are characterized by a high variety of food products offered in very different sorts of packaging which guarantee their preservation. Plastics have already been in use for over 50 years in ever increasing quantities for food and drink packaging. Especially in the field of foodstuffs plastic packaging has to fulfill a series of important tasks necessary for protection and distribution. Two functions of plastic packaging are of major importance: on the one hand they have to guarantee that the packaged foodstuffs reach the consumer in their most original composition, i.e. without loss of ingredients – on the other hand they have to prevent shortening of shelf-life and impairment of characteristic qualities.

In order to fulfill the functions mentioned above, the packaging plastic comes in most cases in direct contact with foodstuffs. For this reason it is necessary to reflect on that the packaging itself is not totally inert and can transfer substances particularly mobile compounds to the packaged food. Since there are interactions between the system environment, packaging and food it is necessary to choose carefully a plastic packaging material which is compatible with the foodstuff. The use of certain plastic materials for food packaging presupposes that any migration of substances is not going to render the food unsafe to eat or make it organoleptically unacceptable to the consumer.

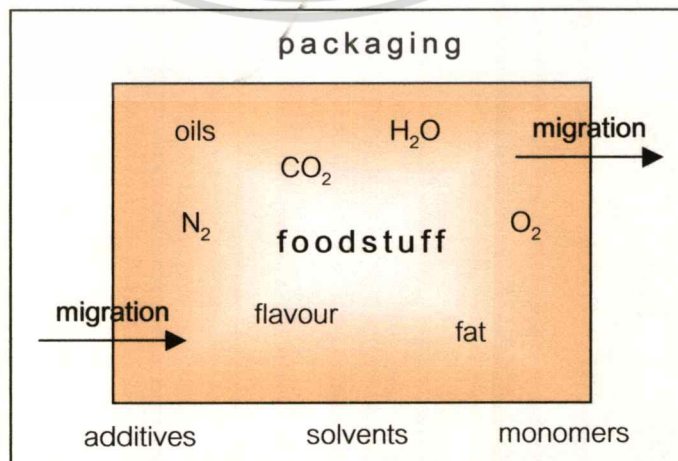


Figure 2.10 Migration process between foodstuff component and packaging materials.

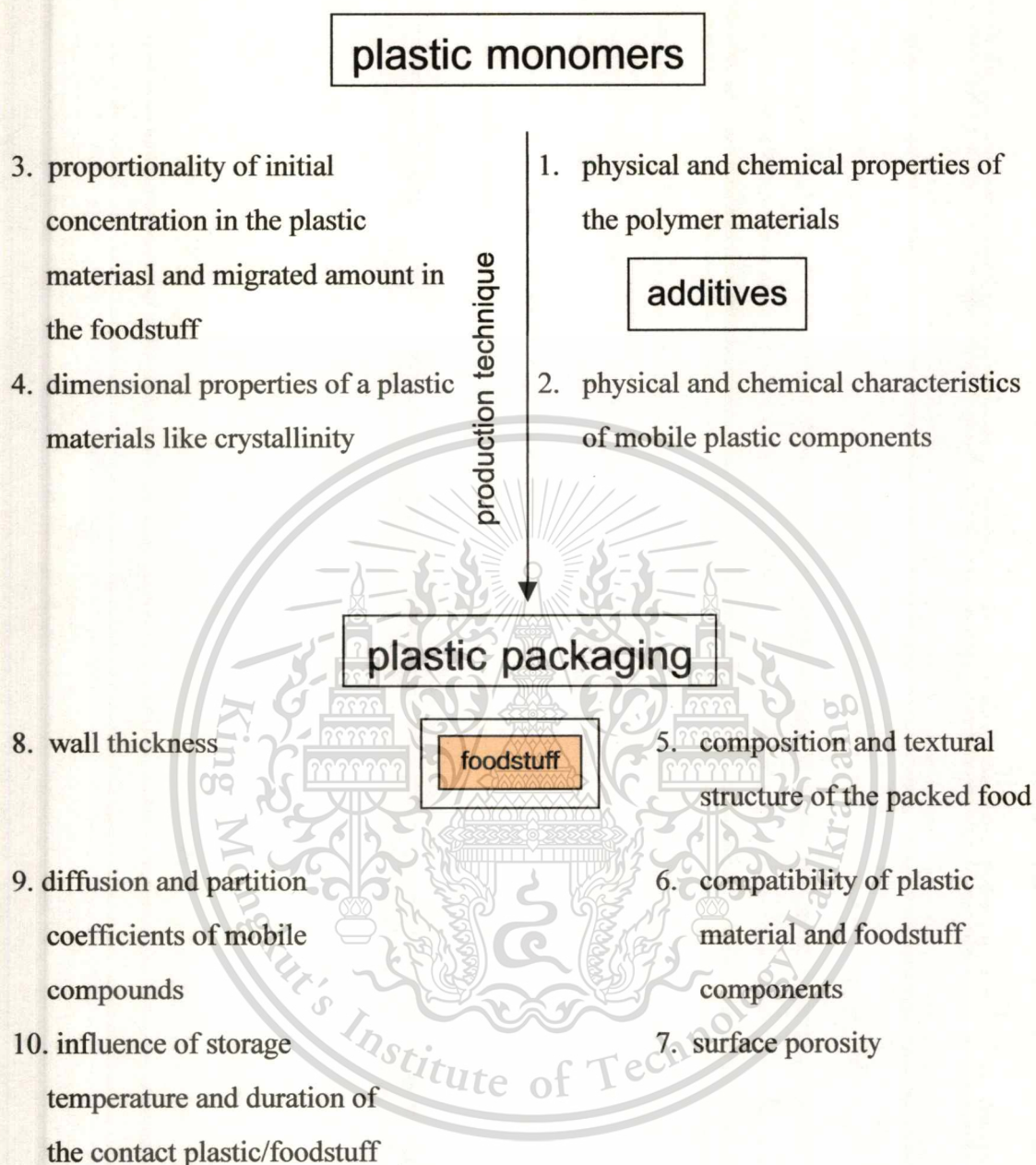


Figure 2.11 Migration potential between foodstuff component and packaging materials.

2.8 Literature Review

Cao, et al. (2002) synthesized water absorption resins of carboxymethyl starch graft acrylamide (CMS-g-AM) by a free radical initiating process. The free radicals were produced by the chemical initiation method in which ceric ammonium nitrate was used as an initiator. Firstly, sample of maize starch and chloroacetic acid in sodium hydroxyl-methanol media. Then, carboxymethyl starch was incorporated in graft polymerization with acrylamide. The evidence of graft copolymers was investigated by using infrared spectra. The effect of the preparation conditions on the substituent degree of starch and the water absorption capacities of carboxymethyl starch graft acrylamide were investigated. The results showed that substituent degree of starch first increased remarkable and then gradually with increased addition capacity of carboxymethyl starch graft acrylamide is 350 g/g and the corresponding substituent degree is 0.75 [4].

Lahman, et al. (2000) carried out the graft copolymerization by methyl acrylate with sago starch in which ceric ammonium nitrate was used as an initiator based on a free radical reaction. The effect of concentration of ceric ammonium nitrate (CAN), concentration of methyl acrylate (MA), sago starch (AGU), studied in terms of the percentages of grafting, grafting efficiency, and rate of grafting. The optimum yield of grafting was obtained when the concentration of CAN, MA, AGU, and H_2SO_4 were used at 8.77×10^{-3} , 0.803, 0.135, and 0.175 mol L^{-1} , respectively. The rate of graft polymerization was explored on the basis of experimental results and reaction mechanism. The graft copolymers were characterized by FTIR spectroscopy, TGA and DSC analysis showed that confirmation of the occurrence of polymer (methyl acrylate) onto sago starch [21].

Athawale and Lele (1998) prepared the grafting of acrylic acid (AA) onto granular maize starch using ceric ammonium nitrate (CAN) as an initiator. The synthetic condition has been studied gravimetrically under nitrogen atmosphere in aqueous medium. It was found that the percentage of grafting and grafting efficiency were all dependent on concentration of ceric ammonium nitrate, concentration

of acrylic acid, concentration of ceric ion, concentration of AA, reaction temperature, polymerization time and material-to-liquor ratio. The variables effecting the graft copolymerization were thoroughly examined. The optimum conditions for effective grafting of acrylic acid onto 2.0g of granular maize starch were initiator concentration = 0.004 mol/L in 0.1 molar HNO_3 , monomer concentration = 0.2775 mol/L, reaction temperature = 35°C , polymerization time = 240 minutes and material-to-liquor ratio = 1:10. The graft copolymers were analyzed by infra-red spectroscopy, x-ray diffraction (XRD), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). XRD studies show that the crystallinity of the starch reduces on grafting. As can be seen from the thermal analysis, grafting of acid onto maize starch reduced its thermal stability. SEM reveals that grafting is purely a surface phenomenon. Hydrogels were prepared by grafting AA onto gelatinized followed by neutralization with NaOH. The maximum water absorption obtained was 250 g/g [1].

Athawale and Rathi.(1997) prepared graft-polymerization of methacrylic acid (MAA) using tetravalent cerium as initiator. The factors affecting the graft polymerization have also been investigated, such as monomer and initiator concentration, time and temperature. The grafting efficiency exhibits progressive improvement with increasing temperature and initiator concentration and time up to 150 min. The confirmation for graft copolymer formation was studied by using acid hydrolysis and infrared spectroscopy. Further, a representative graft copolymer was characterized by X-ray diffraction, thermogravimetric analysis and differential scanning calorimetry [2].

Gao et al. (1994) used canna - starch to prepare starch graft copolymers with methyl methacrylate (MMA) by using manganese pyrophosphate as an initiator. The first effect to graft copolymerization was initiator concentration; to increase concentration increased percentage of grafting. The second was monomer concentration; the highest percentage of grafting was monomer concentration at 3.0 mol/l. The third was canna-starch concentration; percentage of grafting decreased

with increasing starch concentration because ratio of monomer to canna-starch was lower but the grafting efficiency increased when temperature raised from 20 to 50 °C. To raising temperature will improve the swelling capability of canna starch, increase the diffusion rate of the monomer and initiator onto starch granular and raise the rate of grafting [9].

D.R. Patil, M.N. Crookston and G.F. Fanta (1994) reported the preparation of starch graft poly (methyl acrylate),(PMA) 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 copolymer 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 prepared 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 [19].

Liu, et al.(1993) studied graft copolymerization of methyl acrylate(MA) onto potato starch by using ceric ammonium nitrate(CAN) as initiator. The variables effecting the graft were investigated such as reaction time, reaction temperature, initiator, monomer and nitric acid concentrations. The optimum conditions were 2 hr, 50°C, 5.0×10^{-3} , 1.08 and 0.081 mol/l, respectively [14].

Patil and Fanta (1993) characterized starch graft poly (methyl acrylate) copolymer containing 55-60% PMA which prepared from corn starch using ceric ammonium nitrate(CAN) as initiator by examination of reaction variables. Nitric acid concentration was found no significant in graft copolymerization. To increase CAN concentration showed increasing % add-on and % conversion until reached optimum

level (1.5×10^{-3} mol/l or 1 mol of ceric ion per 200 AGU). Percent conversion and add-on increased with reaction carried out with long time and low CAN concentration (1.5×10^{-3} mol/l). These values slightly decreased when reaction temperature was raised from 25 to 40 °C. At high reactant concentration, high conversion of methyl acrylate to grafted PMA could be obtained in less than 0.5 hr at 25 °C [18].

Goni et al. (1993) used ^{13}C n.m.r. spectroscopic methods to characterize the graft copolymer of methyl methacrylate and ethyl acrylate onto amylose corn starch by using ceric ammonium nitrate initiator. The grafting values obtained by gravimetric methods and by ^{13}C n.m.r. spectroscopic methods were compared and similar result were obtained. A study of microstructure of grafted product obtained involving either the quantitative determination of the grafted copolymer composition or the qualitative study of sequence distribution and the stereochemical configuration of grafted copolymer sequences has been carried out. The α -methyl carbon, the quaternary carbon and the carbonyl carbon have been found to be sensitive to the relative stereochemical configuration of the chain segments [10].

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-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 °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 (%EB) and DSC data were evaluated [23].

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, 45 and 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 summarized [11].

Chinnaswamy and Hanna(1991) presented the review outlines the rationale behind starch polymer based thermo-plastic resin production using reactive extrusion processing techniques, as well as characterization of these polymers. They are also reported reactive extrusion processing techniques for starch grafting onto polystyrene. The mixtures of starch, polystyrene, styrene, sodium bicarbonate, citric acid and water were extrusion processed at temperatures of 100 to 200°C, a combination of molecular mechanisms produced a starch graft onto polystyrene and/or copolymer. This product contained about 60% starch on dry weight basis[5].

CHAPTER 3

EXPERIMENT

3.1 Materials

Materials used in this study are described below.

3.1.1 Tapioca Starch and Monomers

3.1.1.1 Tapioca starch(super high grade) was kindly supplied by Thai Wah Public Co.,Ltd. with moisture content 13.5%, starch 84% and viscosity 550 B.U.

3.1.1.2 Styrene monomer was purchased from Industrial Chemicals Promotion Co.,Ltd. with purity 99.6% (by wt) and inhibitor 25 to 30 ppm. This monomer was commercial grade but used without further purification.

3.1.2 Initiator

3.1.2.1 Potassium persulphate ($K_2S_2O_8$) was analytical grade purchased from Famitalia Colo Erba Co.,Ltd. The initiator solution was prepared by dissolving 27.0 g of $K_2S_2O_8$ in 1000 ml of 1 N nitric acid (HNO_3).

3.1.3 Emulsifier

3.1.3.1 Nonyl phenol ethoxylate (40 mole ethoxylate group, NP-40) was commercial grade used as emulsifier.

3.1.3.2 Sodium lauryl ether sulfate

3.1.4 Other Chemicals

3.1.4.1 0.54 M Na_2EDTA (prepared from commercial grade)

3.1.4.2 Propylene glycol (Commercial grade)

This material is for research use only. It is not to be used for commercial use.

Forbidden to modify the content, and cite the document when use.

- 3.1.4.3 Sodium hydroxide (analytical grade)
- 3.1.4.4 Ethylene glycol (commercial grade)
- 3.1.4.5 Butyl acrylate (commercial grade)
- 3.1.4.6 Perchloric acid (analytical grade)
- 3.1.4.7 Acetone (distilled from commercial grade)
- 3.1.4.8 Polypropylene (commercial grade, PP 1100NK)
- 3.1.4.9 High density polyethylene (commercial grade, HDPE G2855)
- 3.1.4.10 Low density polyethylene (commercial grade, LDPE J4324)
- 3.1.4.11 Linear low density polyethylene (commercial grade, LLDPE L2009F)
- 3.1.4.12 Polystyrene (commercial grade for injection)

3.2 Instruments

The instruments used in this study are listed below:

- 3.2.1 Four necked 2 L glass reactor with paddle type agitator and very rotor speed motor.
- 3.2.2 Hot-Air Oven
- 3.2.3 Granulator (BOSCO)
- 3.2.4 Two-Rolls Mill (Lab Tech)
- 3.2.5 Injection Molding Machine (Cosmo; TTI-220/80 HITECH)
- 3.2.6 Tensile Testing Machine. (LLOYD; 30 kN)
- 3.2.7 Capillary Rheometer (Rosand Precision Advanced Capillary Extrusion Rheometer)
- 3.2.8 Fourier Transform Infrared Spectrometer (Brücker IFS 28)
- 3.2.9 Differential Scanning Colorimeter (Shimadzu)
- 3.2.10 Izod Impact Resistance (YASUDA)
- 3.2.11 Shore D Durometer
- 3.2.12 Deflection Temperature under load (YASUDA)
- 3.2.13 Particle Size Analyzer (Mavern 1.1a, Mastersizer X)

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

3.2.14 Gel Permeation Chromatography (GPC 150, Waters)

3.2.15 Soxhlet Extraction Apparatus.

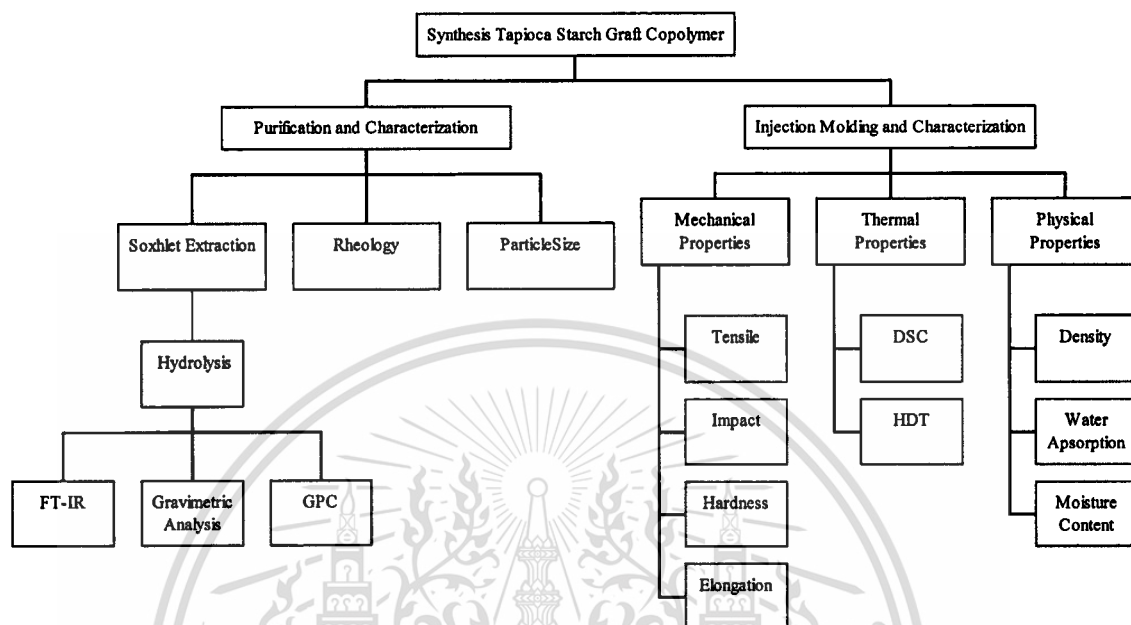


Figure 3.1 Flow chart of the experiments.

3.3 Synthesis of Tapioca Starch Graft Copolymer and Purification

3.3.1 Graft Copolymerization

In graft copolymerization reaction, tapioca starch (150 g) in 1800 ml of distilled water was gelatinized for 1 hr. at the temperature 90°C, in 2L four-necked glass reactor under nitrogen atmosphere. A rotor speed was at 300 rpm. After cooled down to 60°C, NP-40 (10% by weight of monomer) was added and stirred until it became homogeneous solution, followed by the required amount of monomers, Na₂EDTA (37.5 ml) and propylene glycol (1.5 ml), respectively. The mixture was stirred at the rotor speed 500 rpm for 10 min and then 150 ml of initiator solution was added. The reaction was allowed to stir continuously for 3 hrs at 60°C and 1 hr at 90°C. After completion of the reaction, 1 N NaOH was added to neutralize the

solution and dried with hot air oven at temperature between 50-55°C until its weight constant.

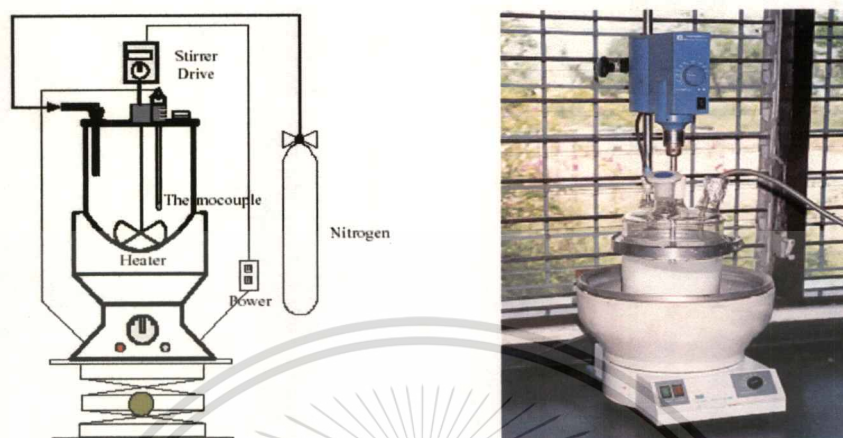


Figure 3.2 The 2 L reactor for preparation of tapioca starch graft copolymer

3.3.2 Ungrafted Polymer Separation

To remove ungrafted polymer, the dried sample was weighed accurately 2 g and extracted in soxhlet extractor with acetone for 72 hrs. Ungrafted polymer was solubilized in acetone-extracted solvent in round bottom flask and then dried by rotary evaporator. The weight of this fraction was used to calculate the percentage of ungrafted polymers in the tapioca starch graft copolymer.

3.3.3 Side Chain Grafted Copolymer Separation

The side chain grafted copolymer was separated from tapioca starch graft copolymer by hydrolysis. The purified tapioca starch graft copolymer was weighed accurately 1 g added to 100 ml of glacial acetic acid. The mixture was stirred for 1 hr at temperature about 90-100°C to swell the graft copolymer, followed by hydrolysis by adding dropwise 2 ml of 60% perchloric acid within 1-2 min. The mixture became clear and then poured into cooling water immediately to precipitate the side chain copolymer. The precipitate was isolated by filtration, thoroughly washed several times with water and dried at 60°C to constant weight.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

3.4 Characterizations

3.4.1 The Particle Size of Tapioca Starch Graft Copolymer.

The average size was studied by particle size analyzer model MasterSizer X (Mavern Instruments Ltd., UK.) and calculated with MAVERN Ver. 1.1 a. The emulsion of tapioca starch graft copolymer was suspended in deionized water.

3.4.2 Molecular Weight Determination

Size exclusion chromatography was the GPC model Waters 150C equipped with the styragel column and the refractive index detector. The molecular weight of styragel in the column is between 5×10^2 to 1×10^7 . The column was calibrated with polystyrene standard. Approximation 15 mg of side chain grafted polymer was weighed and stirred with 10 ml of tetrahydrofuran (THF) solvent for 3 days at room temperature. Insoluble material was separated by centrifugation and supernatant was filtered through a $0.45 \mu\text{m}$ nylon filter before injection. THF was used as an eluent at a flow rate 1.0 ml/min, at 40°C

3.4.3 Gravimetric Characterization

Grafting yield parameters were calculated as following:

$$\text{percent grafting (\%G)} = \frac{W_1 - W_0}{W_1} \times 100$$

$$\text{percent grafting efficiency (\%GE)} = \frac{W_3}{W_1 + W_3} \times 100$$

where W_0 = tapioca starch weight
 W_1 = tapioca starch graft copolymer
 W_2 = ungrafted copolymer
 W_3 = side chain grafted copolymer

3.4.4 Total Solid Content and Conversion

The total solid content of tapioca starch graft copolymer was determined by weighing 2 g of the resulting product after complete polymerization into a dish and drying with hot-air oven at 110°C for 2 hrs. Then cooled down to room temperature in desiccator and weight accurately. After drying the sample weight was constant.

The percentage of total solid content (%TSC) and percentage of conversion (%C) were calculated by the following formulas:

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

where A = weight of dish (g)
 B = weight of dish with sample before drying (g)
 C = weight of dish with sample after drying (g)

$$\%C = \frac{x}{y} \times 100$$

where x = total solid content from experiment
 y = total solid content from the calculation

3.4.5 Identification of Grafting

Fourier Transform Infrared spectrophotometer (Brücker IFS 28) was used to characterize the tapioca starch graft copolymer. The KBr pellets were prepared for the IR spectra recording in the frequency range of 4000-400 cm⁻¹.

3.4.6 Thermal Properties Determination

3.4.6.1 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter (DSC 50, Shimadzu, Japan) was used to determine glass transition temperature (T_g) of tapioca starch graft copolymer, approximately 10 mg of each sample was sealed inside aluminum DSC pan and

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

empty aluminium pan was used as reference. The sample was run from 30°C to 250°C at heating rate 10°C /min.

3.4.6.2 Heat Distortion Temperature (HDT)

The sample was cut from a molding specimens by using the punching machine following ASTM D648. The sample bar of size is 13.00 mm wide × 4.00 mm thick × 127 mm long. Three specimens were tested under a load of 66 psi (0.45 MPa) and the temperature raised at 2°C /min

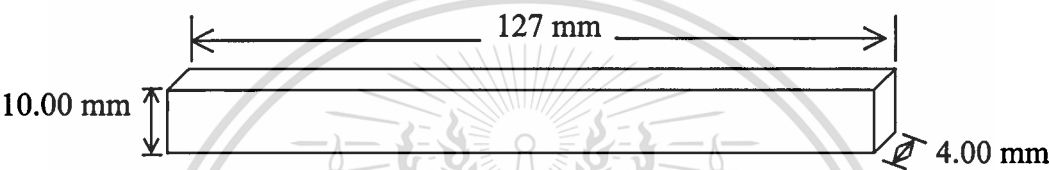


Figure 3.3 Dimensions of HDT specimen.

3.4.7 Mechanical Properties Testing

The tapioca starch graft copolymer obtained from the hot air oven at temperature about 50-55 °C until its constant weight. The dried tapioca starch graft copolymer was granulated by using Bosco granulator. Tensile and impact specimens were prepared using injection molding machine. The tensile and impact molds were used in accordance with ASTM D 638M and ASTM D 256, respectively.

3.4.7.1 Tensile Testing

The tensile specimen of size 10 mm wide ×2.50 mm thick × 151 mm long was tested on a tensile testing machine. Five specimens were tested at maximum load of 30 kN, crosshead speed of 50 mm/min and gauge length of 50 mm.

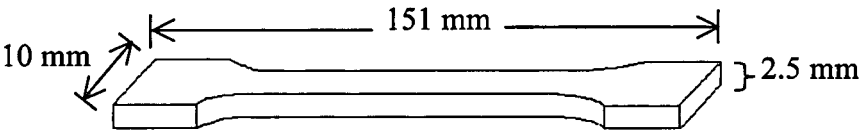


Figure 3.4 Dimensions of the tensile specimen.



Figure 3.5 Tensile testing machine (LLOYD; 30 kN).

Tensile Strength

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

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

where σ = tensile strength (MPa or N/mm²)

F = force at yield or at break(N)

A = initial cross-sectional area of the test specimen (mm²)

Elongation at Break

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

$$\%EB = \frac{(I - I_0)}{I_0} \times 100$$

where $\%EB$ = elongation at break (%)

I = the distance between gauge marks at break (mm)

I_0 = the initial distant between gauge marks or gauge length, which set at 50 mm.

Modulus

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

$$E = F/A$$

Where E = modulus (MPa)

F = load (N)

A = initial cross-section area of the test specimen (mm^2)

3.4.7.2 Impact Testing



Figure 3.6 Impact Tester

Notched izod impact strengths of ten specimens of impact bar were measured on Yasuda pendulum type impact tester following ASTM D256. The impact strength (IS) of each specimen could be calculated from the equation as follow:

$$IS = W/A$$

Where IS = impact strength (kJ/m^2)

W = loss energy (kJ)

A = cross-section area of the notched test specimen(m^2)

3.4.7.3 Hardness Testing

The hardness value was measured from Shore D-type hardness tester following ASTM D785. The sample was laid down on the pan and then pressed under 5 kg of load for 10 second, read the result. Mean values of five specimens were determination.

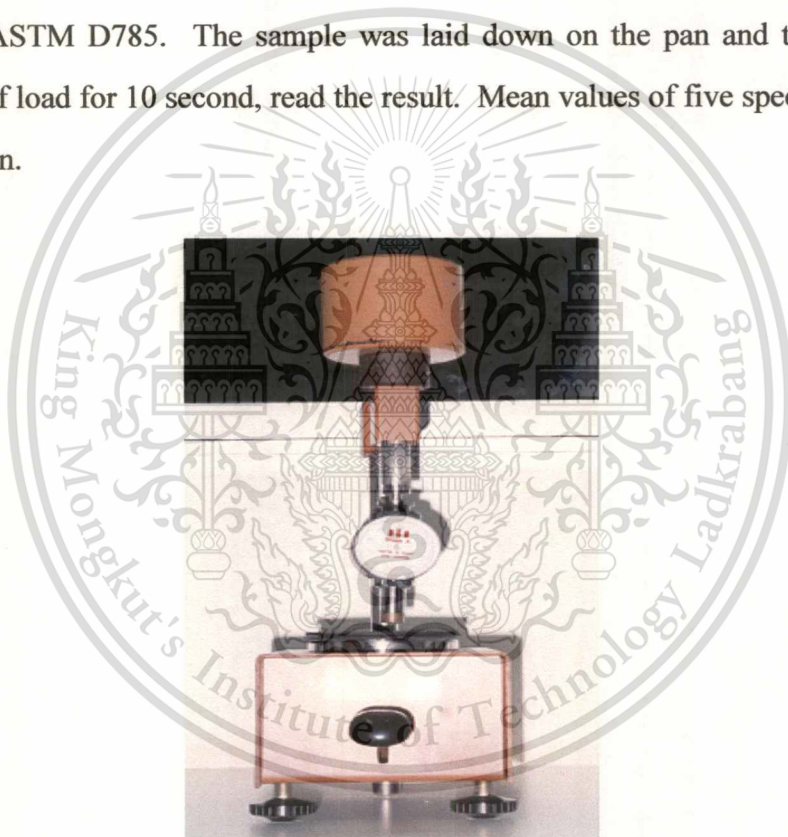


Figure 3.7 Shore D hardness tester



Figure 3.8 Analytical balance for density determination

3.5 Food Packaging Properties

3.5.1 Lead Determination

1.0 g of the tapioca starch graft copolymer sample was added in a quartz evaporating dish. Added 10 drops of sulfuric acid and heated slowly to evaporate most of the sulfuric acid. Dry over a direct flame and increasing the flame, then continue to heat at approximately 450 °C to incinerate. Moisten the content of the evaporating dish with sulfuric acid and heated again. Repeat this procedure until almost white ash is obtained. The residue was dissolved in 10 ml of 0.1 N nitric acid and then lead was determined by atomic absorption spectrophotometer.

3.5.2 Migration Test

3.5.2.1 The Residue on Evaporation Test Method

To extracted sample used the leaching solution in Table 3.1 by using volume of leaching solution (ml) to surface area (cm²) of sample was 2:1. The extracted condition was conducted at temperature 60 °C for 30 minutes, except heptane extracted at room temperature for 60 minutes. Then removed the sample from the leaching solution and allowed to stand in room temperature.

3.4.8 Physical Properties Testing

3.4.8.1 Moisture Content

Take specimen to dried in a hot air oven at 50°C for constant weight, record their masses and then stand in normal atmosphere for 1 day, after that weight and record. Moisture content was calculated as follow:

$$\% \text{ moisture content} = \frac{m_1 - m_0}{m_1} \times 100$$

Where m_0 = weight of sample after dried

m_1 = weight of sample after stand in normal atmosphere

3.4.8.2 Water Absorption

Take specimen to dried in a hot air oven at 50°C for constant weight, record their masses and then immersed in container containing water for 1 day. After that removed the excess water and weight. Water absorption was calculated as follow:

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

3.4.8.3 Density

The density of sample was determined by immersion method. The immersion liquid should be freshly distilled water, or distilled water free from air by boiling before the test.

Calculate the density from the following formula :

$$\text{Density (g/cm}^3\text{)} = \frac{a \times d_s}{a - b}$$

Where a = mass of test piece in air (g)

b = mass of test piece in immersion liquid (g)

d_s = density of immersion liquid (g/cm³)

Table 3.1 The leaching solution used in the residue on evaporation test method.

Type of food	Leaching solution
Oils, fats and fatty food	heptane
Alcoholic drink	20% ethanol
Food other than oils, fats, fatty food and other than alcoholic drink	
Food with pH over 5	Water
Food with pH below 5	4% acetic acid

Transferred 200 ml of test solution (if heptane is used as the leaching solution) to a round-bottom flask and concentrated under reduced pressure to several millilitres. Washed the flask twice each time with approximately 5 ml of heptane. Transferred the concentrate to quartz evaporating dish of known weight, dried at 105° C for 2 hrs, and allowed to cool in a desiccator. After that, weighed the content.

Other leaching solution, 200ml of test solution transferred to quartz evaporating dish of known weight, evaporated with water bath, dried at 105°C for 2 hours, and allowed to cool in a desiccator. After that cooling, weighed the content.

The amount of residue on evaporation was calculated by the following formula.

$$\text{Residue on evaporation (ppm)} = \frac{(a-b) \times 1,000}{\text{Amount of test solution (ml)}}$$

Where :

- a = weight of dried quartz evaporating dish after using leaching test solution (mg)
- b = blank test value obtained by using the same amount of leaching test solution (mg)

3.5.2.2 Consumption of Potassium Permanganate

Added 100 ml water, 5 ml diluted sulfuric acid (concentrate sulfuric acid : water = 1:2), and 5 ml 0.002M potassium permanganate solution to clean an erlenmeyer flask. The mixture was boiled for 5 minutes, then discard the solution and washed the flask with water. To this erlenmeyer flask, added 100 ml test solution, 5 ml diluted sulfuric acid (concentrate sulfuric acid : water = 1:2), 10 ml 0.002M potassium permanganate solution and heated to boil for 5 minutes. Stop heating and immediately added 10 ml of 0.01N sodium oxalate solution to decolor. Titrated with 0.002M potassium permanganate solution until a slight crimson color persists.

A blank test under the same condition was performed separately. The consumption of potassium permanganate was calculated from the following formula.

$$\text{Consumption of potassium permanganate (ppm)} = \frac{(a-b) \times 1,000}{100} \times 0.316$$

Where :

a = volume of 0.002 M potassium permanganate solution used in the actual titration (ml)

b = volume of 0.002 M potassium permanganate solution used in the blank titration (ml)

3.5.2.3 Lead in 4% Acetic Acid Extracted .

Prepared the test solution using 4% acetic acid as the leaching solution and then the test for lead was performed.

3.5.2.4 Migration of Color Extracted by Test Solution.

50 ml of the test solution in a nessler tube with internal diameter of 20 mm, external diameter of 24 mm, distance of 20 cm from bottom to lower face of stopper, and with the graduation by 5 ml up to 50 ml. Observed against a white background vertically and laterally.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

CHAPTER 4

RESULTS AND DISCUSSIONS

In this study, the result and discussion would be presented in two parts. Firstly, the synthesis of tapioca starch graft copolymer by emulsion polymerization involved the determination and processing of tapioca starch graft copolymer by injection molding will be presented. The second part was about the study of tapioca starch graft copolymer characterization.

4.1 Synthesis of Tapioca Starch Graft Copolymer and Determination

4.1.1 Effect of Monomers Ratio

Tapioca starch was used to graft polymerization with a mixed monomers between styrene (St) and butyl acrylate monomers(BA). The mixed monomers was used for 2 mole of starch . The effect of synthetic time on percentage of total conversion of starch graft polymerization at various St/BA ratios are shown in Figure 4.1-4.2 . For data, these are given in the Appendix A, Table A-1 – A-3.

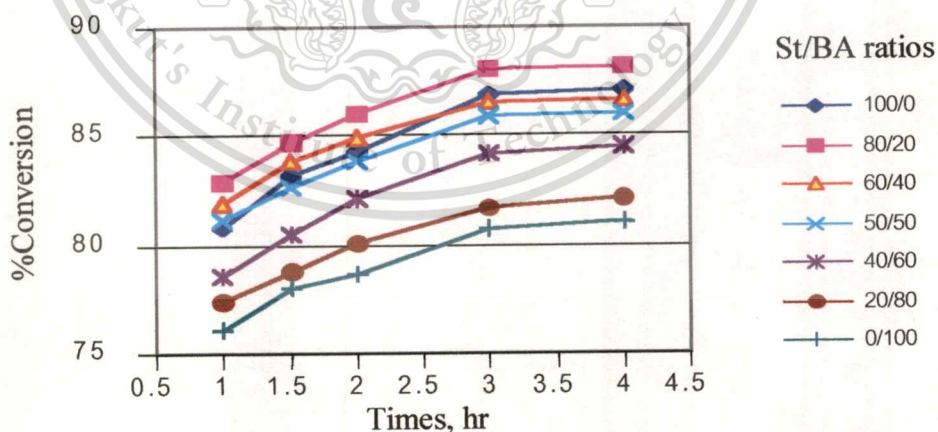


Figure 4.1 The percentage of total conversion of St/BA ratios on tapioca starch graft copolymerization at different time.

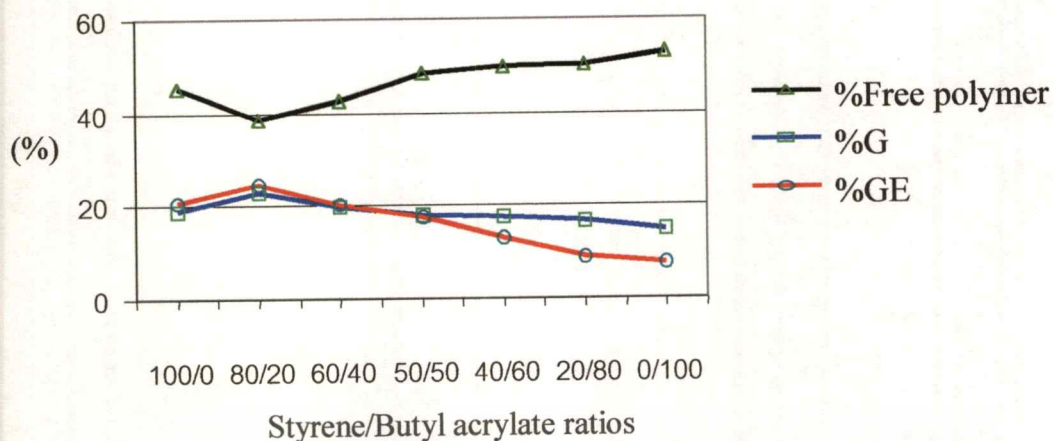


Figure 4.2 Effect of styrene and butyl acrylate monomers on tapioca starch graft copolymerization.

Figure 4.1 highlights the consistent increase in the rate of conversion from 1 up to 3 hrs. The conversion is observed beyond 1 hrs., leading to an optimum %conversion at 3 hrs.

Figure 4.2 exhibits the dependence of %free polymer, %G and %GE on the monomer ratio. The monomer ratio was changed by decreasing the quantity of styrene and increasing the quantity of butyl acrylate in the reaction mixture.

It is evident that the decrease in the percentage of free polymer favours the rate of grafting, presumably due to the formation of less homopolymer in the growing grafted chain. The optimum values for %G of 22.70% and for %GE go 24.80% were obtained at 80/20 of St/BA monomer ratio.

4.1.2 Effect of Injection Condition for Preparing Tensile and Impact Specimens

Injection molding technique was to prepare the sample for tensile and impact test. Injection temperatures, pressure, time, cooling time and plunger speed of the injection molding machine were varied. The external features of specimens were chosen to use as the criteria to obtain the optimum shaping condition. The resulting are shown in Table 4.1–4.5.

Table 4.1 Varying injection molding temperature at nozzle, zone 1, zone 2 and zone 3.

Injection temperature, °C				Visual test results of specimens
Nozzle	Zone 1	Zone 2	Zone 3	
150	150	140	130	Received specimen was burn due to the temperature was too high consequently polymer was degraded.
150	140	130	120	Received specimen was complete.
150	130	120	110	Received specimen was not complete due to the temperature was not high enough to make the polymer melt and flow.

The effect of injection temperature on completed specimen of tapioca starch graft copolymer was shown in Table 4.1. It can be seen that the injection temperature of the processing was optimized when injected at 140°C, 130°C and 120°C of injection zone 1,2 and 3, respectively and nozzle temperature was 150°C. It was found that the specimens had dark brown color when the injection temperature was higher than the optimum conditions.

Table 4.2 Varying injection molding time of 1st STG INJ, 2nd STG INJ and 3rd STG INJ.

Injection time ,second			Visual test results of specimens
1 st STG INJ	2 nd STG INJ	3 rd STG INJ	
45	40	35	Received specimens were complete.
40	35	30	Received specimens were not complete.
35	30	25	Received specimens were not complete.

Table 4.2 shows the effect of injection molding time on visual test results of specimens. The injection molding time at the first, the second and the third injection stages of the tapioca starch graft copolymer were optimized when injected at 45, 40 and 35 seconds, respectively.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

Table 4.3 Varying cooling time of injection molding condition.

Cooling time, second	Visual test results of specimens
200	Not able to take specimen from the mold because of some part of the specimen struck at the gate.
100	Difficult to take specimen from the mold.
50	Easily to take specimen from the mold.

From the experiment by changing the cooling time as shown in Table 4.3, 50 second was the best cooling time for good specimen if the time longer than 50 second the specimen will be stick the mold.

Table 4.4 Plunger speed of injection molding condition.

Plunger speed, mm/second	Visual test results of specimens
10	Received specimens were not complete.
20	Completed specimen.

Outcome from changing plunger speeds as shown in the Table 4.4. It found that twenty percentage was the optimum plunger speed if the speed lower than the optimum speed the polymer was not flow.

Table 4.5 Varying injection pressure 1st INJ, 2nd INJ, 3rd INJ.

Injection pressure ,N/m ²			Visual test results of specimens
1 st INJ	2 nd INJ	3 rd INJ	
3.92×10 ⁶	3.43×10 ⁶	2.94×10 ⁶	Not able to injection completed specimen.
4.41×10 ⁶	3.92×10 ⁶	3.43×10 ⁶	Enable injection.

The effect of injection pressure on appearance of the tapioca starch graft copolymer was investigated (Table 4.5). It was found that the specimen had brown

color and good shape when the injection pressure at the first, the second and the third injection stages were 4.41×10^6 , 3.92×10^6 and 3.43×10^6 N/m², respectively.

Table 4.6 The optimum conditions of injection molding machine for preparing tensile and impact specimens were shown below :

Injection temperatures	Nozzle	150 °C
	Zone 1	140 °C
	Zone 2	130 °C
	Zone 3	120 °C
Injection time	1 st STG INJ	45 second
	2 nd STG INJ	40 second
	3 rd STG INJ	35 second
	Cooling time	50 second
Plunger speed	20 mm/second	
Injection pressure	1 st INJ	4.41×10^6 N/m ²
	2 nd INJ	3.92×10^6 N/m ²
	3 rd INJ	3.43×10^6 N/m ²

4.1.3 Varying Condition for Synthesis Tapioca Starch Graft Copolymers

In this study, all tapioca starch graft copolymers were prepared at the mixture of styrene and butyl acrylate was 80/20. As studied in the previous section, polymerization reactions were six conditions as following:

Condition 1, tapioca starch graft copolymer was synthesized by reacting a mixture of gelatinized tapioca starch and styrene with butyl acrylate by emulsion polymerization. Potassium persulfate in 1N HNO₃ was used as an initiator and NP-40 used as a surfactant followed by neutralization with 1N NaOH. The drying product from synthesis was not removed monomers. before injection molding.

Condition 2, the tapioca starch graft copolymer was prepared with the same process as condition 1, except changing surfactant type from NP-40 to sodium lauryl ether sulfate.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

Condition 3, the tapioca starch graft copolymer was the same process as condition 1, but using tapioca starch flour directly without gelatinization.

Condition 4, the tapioca starch graft copolymer the same process as condition 1, but dissolved the initiator with water.

Condition 5, the tapioca starch graft copolymer was prepared the same condition 1, but adding a step to clean monomer with water.

Condition 6, tapioca starch graft copolymer was prepared the same as condition 1, after that removed the monomer with isopropanol.

Table 4.7 The tapioca starch graft copolymer was synthesized as reaction conditions 1-6.

Reaction condition	Compound			Note
	Starch condition	Surfactant	Initiator	
1	gelatinized tapioca starch	NP-40	$K_2S_2O_8$ in 1 N HNO_3	normal condition
2	gelatinized tapioca starch	Sodium lauryl ether sulfate	$K_2S_2O_8$ in 1 N HNO_3	vary surfactant type
3	granular tapioca starch	NP-40	$K_2S_2O_8$ in 1 N HNO_3	minimized process
4	gelatinized tapioca starch	NP-40	$K_2S_2O_8$ in distilled water	vary solvent of initiator
5	gelatinized tapioca starch	NP-40	$K_2S_2O_8$ in 1 N HNO_3	washed monomer of tapioca starch graft copolymer with water
6	gelatinized tapioca starch	NP-40	$K_2S_2O_8$ in 1 N HNO_3	washed monomer of tapioca starch graft copolymer with isopropanol

The data of %TSC, %conversion, %free polymer, %G and %GE were shown in Appendix A, Table A-4. The specimens after injected have brown color.

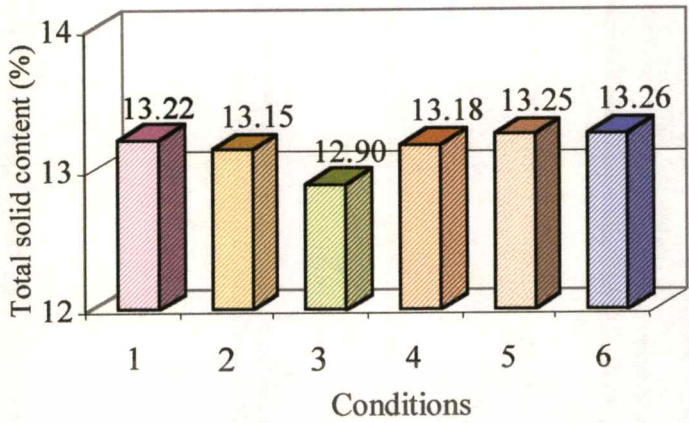


Figure 4.3 %Total solid content of tapioca starch graft copolymers 1-6.

Figure 4.3 showed that effect of synthetic tapioca starch graft copolymer six conditions on the total solid content . It can be seen that the percentage of total solid content range were 12.9-13.26%, which all tapioca starch graft copolymer were not exhibited different significant. But tapioca starch graft copolymer 3 was the lowest percentage of total solid content. The difference value between tapioca starch graft copolymer 1 and 3 was 2.5%

The effect of the synthetic condition on the % conversion has been shown in Figure 4.4. It can be noted that % conversion reaches a maximum of 88.40% from the tapioca starch graft copolymer 6 in the same manner as the %total solid content.

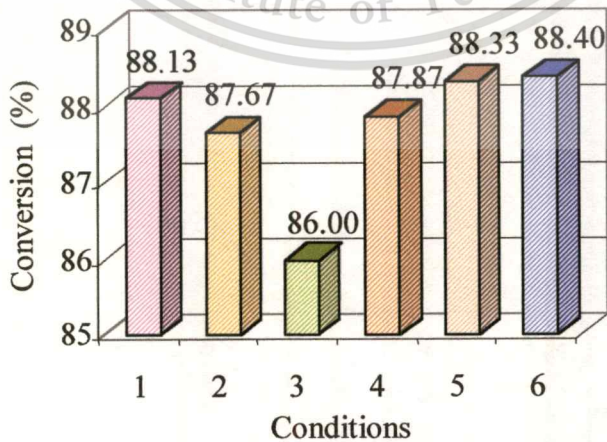


Figure 4.4 %Conversion of tapioca starch graft copolymers 1-6.

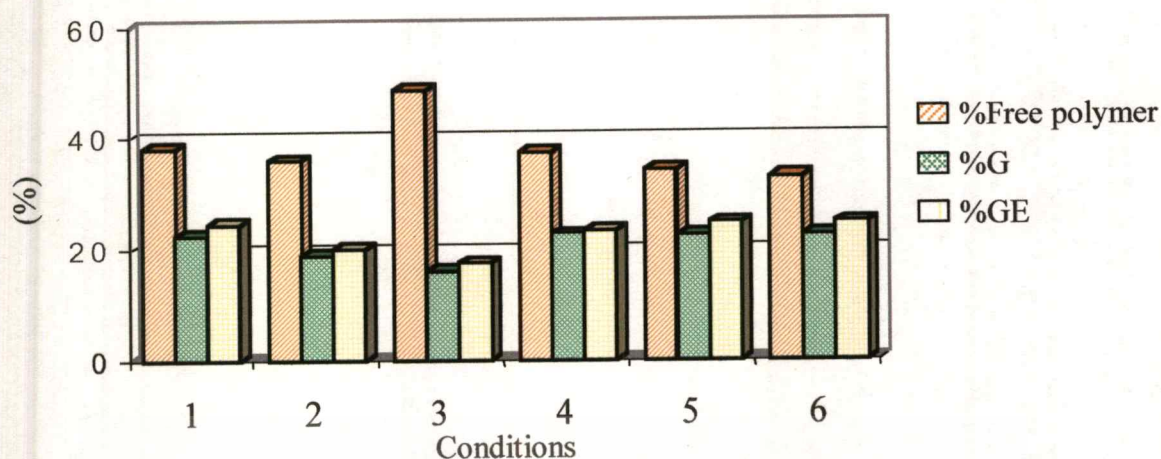


Figure 4.5 %free polymer, %G and % GE of tapioca starch graft copolymers 1-6.

Figure 4.5 exhibits the dependence of %free polymer, %G and %GE on tapioca starch graft copolymers 1-6. It is evident that both %G and %GE decreased because the highest %free polymer was formed in the tapioca starch graft copolymer 3. Because of it was used both monomers in the formation of large amount of homopolymer. Therefore homopolymer molecule prevented the rate of diffusion of monomer to the tapioca starch macroradicals. However, the tapioca starch graft copolymer 3 was prepared by grafting St/BA onto granular tapioca starch without gelatinized tapioca starch. The gel effect should help the swelling tapioca starch molecule, which ultimately facilitates backbone, thereby enhanced the grafting.

4.2 Characterization of Tapioca Starch Graft Copolymer

This section present and discuss results from the characterization of tapioca starch graft copolymer, which were synthesis by emulsion polymerization. There were two monomers(St and BA) using to graft onto tapioca starch. Techniques applied to study structure and properties of tapioca starch graft copolymer include furrier transform infrared spectroscopy (FT-IR), particle size distribution and gel permeation chromatography(GPC). Data presented in this section provide information on tapioca starch graft copolymer structure features and properties, factors that are crucial in understanding and predicting tapioca starch graft copolymers behaviors.

4.2.1 Rheological Properties

Rheological properties are important to estimate the behaviors of tapioca starch graft copolymer during processing. The flow curve of tapioca starch graft copolymers 1-6 in Figure 4.6 shows the relation between shear stress and shear rate. Figure 4.7 shows the relation between apparent viscosity and shear rate. The viscosity of tapioca starch graft copolymers 1-6 drops with an increase of shear rates irrespective of tapioca starch graft copolymer concentrations. The highest viscosity was observed at lowest shear rate (8.9 s^{-1}). It suggests that tapioca starch graft copolymer exhibited shear thinning properties. From these results, it could be explained that the reason for drop in viscosity of tapioca starch graft copolymers with an increase of shear rates, on the basis of tapioca starch network entanglement mechanism during shearing. In an entangled network system the viscosity remained constant at low shear rates because there was a sufficient time to form a new entanglement between the chain partners. At higher shear rates, the rate of re-entanglement falls behind the rate of disruption of the exiting entanglements. The extent of entanglement coupling decreased progressively with increasing shear rates as a result viscosity drops. The decrease in viscosity with the increase in shear rates indicated that the breakage of intra or intermolecular associative bonding systems in the tapioca starch graft copolymer network micelle was higher at higher shear rates.

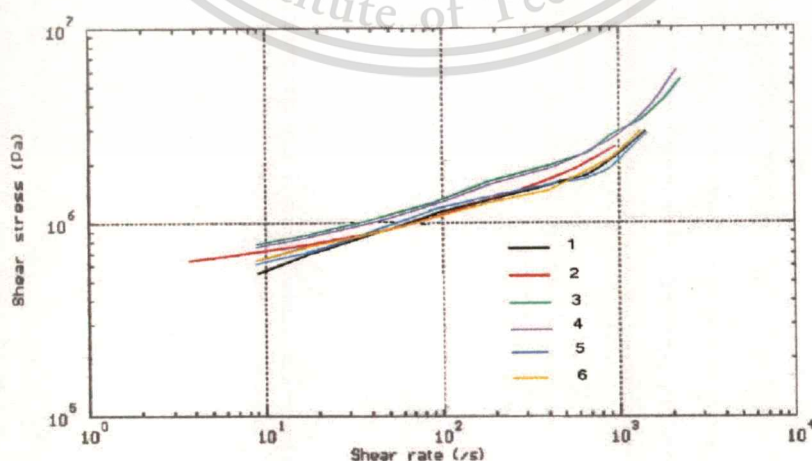


Figure 4.6 Relation of shear stress and shear rate of tapioca starch graft copolymers 1-6.

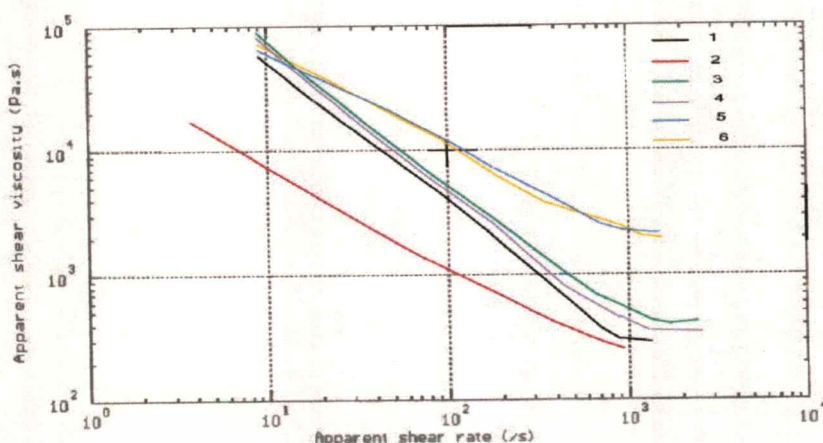


Figure 4.7 Relation of shear rate and shear viscosity of tapioca starch graft copolymers 1-6.

4.2.2 Identification of Grafting

The tapioca starch and tapioca starch graft copolymer spectra are shown in Figure 4.8 and 4.9, respectively. The infrared spectrum was recorded in the frequency region of $4000\text{--}400\text{ cm}^{-1}$. Table 4.8 summarizes the peak assignment of the infrared vibrational bands. From the result presented are shown characteristic FT-IR peak of C=O of grafted butyl acrylate polymer appeared between $1730\text{--}1750\text{ cm}^{-1}$.

Table 4.8 Infrared spectroscopy characterization.

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

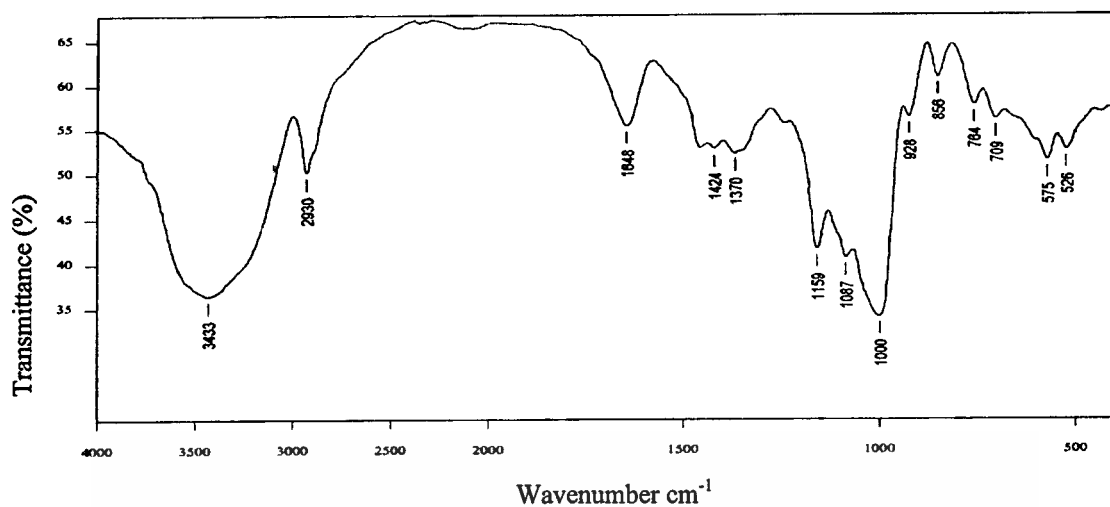


Figure 4.8 FT-IR spectrum of tapioca starch.

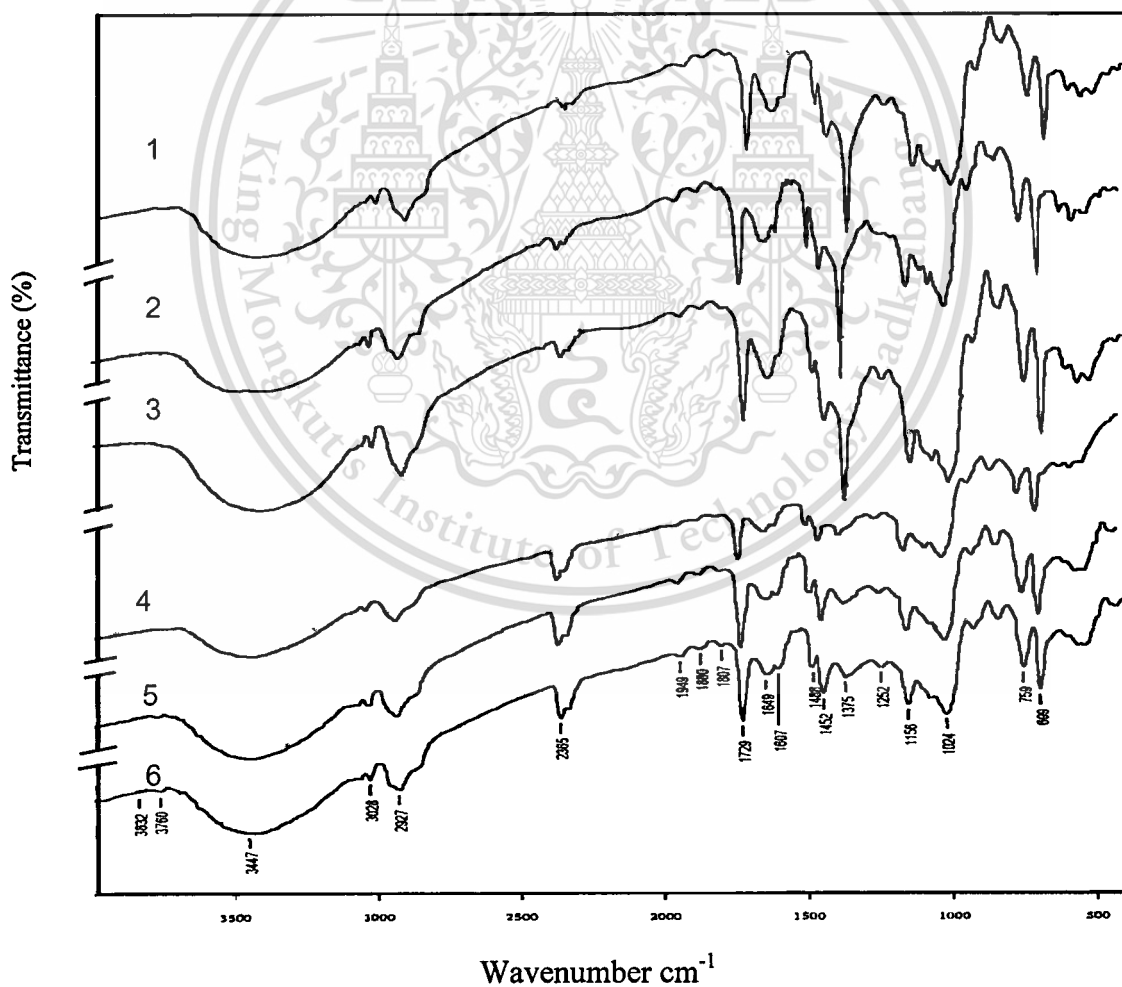


Figure 4.9 FT-IR-spectra of tapioca starch graft copolymers 1-6.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

4.2.3 Molecular Weight Determination of Side Chain Polymer.

Molecular weight is an extremely important characteristic because it relates directly to a chemical structure of tapioca starch side chain graft copolymer. Gel permeation chromatography (GPC) was used to determine average molecular weight (Mw and Mn), molecular weight distribution and polydispersity index (Mw/Mn). In this analysis, average molecular weight of side chain polymers were measured and reported in Table 4.9

Table 4.9 The average molecular weight of side chain polymers 1-6.

Samples	Mn	Mw	Mw/Mn
side chain polymer 1	49,979	75,613	1.512
side chain polymer 2	47,568	71,385	1.500
side chain polymer 3	32,254	42,795	1.326
side chain polymer 4	45,617	67,057	1.470
side chain polymer 5	49,502	76,086	1.537
side chain polymer 6	49,678	77,101	1.552

The Mn is influenced more by the low molecular weight species whereas the Mw reflects the higher molecular weight molecules. However, this section discuss on average molecular weight (Mw) of side chain polymers in the range of 42,795-77,101. The observed average molecular of tapioca starch side chain graft copolymer could be determined its melting point or viscosity and processing properties of tapioca starch graft copolymer. In general, melt viscosity increases with molecular weight. Based on the lower Mw of tapioca starch side chain graft copolymer 3, this implies a tendency of tapioca starch graft copolymer 3 being less viscous than the other.

4.2.4 The Particle Size of Tapioca Starch and Tapioca Starch Graft Copolymer.

As seen in Table 4.10, the average particle size of tapioca starch graft copolymers 1-6 were 51.75-72.92 μm , which tapioca starch graft copolymer 4 was the smallest while tapioca starch graft copolymer 3 was the largest average particle size. But tapioca starch graft copolymer 3 had two groups of particle size (Figure C-4) so the received average particle size was not correctly.

Table 4.10 The average particle size of tapioca starch and tapioca starch graft copolymers 1-6.

Sample	Average particle size (μm)
tapioca starch	14.53
tapioca starch graft copolymer 1	62.37
tapioca starch graft copolymer 2	56.88
tapioca starch graft copolymer 3	72.92
tapioca starch graft copolymer 4	51.75
tapioca starch graft copolymer 5	61.21
tapioca starch graft copolymer 6	58.93

4.2.5 Thermal Properties

Differential scanning calorimeter (DSC) and heat distortion temperature are two thermal analysis techniques applied to study tapioca starch graft copolymers. The DSC thermogram of tapioca starch and tapioca starch graft copolymer are given in the Table 4.11 and APPENDIX D, Figure D-14 - D-19. The observed endothermic transition should represent glass transition temperature (T_g). Tapioca starch showed an endothermic transition at 70.7°C , and tapioca starch graft copolymers 1-6 exhibited a board endothermic transition temperature in a range of 140.6 - 166.2°C .

The results of heat distortion temperature (HDT) were shown in Figure 4.9 and the data are listed in Table 4.11. It can be seen that there were no significant difference between tapioca starch graft copolymers 1-6. Comparison of the HDT of each tapioca starch graft copolymers 1-6 with those commercial plastics shown that the HDT of all tapioca starch graft copolymer were significant lower than commercial plastics because of poor thermal stability of the tapioca starch.

Table 4.11 Thermal properties determination.

Sample	T_g ($^\circ\text{C}$)	HDT ($^\circ\text{C}$)
tapioca starch graft copolymer 1	163.0	51.1
tapioca starch graft copolymer 2	152.9	51.5
tapioca starch graft copolymer 3	155.4	51.3
tapioca starch graft copolymer 4	140.6	51.5
tapioca starch graft copolymer 5	166.2	51.7
tapioca starch graft copolymer 6	157.2	51.8
PS	109.0	79.0
PP	170.2	89.0
LLDPE	127.9	90.0
HDPE	131.1	81.0
LDPE	110.8	85.0
tapioca starch	70.7	N/A

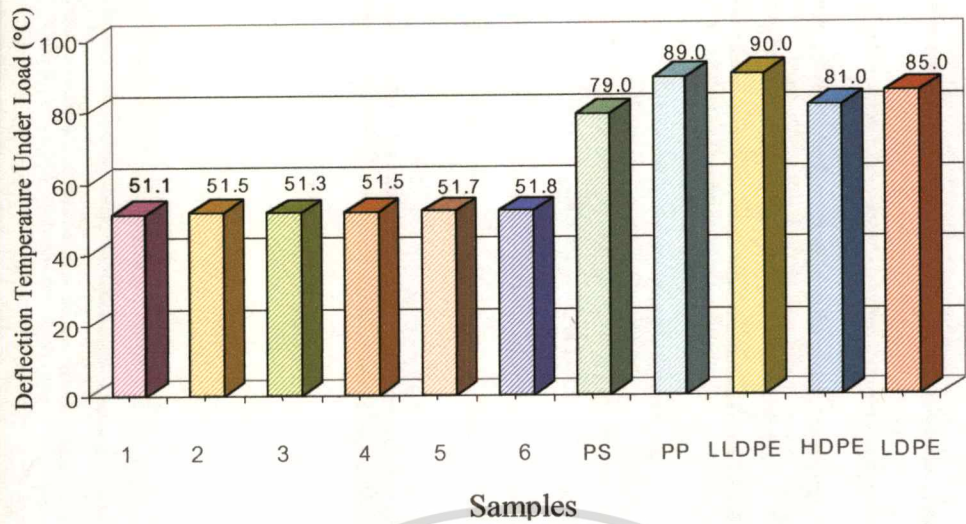


Figure 4.10 Heat distortion temperature (°C) of tapioca starch graft copolymers 1-6 and commercial plastics.

4.2.6 Mechanical Properties Testing

Mechanical properties of tapioca starch graft copolymer are presented in Figure 4.11– 4.15 and the results are given in Appendix A, TableA-11. In This study, all tapioca starch graft copolymers were injected at the temperature at nozzle, zone 1, zone 2 and zone 3 equal 150 140, 130, 120°C, respectively. The migration properties from commercial plastics (PP, PS, LLDPE, HDPE and LDPE) used for food packaging was studied.

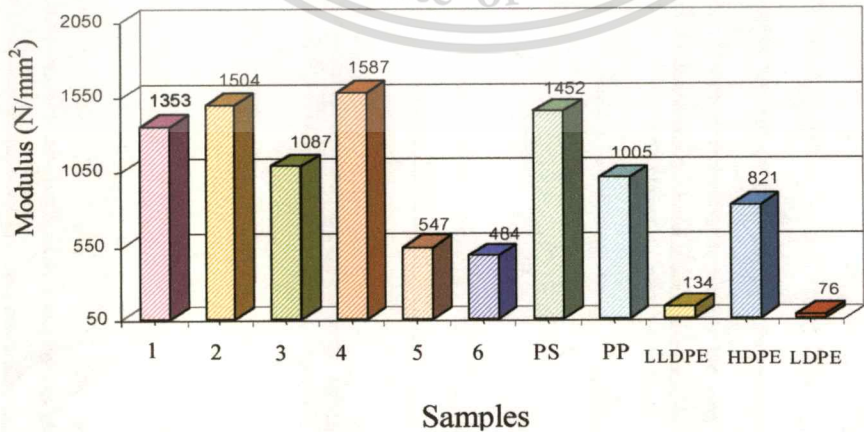


Figure 4.11 Young's Modulus of tapioca starch graft copolymers 1-6 and commercial plastics.

From the results presented in Figure 4.11, it can be seen that there was a little difference in the Young's Modulus between the tapioca starch graft copolymers 1-6. The Young's Modulus values of commercial plastics (PS, PP and HDPE) were significantly similar to the above values but commercial plastics (LLDPE and LDPE) were lower.

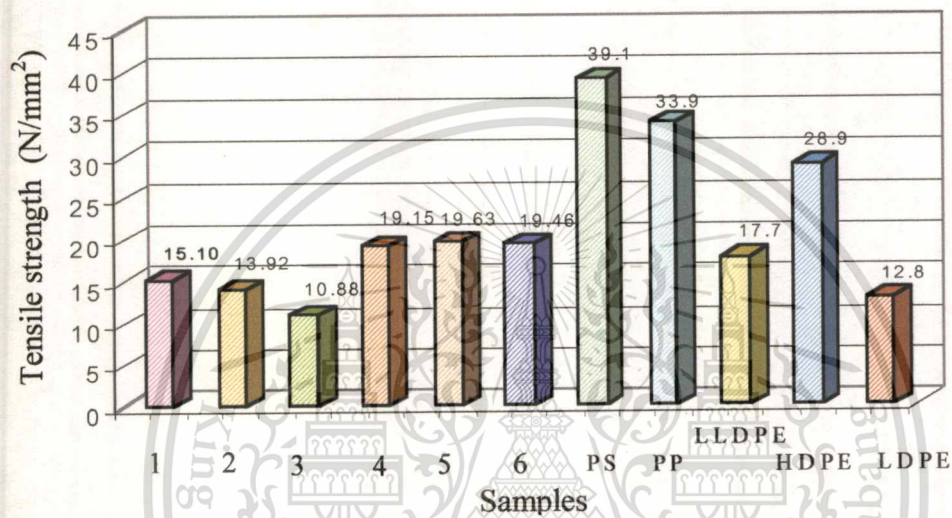


Figure 4.12 Tensile strength of tapioca starch graft copolymers 1-6 and commercial plastics.

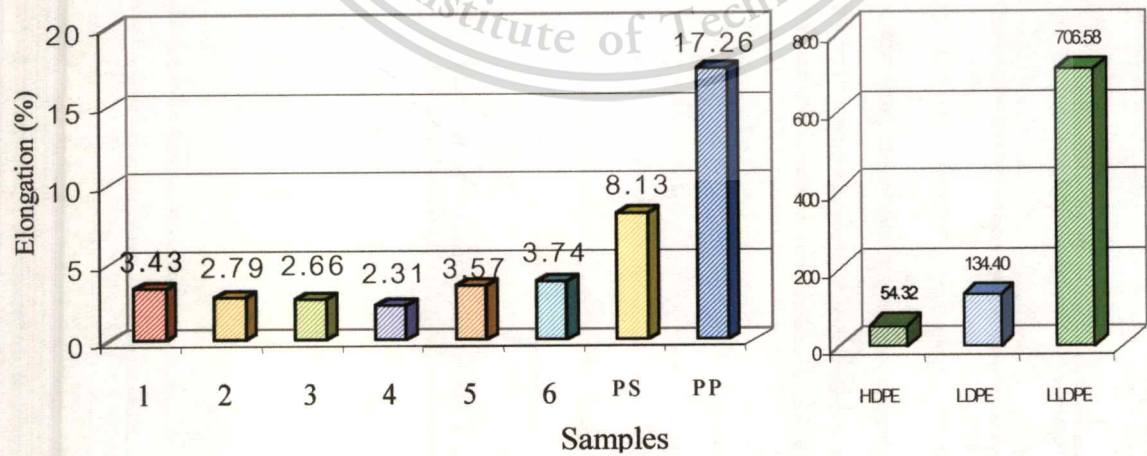


Figure 4.13 Elongation at break of tapioca starch graft copolymers 1-6 and commercial plastics.

The tensile strength was shown in Figure 4.12 . The result shown that the tensile strength of commercial plastics were higher than tapioca starch graft copolymers. The results of elongation at break of tapioca starch graft copolymer were shown in Figure 4.13 . It appears that there was obvious differences from commercial plastics values between 8.13 to 706.58%. Figure 4.14 shows the Shore D hardness of tapioca starch graft copolymers in a range of 65-68. For commercial plastics PS, PP, LLDPE, HDPE and LDPE were 74, 95, 91, 95 and 91, respectively. The result of impact strength was shown in Figure 4.15, which did not exhibit any significant change for varying the synthetic conditions. The mechanical properties of the tapioca starch graft copolymers were fairly good.

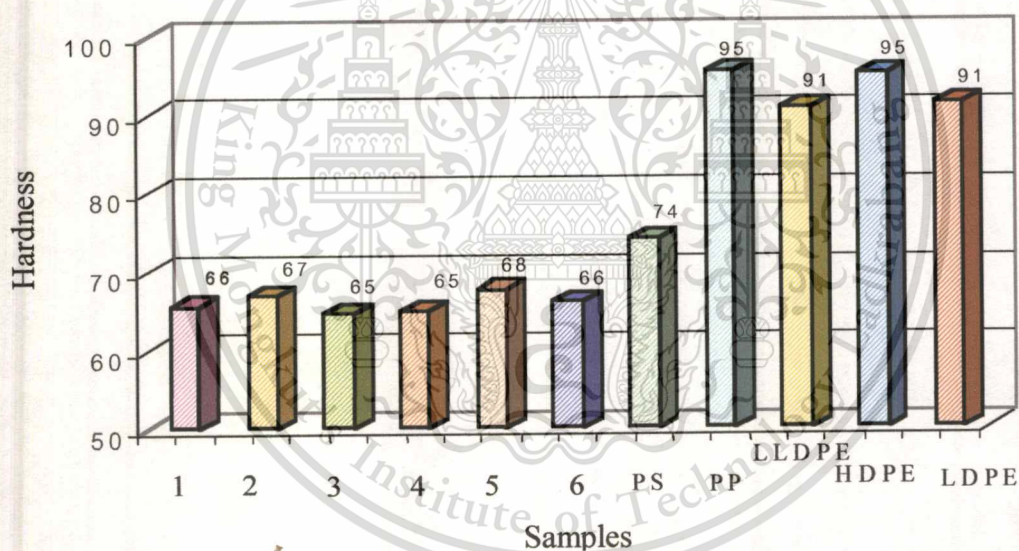


Figure 4.14 Hardness of tapioca starch graft copolymers 1-6 and commercial plastics.

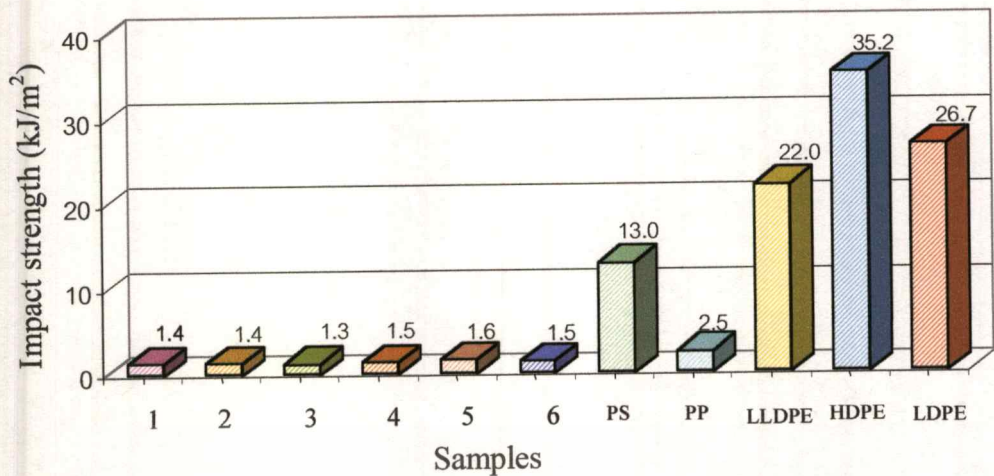


Figure 4.15 Impact strength of tapioca starch graft copolymers 1-6 and commercial plastics.

4.2.6 Physical Properties Testing

Physical properties of tapioca starch graft copolymer including density, moisture content and water absorption are present in Figure 4.16-4.18 and the data listed in Appendix A, Table A-6.

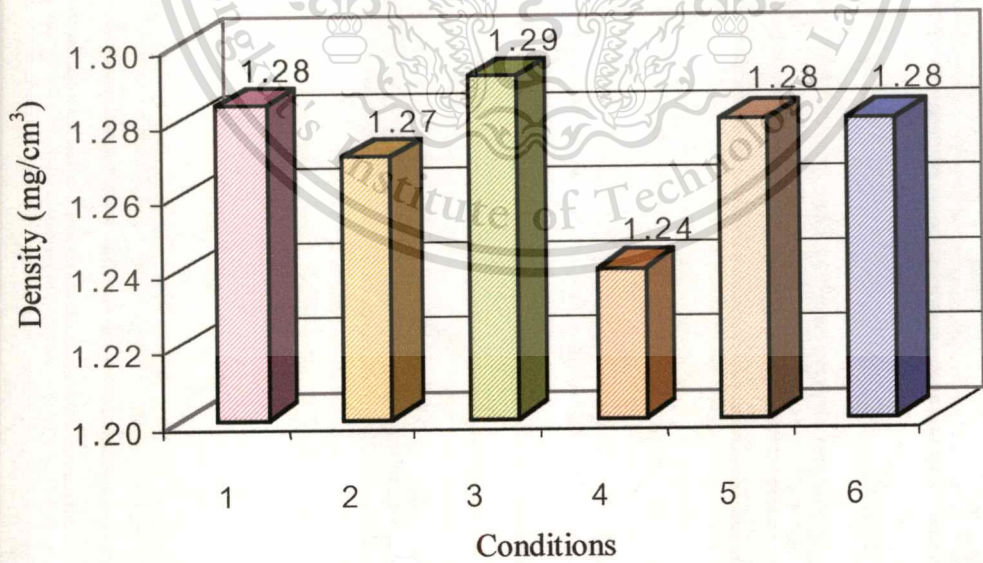


Figure 4.16 Density of tapioca starch graft copolymers 1-6 .

From the result presented above it can be seen that the density (Figure 4.16), and moisture content of tapioca starch graft copolymers 1-6 in range 1.24-1.29

mg/cm³ and 3.61-3.88%, respectively. This result did not exhibit any significant change for varying the condition of synthesis. But the result of grating tapioca starch lead to decrease in moisture content when compared with tapioca starch (Figure 4.17) which decrease from 13.5% to 3.61-3.88%. These are content that tapioca starch graft copolymer was increased water resistant because the molecule of tapioca starch was increased the hydrophobic segments. Water absorption properties of this tapioca starch graft copolymers are shown in Figure 4.18 .

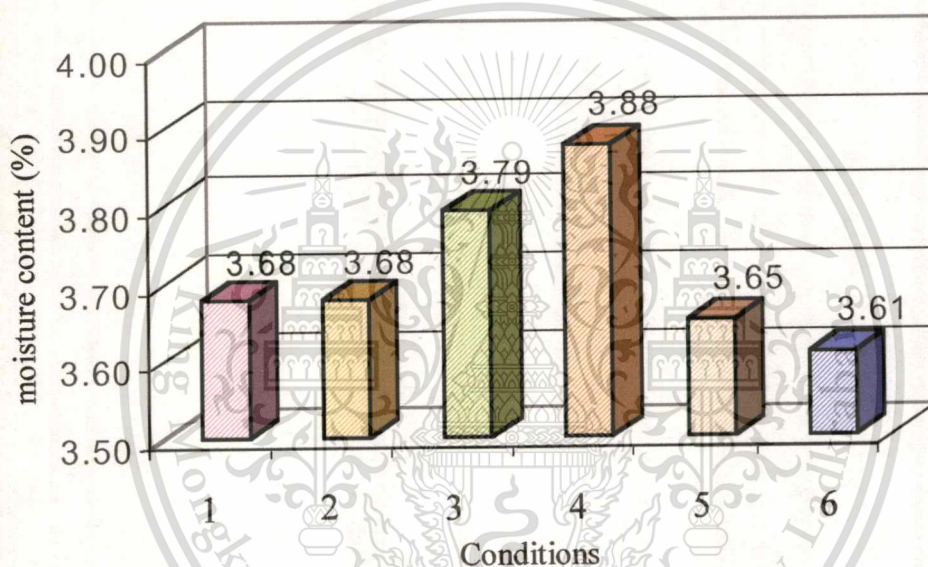


Figure 4.17 Moisture content of tapioca starch graft copolymers 1-6.

The result was found that the water absorption was about 14.72-16.90% after submerging 24 hrs in water at 25°C. This result was observed higher than the petroleum derived polymer. It has been believed that tapioca starch consists of a mixture of amylose and amylopectin that have many hydroxyl groups. The abundant of hydroxyl groups on the tapioca starch molecules impart hydrophilic properties which giving it an affinity for moisture and dispersibility in water.

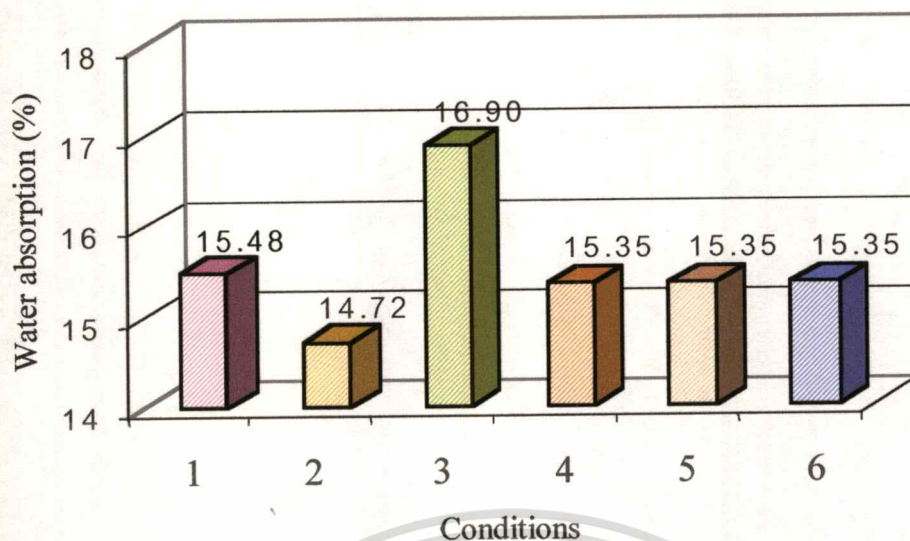


Figure 4.18 Water absorption of tapioca starch graft copolymers 1-6.

4.2.8 Food Packaging Properties

In this study, lead determination and migration test are two analysis techniques applied to tapioca starch graft copolymer with the aim to find the safety for food packaging. Since human health as well as safety and of highest importance, notification of the Ministry of Public Health No.111 (B.E. 2531(1988)) according to the Thai FDA has to ensure that there is an effective control on any substances which might be transferred to the packaging food. The essential principle of this framework is the preservation of food purity and the inertness of packaging materials and articles intended to come into contact with foodstuffs. At the notification of the Ministry of Public Health No.111 (B.E. 2531(1988)) all necessary migration tests are carried out depending on type, subject and requirement of the plastic packaging material.

4.2.8.1 Lead Determination

Lead studies were carried out using a atomic absorption spectrophotometry. This system makes use of the phenomenon that the atoms in a ground state absorb a unique wavelength of light when light is pass though an atomic vapor layer and measures the concentration of the element under examination in a test solution. The flame method is employed here. The quantities of lead in tapioca starch graft copolymers 1-6 are given in a Table 4.12. No difference can be seen among the

various types of tapioca starch graft copolymers. It, therefore, appears that heavy metal has no effect on composition and contaminant.

4.2.8.2 Migration Tests

The residue on evaporation test method determines the amount of substances migration from a sample to a leaching solution. The migration of plastic packaging components into foodstuffs is essentially a problem of diffusion. The extent of migration of a particular plastics component from a food packaging material into the contained foodstuff depends on a number of variable factors such as concentration of the components in the plastics material, the temperature in the contact system of plastic/foodstuff, and the duration of contact between the system components. Generally, if the contact time and the temperature of the contact system are constant.

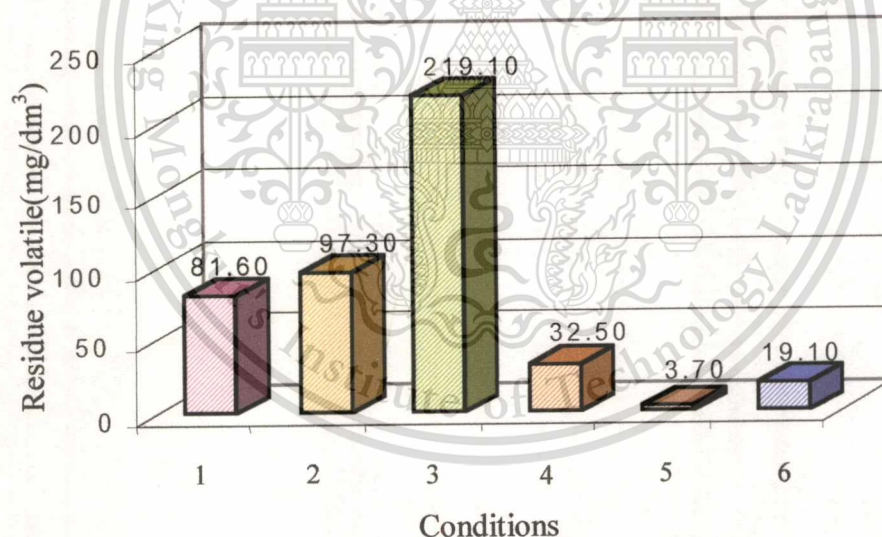


Figure 4.19 Residue volatile in distill water of tapioca starch graft copolymers 1-6.

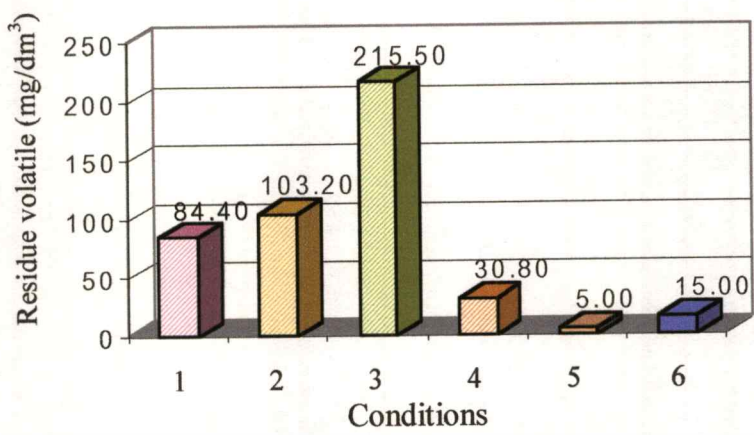


Figure 4.20 Residue volatile in 4% acetic acid of tapioca starch graft copolymers 1-6.

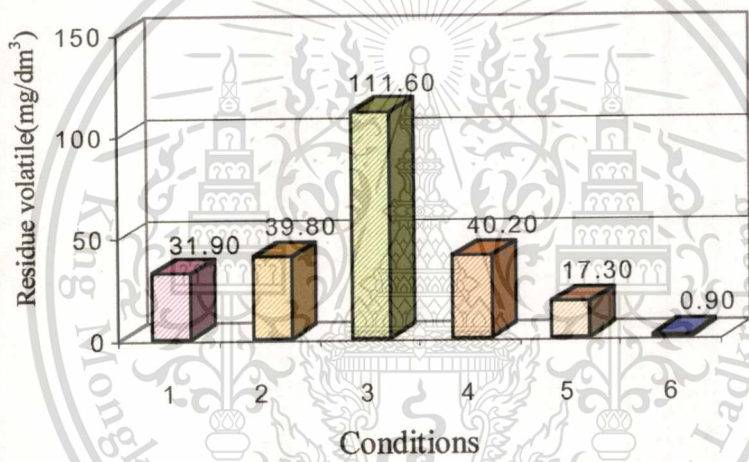


Figure 4.21 Residue volatile in 20% ethanol of tapioca starch graft copolymers 1-6.

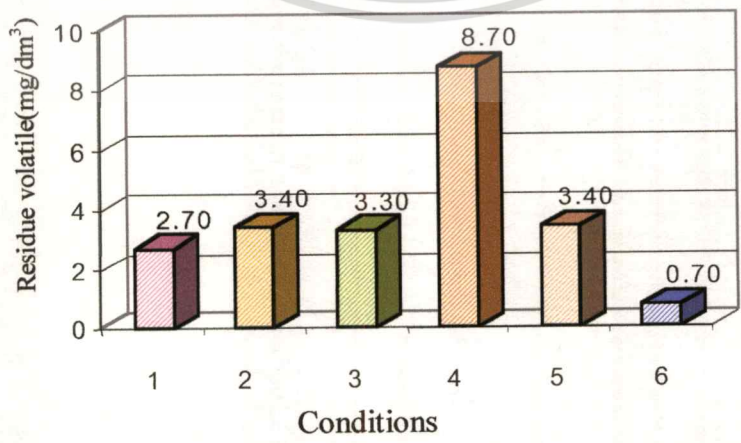


Figure 4.22 Residue volatile in heptane of tapioca starch graft copolymers 1-6.

The migration test of tapioca starch graft copolymer into aqueous food simulant (distilled water, 4% aqueous acetic acid and 20% ethanol) and fatty food simulant (heptane) was studied. Test condition for packaging material/food simulant contact and method of migration analysis were according to the notification of the Ministry of Public Health No.111 (B.E. 2531(1988)).

The migration test led to the result shown in Table 4.12 and Figure 4.19-4.22. The result showed that for four tested tapioca starch graft copolymer (condition 1,2,3 and 4) values of migration into aqueous simulants ($31.9-84.4 \text{ mg/dm}^3$, $39.8-103.2 \text{ mg/dm}^3$, $111.6-219.1 \text{ mg/dm}^3$ and $30.8-40.2 \text{ mg/dm}^3$) were significantly higher than the upper limit (30 mg/dm^3) for migration from plastic packaging materials and articles into food and food simulants. The maximum amount of migration is from the tapioca starch graft copolymer 3. This could be explained by the percentage of grafting. In corresponding test, the smallest percentage of grafting gives a higher migration into the food simulants. The migration values from tapioca starch graft copolymers 4 and 6 were significantly lower ($3.7-17.3 \text{ mg/dm}^3$ and $0.9-19.1 \text{ mg/dm}^3$) than the above values which lower than the upper limit for migration. It has believed that most residual tapioca starch and remaining monomers were eliminated by washing before injecting molding. From Table 4.12 also showed that the migration values from all tested into heptane were significantly very lower than the upper limit for food packaging.

Potassium permanganate used for making chemical reaction. The test method for potassium permanganate consumption determine by the amount of substances oxidized by potassium permanganate exiting in the substances migration from the sample to water. The amount of potassium permanganate were shown in Figure 4.23. The consumption of potassium permanganate from six materials were significantly higher than the upper limit (10 mg/dm^3). Because all sample were made from tapioca starch which were organic substance.

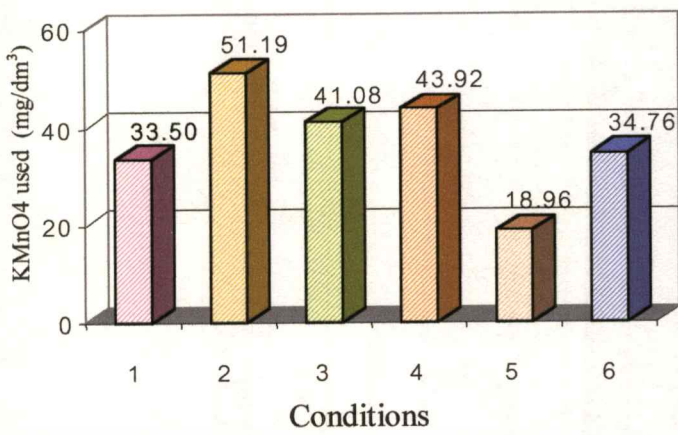


Figure 4.23 Potassium permanganate consumption for making chemical reaction of tapioca starch graft copolymers 1-6.

The lead migration in 4% acetic acid was shown in Table 4.12. It can be seen that the same behavior was observed in lead determination, lead migration in 4% acetic acid were not detected. Table 4.12 also shown that the migration of color extracted by distilled water, 4% acetic acid and 20% ethanol were observed in sample 1-4. In corresponding tests, all tested six sample (1-6) color of migration into heptane were not detected.

4.2.9 Biodegradable Properties

Soil and water play an irreplaceable role in the global nutrient cycling due to the biochemical activity of microorganisms indigenous to the individual terrestrial and aquatic environments. These microorganisms are capable of degrading not only simple organic compounds but also several natural polymers such as starch, cellulose and humic substances. Degradation was thus investigated by monitoring the appearance of plastic.

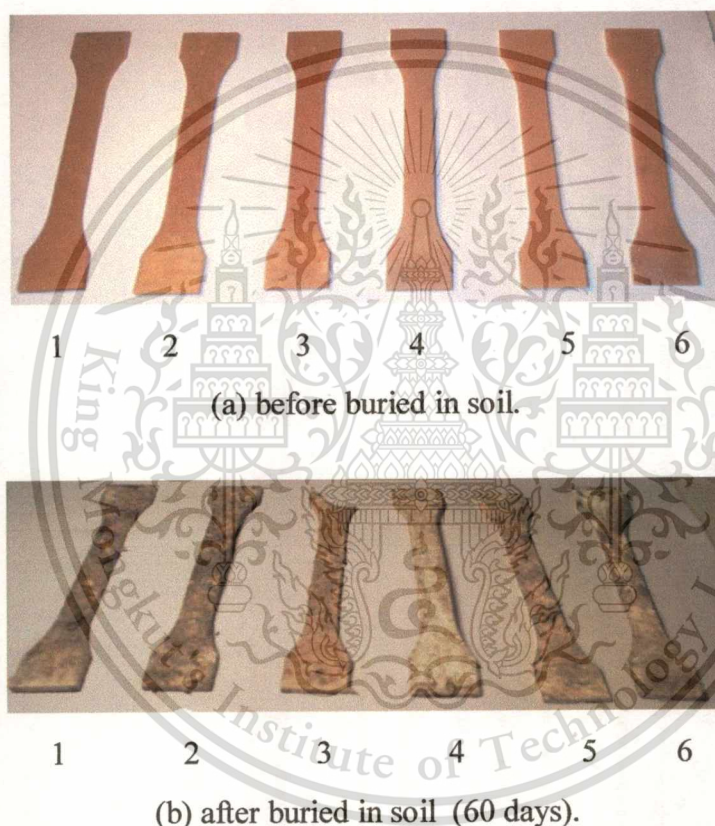
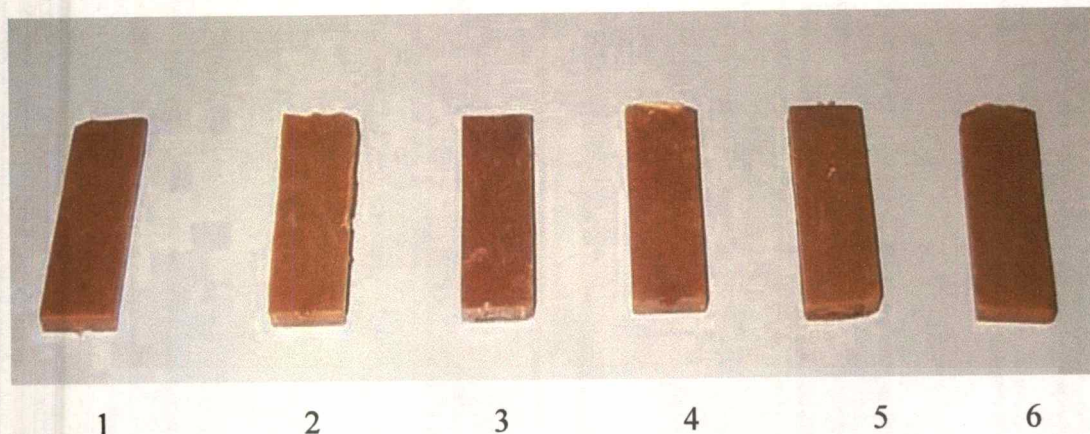


Figure 4.24 Biodegradability of tapioca starch graft copolymers by buried in soil .

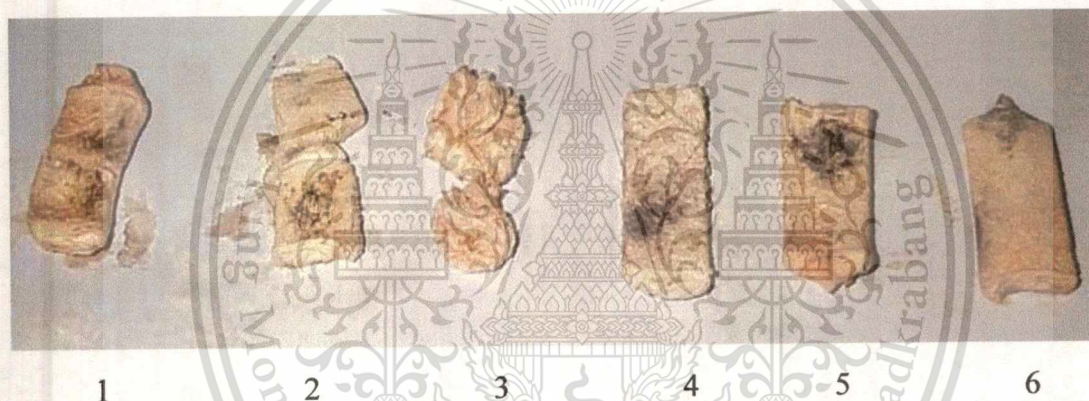
(a) before buried in soil.

(b) after buried in soil.

Form the Figure 4.24, it obviously seen that all samples were degraded in only 60 days which were exposed in natural soil.



(a) before immersed in water.



(b) after immersed in water (60 days).

Figure 4.25 Biodegradability of tapioca starch graft copolymers by immersed in water.

(a) before immersed in water.

(b) after immersed in water.

Correspondingly, fungi was found in the sediment from tapioca starch graft copolymer which were immersed for 60 days in water as shown in Figure 4.25 .

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

The following conclusions could be made from the present studies

1. The study of the simultaneous grafting of styrene with butyl acrylate onto gelatinized tapioca starch in aqueous medium was carried out by the chemical initiation method in which potassium persulfate was used as an initiator in nitrogen blanket for six conditions.

Tapioca starch graft copolymer condition 1 was prepared by using emulsion polymerization. The gelatinized tapioca starch was stirred with a mixture of styrene and butyl acrylate using potassium persulfate in 1 N nitric acid as an initiator and NP-40 as surfactant.

Tapioca starch graft copolymer condition 2 was prepared with the same process as condition 1, except changing surfactant type from NP-40 to sodium lauryl ether sulfate.

Tapioca starch graft copolymer condition 3, the same as condition 1 but the tapioca starch was not gelatinized.

Tapioca starch graft copolymer condition 4, the same process as 1, but prepared by using initiator dissolved in water.

Tapioca starch graft copolymer condition 5 and 6 were samples obtained from synthesis condition 1, but adding a step in removing monomer with water and isopropanol, respectively.

The effect of synthetic tapioca starch graft copolymer six conditions found that the tapioca starch graft copolymer 3 was the lowest percentage of grafting efficiency.

2. The optimum condition of injection molding machine for preparing complete tapioca starch graft copolymer specimens were shown below:

Injection temperatures	Nozzle	150°C
	Zone 1	140 °C
	Zone 2	130 °C
	Zone 3	120 °C
Injection time	1 st STG INJ	45 second
	2 nd STG INJ	40 second
	3 rd STG INJ	35 second
	Cooling time	50 second
Plunger speed		20 mm/second
Injection pressure	1 st INJ	4.41×10 ⁶ N/m ²
	2 nd INJ	3.92×10 ⁶ N/m ²
	3 rd INJ	3.43×10 ⁶ N/m ²

3. The starch consists of a mixture of amylose and amylopectin that has many hydroxyl groups. The abundant hydroxyl groups in the tapioca starch molecules imparting hydrophilic properties caused it to absorb water and swell.
4. Thermal properties testing of tapioca starch graft copolymers were decreased as compared with commercial plastics because of poor thermal stability of the tapioca starch.
5. The tensile strength was increased, while elongation at break and impact strength were decreased. No significant change of young's modulus was observed as compared with polystyrene.
6. In the cause of residue migration that do not fit to the standard of the notification of the Ministry of Public Health No.111(B.E 2531(1988)) by higher than the limit 30 ppm. This may cause by the presence of starch.
7. The biodegradation behavior of the starch graft copolymer was investigated through outdoor soil burial test and immersed in water. The test results showed that all the tapioca starch graft copolymers could be degraded under the test conditions.

Suggestion for future work.

1. Further study of the packaging using the material would involve the production costs for the purpose of scaling up the production to commercialization.
2. Study kinetics and mechanism of free radical reaction by grafting styrene and butyl acrylate onto tapioca starch for explaining the properties of tapioca starch graft copolymer correctly.
3. The packaging made of tapioca starch graft copolymer coated with paraffin or wax should be investigated for its durability when contacted with water.

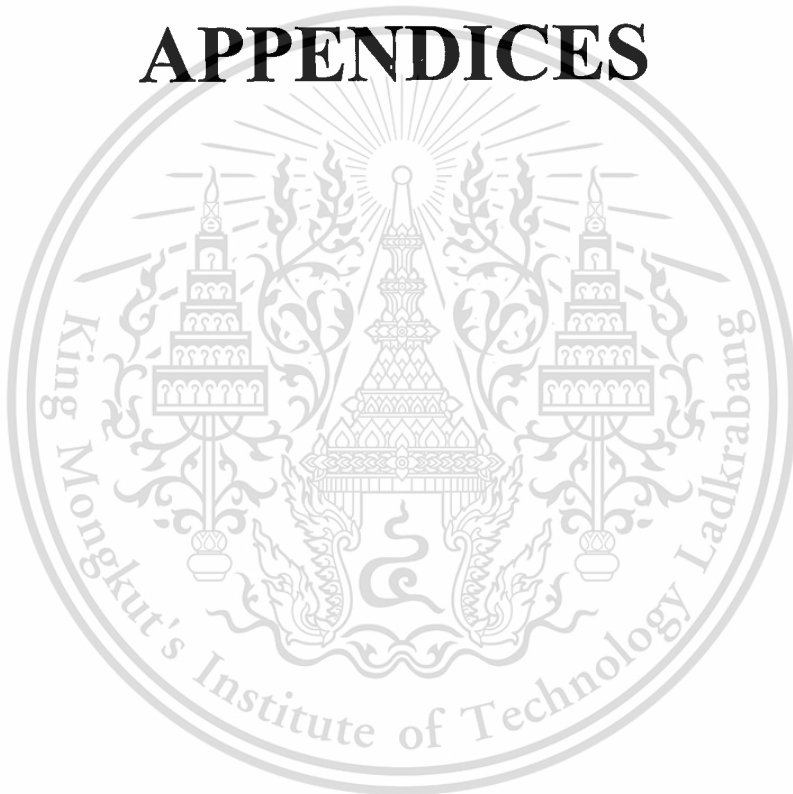


REFERENCES

- [1] Athawale, V.D. and Lele, V. "Graft copolymerization on to starch. II. Grafting of acrylic acid and preparation of it's hydrogels". **Carbohydr. Polym.** 1998(35) : pp.21-27
- [2] Athawale, V.D. and Rath, S.C. **J.Appl.Polym.Sci.** 1997(66) pp.1399-1403.
- [3] Briley, A.W, Haworth, B. and Batchelor, J. **Physics of Plastics.** New York. 1992.
- [4] Cao, Y. et al "Graft copolymerization of acrylamide onto carboxymethyl starch" **European Polymer Journal.** 2002(38) : pp.1921-1924.
- [5] Chinnaswamy, R. and Hana, M.A. "Extrusion - Grafting Starch onto Vinyl Polymer" **Starch/Stärke.**1991(43) pp.396-402.
- [6] Crompton, T.R. **Additive Migration From Plastics into Food.** Oxford : Pergamon Press. 1979.
- [7] Diraddo R.W. and Laroche I., "Physical Properties of Virgin HDPE and Recycled Polymers", **Plastics, Rubber and Composites Processing and Applications.** 1995(4) pp.197-200.
- [8] Ehrig, R.J. **Plastics Recycling.** New York. 1992.
- [9] Gao, J.P. et al. "Graft Copolymer of Methyl Methacrylate onto Canna Starch Using Manganic Pyrophosphate as an Initiator." **J.Appl. Polym. Sci.** 1994(53) pp.1091-1102.
- [10] Goni, I. et al. "¹³C n.m.r. Study of the Graft Copolymerization of a Mixture of Methyl Methacrylate with Ethyl Acrylate on Amylose." **Polymer.** 1993(34) : pp.512-517.
- [11] Henderson, A.M. and Rudin, A. "Effects of Water on Starch-g- Polystyrene and Starch - g - Poly(Methyl Acrylate) Extrudates" **J.Appl. Polym. Sci.** 1982(27) : pp.4115-4135.
- [12] Jesse, E. **Plastics Additives and Modifiers Handbook.** New York. 1992.
- [13] John, H. B. et. al. **Plastics in Contact with Food.** London : Food Trade Press. 1974.

- [14] Liu, M. et al. "Graft Copolymerization of Methyl Acrylate onto Potato Starch Initiated by Ceric Ammonium Nitrate." **J. Polym. Sci. Part A : Polym. Chem.** 1993(31) pp.3181–3186.
- [15] Michaeli, W. **Traning in injection molding**. New York. Hamser/Gerdner Pulication, Inc. 1995.
- [16] Morton-Jones, D.H., **Polymer Processing**. New York : Chapman and Hall. 1989.
- [17] Narayan, R. **Starch - Based Plastics**. New Jersey. 1991.
- [18] Patil, D.R. and Fanta, G.F. "Graft Copolymerization of Starch with Methyl Acrylate : An Examination of Reaction Variables. **J. Appl. Polym. Sci.** 1993(47) : pp.1765–1772.
- [19] Patil, D.R., Crookston, M.N. and Fanta, G.F. "Synthesis and Processing of Graft Copolymers from Cornstarch and Methyl Acrylate : Physical and Mechanical Preperities" **Starch/ Stärke**. 1994(46) : pp.142-146.
- [20] Piirma, I. **Emulsion Polymerization**. New York : Academic Press. 1982.
- [21] Rahman, L. et. al. " Graft Copolymerization of Methyl Acrylate onto Sago Starch Using Ceric Ammonium Nitrate as an Initiator". **J. Appl. Polym. Sci.** 2000(76) : pp.516-523.
- [22] Rivard, C. and Himme, M. **Biodegradation of Plastics**. New Jersey. 1991.
- [23] Trimnell, D., Swanson, C.L., Shogren, R.L. and Fanta, G.F. "Extrusion Processing of Granular Starch-g - Poly (Methy Acrylate) : Effect of Extrusion Conditions on Morphology and Properties" **J. Appl. Polym. Sci.** 1993(48) : pp.1665-1676.
- [24] Vert, M. et. al. **Biodegradable Polymers and Plastics**. Cambridge : The Royal Society of Chemistry. 1991.
- [25] Wu, C.S. **Hanbook of Size Exclusion Chromatography**. New York : Marcel Dekker, 1995. pp.381-406.
- [26] Wurzburg, O.B., editor. **Modified Starches : Properties and Uses**. 3rd ed., USA : CRC Press. 1987.

APPENDICES



This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

APPENDIX A

The Tables of Synthetic Data onTapioca Starch Graft Copolymer and Characterization.



Table A-1 The percentage of total solid content (%TSC) of St/BA monomers ratio on tapioca starch graft copolymerization at different reaction time.

St/BA	%TSC at different reaction time(hrs.)				
	1	1 ½	2	3	4
100/0	12.53	12.89	13.06	13.46	13.50
80/20	12.84	13.13	13.34	13.65	13.66
60/40	12.69	13.00	13.16	13.42	13.43
50/50	12.58	12.80	13.00	13.32	13.33
40/60	12.18	12.47	12.73	13.05	13.09
20/80	12.00	12.22	12.41	12.66	12.73
0/100	11.79	12.09	12.20	12.51	12.56

Table A-2 The percentage of total conversion of St/BA monomers ratio on tapioca starch graft copolymerization at different time.

St/BA ratio	%Conversion at different reaction time (hrs.)				
	1	1 ½	2	3	4
100/0	80.83	83.18	84.27	86.82	87.11
80/20	82.85	84.69	86.04	88.06	88.15
60/40	81.89	83.88	84.91	86.56	86.65
50/50	81.17	82.61	83.84	85.91	86.00
40/60	78.61	80.45	82.15	84.20	84.48
20/80	77.40	78.82	80.09	81.67	82.11
0/100	76.06	78.00	78.68	80.73	81.00

Table A-3 Effect of St/BA monomers ratio on tapioca starch graft copolymerization at 3 hours.

St/BA	% Free polymer	%G ^a	%GE ^b
100/0	45.30	19.02	20.74
80/20	38.30	22.70	24.80
60/40	42.50	19.70	20.02
50/50	48.56	17.93	17.41
40/60	49.80	17.49	13.19
20/80	50.30	16.54	9.12
0/100	52.86	14.58	7.39

G^a = Percentage of grafting

GE^b = Grafting efficiency

Table A-4 Polymerization parameter of tapioca starch graft copolymers 1-6.

Sample	% TSC	% Conversion	% Free polymer	%G	%GE
1	13.22	88.13	38.30	22.53	24.62
2	13.15	87.67	36.03	18.89	20.19
3	12.90	86.00	48.59	16.21	17.57
4	13.18	87.87	37.50	22.71	23.40
5	13.25	88.33	34.20	22.57	24.73
6	13.26	88.40	33.02	22.59	24.76

Table A-5 Mechanical properties testing .

Sample	Tensile Modulus (N/mm ²)	Tensile Strength (N/mm ²)	Elongation (%)	Impact strength (kJ/m ²)	Hardness shore D
Condition 1	1353	15.10	3.43	1.4	65.67
Condition 2	1504	13.92	2.79	1.4	67.00
Condition 3	1087	10.88	2.66	1.3	64.67
Condition 4	1587	19.15	2.31	1.5	65.00
Condition 5	547	19.63	4.57	1.6	67.60
Condition 6	484	19.46	3.83	1.5	66.00
PS	1452	39.13	8.13	13.0	74.20
HDPE	821	28.90	54.32	35.2	95.17
LDPE	76	12.78	134.40	22.0	91.40
LLDPE	134	17.66	706.58	26.7	90.83
PP	1005	33.90	17.41	2.5	95.37

Table A-6 Physical properties of tapioca starch graft copolymers 1-6.

Conditions	Moisture content (%)	Water absorption (%)	Density at 23 °C (g/cm ³)
1	3.68	15.48	1.28
2	3.68	14.72	1.27
3	3.79	16.90	1.29
4	3.88	15.35	1.24
5	3.65	15.35	1.24
6	3.61	15.35	1.24

APPENDIX B

FT-IR Spectra of Tapioca Starch Graft Copolymers 1-6



APPENDIX C

The Particle Size of Tapioca Starch and Tapioca Starch Graft Copolymers 1-6



This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

APPENDIX D

DSC Thermograms of Tapioca Starch Graft Copolymers 1-6 and Commercial Plastics



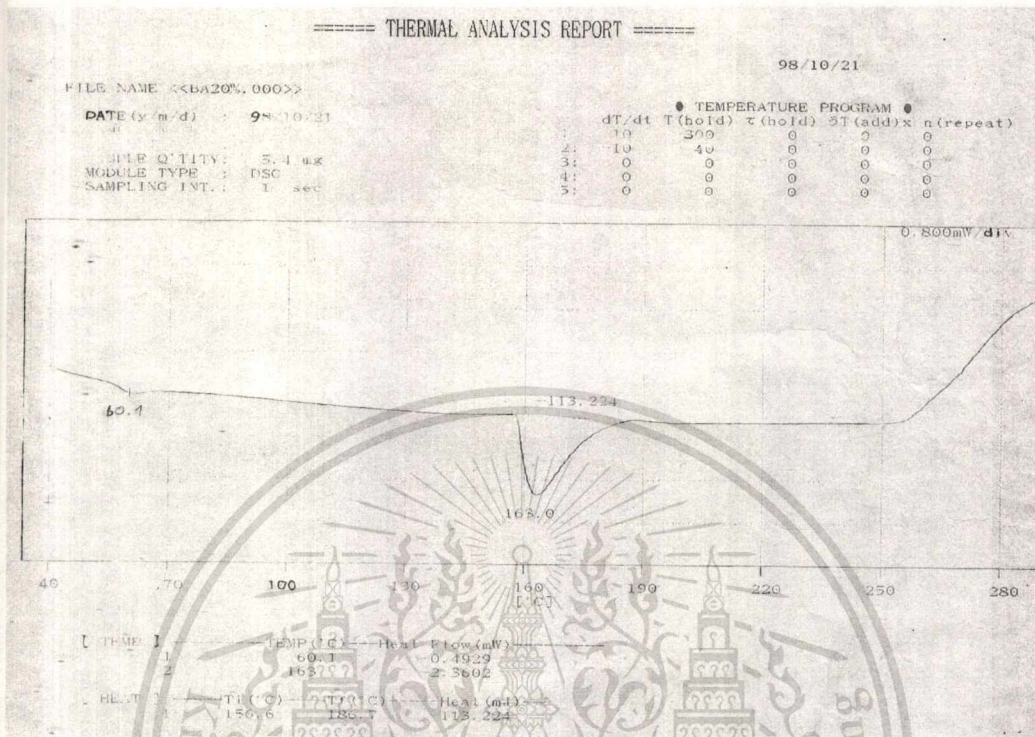


Figure D-1 DSC thermogram of tapioca starch graft copolymer 1.

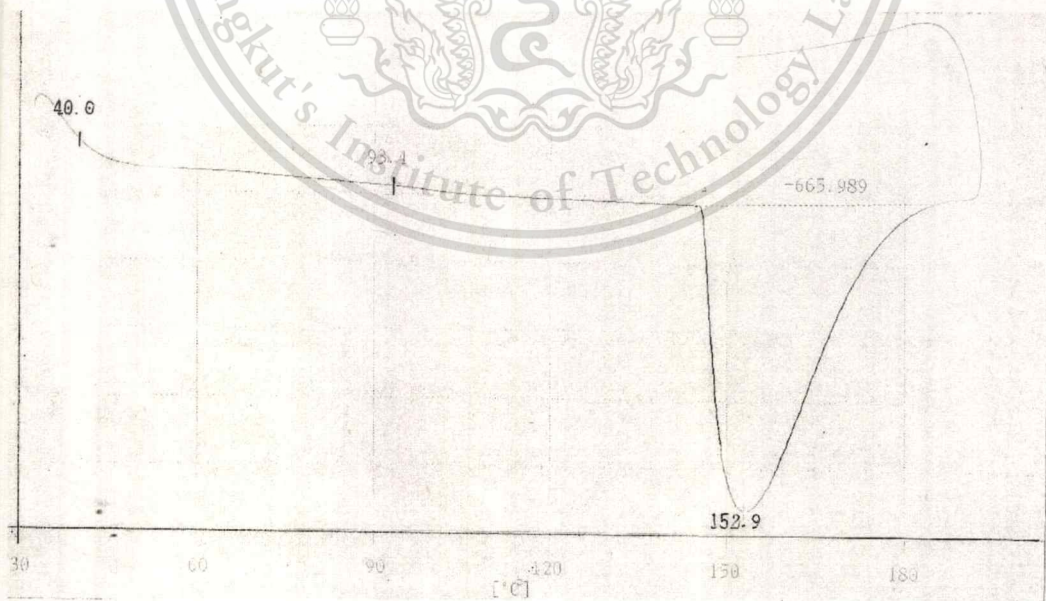


Figure D-2 DSC thermogram of tapioca starch graft copolymer 2.

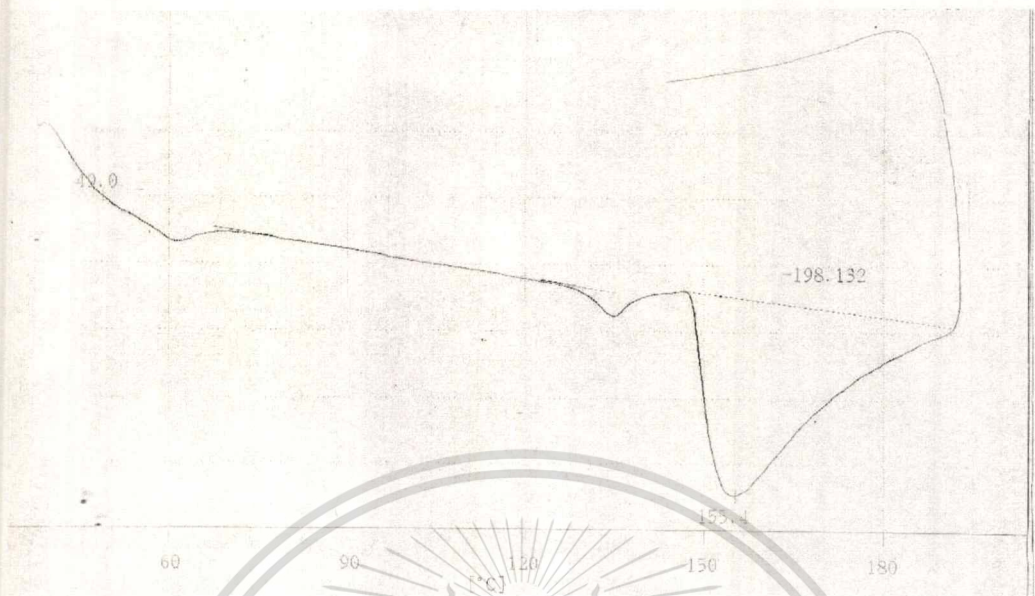


Figure D-3 DSC thermogram of tapioca starch graft copolymer 3.

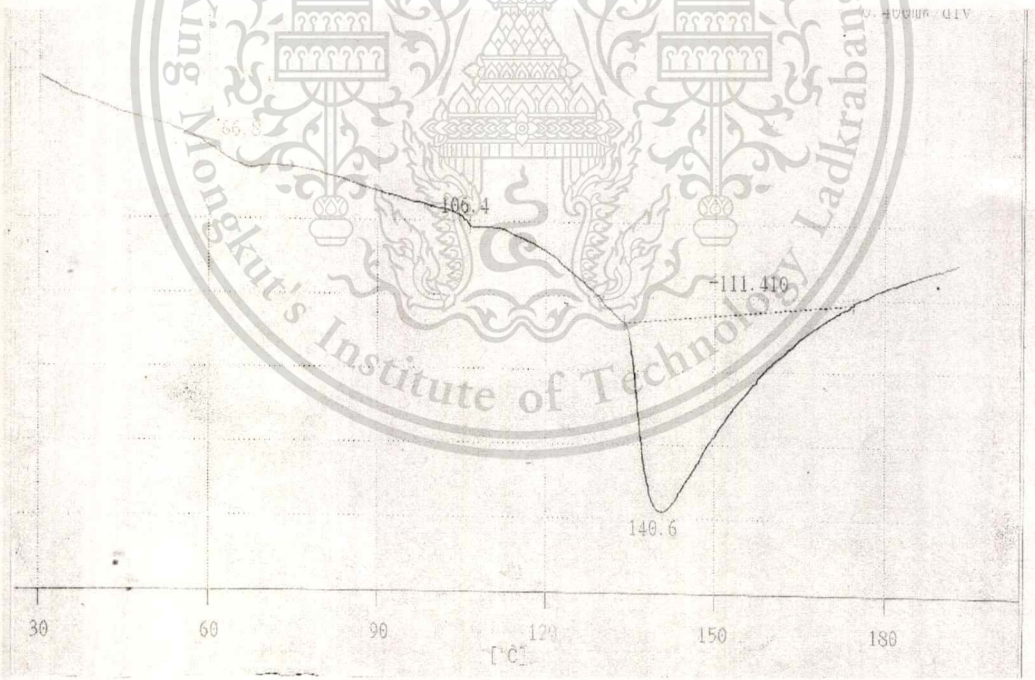


Figure D-4 DSC thermogram of tapioca starch graft copolymer 4.

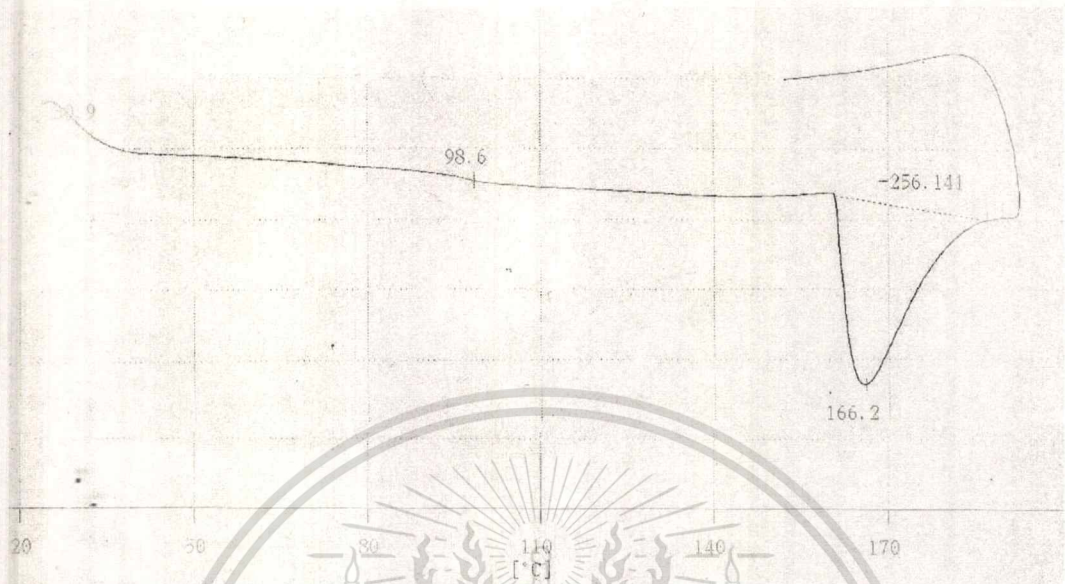


Figure D-5 DSC thermogram of tapioca starch graft copolymer 5.

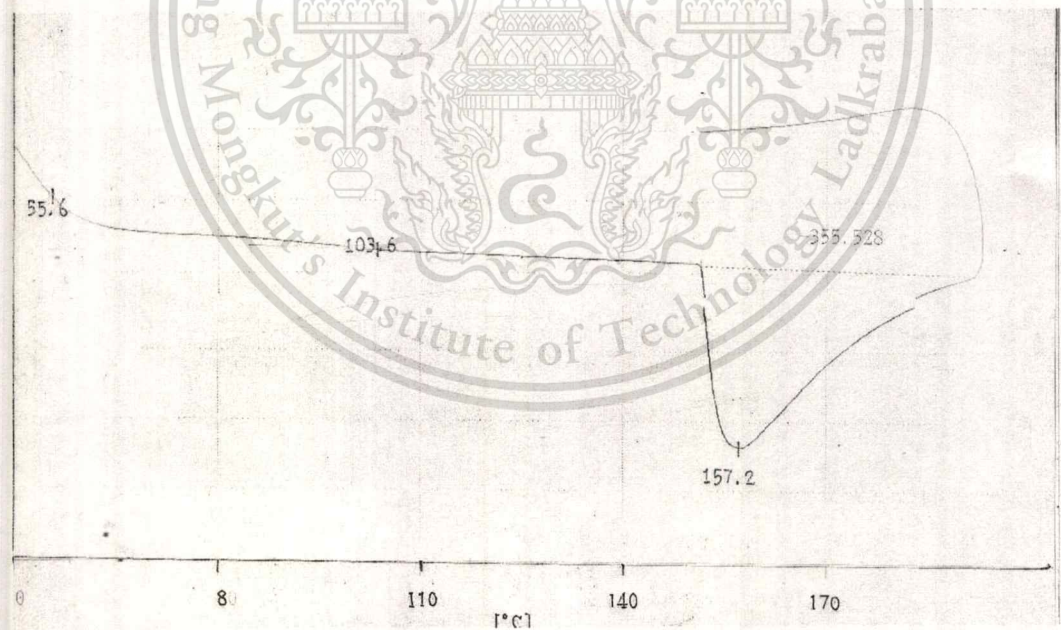


Figure D-6 DSC thermogram of tapioca starch graft copolymer 6.

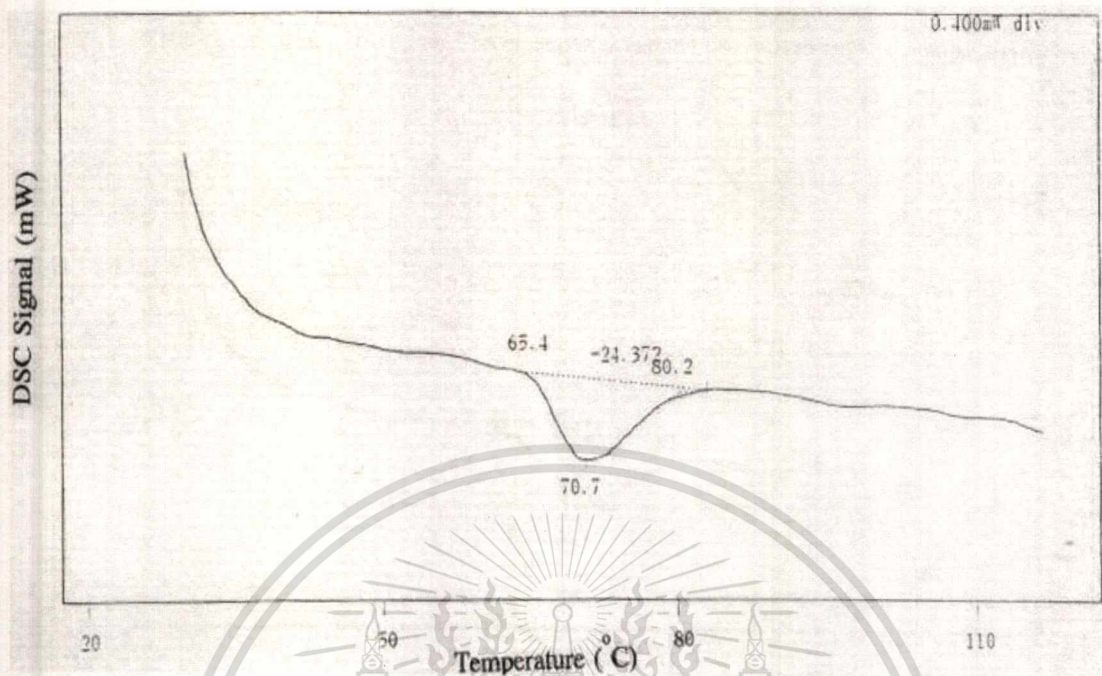


Figure D-7 DSC thermogram of tapioca starch.

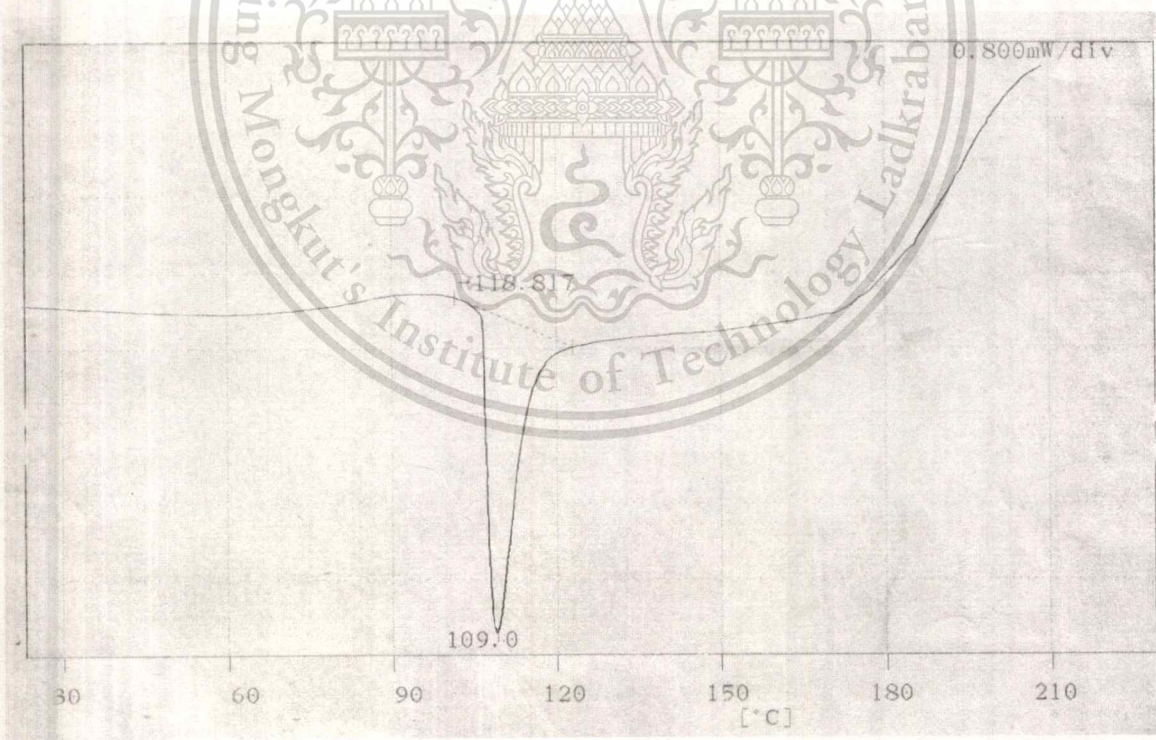


Figure D-8 DSC thermogram of PS.

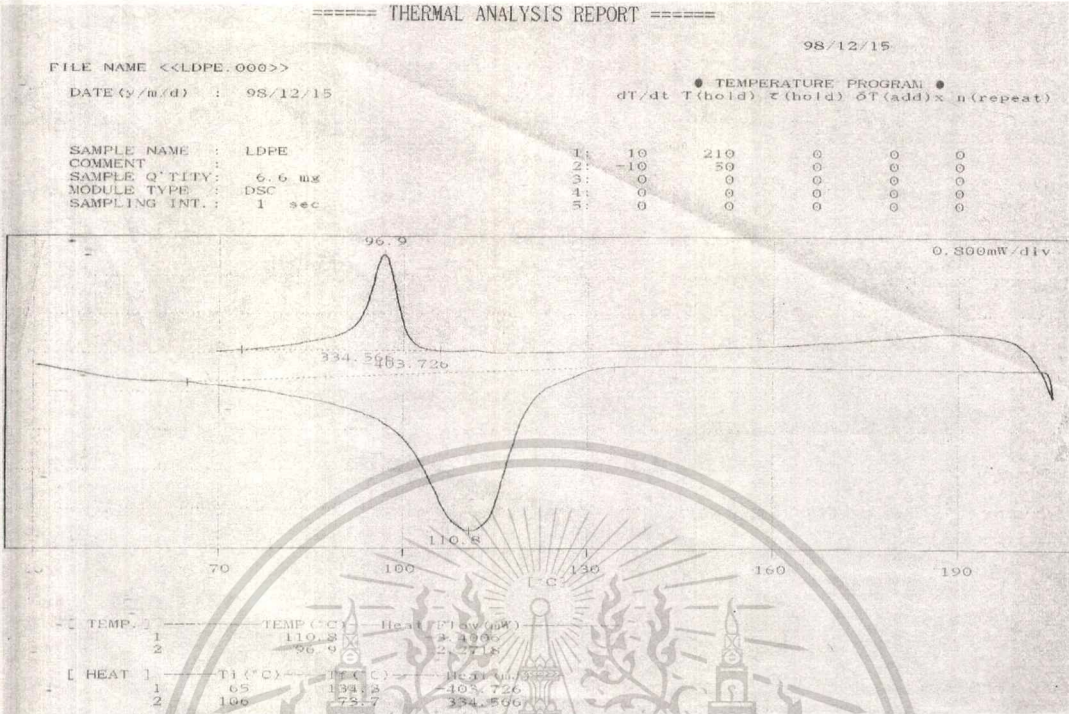


Figure D-11 DSC thermogram of LDPE.

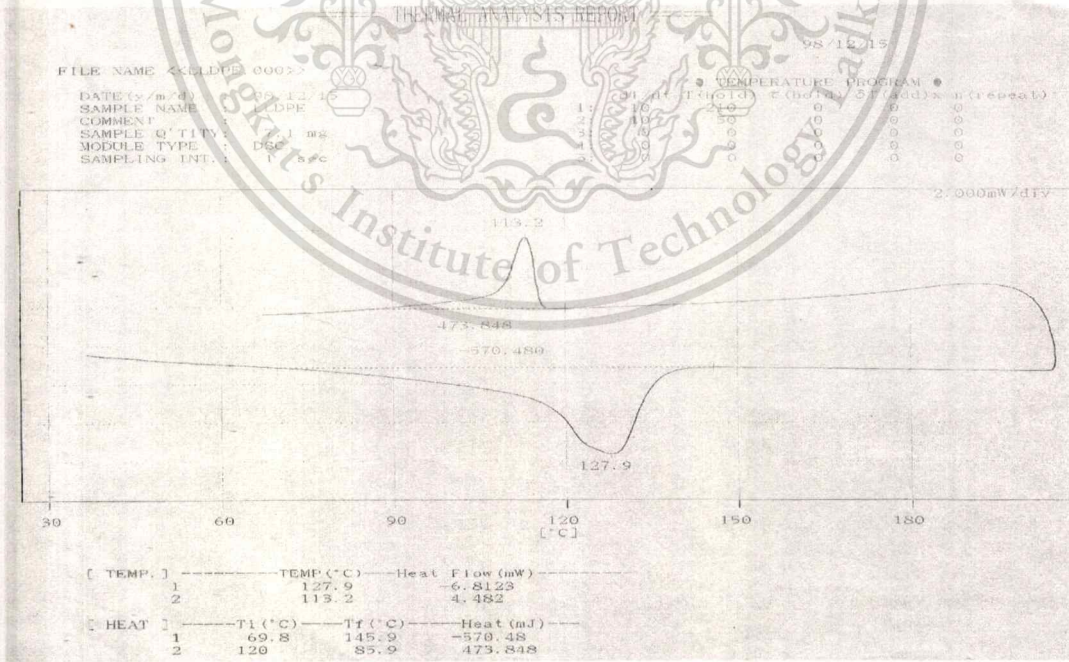


Figure D-12 DSC thermogram of LLDPE.

APPENDIX E

Rheological Properties of Tapioca Starch

Graft Copolymers 1-6



ROSAND PRECISION-CAPELLARY-RHEOMETER

16th Sep 1998 3:22pm

TEST INFORMATION

Polymer type..... 1
 Trade name.....
 Grade.....
 Batch number.....

Lab code number.....
 Molecular weight Mw.....
 Filler percentage.....
 Filler types.....
 Sample origin.....
 Additional information...

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

TEST TEMPERATURE

Top zone temp (°C)..... 150
 Middle zone temp (°C)..... 150
 Bottom zone temp (°C)..... 150
 Bottom actual temp (°C)... 150.0

TEST GEOMETRY

Long die length (mm).... 36
 Long die diameter (mm).. 2.0
 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.....
 Transducer at short die...
 Max pressure (psi)..... 1500
 Information.....

PREHEAT SEQUENCE

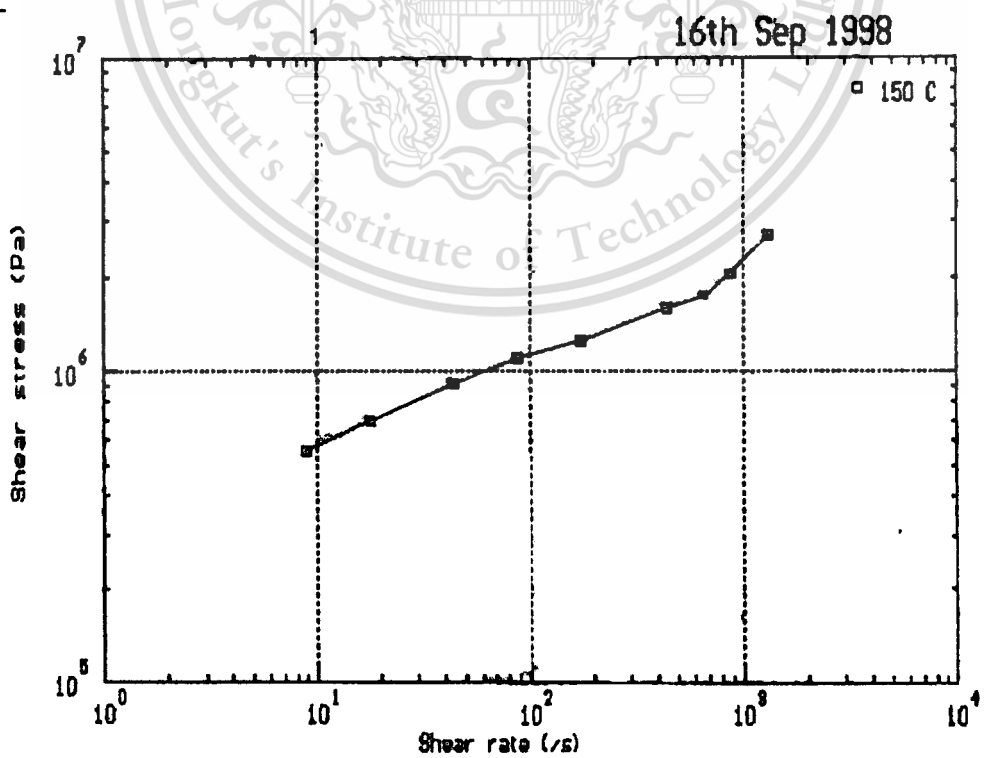
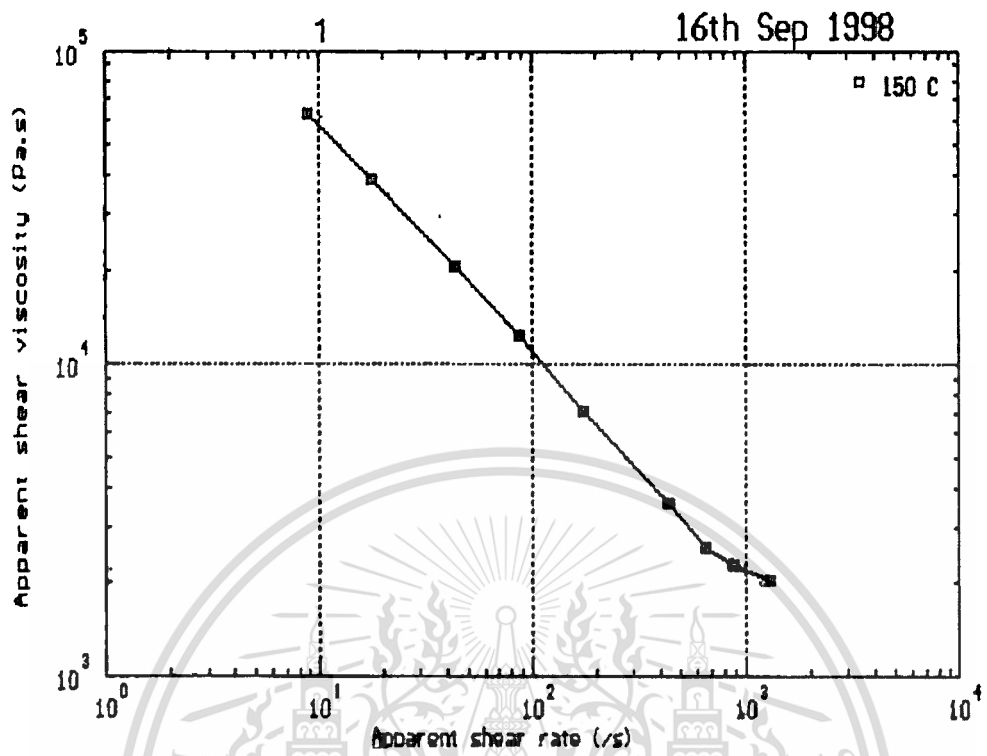
Initial pressure long die (MPa).... 0.5
 Initial pressure short die (MPa)... 0.5
 Time before 2nd compression (min).. 6
 Final pressure long die (MPa)..... 0.6
 Final pressure short die (MPa)..... 0.5
 Preheat time (min)..... 2

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.... PP
 File title.... PP 26

RECALLED TEST RESULTS

	Shear rate /s	Time s	P1 MPa	Ps MPa	Po MPa	Shear Stress kPa	Shear Visc Pa.s	Exten Stress kPa	Elong Visc kPa.s	n
M	3.7	275.4	9.72	0	0	135.03	36009	0	0	0.15
	7.5	323.4	10.96	0	0	152.21	20294	0	0	0.18
	18.7	339.9	13.06	0	0	181.33	9671	0	0	0.21
	37.5	355.0	15.77	0	0	219.05	5841	0	0	0.24
	75.0	360.5	18.96	0	0	263.34	3511	0	0	0.26
	187.5	366.5	23.64	0	0	328.39	1751	0	0	0.30
	281.2	372.0	26.56	0	0	368.91	1312	0	0	0.31
	375.0	375.5	28.56	0	0	396.72	1058	0	0	0.32
	562.5	381.0	32.55	0	0	452.08	804	0	0	0.34
	750.0	384.6	36.26	0	0	503.55	671	0	0	0.35
	937.5	391.5	40.71	0	0	565.42	603	0	0	0.36
	1125.0	395.0	45.28	0	0	628.90	559	0	0	0.36



ROSAND PRECISION CAPILLARY RHEOMETER

8th-Oct 1998 1:33pm

TEST INFORMATION

Polymer type..... 2
 Trade name.....
 Grade.....
 Batch number.....

Lab code number.....
 Molecular weight Mw.....
 Filler percentage.....
 Filler types.....
 Sample origin.....
 Additional information... RUN TEST

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

TEST TEMPERATURE

Top zone temp (°C)..... 150
 Middle zone temp (°C)..... 150
 Bottom zone temp (°C)..... 150
 Bottom actual temp (°C)... 150.0

TEST GEOMETRY

Long die length (mm).... 36
 Long die diameter (mm).. 2.0
 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

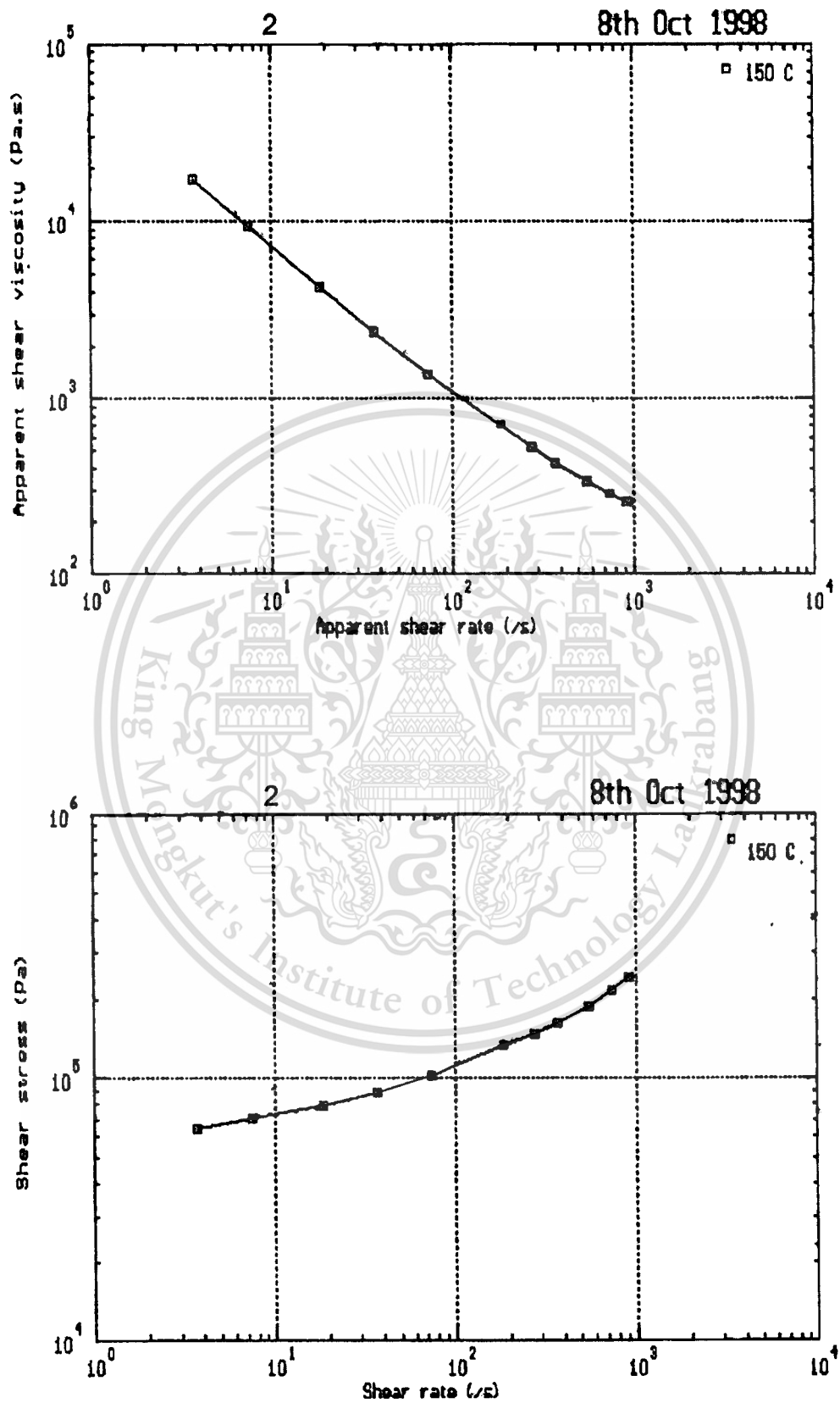
Initial pressure long die (MPa).... 0.5
 Initial pressure short die (MPa)... 0.5
 Time before 2nd compression (min).. 6
 Final pressure long die (MPa)..... 0.5
 Final pressure short die (MPa)..... 0.5
 Preheat time (min)..... 2

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.... PP
 File title.... 3 41

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
3.7	82.6	4.62	0	0	64.16	17110	0	0	0.05
7.5	103.6	5.06	0	0	70.23	9364	0	0	0.10
18.7	115.7	5.65	0	0	78.52	4188	0	0	0.16
37.5	123.7	6.36	0	0	88.36	2356	0	0	0.20
75.0	130.2	7.36	0	0	102.26	1364	0	0	0.24
187.5	136.7	9.58	0	0	133.01	709	0	0	0.30
281.2	141.2	10.59	0	0	147.11	523	0	0	0.33
375.0	144.7	11.57	0	0	160.71	429	0	0	0.35
562.5	148.7	13.46	0	0	186.95	332	0	0	0.37
750.0	154.2	15.45	0	0	214.59	286	0	0	0.39
937.5	164.2	17.35	0	0	240.99	257	0	0	0.41
N 1125.0	181.8	34.74	0	0	482.49	429	0	0	1.00



ROSAND PRECISION-CAPILLARY-RHEOMETER

8th Oct 1998 4:47pm

TEST INFORMATION

Polymer type..... 3
 Trade name.....
 Grade.....
 Batch number.....

Lab code number.....
 Molecular weight Mw.....
 Filler percentage.....
 Filler types.....
 Sample origin.....
 Additional information...

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

TEST TEMPERATURE

Top zone temp (°C)..... 150
 Middle zone temp (°C)..... 150
 Bottom zone temp (°C)..... 150
 Bottom actual temp (°C)... 150.0

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

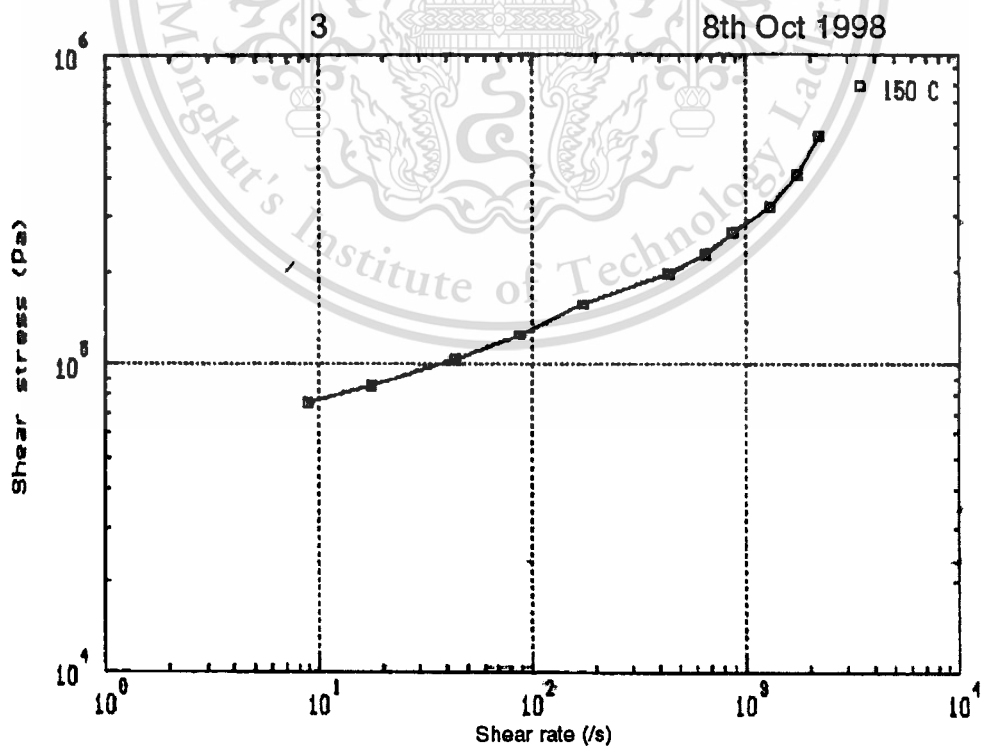
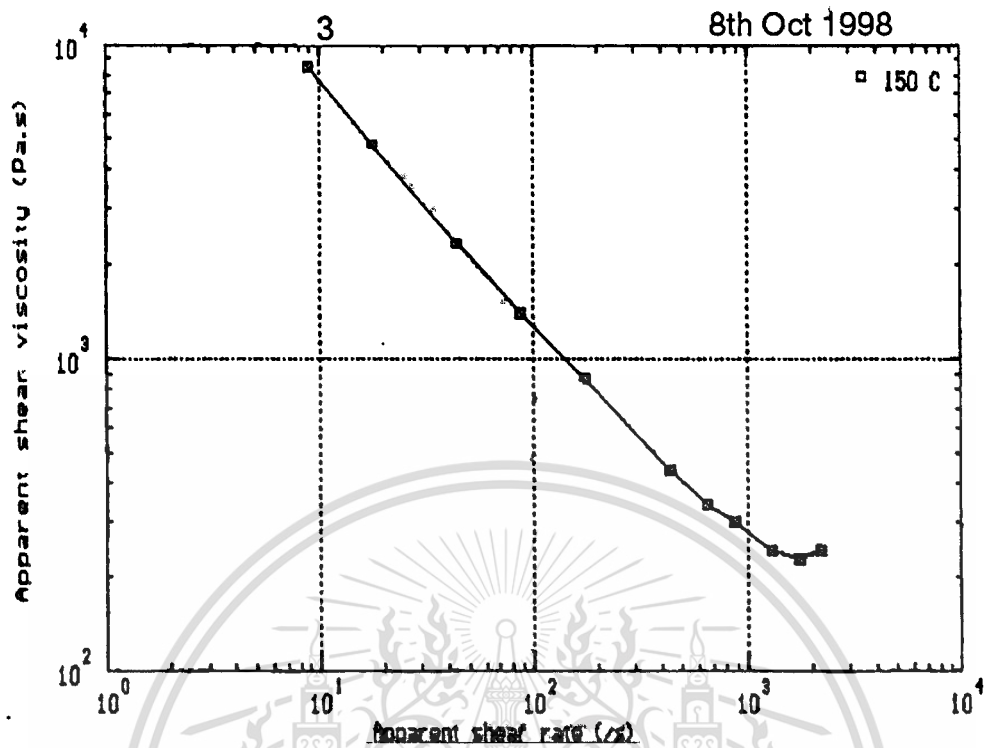
Initial pressure long die (MPa).... 0.5
 Initial pressure short die (MPa)... 0.5
 Time before 2nd compression (min).. 6
 Final pressure long die (MPa)..... 0.5
 Final pressure short die (MPa)..... 0.5
 Preheat time (min)..... 2

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... PP
 File title.... 5 43

CURRENT TEST RESULTS

Shear rate /s	Time s	P1 MPa	P2 MPa	P0 MPa	Shear Stress kPa	Shear Visc Pa.s	Exten Stress kPa	Elong Visc kPa.s	n
8.9	104.7	4.81	0	0	75.12	8451.5	0	0	0.06
17.8	137.7	5.47	0	0	85.40	4803.6	0	0	0.12
44.4	152.7	6.57	0	0	102.67	2310.0	0	0	0.21
88.9	164.7	7.94	0	0	124.02	1395.2	0	0	0.28
177.8	171.3	9.93	0	0	155.16	872.8	0	0	0.34
444.4	176.3	12.44	0	0	194.38	437.4	0	0	0.43
666.7	181.8	14.37	0	0	224.51	336.8	0	0	0.47
888.9	188.2	16.95	0	0	264.78	297.9	0	0	0.49
1333.3	200.3	20.60	0	0	321.84	241.4	0	0	0.53
1777.8	213.3	26.02	0	0	406.56	228.7	0	0	0.56
2222.2	235.3	34.48	0	0	538.69	242.4	0	0	0.58
N 2666.7	236.8	22.73	0	0	355.23	133.2	0	0	1.00



ROSAND PRECISION CAPILLARY RHEOMETER

8th Oct 1998 3:40 am

TEST INFORMATION

Polymer type..... 4
 Trade name.....
 Grade.....
 Batch number.....

Lab code number.....
 Molecular weight Mw.....
 Filler percentage.....
 Filler types.....
 Sample origin.....
 Additional information...

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

TEST TEMPERATURE

Top zone temp (°C)..... 150
 Middle zone temp (°C)..... 150
 Bottom zone temp (°C)..... 150
 Bottom actual temp (°C)... 150.0

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

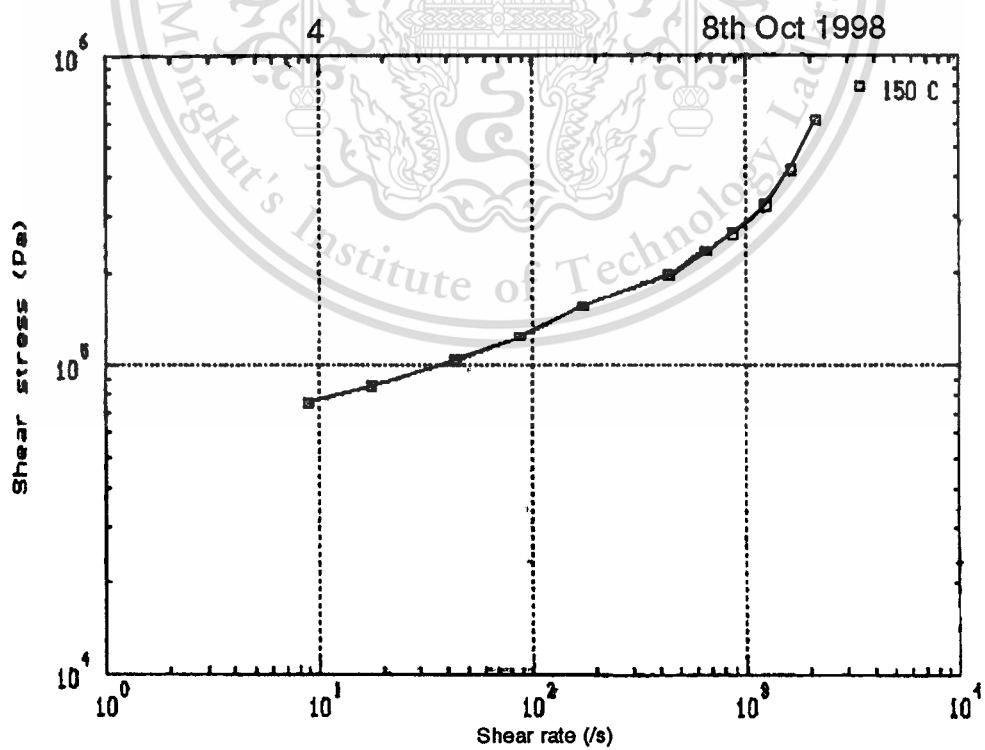
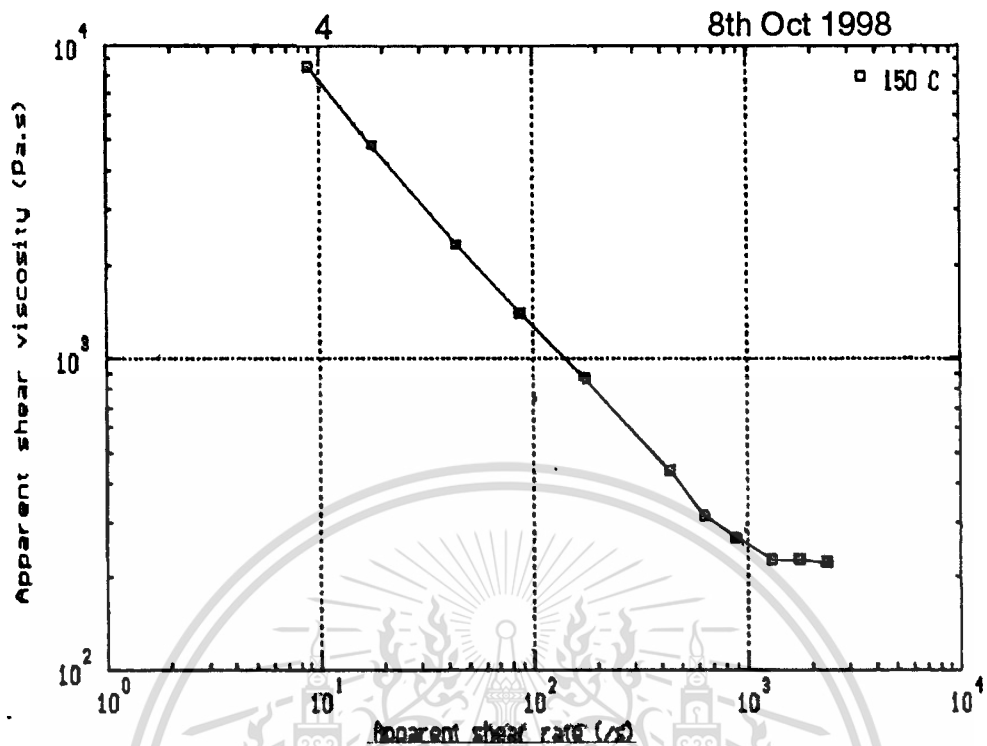
Initial pressure long die (MPa).... 0.5
 Initial pressure short die (MPa).... 0.5
 Time before 2nd compression (min).. 6
 Final pressure long die (MPa)..... 0.5
 Final pressure short die (MPa)..... 0.3
 Preheat time (min)..... 2

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.... PP
 File title.... 5 43

CURRENT TEST RESULTS

Shear rate /s	Time s	P1 MPa	P2 MPa	P0 MPa	Shear Stress kPa	Shear Visc Pa.s	Exten Stress kPa	Elong Visc kPa.s	n
8.9	104.7	4.81	0	0	75.12	8451.5	0	0	0.06
17.8	137.7	5.47	0	0	85.40	4803.6	0	0	0.12
44.4	152.7	6.57	0	0	102.67	2310.0	0	0	0.21
88.9	164.7	7.94	0	0	124.02	1395.2	0	0	0.28
177.8	171.3	9.93	0	0	155.16	872.8	0	0	0.34
444.4	176.3	12.44	0	0	194.38	437.4	0	0	0.43
666.7	181.8	14.37	0	0	224.51	336.8	0	0	0.47
888.9	188.2	16.95	0	0	264.78	297.9	0	0	0.49
1333.3	200.3	20.60	0	0	321.84	241.4	0	0	0.53
1777.8	213.3	26.02	0	0	406.56	228.7	0	0	0.56
2222.2	235.3	34.48	0	0	538.69	242.4	0	0	0.58
N 2666.7	236.8	22.73	0	0	355.23	133.2	0	0	1.00



RODAND PRECISION-CAPILLARY MOUNTED

16th Sep 1998 12:51pm

TEST INFORMATION

Polymer type..... 5
 Trade name.....
 Grade.....
 Batch number.....

Lab code number.....
 Molecular weight Mw.....
 Filler percentage.....
 Filler types.....
 Sample origin.....
 Additional Information...

Operator's initials.....
 Mu/In.....
 Drying temperature.....
 Drying-atmosphere.....
 Drying hours.....

TEST TEMPERATURE

Top zone temp (°C)..... 150
 Middle zone temp (°C)..... 150
 Bottom zone temp (°C)..... 150
 Bottom actual temp (°C)... 150.0

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/cm/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

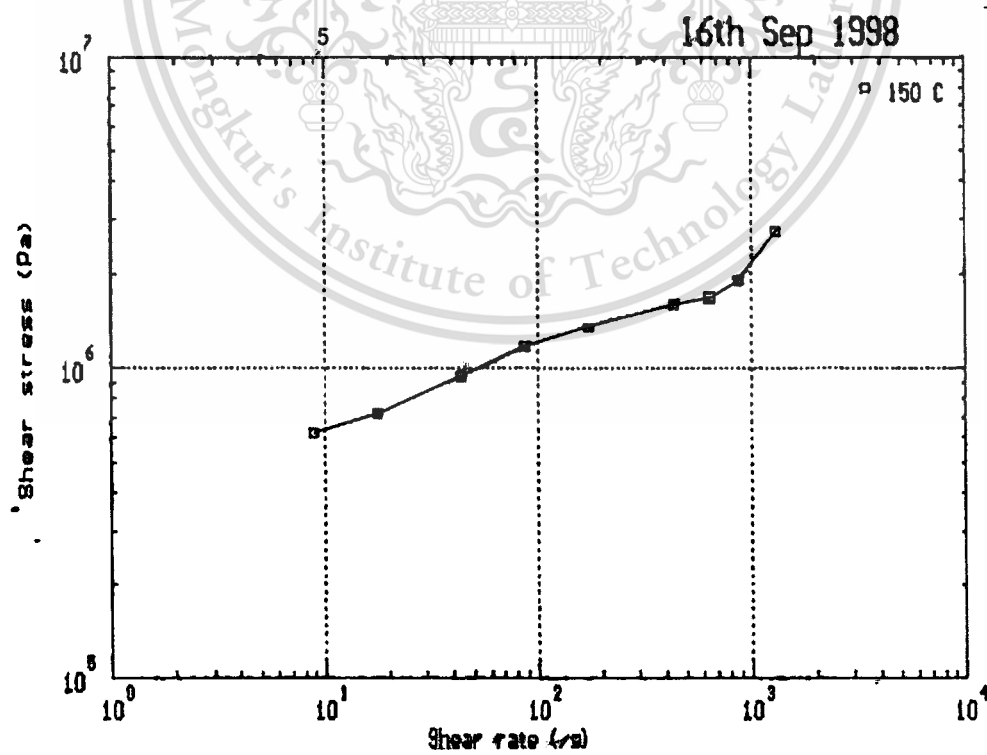
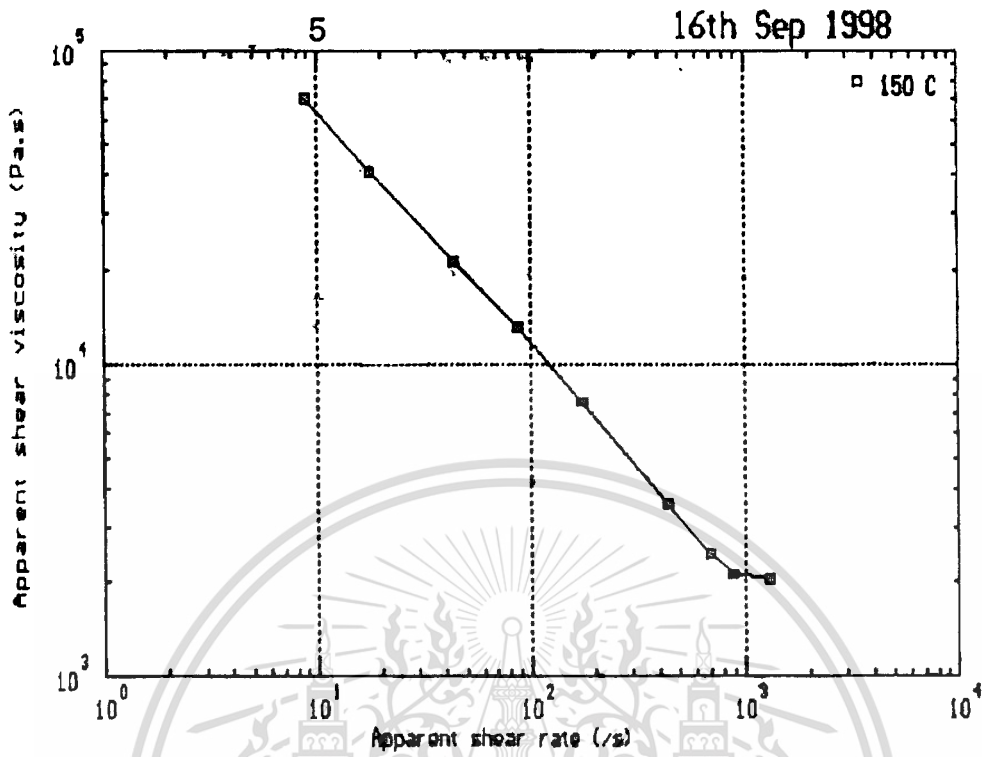
Initial pressure short die (MPa)... 0.5
 Time before 2nd-compression (min).. 6
 Final pressure long die (MPa)..... 0.5
 Final pressure short die (MPa)..... 0.5
 Preheat time (min)..... 2

CONTROL FACTORS

Initial pressure long die (MPa).... 0.5 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.... c
 File title.... PP 60

RECALLED TEST RESULTS

Shear rate /s	Time s	P1 MPa	P2 MPa	P3 MPa	Shear Stress kPa	Shear Visc Pa.s	Exten Stress kPa	Elong Visc kPa.s	n
8.9	99.1	7.98	0	0	135.03	36009	0	0	0.09
18.7	132.1	9.71	0	0	152.21	20294	0	0	0.15
37.5	145.7	12.37	0	0	181.33	9671	0	0	0.23
75.0	158.7	14.44	0	0	219.05	5841	0	0	0.28
187.5	163.2	17.63	0	0	263.34	3511	0	0	0.34
281.2	169.2	21.69	0	0	328.39	1751	0	0	0.42
375.0	172.2	25.67	0	0	368.91	1312	0	0	0.45
562.5	181.7	30.11	0	0	396.72	1058	0	0	0.48
750.0	192.7	33.44	0	0	452.08	804	0	0	0.51
937.5	196.2	36.26	0	0	503.55	671	0	0	0.53
1125.0	205.7	40.71	0	0	565.42	603	0	0	0.55
1333.3	212.7	45.28	0	0	628.90	559	0	0	0.57



ROSAND PRECISION-CAPILLARY-RHEOMETER

16th Sep 1998 1:05 pm

TEST INFORMATION

Polymer type..... 6
 Trade name.....
 Grade.....
 Batch number.....

Lab code number.....
 Molecular weight Mw.....
 Filler percentage.....
 Filler types.....
 Sample origin.....
 Additional information...

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

TEST TEMPERATURE

Top zone temp (°C)..... 150
 Middle zone temp (°C)..... 150
 Bottom zone temp (°C)..... 150
 Bottom actual temp (°C)... 150.0

TEST GEOMETRY

Long die length (mm).... 36
 Long die diameter (mm).. 2.0
 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.....
 Transducer at short die...
 Max pressure (psi)..... 1500
 Information.....

PREHEAT SEQUENCE

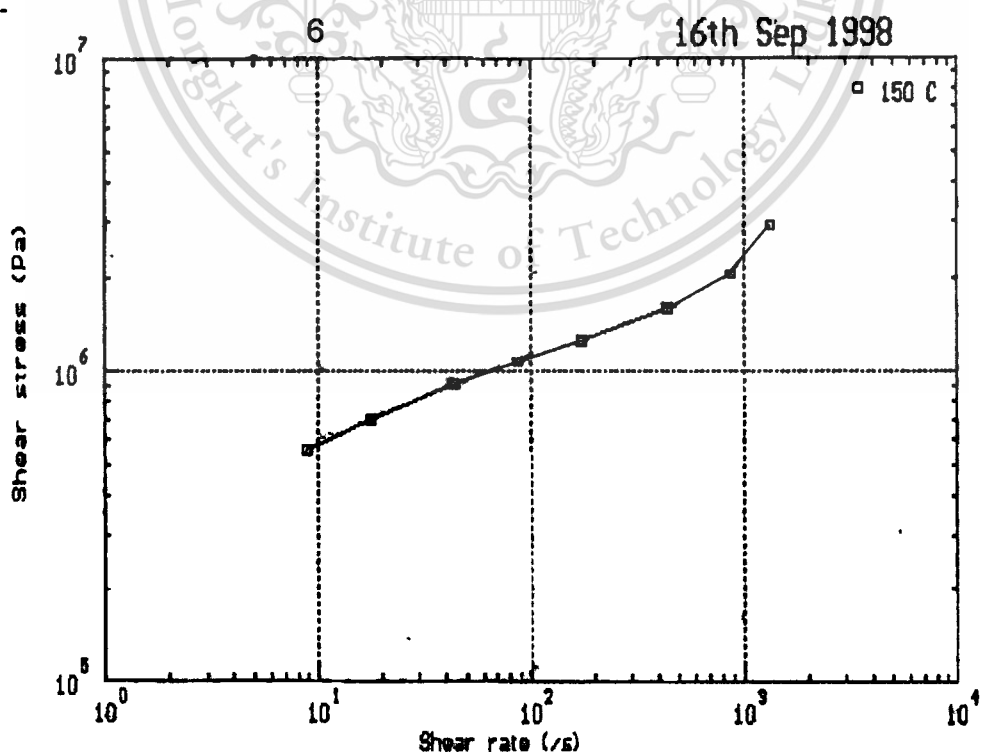
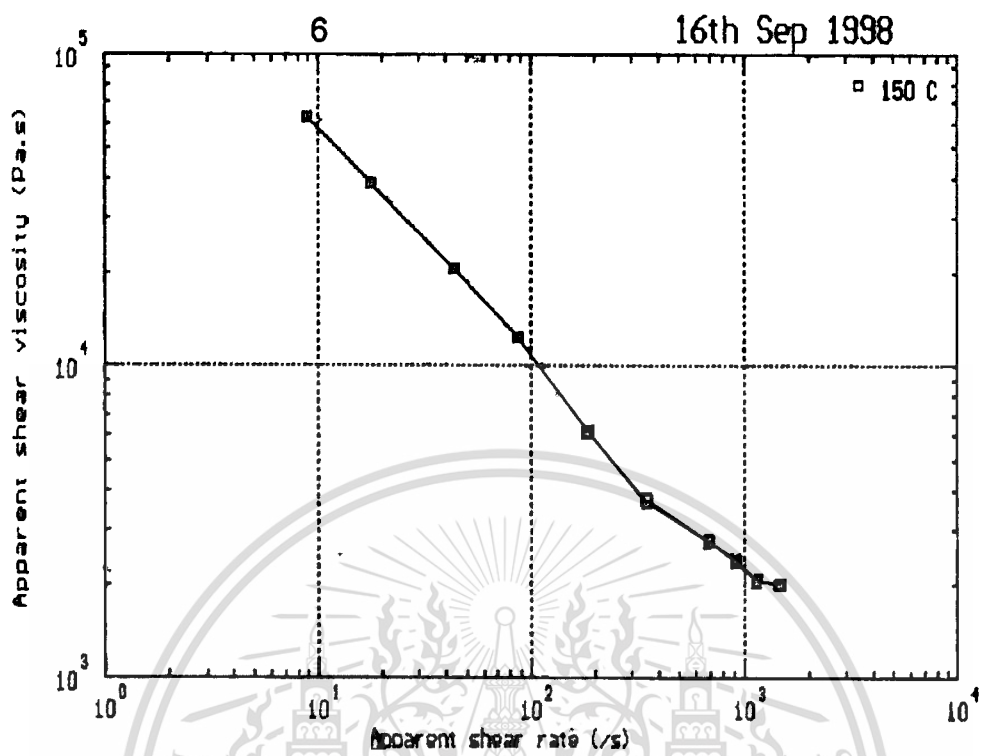
Initial pressure long-die (MPa).... 0.5
 Initial pressure short die (MPa).... 0.5
 Time before 2nd compression (min).. 6
 Final pressure long die (MPa)..... 0.5
 Final pressure short die (MPa)..... 0.5
 Preheat time (min)..... 2

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.... PP
 File title.... PP 26

RECALLED TEST RESULTS

	Shear rate /s	Time s	P1 MPa	P2 MPa	P3 MPa	Shear Stress kPa	Shear Visc Pa.s	Exten Stress kPa	Elong Visc kPa.s	n
M	3.7	275.4	9.72	0	0	135.03	36009	0	0	0.15
	7.5	323.4	10.96	0	0	152.21	20294	0	0	0.18
	18.7	339.9	13.06	0	0	181.33	9671	0	0	0.21
	37.5	355.0	15.77	0	0	219.05	5841	0	0	0.24
	75.0	360.5	18.96	0	0	263.34	3511	0	0	0.26
	187.5	366.5	23.64	0	0	328.39	1751	0	0	0.30
	281.2	372.0	26.56	0	0	368.91	1312	0	0	0.31
	375.0	375.5	28.56	0	0	396.72	1058	0	0	0.32
	562.5	381.0	32.55	0	0	452.08	804	0	0	0.34
	750.0	384.6	36.26	0	0	503.55	671	0	0	0.35
	937.5	391.5	40.71	0	0	585.42	603	0	0	0.36
	1125.0	395.0	45.28	0	0	638.90	559	0	0	0.36



APPENDIX F

Molecular Weight Determination of Side Chain Polymers



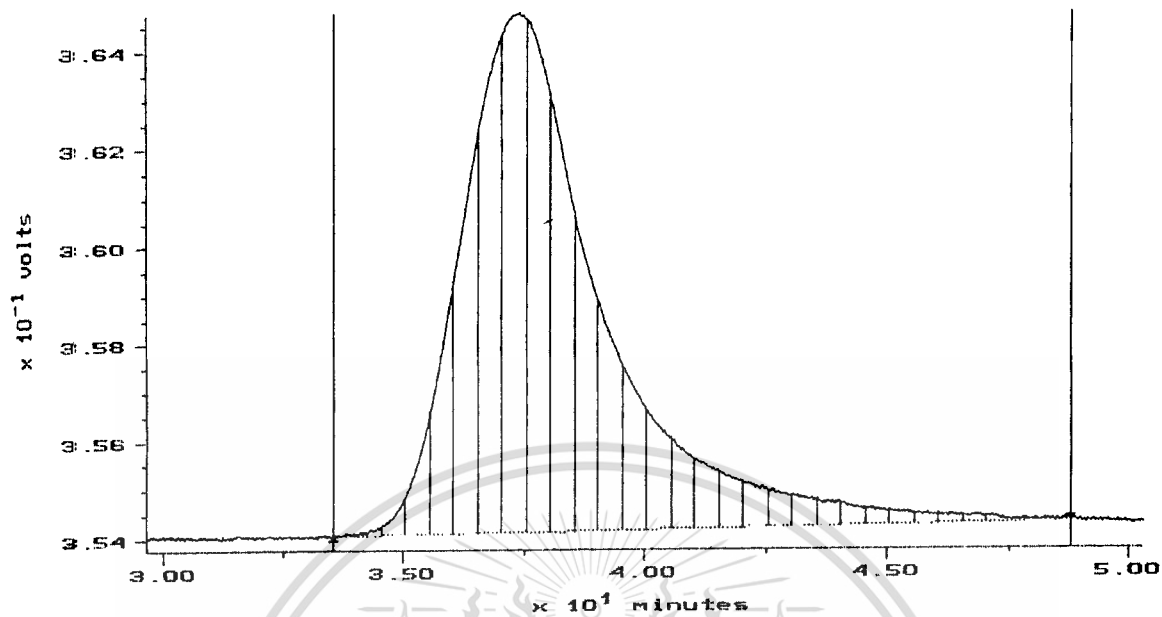


Figure F-1 Molecular weight determination of side chain polymers condition 1.

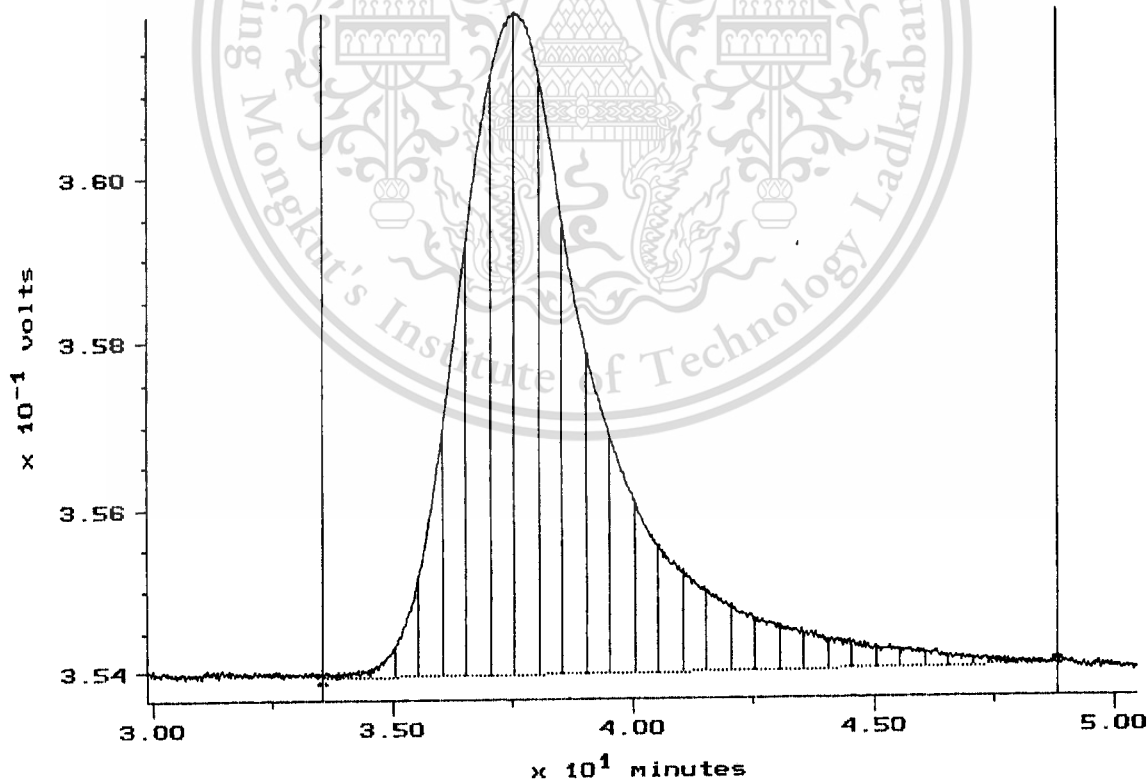


Figure F-2 Molecular weight determination of side chain polymers condition 2.

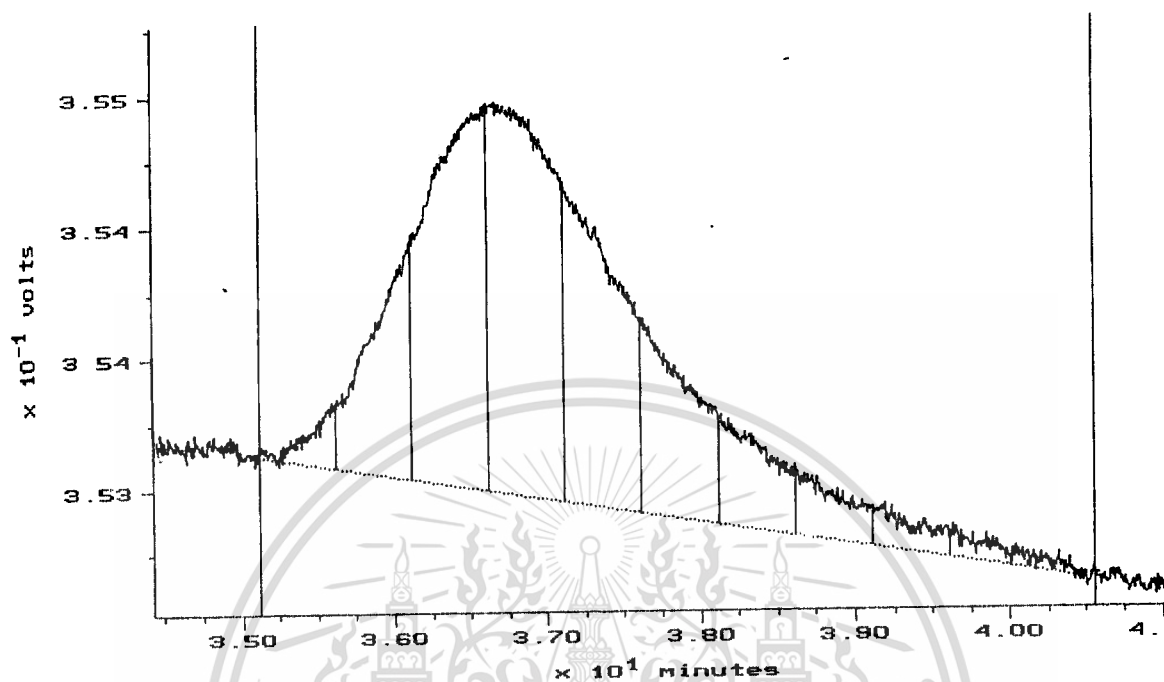


Figure F-3 Molecular weight determination of side chain polymers condition 3.

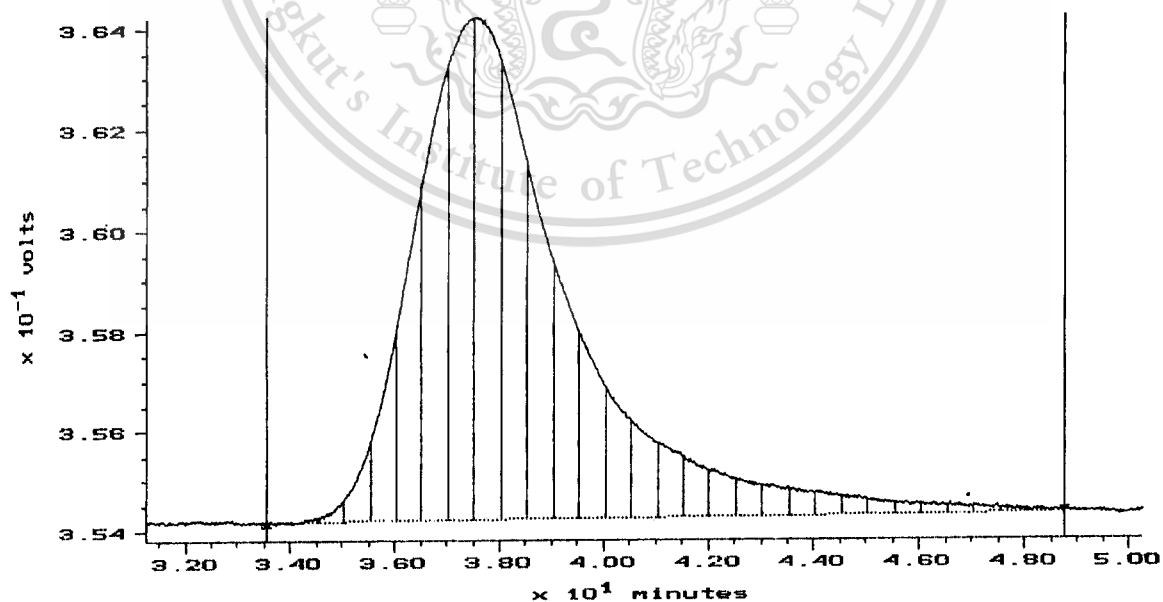


Figure F-4 Molecular weight determination of side chain polymers condition 4.

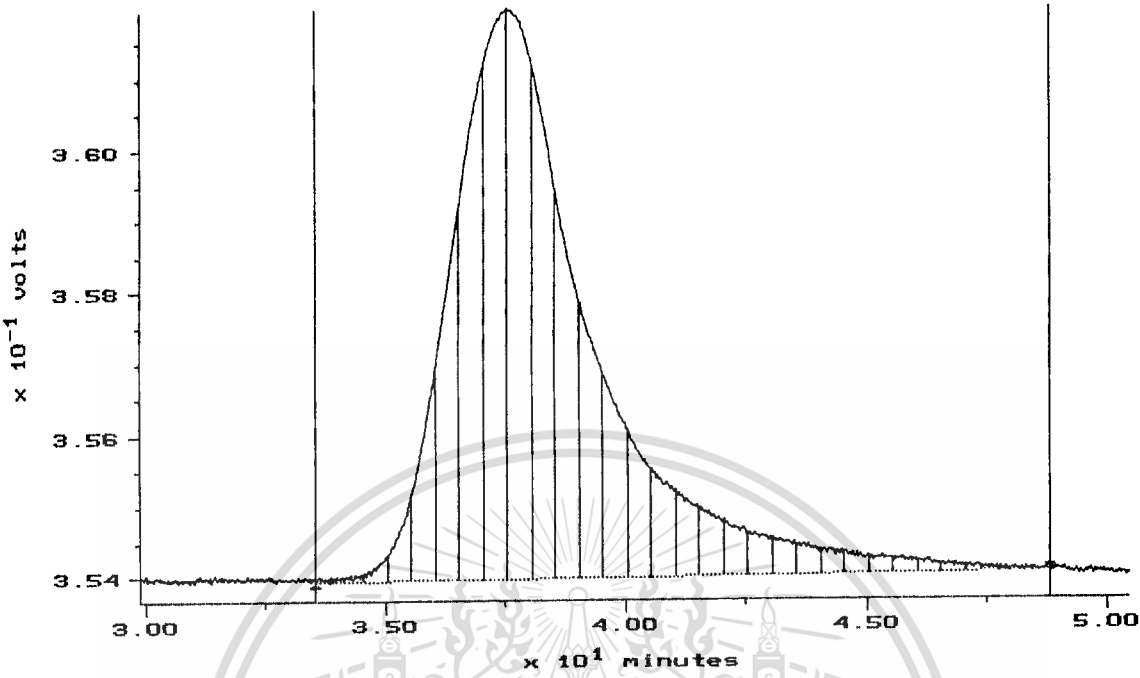


Figure F-5 Molecular weight determination of side chain polymers condition 5.

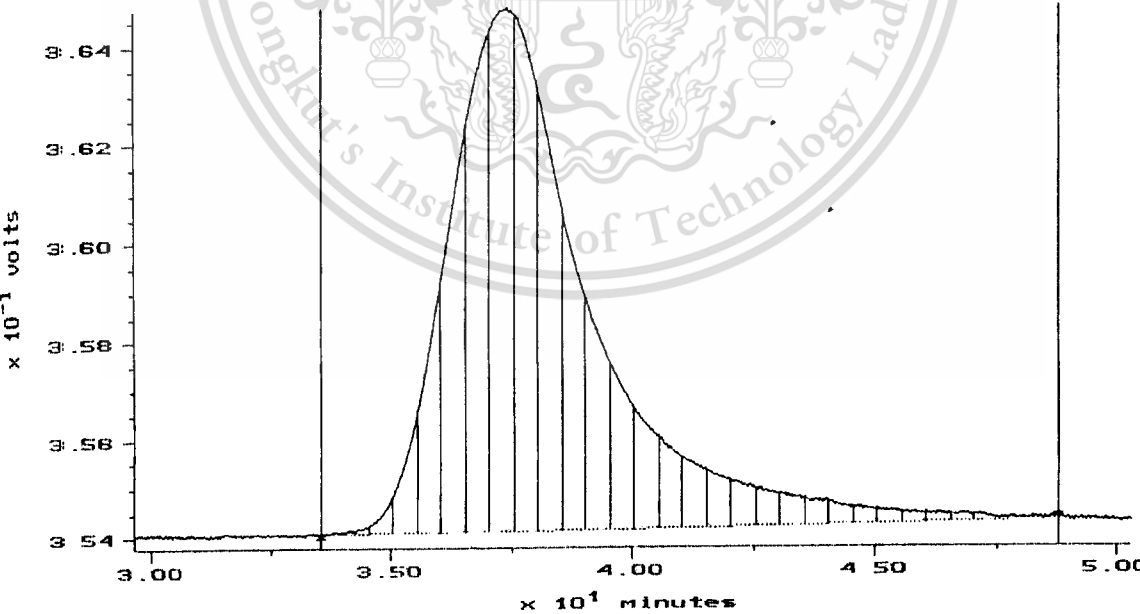


Figure F-6 Molecular weight determination of side chain polymers condition 6.

APPENDIX H

Monthly FOB Price of Tapioca Starch (Unit : Baht / kg)

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Avg.
2002	7.78	7.91	8.10	8.70	8.64	8.31	7.75	7.63	7.46	7.61	-	-	-
2001	6.66	6.58	7.03	7.64	7.78	8.22	8.51	8.39	7.78	7.79	7.80	7.59	7.65
2000	6.09	6.10	5.84	6.13	6.37	6.41	6.40	6.40	6.10	6.00	6.50	6.55	6.24
1999	7.25	7.35	7.68	7.85	7.51	6.97	6.27	6.11	6.15	6.30	6.17	6.31	6.83
1998	12.74	16.65	12.85	12.94	12.74	13.23	12.89	12.17	9.82	8.17	7.80	7.70	11.31
1997	6.53	6.49	6.46	6.49	6.45	6.43	7.27	7.35	8.55	8.90	9.36	10.52	7.57
1996	8.16	8.05	7.79	7.80	7.81	7.83	7.52	6.92	6.82	6.47	6.46	6.48	7.34
1995	8.73	8.69	8.63	8.67	8.81	9.52	10.00	9.82	8.82	8.25	8.27	8.21	8.87
1994	5.03	5.31	5.83	5.88	5.77	6.14	6.05	5.98	6.06	6.41	7.16	8.58	6.18
1993	5.52	5.45	5.70	5.52	5.41	5.27	5.12	4.70	4.45	4.37	4.54	4.63	5.06
1992	5.75	5.90	5.93	6.06	6.29	6.27	6.25	5.96	5.65	5.60	5.55	5.52	5.89
1991	6.01	5.97	6.18	6.17	6.19	6.41	6.35	6.0	5.92	5.91	5.99	5.74	6.07
1990	5.03	5.16	5.57	5.89	5.61	5.73	5.44	5.55	5.78	6.18	6.2	6.49	5.74
1989	4.10	4.11	4.13	4.23	4.59	47.61	4.22	4.17	4.07	4.04	4.66	4.26	4.22
1988	4.06	4.04	4.00	4.27	4.33	4.28	4.29	4.39	4.18	4.13	4.22	4.12	4.19

Source : Office of Agricultural Economics

APPENDIX G
Notification of The Ministry of Public Health
No. 111 (B.E. 2531 (1988))



UNOFFICIAL
NOTIFICATION OF THE MINISTRY OF PUBLIC HEALTH
No. 111 (B.E. 2531 (1988))

Re : Qualities or Standards of Plastic Containers, Usage
 Of Plastic Containers, and Prohibition of Usage of
 Articles as Food Containers.

* * * *

Whereas it is deemed appropriate to revise the prescription respecting the qualities or standards of plastic containers to be used as food containers,

By virtue of Section 5 and Section 6 (6) and (9) of the Food Act B.E. 2522 (1979), the Minister of Public Health hereby notifies that :

No. 1 The provisions of No. 5 of the Notification of the Ministry of Public Health No. 92 (B.E. 2528 (1985)) Re Qualities of Standards of Containers, Usage of Containers, and Prohibition of Usage of Articles as Food Containers, dated 19th January 1985, shall be repealed and replaced by this Notification.

NO.2 In this Notification, container means an article used to contain food, irrespective of whether it be used by putting the food therein, or by wrapping the food, or by any other method, and it shall mean to include cover or stopper as well.

No. 3 Plastic container shall have the following qualities or standards :

- (1) shall be clean ;
- (2) shall give out no other substance to contaminate with the food in a quantity that may be hazardous to health;
- (3) shall have no microorganism that causes diseases;
- (4) shall give out no colour to contaminate with the food.

No. 4 Plastic container, which must have the qualities or standards under No. 3, shall also be subject to the qualities of standards per List No.1 annexed hereto.

No. 5 The analysis of qualities or standards of dissemination of plastic container shall be carried out by the method prescribed by the Food and Drug Administration.

No. 6 Plastic which is in sheet or bag form and is used as food container shall not be made from used plastic. Except :

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

- (1) laminate plastic. specifically the layer that does not contact directly with the food ;
- (2) plastic used to contain fruits with peel.

NO. 7 It is prohibited to use coloured plastic container to contain food, except :

- (1) laminate plastic in sheet or bag form, specifically the layer that does not contact directly with the food;
- (2) plastic used to contain fruits with peel;
- (3) where an approval has been obtained from the Food and Drug Administration.

No. 8. Plastic container used to contain milk, milk products or product of the like. Namely soya bean milk. Ready-made coconut milk, shall be polyethylene, polypropylene, polystyrene or polycarbonate plastic.

For the purpose of paragraph one, milk product means cultured milk, modified milk for infant, flavoured milk, ice cream and milk product under the Notification of the Ministry of Public Health governing such; and milk, milk product and product of the like shall not include those in the form of powder, or of dry type.

No. 9 It is prohibited to use plastic container which had been used to contain or wrap fertilizer, poisonous articles or articles that may be hazardous to health as food container.

No. 10 It is prohibited to use plastic container made up for containing other things than food. Or plastic container with picture, design, or statement that could lead to misinterpretation of the significant part of the food contained therein, as food container.

This Notification shall be enforced on and from the day following the date of its publication in the Government Gazette.

Notified this 22nd day of January 1988

THOEDPONG CHAIYANAN

Minister of Public Health

(Ref. : Government Gazette. Volume 105. Part 46. Of 24th March 1988)

Annexed to the Notification : of the Ministry of Public Health No 11 (B.E. 2531 (1988))

Table 1 : Qualities or Standards of Plastic.

Particulars	Maximum quantity allowed (Mg./1 kg.)					
	Polyvinyl- chloride	Polyethylene : Polypropylene	Polystyrene	Polyvinyl lidene	Polyethylene teraphthalate	Of the type that the layer that contacts with the food is polyethylene and polypropylene plastic, for containing milk, milk product or product of the like
(a) Lead	100	100	100	100	100	-
(b) Heavy metal (calculated as lead)	-	-	-	-	-	20
(c) Barium	-	-	-	100	-	-
(d) Dibutyltin compound	50	-	-	-	-	-
(e) Cresyl phosphate	1,000	-	-	-	-	-
(f) Vinyl chloride monomer	1	-	-	-	-	-
(g) Volatile substances, i.e., toluene, ethyl benzene, isopropyl benzene, propyl benzene and styrene	-	-	5,000 2,000**	-	-	1,500
(h) Vinylidene chloride	-	-	-	6	-	-
(i) Arsenic	-	-	-	-	2	2
(j) Extracts by Hexane	-	-	-	-	26,000	-
(k) Substances soluble in xylene	-	-	-	-	113,000	-

Remarks : - No analysis needed

* Other plastic the qualities or standards of which have not been prescribed shall have the qualities or standards as approved by the Food and Drug Administration.

** In case of using it at temperature higher than 100°C, Whereby the quantity of styrene must not exceed 1,000 mg./ 1 kg. And the quantity of ethyl benzene must not exceed 1,000 mg./ 1 kg.

Table 2 : Qualities or standards of migration of plastic.

Particulars	Type of Plastic*	Maximum quantity allowed (mg./l kg.)						Of the type that the layer that contacts with the food is polystyrene plastic, for containing milk, milk product and product of the like	Of the type that the layer that contacts with the food is polyethylene and polypropylene plastic, for containing milk, milk product or product of the like
		Polyvinyl-chloride	Polyethylene Polypropylene	Polystyrene	Polyvinylidene	Polyethylene teraphthalate	Melamine **		
(a) Phenol	-	-	-	-	-	-	30	-	-
(b) Formaldehyde	-	-	-	-	-	-	2	-	-
(c) Antimony	-	-	-	-	-	0.05	-	-	-
(d) Germanium	-	-	-	-	-	0.1	-	-	-
(e) Heavy metals(calculated as metal)	1	1	1	1	1	1	1	1	-
(f) Potassium permanganate used for making chemical reaction	10	10	10	10	10	10	10	5	5
(g) Residues volatile in water (in case of food with pH value more than 5)	30	30	30	30	30	30	30	15	15
(h) Residues from substance volatile in acetic acid of 4% concentration (in case of food with pH value not more than 5)	30	30	30	30	30	30	30	15	15
(I) Residues from substance in alcohol of 20% concentration (in case of food with alcohol)	30	30	30	30	30	30	30	15	15
(J) Residues from substance volatile in heptane (in case of fat, oil and food with fat)	150	150	30***	240	30	30	30	15	15

Remarks :

- No analysis needed.
- * Other plastic the qualities or standards of which have not been prescribed shall have the qualities or standards as approved by the Food and Drug Administration.
- ** Must be analyzed at working temperature.
- *** In case of using it at temperature higher than 100°C.

APPENDIX I

Condition of Injection Molding Machine for Preparing Tensile and Impact Specimens.

Temperature programming

NOZZLE TEMP.	150
ZONE 1 TEMP.	140
ZONE 2 TEMP.	130
ZONE 3 TEMP.	120

Time programming

DIE CLS/OPN TIME	60	MELTING TIME	120
SID-COR ACT TIME	20	DECOMPRS TIME	2
1 th STG. INJ. TIME	45	COOLING TIME	50
2 ND STG. INJ. TIME	40	EJECTOR COUNT	2
3 RD STG. INJ. TIME	35	SCW. FEW. TIME	0
EJE. FWD. DLY TIME	0	SCW. BWD. TIME 1	0
MEL. FWD. DLY TIME	0	SCW. BWD. TIME 2	0
EJE. BKD. DLY TIME	0	ALARM TIME	500

Programming flow speed

RAPID CLS. SPD.	40	1 ST STG. INJ. SPD.	30
HIGH CLS. SPD.	25	2 ND STG. INJ. SPD.	20
CLAMPING SPD.	15	3 RD STG. INJ. SPD.	25
DIE OPN. SLW.1	5	MELTING SPD.	35
RAPID OPN. SPD.	25	DECOMP. SPD.	50
DIE OPN. SLW.	15	EJECTOR SPD.	20
PLUNGER SPD.	20	SCREW-IN SPD.	0
DIE ADJ. SPD.	25	DIE CHANGE SPD.	0

Pressure programming

DIE CLS. PRESR.	26	MELTING PRESR.	80
CLS. LOW PRESR.	30	DECOMP. PRESR.	100
CLS. HI PRESR.	50	PLUNGER PRESR.	20
DIE OPN. PRESR.	30	EJECTOR PRESR.	5
1 ST INJ. PRESR.	45	SCW-IN PRESR.	10
2 ND INJ. PRESR.	40	DIE ADJ. PRESR.	50
3 RD INJ. PRESR.	35		

