

การปรับปรุงความทนแรงกระแทก เสถียรภาพเชิงความร้อนและต่อรังสียูวีของแผ่นอะคริลิกโดย
การเติมพอลิ(สไตรีน-โค-เมทิลเมทาคริเลต)-กราฟต์-ยางอีพิตีเอ็ม



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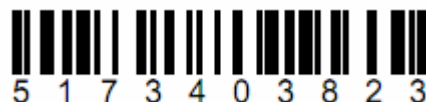
วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

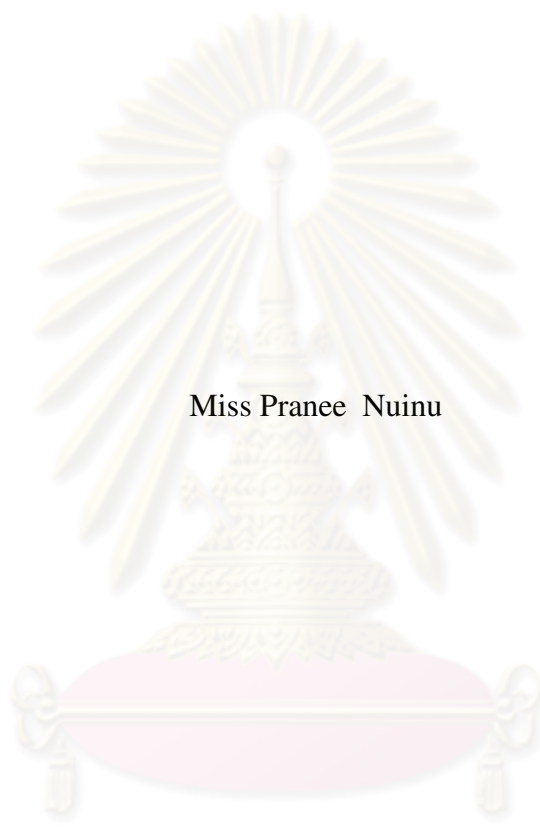
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2553

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย



IMPROVEMENT OF IMPACT STRENGTH, THERMAL AND UV STABILITIES
OF ACRYLIC SHEETS BY ADDITION OF POLY(STYRENE-*co*-METHYL
METHACRYLATE)-*g*-EPDM RUBBER



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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2010
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ปราณี นุ้ยหนู : การปรับปรุงความทนแรงกระแทก เสถียรภาพเชิงความร้อนและต่อรังสียูวี
ของแผ่นอะคริลิกโดยการเติมพอลิ(สไตรีน-โค-เมทิลเมทาคริเลต)-กราฟต์-ยางอีพีดีเอ็ม.

(IMPROVEMENT OF IMPACT STRENGTH, THERMAL AND UV STABILITIES OF
ACRYLIC SHEETS BY ADDITION OF POLY(STYRENE-co-METHYL
METHACRYLATE)-g-EPDM RUBBER) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ. ดร.นพิตา
หิญาธิระนันท์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร.สมหมาย ผิวสะอาด, 92 หน้า.

งานวิจัยนี้ศึกษาสมบัติเชิงกลรวมทั้งเสถียรภาพเชิงความร้อนและรังสียูวีของแผ่นอะคริลิกที่
ปรับปรุงแล้วซึ่งมีกราฟต์โคพอลิเมอร์ของพอลิเมทิลเมทาคริเลตและสไตรีนบนยางอีพีดีเอ็ม
(GEPDM) ซึ่งสังเคราะห์ด้วยกระบวนการพอลิเมอไรเซชันแบบสารละลาย เตรียมแผ่นอะคริลิก
(เมทิลเมทาคริเลต/สไตรีน = 80/20 %โดยน้ำหนัก) ด้วยกระบวนการพอลิเมอไรเซชันแบบบัลค์ โดย
ใช้เบนโซอิลเปอร์ออกไซด์และสารประกอบเอโซเป็นตัวริเริ่มปฏิกิริยา ตัวแปรที่ใช้ในการกำหนดการ
กราฟต์โคพอลิเมอร์คือ เวลาในการทำปฏิกิริยา พบว่าเวลาในการทำปฏิกิริยาที่ 16 ชม. เป็น
เวลาที่ทำให้ประสิทธิภาพการกราฟต์ของ GEPDM สูงสุดที่ 88.1% จากนั้นศึกษาผลของประสิทธิภาพ
การกราฟต์ และปริมาณของยางกราฟต์ต่อสมบัติเชิงกลและทางกายภาพก่อนและหลังการบ่มเร่ง
ด้วยความร้อนและแสงอัลตราไวโอเล็ตของแผ่นอะคริลิก สมบัติความทนทานต่อแรงกระแทกและ
การดัดโค้งของแผ่นอะคริลิกเพิ่มขึ้นตามปริมาณ GEPDM โดยให้ค่าสูงสุดที่ 52.1 กิโลจูล/ตาราง
เมตรและ 96.8 เมกะปาสคาล ตามลำดับ เมื่อเติม GEPDM ในแผ่นอะคริลิกที่ 2% โดยน้ำหนัก
ความทนทานต่อแรงดึงและระยะยืด ณ จุดขาดลดลงเมื่อปริมาณของ GEPDM เพิ่มขึ้นโดยมีค่าสูง
ที่สุดที่ 73.3 เมกะปาสคาล และ 5.71% ที่ปริมาณยาง GEPDM 1 และ 2% โดยน้ำหนักตามลำดับ
ความเสถียรของสมบัติเชิงกลของแผ่นอะคริลิกที่มี GEPDM หลังการบ่มเร่งด้วยความร้อนและรังสี
ยูวีดีกว่าแผ่นอะคริลิกที่ปรับปรุงโดยการเติมยาง EPDM ที่ 1% โดยน้ำหนัก จากข้อมูลทาง
จลนพลศาสตร์ของการสลายตัวด้วยความร้อน พบว่าแผ่นอะคริลิกที่เติม GEPDM มีค่าพลังงาน
กระตุ้นในการสลายตัว (210.7 กิโลจูล/โมล) มากกว่าแผ่นอะคริลิกที่ไม่ได้เติม GEPDM (183.4 กิโล
จูล/โมล) นอกจากนี้การเติม GEPDM เพิ่มความทึบแสงของแผ่นอะคริลิกทำให้เกิดการยับยั้งการ
ส่องผ่านของรังสียูวี ส่งผลให้แผ่นอะคริลิกที่มี GEPDM มีความต้านทานต่อรังสียูวีมากขึ้น จาก
ข้อมูลการทดลองแสดงว่ายาง GEPDM สามารถนำมาประยุกต์ใช้ในการปรับปรุงสมบัติเชิงกลและ
เสถียรภาพเชิงความร้อนและรังสียูวีของแผ่นอะคริลิกได้

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อผู้ผลิต.....ปราณี นุ้ยหนู.....

ปีการศึกษา..2553.....

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....*สมหมาย*

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม.....*นพิตา*

5173403823 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
 KEYWORDS : ACRYLIC / GRAFT COPOLYMER / EPDM RUBBER / METHYL
 METHACRYLATE / STYRENE

PRANEE NUINU : IMPROVEMENT OF IMPACT STRENGTH, THERMAL
 AND UV STABILITIES OF ACRYLIC SHEETS BY ADDITION OF
 POLY(STYRENE-*co*-METHYL METHACRYLATE)-*g*-EPDM RUBBER.
 THESIS ADVISOR : ASST. PROF. NAPIDA HINCHIRANAN, Ph.D.,
 THESIS CO-ADVISOR: ASST. PROF. SOMMAI PIVSA-ART, Ph.D., 92 pp.

This research studied the mechanical properties including thermal and UV stability of the modified acrylic sheet containing graft copolymer of poly(methyl methacrylate-*co*-styrene) on EPDM (GEPDM) synthesized via solution polymerization. The modified acrylic sheet (methyl methacrylate/styrene = 80/20 wt%) was prepared by bulk polymerization using benzoyl peroxide and azo-compounds as initiators. The parameter for controlling the level of graft copolymerization was reaction time. It was found that the 16 h of reaction time gave the maximum %grafting efficiency as 88.1%. Then, the mechanical properties and their stability of the modified acrylic sheets before and after thermal and UV aging were reported as functions of %GE and GEPDM content. The impact and flexural strength of the modified acrylic sheets increased with increasing GEPDM content. The maximum impact strength and flexural strength of the modified acrylic sheet were 52.08 KJ/m² and 96.75 MPa, respectively when GEPDM was applied as 2 wt%. The tensile strength and elongation at break of the modified acrylic sheet decreased with increasing GEPDM content. It reached to the maximum values at 73.32 MPa and 5.71% when the modified acrylic sheet contained GEPDM content at 2 and 1 wt%, respectively. The mechanical properties retention of the modified acrylic sheets after thermal and UV aging was better than that of ones containing 1 wt% of EPDM. From the kinetic data of the thermal degradation, the activation energy of the acrylic sheets containing GEPDM (210.7 kJ/mol) was higher than that of ones without GEPDM content (183.4 kJ/mol). Moreover, the addition of GEPDM increased the opacity of the acrylic sheet resulting to inhibit the UV penetration. This could increase the UV resistance of the modified acrylic sheet. These experimental results implied that GEPDM could act as the mechanical properties improver including thermal and UV stabilizer for the acrylic sheets.

Field of Study :...Petrochemistry and
 Polymer Science.....
 Academic Year : 2010.....

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ACKNOWLEDGMENTS

The author would like to express her gratitude to her advisor, Assistant Professor Napida Hinchiranan, Ph.D. and co-advisor, Assistant Professor Sommai Pivsa-Art, Ph.D. for their encouraging guidance, supervision and helpful suggestion throughout this research. In addition, she is also grateful to Assistant Professor Warinthorn Chavasiri Ph.D., Associate Professor Wimonrat Trakarnpruk, Ph.D. and Assistant Professor Kitikorn Charmondusit, Ph.D., for serving as an external examiner of thesis committee.

The author also thanks for the research financial supports from the Petrochemistry and Polymer Science Program of Chulalongkorn University and Center for Petroleum, Petrochemical, and Advanced Materials, Thailand Research Fund Window II (MAG-WII525S018), the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund). The author wishes to express her thankfulness to the Department of Materials and Metallurgical Engineering of Rajamangala University of Technology Thanyaburi and Pan Asia Industrial Co., Ltd for their hospitality in providing equipment. Many thanks are going to Ms. Weraporn Pivsa-Art and Mr. Chaiwute Vudjung for their assistance during the period of this research.

Thanks are going towards her friends whose names are not mentioned here but and contributed their assistance, suggestion, advice concerning the experimental techniques and the encouragement during the period of this work.

Finally, and most of all, the author wishes to express her deepest gratitude to her family; especially her parents for their love, support and encouragement throughout graduate study.

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LIST OF ABBREVIATIONS

EPDM	:	Ethylene propylene methylene diene rubber
GEPDM	:	Grafted ethylene propylene methylene diene rubber
ST	:	Styrene
MMA	:	Methyl methacrylate
LPE	:	Light petroleum ether
MEK	:	Methyl ethyl ketone
ABVN	:	2,2'-Azobis-(2,4-dimethylvaleronitrile)
BPO	:	Benzoyl peroxide
GE	:	Grafting efficiency
FT-IR	:	Fourier-Transform Infrared Spectrometer
NMR	:	Nuclear Magnetic Resonance Spectrometer
SEM	:	Scanning Electron Microscope
EB	:	Elongation at break
TS	:	Tensile strength
b.p.	:	Boiling point
°C	:	Degree celsius
phr	:	Part per hundred
wt	:	Weight
wt%	:	% by weight
h	:	Hour
min	:	Minute

CHAPTER I

INTRODUCTION

1.1 Purpose of investigation

Poly(methyl methacrylate) (PMMA) or acrylic is a thermoplastic, which is a high amorphous. The production of the acrylic sheets is carried out by bulk polymerization via casting process. Due to its advantages in terms of high clarity and safety with light weight and high resistance to outdoor environment, it is used in various applications such as aircraft window, car components, laminated glass, laminated roof, protective coating, lens, transparency roof tile, dyed interior decorated product, dental materials, optical equipment, instrument, light box, furniture, stand menu, aquarium and appliance covers, home furnishings etc (Billmeyer, 1984 and Fred, 1971). Polystyrene (PS) is also thermoplastic material, which has similar properties to PMMA (Charmondusit et al., 2009). To compare the price of methyl methacrylate (MMA) and styrene (ST) monomers in mid-May of 2010, the price of MMA was \$2,250 -2,300/ton while ST was \$1,250-1,300/ton (Asian market review by Clive Ong, ICIS pricing, 2010). It was also reported that the price of MMA monomer will be more expensive than that of ST as 77% per year. This will directly affect on the production cost of acrylic products. In order to decrease the cost of the acrylic sheet production, the copolymerization technique of MMA and ST has been considered. However, the resulting product exhibit the brittle property and low impact strength (Oommen et al., 1993).

There are many attempts to improve mechanical properties of brittle materials by blending with elastic polymers such as butadiene rubber, styrene-butadiene rubber (Sriprachuabwong et al., 2006), ethylene-vinyl acetate copolymer, natural rubber (Prasertpong et al., 2008) and polyurethane (Heim et al., 1993). However, these rubbers contain unsaturated C=C bonds resulting in poor thermal and oxidation stability which limit to outdoor applications. Thus, the saturated elastomers are attractive materials to use for improving the mechanical properties including

oxidative and thermal stability of the brittle materials. Ethylene-propylene-diene rubber (EPDM), one of saturated rubbers, shows outstanding thermal resistance to heat, light, oxygen and ozone according to its less content of C=C bonds and non-conjugated diene component (Indian Rubber Institute, 1998). EPDM has been used as a toughen agent for non-polar polymers, such as polypropylene (PP) (Bassani and Pessan, 2002). To get satisfied toughening properties, EPDM is often grafted with vinyl and/or acryl monomers to increase its polarity to blend with plastics for preparing the high impact engineering material with excellent resistance to weatherability, yellow discoloration and aging property (Morton, 1973).

Generally, the blend of polymer with highly different polarity exhibits poor mechanical properties of final product due to incompatibility and phase separation (Bemiller, 1976). To minimize phase separation and increase interfacial adhesion, the addition of a compatibilizing agent such as a third polymer, a graft or block copolymer, could improve the interaction between the constituent polymers. It is well known that the graft copolymers promote the adhesion between the rubbery and glassy phases resulting in mechanical property improvement of the blends (Collyer, 1994). Therefore, the objective of this research was to prepare graft copolymer of MMA and ST on EPDM rubber via solution polymerization initiated by benzoyl peroxide. The modified acrylic sheets were prepared by bulk polymerization of MMA with a small amount of graft rubber and then casted in a two-glass plate mold. The mechanical, and physical properties including morphology of the modified acrylic sheets were investigated in terms of percentage of grafting efficiency and graft EPDM content. The thermal and ultraviolet (UV) resistance including kinetics of thermal degradation were also reported.

1.2 Research objectives

The objectives of this research could be summarized as follows:

1. To prepare the graft copolymer of MMA and ST on EPDM rubber at various reaction time to achieve the desired grafting level.

2. To investigate the mechanical properties and morphology of the modified acrylic sheets containing graft EPDM (GPDM) with various contents and grafting levels.
3. To study the thermal and UV stability of the modified acrylic sheets containing GEPDM with various contents and grafting levels. The kinetics of thermal degradation of the modified acrylic sheets was also reported.

1.3 Scope of investigation

In preparation of GEPDM, the effect of the reaction time of graft copolymerization step on the grafting properties was investigated. Subsequently, the GEPDM was added into the monomer mixture of MMA and ST at 80/20 wt% for preparing the modified acrylic sheets. The effect of the GEPDM content and percentage of grafting efficiency (%GE) on the mechanical and physical properties of the modified acrylic sheets was examined before and after thermal and ultraviolet ageing. The morphology of the modified acrylic sheet before ageing was also reported. The step experiments were as follows:

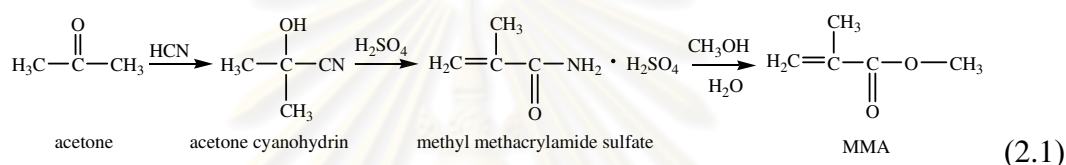
1. Literature survey and in-depth study of this research work.
2. Preparation of graft copolymer of MMA and ST on EPDM rubber via solution copolymerization initiated by using benzoyl peroxide.
3. Structure characterization of the GEPDM.
4. Preparation of the modified acrylic sheets containing various contents and grafting levels of GEPDM by bulk polymerization.
5. Investigation of the effect of GEPDM content and %GE of GEPDM on the mechanical and physical properties of the modified acrylic sheets before and after thermal and UV ageing.
6. Study of the kinetics of thermal degradation of the modified acrylic sheets.
7. Summary of results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Methyl methacrylate and poly(methyl methacrylate) (Fred, 1971)

Methyl methacrylate (MMA) is a monomer used for production of the transparent plastic poly(methyl methacrylate) (PMMA). Generally, MMA is synthesized from acetone and hydrogen cyanide as shown in eq. 2.1:



In a typical process, acetone is treated with hydrogen cyanide at 40°C in the presence of ammonia used as a catalyst to produce acetone cyanohydrin. Then, the acetone cyanohydrin is treated with concentrated sulfuric acid at 100°C to form methyl methacrylamide sulfate which is directly fed into an aqueous methanol to produce MMA. The MMA product is separated by steam and purified by distillation. The MMA or acrylic monomer is colorless liquid with a characteristic sweet odor. Its boiling point is ca. 100.5°C. For shipping and storage, hydroquinone or *p*-methoxyphenol is commonly used as an inhibitor for MMA monomer to inhibit the self-polymerization of MMA (Ghosh, 1990).

The first acrylic polymer commercially produced was poly(methyl acrylate). Its production was begun in 1927 by Rohm and Haas AG in Germany. In about 1930, Hill of Imperial Chemical Industries Ltd. (UK) prepared acrylic or MMA sheets which are potentially useful material for various applications. However, the high raw material cost prohibited the commercial development. At that time, MMA was obtained by dehydrogenation of hydroxyisobutyric ester. In 1932, Crawford synthesized MMA based on cheap raw materials: acetone and hydrogen cyanide. Thus, PMMA or acrylic plastic became a feasible proposition and commercial

production in 1934. The acrylic sheets were used during the Second World War for aircraft glazing. After the world war, the acrylic sheets have been used in various applications such as display signs, lighting fittings and bathroom fittings. PMMA can be melted by heat to replace the casting process. This causes the enhancement of the cost effective means. PMMA is also extensively used for the production of dentures.

The polymerization of MMA is readily accomplished by bulk, solution, suspension and emulsion techniques. Among these methods, bulk and suspension polymerization methods are mainly used for the production of the homopolymer. The production of cast sheets, rods and tubes is carried out by bulk polymerization, starting in most cases with syrup of partially polymerized MMA with a convenient viscosity for handling. In addition, the shrinkage and heat evolution during polymerization are reduced by the use of syrup. PMMA sheets are also commonly made by extrusion. Alternatively, they may be casted in cells consisting of two glass sheets separated by a coated rubber gasket. The polymerization is carried out at 60-70°C in an air oven or water bath, with a finishing treatment at 100°C. Normally, peroxide or azo initiators may be applied as initiators. PMMA prepared by free radical polymerization is amorphous because of its lack of complete stereoregularity and its bulky side groups. It is therefore soluble in aromatic and chlorinated hydrocarbons including esters. However, it has high resistance to water, alkali, solution, inorganic solvent and most dilute acids. PMMA has more resistance to hydrolysis than poly(methyl acrylate), probably by virtue of the shielding presented by the α -methyl group (Brinkmann, 2006).

PMMA is a linear, hard, polar and rigid transparent thermoplastic with a higher softening point, better impact strength, and better weatherability than PS. The typical properties of PMMA are given in Table 2.1. An outstanding property of PMMA is its clarity. Thus, the transmission of normal incident light through a sheet of the polymer is about 92%. A further outstanding property of PMMA is the good outdoor weathering. After several years under tropical conditions, the color change is extremely small. The mechanical and thermal properties of PMMA such as tensile

Table 2.1 Typical properties of poly (methyl methacrylate) (Katsikis et al., 2007)

Property	Value
Density, g/cm ³	1.15-1.19
Water absorption, %	0.3-2
Hardness, Rockwell M	63-97
Young's modulus, GPa	1.79-3.38
Tensile strength, MPa	55-85
Elongation at break, %	1-30
Charpy Impact, J/cm ²	0.2-0.4
Specific heat capacity, J/(g·K)	1.46-1.47
Thermal conductivity, W/(m·K)	0.19-0.24
Glass temperature, °C	100-105
Melting point, °C	130-140
Vicat Softening Point, °C	47-117
Transmission, %	80-93
Refractive index	1.49-1.498

strength, impact strength, etc. are also good. Electrical properties are fair. A limitation of the optical uses of PMMA is its poor abrasion resistance compared to glass. Although it has been found the techniques to improve the scratch resistance, it also deteriorated other properties such as impact strength.

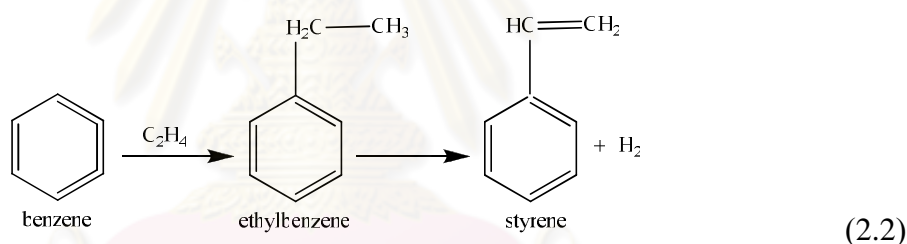
It is generally accepted that the decomposition of PMMA in nitrogen atmosphere consists of three stages: the first stage (100–200°C) is ascribed to the rupture of weak head-to-head linkages in the main chain. The second stage (200–300°C) is decomposition of the terminal vinyl group. Finally, the degradation in the third stage (300–400°C) is related to the random scission of polymer main chain (Hwu et al., 2002). For the decomposition of PMMA in the presence of oxygen, the first peak disappears and the second peak either merges with the third peak or becomes a shoulder to the third peak depending on the heating rate. This phenomenon has been explained by the dual function of oxygen in PMMA decomposition.

At lower temperatures, oxygen inhibits PMMA decomposition by reacting with a polymeric radicals and forming new polymeric radicals with higher stability. Above 270°C, these new polymeric radicals are decomposed and release more reactive radicals resulting to the acceleration of PMMA decomposition (Peterson et al., 1999).

2.2 Styrene and polystyrene (Ghosh, 1990)

Styrene (ST) or vinyl benzene is an organic compound with the chemical formula $C_6H_5CH=CH_2$. Under normal conditions, this aromatic hydrocarbon is an oily liquid and slightly polar compared to ethylene and α -olefins. It is also easily evaporated and smells sweet. It often contains other chemicals having sharp and unpleasant smell.

The bulk of commercial ST is prepared from benzene by the following route (eq. 2.2):



In the first stage, Friedel-Crafts reaction is commonly carried out by treating benzene with ethylene in the liquid phase at 90-100°C at slightly above atmospheric pressure. The catalyst is aluminum chloride (with ethyl chloride as catalyst promoter) to produce ethylbenzene. The second stage involves with the dehydrogenation of ethylbenzene. This reaction is carried out in the vapor phase at 600-650°C over catalyst based on either ferric or zinc oxide with lesser amounts of other metallic oxides such as chromic, cupric, and potassium oxides. The reaction is favored by low pressure. In order to reduce the partial pressure of the ethylbenzene, the feed is mixed with superheated steam before passing over the catalyst. ST is colorless liquid with a characteristic odor and could be refined by distillation.

The production of ST in the United States was dramatically increased during the 1940's to supply the war to be used as the raw material for synthetic

rubber. Because the ST molecule has a vinyl group with a double bond, it can be polymerized. It is normally used as a monomer to make plastics such as polystyrene (PS), acrylonitrile-butadiene-styrene rubber (ABS), styrene-butadiene rubber (SBR) and unsaturated polyesters. These materials are used in rubber, plastic, insulation, fiberglass, pipes, automobile parts, food containers and carpet backing etc.

Polystyrene (PS) is a polymer made from polymerization of ST in four techniques: bulk, solution, suspension, and emulsion polymerizations. Although solution or emulsion polymerization may generally be used, most PS is made either by suspension or bulk polymerization. The chemical structure of PS is shown in Figure 2.1. At room temperature, PS is normally a solid thermoplastic. It can be melted at higher temperature for molding or extrusion.. Commercial interest in PS began in the 1930s when the material was found to have good electronic insulation characteristics. The production was started by I.G. Farben industries (Germany) and Dow Chemical Company (USA) before the Second World War. Application of PS was vigorously explored and quickly adopted in many fields. PS is now one of the major commercial plastics, which are very extensively used such as food containers, packaging, toys and thermal insulation. Straight PS is a hard, rigid and rather brittle material. Some properties of PS are shown in the Table 2.2. It has a relatively low softening point and cannot withstand the temperature of boiling water. PS is a low cost material with high transparent property with 90% of transmission value (Billmeyer, 1984).

2.3 Ethylene propylene diene rubber (EPDM) (Morton, 1973)

The first commercial ethylene propylene rubbers were made by the random copolymerization of ethylene and propylene in solution catalyzed by using Ziegler-Natta catalyst. The dienes most commonly used today to produce the ethylene-propylene diene rubber (EPDM) are 1,4 hexadiene, ethylidene, norbornene and dicyclopentadiene, each conferring a different rate and state of cure to the polymer.

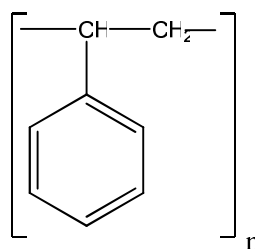


Figure 2.1 Structure of polystyrene.

Table 2.2 Typically properties of polystyrene (O dian, 1991)

Property	Value
Density, g/cm ³	1.04-1.07
Water absorption, %	0-0.1
Hardness, Rockwell M	70-74
Young's modulus, GPa	1.79-3.38
Tensile strength, MPa	25-69
Elongation at break, %	1-45
Charpy impact, J/cm ²	0.2-0.4
Specific heat capacity, J/(g.K)	1.2-2.1
Thermal conductivity, W/(m.K)	0.12-0.193
Glass temperature, °C	83-100
Melting point, °C	240
Vicat softening point, °C	1.03-110
Transmission, %	80-90

In general, the ethylene propylene rubbers are compounded to provide good low-temperature flexibility, high tensile strength, high tear and abrasion resistance, excellent weatherability (ozone, water, and oxidation resistance), good electrical properties, high compression set resistance, and high heat resistance. Many different types of EPDM are available with different properties. The ethylene content ranges between 45 (amorphous types) to 55-65 wt% (semi-crystalline types) and 70 wt% (crystalline types). For EPDM containing ethylene content below 50 wt%, the crystalline fraction is zero, but it can increase to 20% for EPDM with 80 wt% of

ethylene. The high molecular mass crystalline EPDM can incorporate high levels of fillers. Ethylene propylene rubber (EPMs) and EPDM have low resistance to hydrocarbon oils and their lack of building tack must be compensated by using the addition of resin. In this work, the EPDM containing 9.2 wt% of 5-ethylidene-2-norbornene (ENB) (Figure 2.2) was used as a raw material for graft copolymerization.

EPDM rubber was developed and commercialized in the late 1950s. With an annual production capacity of more than 1,000 kilotons in 1998. EPDM is currently counted as the fourth elastomer by volume to become a commodity rubber. Actually, EPDM is the largest non-tire rubber. The annual growth rate is about 4%. Exxon mobil, Dow and DSM are market leaders. The outstanding property of the ethylene-propylene rubber (EPM) and EPDM are their good weather-resistance compared with polybutadiene, polyisoprene and styrene/butadiene copolymer, due to less C=C double bond content in the structure of the polymer chains. Thus, they are less sensitive to oxygen and ozone including UV-light. Other excellent properties of these rubbers are high resistance to acid and alkali with high insulation properties. Some properties of rubber are shown in the Table 2.3. The EPM and EPDM are also used in the automotive industry for windows, hoses, gaskets, wipers, bumpers, belts, door seals, etc. They are also used for cable insulation and roofing. Moreover, this can be applied for white sidewall compounds of tire production. A large number of commercial EPM and EPDM grades are produced. The main structural characteristics are depended on the factors as followed (Noordermeer, 2002).

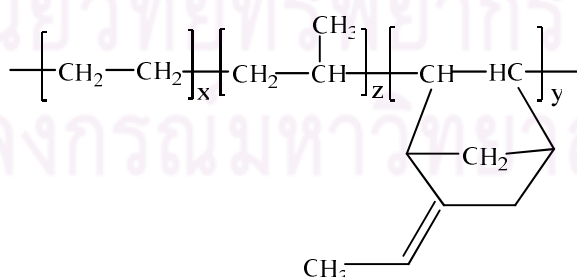


Figure 2.2 Structure of ethylene-propylene-diene rubber (Morton, 1973 and Ciesielski, 1999).

- Concentration ratio of ethylene and propylene chain units (amorphous or crystalline grades)
- Co- or terpolymerization of ethylene, propylene and diene monomers (EPM or EPDM)
- Type and amount of termonomer (chain branching, type of crosslinking and mechanical properties)
- Molecular weight and molecular weight distribution
- Chain branching (differences in viscosity and processability)
- Processability and price

EPM and EPDM containing below 55 wt% of ethylene section are completely amorphous and are not self-reinforcing. At higher ethylene contents of (60-70 wt.%), the polymers can form crystalline domains. These polymers are referred as “sequential” grades and their processing behavior considerably differs from that of the normal amorphous grades. The form with partially crystalline domains is thermally reversible physical crosslinks, which is thermoplastic elastomer to provide higher mechanical strength without chemical crosslinks. However, its tensile properties in vulcanisates are low. Most applications require crosslinking. Traditionally, sulfur vulcanization requires unsaturation and therefore fully saturated EPM cannot be crosslinked by using sulfur. Non-conjugated diene monomers have been introduced in EPM, yielding EPDM for sulfur vulcanization. For peroxide crosslinking, the presence of the diene increases the crosslinking efficiency. The termonomer used must have one of its C=C double-bonds sufficiently reactive to copolymerize randomly with ethylene and propylene, while the other must be unreactive in the polymerization. Normally, the unsaturated termonomer is present on the side chain rather than in the main chain. For various compounds in tire industry, only three types of unsaturated termonomer are widely used (Figure 2.3). From a practical point of view, ethylidene norbornene (ENB) and dicyclopentadiene (DCPD) are the most important diene termonomers due to the high amounts of diene that can be easily incorporated in commercial EPDMs (Hofmann, 1989).

Table 2.3 Qualitative comparison of properties of rubbers (Indian Rubber Institute, 1998)

Properties	Class				
	Unsaturated carbon chains				Saturated carbon chains
	NR	BR	NBR	SBR	EPDM
Glass transition temperature (T _g , K)	203	168	232	217	213
Density (Kg/m ³)	920	910-940	1,000	933	860
Tensile strength (MPa)	22-25	5	3	2-3	5
Hardness (IRHD)	30-90	35-90	30-90	40-90	40-90
Tear resistance	G	E	F/G	P/F	F/G
Abrasion resistance	G	E	G	VG	E
Compression set	F/G	G	G	P/G	G
Rebound resilience Cold	E	VG	VG	VG	VG
Rebound resilience Hot	E	VG	VG	VG	VG
Electrical properties					
- Dielectric strength	E	E	F	E	VG
- Electrical insulation	E/G	E	F	E	E
Resistance to ageing					
- Oxidation	G	G	F	G	E
- Ozone	P	P	P	P	E
- Sunlight	P	P	P	P	O
- Flame	P	P	P	P	O
- Heat	G	G	G	VG	E
- Cold	E	E	F	G	G

Note: E=excellent F=fair G= good O=outstanding P=poor VG=very good

The increase in the amount of diene causes the enhancement of crosslink densities resulting the corresponding changes in mechanical and elastic properties. The preferred third monomer for peroxide cure is 1,4 hexadiene (VNB).

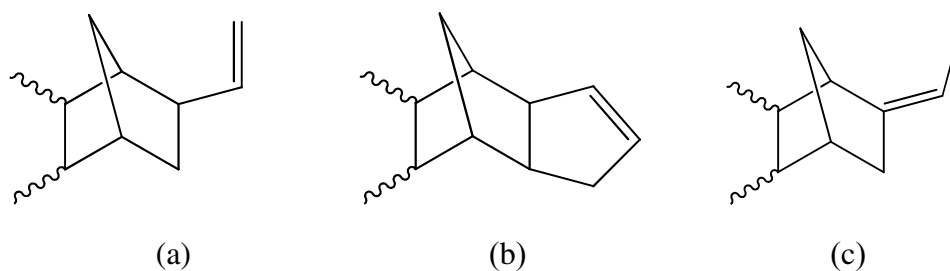


Figure 2.3 Chemical structure of diene third monomers: (a) VNB, (b) DCPD and (c) ENB (Noordermeer, 2002).

The commercial grades of EPDM differ in composition (ethylene and termonomer content), molecular mass and amount of extender. They are broadly following categories:

- (i) Random polymer with roughly equal ethylene/propylene ratio
- (ii) Sequential polymers with higher ethylene content. The ethylene is incorporation ratio into the molecular chain partially in the form of sequences to produce a partially crystalline molecular structure.
- (iii) Oil extended polymers: the advantages of EPDM are that they can tolerate large amounts oil and black in the compound and being fully saturated. They are not subjected to ozone or oxidative attack and have good resistance to heat aging. Characteristic properties of EPDMs are good weatherability and excellent ozone and heat resistance.

2.4 Elastomer blends

Various polymers or rubbers are often blended to reach required properties for any application. To obtain a desired combination of properties, both theoretical and technical aspects should be taken into account. Compatibility of rubber ingredients is vital for rubber blends to achieve optimum properties. Blending is an effective and economic approach to achieve desired properties compared to synthesize new elastomers. Potential merits of rubber blends are: (1) improvement of solvent resistance; (2) improvement of processability; (3) better product uniformity; (4) quick formulation changes and manufacture flexibility and (5) improvement of productivity. The rubber blends, based on the miscibility of constituent polymers, can be divided

into three broad classes: a) miscible blends (interpenetrating networks), b) partially miscible blends and c) immiscible blends (e.g. polymer alloys which are immiscible but compatibilized). Although the polymer alloy has two or more different phases on a micro-scale, it exhibits macroscopic properties as a single-phase material (Brydson, 1988). The immiscibility and phase separation are normally occurred in the rubber blends. The homogeneity at a fairly fine level instead of molecular miscibility is sufficient for optimum performance. It is usually desirable to have a certain degree of micro-heterogeneity to preserve the individual properties of the respective rubber components. (Kraus, 1978)

2.4.1 Miscibility of polymers (Brydson, 1988)

Miscibility of polymers is determined by thermodynamic phenomena in a term of the Gibbs free energy change of mixing (ΔG_m) as shown in eq. 2.3

$$\Delta G_m = \Delta H_m - T\Delta S_m \leq 0 \quad (2.3)$$

where, ΔH_m is the enthalpy of mixing (J), ΔS_m is the entropy change of mixing (J/K) and T is the absolute temperature (K). Polymers are only miscible when the Gibbs free energy of mixing is negative. Normally, the most polymer blends are immiscible because mixing is endothermic and the entropic contribution is small due to the high molecular weights of the constituent polymers. Miscibility can also be predicted from the solubility parameters. The relationship between the enthalpy change of mixing and the solubility parameters is governed by eq. 2.4.

$$\Delta H_m / V = k(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (2.4)$$

where, V is the volume of the two polymers, k is a constant value close to 1, δ_1 , ϕ_1 and δ_2 , ϕ_2 are the solubility parameters and volume fractions of components 1 and 2, respectively. Polymer miscibility is possible only when the difference in solubility parameters is small enough ($< 0.1 \text{ (J/cm}^3)^{1/2}$) or if there are specific interactions existing which contribute to a negative ΔH_m . The solubility parameters of some

relevant polymers, determined by Gas Liquid Chromatography (GLC), viscometry, swelling measurements together with the calculated data are given in Table 2.4.

2.4.2 Compatibility of rubber blends (Ghosh, 1990)

The lack of miscibility and technological compatibility of the rubberic component severely restricts the application of rubber blends. It is very often that the rubberic components are grossly immiscible as well as technologically incompatible. The mutual compatibility is essentially governed by the thermodynamic compatibility of the rubber components involved in blending. The better compatibility between two phases in the blend shows the smaller dispersed phase domains. To concern the morphology of phase separated rubber blends, the main influences governing the structure of the entire system are: (1) the interfacial tension, which affects the size and shape of the phases; (2) the viscosity of the matrix; and (3) the shear stress. Co-continuous blend morphology is observed for rubbers with similar viscosities.

Generally, the matrix is formed by the phase with lower viscosity, while the one with higher viscosity forms the dispersed phase. Homogeneity of mixing can be controlled by using either proper mixing conditions or by addition of compatibilizers (Grulke, 1994 and Ebewele, 2000).

Table 2.4 Solubility parameters of various polymers determined with different methods (Hofmann, 1989)

Elastomer types	GLC	Solubility parameters ($(\text{J}/\text{cm}^3)^{1/2}$)		
		Viscometry	Swelling	Calculated*
EPDM	15.9	15.8	15.9	15.8
NR	16.6	16.8	16.7	16.7
Cis-BR	17.2	17.0	16.7	17.1
PS	19.9	-	-	19.0

*calculated from eq. 2.4.

2.5 Graft copolymerization methods (Bemiller, 1976 and Mark, 1994)

For graft copolymerizations, side chains of the backbone polymer are formed by attachment of macromolecules with different chemical composition. The simplest case of graft copolymer can be represented by the model as shown in Figure 2.4 where a sequence of monomer units (A) is referred as the main chain or backbone, a sequence of B units is the side chain of graft and X is the grafting position on the polymeric backbone (Bayer, 1992). Graft copolymerization is defined as a post polymerization. The vinyl monomers such as styrene, acrylonitrile and MMA are normally used to graft on the backbone.

The synthesis of graft copolymers is much more diverse, but it can be divided into 5 groups related to the reaction processes.

2.5.1 Chain transfer

In a free radical polymerization, the chain transfer is an important reaction. The chain transfer to a monomer, solvent, mercaptan, or other growing chain can take place. When the chain transfer reaction to another chain takes place, it creates radicals which act as sites for further chain growth and grafting. The simplest technique is to dissolve the polymer in the appropriate solvent and initiate with the peroxide initiator to abstract a hydrogen radical and generate a radical on the polymer chain as the grafting sites for the fresh monomer. In many cases, when grafting is carried out in latex form, it has been product is normally used in thermoplastic applications.

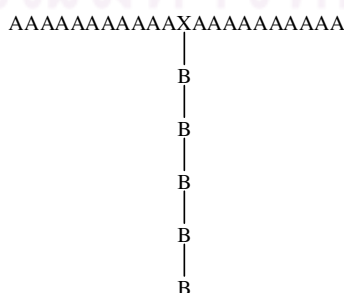


Figure 2.4 Model of graft copolymer (Bayer, 1992).

2.5.2 Copolymerization via unsaturated groups (Schulz, 1982)

Redox polymerization is the most popular techniques for grafting reactions. A hydroperoxide or similar group is reduced to a free radical plus an anion, while the metal ion is oxidized to a higher valency state. At the same time, a monomer is added. When the reducible group is attached to a polymeric chain, the free radical grafting sites formed on the macromolecular backbone acting as initiators for graft copolymerization. Hydroxyl polymers can be grafted by redox polymerization by using water soluble peroxide, such as hydrogen peroxide in conjunction with ferrous ions. The produced hydroxyl radicals abstract hydrogen atoms from the hydroxy groups in the polymer to give free radical grafting sites on the backbone. The advantage of this reaction lies in the fact that only hydroxyls on the polymer are converted into R-O radicals, so that no homopolymer can be produced and pure graft is obtained.

2.5.3 High-energy reaction techniques

The irradiation synthesis may be carried out in solution, either in contact with liquid monomer (with or without a diluent) or in contact with monomer in the absence of air to produce free suspension. The rubber may be pre-irradiated in the absence of air to produce free radicals for later monomer addition, but the life of these radicals is short as a result of mobility within the rubber matrix. The irradiation at very low temperature is possible process to use the trapped radical technique for a variety of synthetic rubbers.

2.5.4 Photochemical synthesis

Macromolecules containing photosensitive groups which can absorb energy from ultraviolet frequencies are often degraded by free radical processes. The degradation processes as a rule is fairly slow, but by the addition of photosensitizer, such as xanthone, benzyl, benzoin and 1-chloroanthraquinone can be speeded up to enable graft copolymerization to take place in the presence of monomers.

2.5.5 Metallation using activated organolithium with chelating diamines

Unsaturated elastomers can be readily metallated with activated organolithium compounds in the presence of chelating diamines or alkoxides of potassium or sodium. They can also be grafted with ionically polymerizable monomers to produce comblike materials.

Although graft copolymerizations are widely practiced with vinyl monomers and polymers, especially for improving compatibility, impact, and low temperature properties of thermoplastics, the technology has been based more upon art than upon science. Often small proportions of actual grafting have been sufficient to give worthwhile modification of properties. If grafting does not give directly the properties desired, it may improve morphology or compatibility with specific added polymers or plasticizers that impart the desired effect. In addition, these graft copolymers have been mixed with other resins such as poly(vinyl chloride) to improve compatibility, impact strength and low temperature properties of thermoplastics.

2.6 Bulk copolymerization (Odián, 1991, Drive, 1979 and Michaeli, 1995)

Bulk or mass polymerization of a pure monomer is the simplest process with a minimum contamination in the resulting product. Monomer, polymer and initiator are the only components in the bulk polymerization. Polymerization apparatus is shown in Figure 2.5. However, the bulk polymerization of vinyl monomer is more difficult, since the reactions are highly exothermic. The usual thermally decomposed initiators proceed at a rate which is strongly dependent on temperature. Thus, the problem of coupled heat transfer is normally incurred because of the viscosity development at the early stage of reaction, resulting to the difficulty in control. The advantages and disadvantages of the commercial polymerization systems are shown in Table 2.5. In the bulk copolymerization, the monomers and initiators are mixed in a reactor consisting of heating or cooling unit. Many reactions are carried

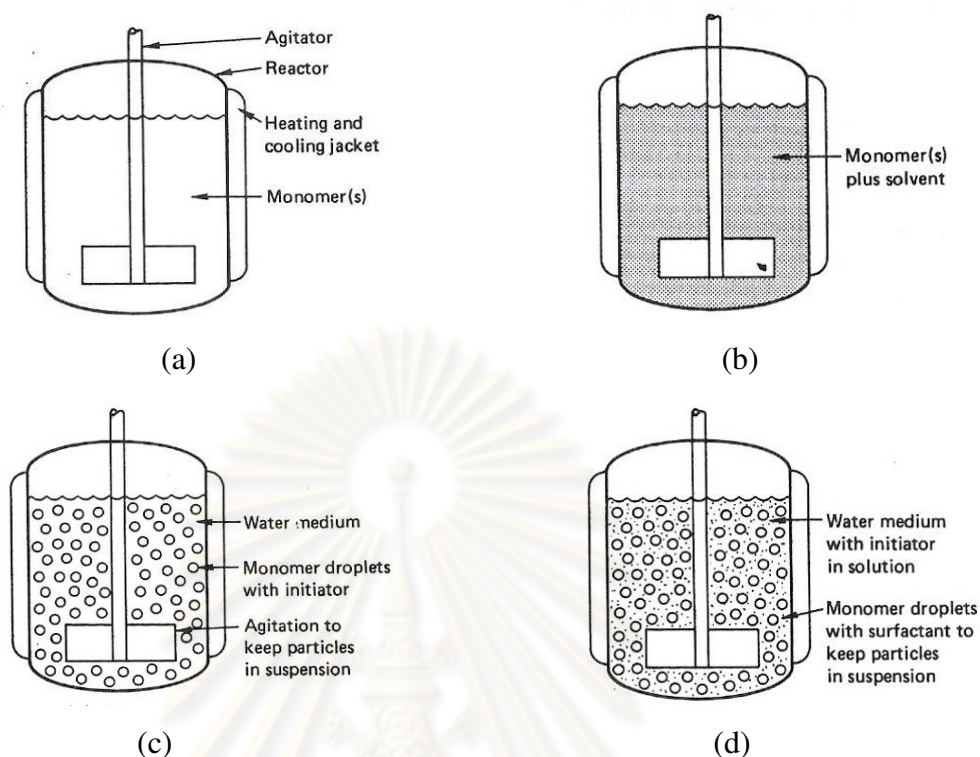


Figure 2.5 Diagrams of polymerization apparatus: (a) bulk, (b) solution, (c) suspension and (d) emulsion polymerization (Gulke, 1994).

out by charging one monomer into the reactor and/or slowly adding the second monomer.

In addition, the reaction is often too exothermic for the bulk process resulting to the requirement of careful temperature control. Therefore, the special steps must be taken to remove heat during polymerization. It can be differentiated between quiescent and stirred bulk polymerization. Both methods are applied to system which polymer is stable in monomer and progressively increases viscosity with conversion. In quiescent systems, gel formation, corresponding to infinite viscosity, can occur. However, the reaction rate of this system is difficult to be controlled due to the released heat during polymerization.

Table 2.5 Commercial polymerization systems (Grulke, 1994)

Type	Advantage	Disadvantages
Bulk: batch	<ul style="list-style-type: none"> • Minimum contamination • Simple equipment for making castings 	<ul style="list-style-type: none"> • Strongly exothermic • Broadened molecular weight distribution at high conversion • Complex if small particles required
Bulk: continuous	<ul style="list-style-type: none"> • Lower conversion per pass leads to better heat control and narrower molecular weight distribution 	<ul style="list-style-type: none"> • Requirement of agitation, material transfer, separation, and recycling
Solution	<ul style="list-style-type: none"> • Ready control of heat of polymerization 	<ul style="list-style-type: none"> • Not useful for dry polymer because of difficulty of complete solvent removal
Suspension	<ul style="list-style-type: none"> • Ready control of heat of polymerization • Suspension or resulting granular polymer may be directly usable 	<ul style="list-style-type: none"> • Requirement of continuous agitation • Contamination by stabilizer • Requirement of washing and drying processes
Emulsion	<ul style="list-style-type: none"> • Rapid polymerization to high molecular weight and narrow distribution with ready heat control 	<ul style="list-style-type: none"> • Contamination with emulsifier, etc., almost inevitable, leading to poor color and color instability • Requirement of stability washing and drying process

2.7 Casting process (Drive, 1979 and Grulke, 1994)

Casting is a manufacturing process and involves the pouring of a liquid resin into a mold to allow it to harden with little or no pressure. The liquid may consist of a melted or dissolved thermoplastic, thermosetting resin, or thermoplastic monomer. Hardening takes place by cooling, evaporation of solvent or chemical reaction (Drive, 1979). Casting method requires simpler machines for making products with more economical practice of small quantities. It is also lower expenses for molds (Michaeli, 1995). The configuration of the conventional mold for preparing the general thermoplastics is shown in Figure 2.6.

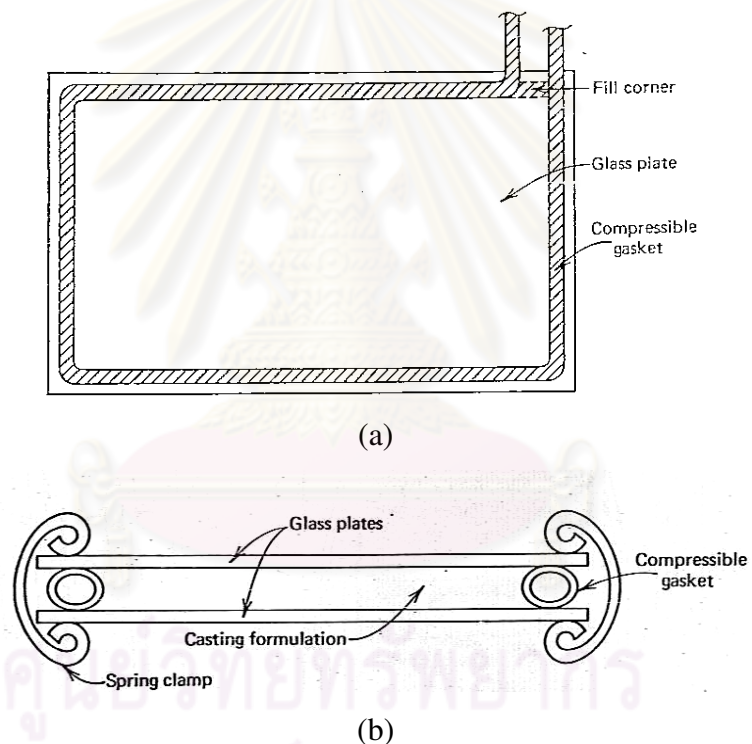


Figure 2.6 Conventional cell casting mold configuration: (a) face view and (b) edge view (Drive, 1979 and Grulke, 1994).

2.8 Impact modifier (Lutz, and Grossman, 2001)

In the early days of the thermoplastic industry, the commercial polymers such as PS, rigid PVC and PMMA exhibited low impact strength in their homopolymer forms. In the case of PS and styrene-acrylonitrile copolymer (SAN), rubbers such as polybutadiene or natural rubber are incorporated to such polymers during polymerization in order to increase their toughness.

2.8.1 Effect of secondary glass transitions temperature

The impact resistance of the brittle polymers is correlated to the presence of a secondary glass transition temperature of polymer. This temperature locates below the primary glass transition temperature. The secondary glass transition temperature is associated with the motion of the polymer backbone, not pendant side-chain groups. This is effective to improve the impact resistance. Because the definition of impact strength is the ability of the material to undergo massive yielding at impact speeds, the main-chain motions that can be activated at impact speed are expected to correlate with impact strength. Thus, a low secondary glass transition temperature is an indication of chain segments that possess some degree of mobility at impact speed. This mobility can be translated into the large-scale deformation of the polymer chains.

2.8.2 Interaction of additive impact modifier and polymer matrix

There are relatively few polymers, such as polycarbonate, that manifest the secondary glass transition temperature that to yield high impact strength with maintaining a sufficiently high primary glass transition temperature for acceptable engineering properties. Polymers having low secondary glass transition are PVC and polyphenylene oxide. These require impact modifiers to yield high impact resistance. However, some polymers, such as PS, do not have the secondary glass transition temperature. Consequently, this concept provides the secondary glass transition temperature in the materials for improving their impact strength by the addition of rubber impact modifiers with a low glass transition temperature.

In general, rubbery materials can be used as impact modifiers due to their shear stresses that arise at the rubber-matrix boundaries. When the large numbers of microscopic rubbery phases inclusions are distributed throughout the matrix, this matrix deformation is delocalized throughout the sample and large amounts of energy can be absorbed. Graft copolymers containing identical segments to the blend components can be applied as the compatibilizer to increase the miscibility between the copolymer segments and the corresponding blend components. In the most cases, the compatibilizer possibly affects the final products such as reduction of the interfacial tension during melt mixing resulting to a finer dispersed phase which increases the adhesion at phase boundaries. This gives the improved stress transfer with strengthening the interface in the solid state and stabilization of the dispersed phase by reducing the rate of domain coalescence during melts processing and annealing (Edenbaum, 1996).

2.9 Literature reviews

2.9.1 Graft copolymerization of ethylene propylene diene rubber

Fu et al. (2008) studied the use of EPDM grafted with MMA and ST (EPDM-*g*-MMA/ST) as a toughen agent for methyl methacrylate styrene resin (MS resin). The graft copolymer was synthesized by solution graft copolymerization in toluene/*n*-heptane co-solvent using benzoyl peroxide (BPO) as an initiator. The effects of reaction conditions on the graft copolymerization such as EPDM/MMA-ST ratio, MMA/ST ratio, initiator dosage, reactant concentration, toluene/*n*-heptane ratio and reaction time were discussed. EPDM-*g*-MMA/ST/MS resin blends were prepared by melt blending. The effect of EPDM-*g*-MMA/ST on the toughening property of MS resin was also investigated. The results showed that the optimized reaction conditions were 50/50 by wt of EPDM/MMA/ST and 75/25 by wt of MMA/ST initiator dosage of 1%, reactant concentration of 20%, toluene/*n*-heptane ratio of 75/25 at 80°C for 20 h and EPDM-*g*-MS with the higher EPDM content (56.8%) and grafting ratio (52.8%) was obtained under the optimized reaction conditions. SEM analysis showed that EPDM-*g*-MMA/ST had good compatibility with MS resin. EPDM-*g*-MMA/ST had

excellent toughening effect on MS resin and could be used for toughen agent of MS resin.

Fu et al. (2008) studied the toughening effect of grafted EPDM with MMA and ST (EPDM-*g*-MMA/ST) as a toughening agent for MS resin. The graft copolymer was synthesized by solution graft copolymerization in toluene/*n*-heptane co-solvent using benzoyl peroxide (BPO) as an initiator. The toughening effects of grafted EPDM on MS resin were discussed. The result showed that the Notched Izod impact strength of MS resin increased with increasing grafting ratio. The differential scanning calorimetry showed that the grafted EPDM and MS resin are partially compatible and the compatibility was improved with increasing grafting chain polarity of grafted EPDM.

Zeng et al., (2004) studies on the synthesis of high rubber styrene-EPDM-acrylonitrile graft copolymer (AES) and its toughening effect on SAN. The graft copolymerization of styrene (ST) and acrylonitrile (AN) onto EPDM were prepared by solution polymerization in *n*-heptane/toluene cosolvent using benzoyl peroxide as an initiator. The effects of reaction conditions, such as reaction temperature, initiator concentration, EPDM content, the solvent component, and reaction time on the graft copolymerization were discussed. In addition, according to the research on mechanical properties of the SAN/AES blend, the toughening effect of AES on SAN resin was found. By means of scanning electron microscopy, the toughening mechanism was proposed to be crazing initiation from rubber particles and shear deformation of SAN matrix. Uniform dispersion of rubber particles, as shown by transmission electron microscopy, the AES was attributed to the good compatibility of SAN.

2.9.2 Modification of acrylic sheet

Charmondusit et al. (2008) studied the preparation of high impact transparent ST-MMA copolymer cast sheet by using natural rubber (NR) as an impact modifier. The copolymer cast sheets were prepared by bulk polymerization via casting process. The influence factors, such as monomer ratio and NR concentration were

studies. The physical and mechanical properties of the modified copolymer cast sheets were investigated. It was found that the appropriate conditions were 90 and 80 wt% of MMA, 10 and 20 wt% of ST, 0.1 wt% of peroxide as an initiator and 0.03 wt% of azocompound initiator. The highest impact strength of copolymer cast sheet was reached when the cast sheet contained 20 wt% of NR.

Cheng et al. (2004) studied transparent EVA/PMMA sheets produced via *in situ* polymerization of MMA. In the presence of the EVA-graft-PMMA (EVA-g-PMMA) prepared by using *tert*-butyl peroctoate (*t*-BO) as an initiator in the EVA/PMMA, EVA can be well dispersed in the PMMA matrix. Both tensile fracture energy and Izod impact strength of the EVA/PMMA blends were higher than those of the neat PMMA. This was confirmed by using Scanning Electron Microscopy (SEM). The copolymer also prevented the dispersed EVA particles from pulling out the fracture surface. The strength of the EVA/PMMA blends were investigated at room temperature over the four stain rates of decadence (from 1.6×10^{-4} to 0.16 s^{-1}). It had an obvious transition, whereas the neat PMMA remained the brittleness over the entire range of strain rates.

Mansour et al. (2004) prepared copolymer films of ST and MMA with different percentage. Differential scanning calorimeter showed a single transition at 50/50 ST/MMA. Thermogravimetry technique was used to compare the thermal stability of the copolymer and homopolymers. The copolymers degradation occurred at higher temperatures than pure PMMA indicating the higher stabilization of the copolymer. FTIR spectroscopy was used to give information on the structural changes consequently upon exposure. This indicated that the copolymerization of ST and PMMA improved the photodegradation behavior of PS. The optical absorption (α) and the band gap (E_g) of film were determined before and after exposure to UV radiation. The optical transmission and reflection data for 50/50 of ST/MMA copolymer were also analyzed to evaluate the refraction index (n) and extinction coefficient (k) before and after exposure to UV radiation.

Hinchiranan et al. (2007) reported the improved properties of modified acrylic sheet via addition the graft NR. The mechanical properties of a modified

acrylic sheet prepared by bulk copolymerization of MMA and ST were improved by the addition of a small amount of graft NR (GNR). The graft copolymerization of MMA and ST onto NR latex was carried out by emulsion polymerization using potassium persulfate as an initiator. The properties of the modified acrylic sheet containing GNR with 22.5 wt% graft copolymer were investigated as a function of GNR content. The results indicated that the impact strength, tensile strength and elongation at break of the modified acrylic sheet increased with increasing the amount of GNR in the range of 0.5–4 parts. From the stress–strain behavior, the characteristics of the modified acrylic sheet shifted from brittle to ductile when the amount of GNR was increased. The scanning electron micrographs of the modified acrylic sheets showed the relatively smooth fracture surface with relatively few small cracks. This implies that the GNR could be used as an impact modifier for acrylic plastics.

Thawornwisit et al. (2006) studied the properties of copolymer sheets containing ST, MMA and modified NR prepared by bulk copolymerization using benzoyl peroxide and 2,2'-azobis-(2,4-dimethylvaleronitrile) as initiators. The modified NRs were prepared by graft copolymerization and hydrogenation. The graft NR prepared by emulsion copolymerization using redox initiator consisted of 66.1 wt% NR-g-(MMA-co-ST), 26.9 wt% of free rubber and 7.0 wt% of free copolymers. The hydrogenation of NR catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)$ was carried out at 140°C and 400 psig, to obtain the hydrogenation level as 56.5%. The effect of ST, rubber and monomer contents on the mechanical and physical properties including morphology of the modified acrylic sheets was investigated. The results showed that the better mechanical properties of the modified acrylic sheet were obtained from the addition of 2 wt% of graft NR and 1 wt% of hydrogenated NR. The optimum content of ST in the modified acrylic sheets for improving the mechanical properties was 20 wt%. Moreover, the modified acrylic sheet containing the hydrogenated NR had the superior thermal resistance. The tensile fracture surface examined by SEM showed the relatively smooth surface with few relatively small cracks. It implied that the modified NR could be used as an impact modifier for the acrylic cast sheet.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

EPDM (NORDEL IP 5565 containing 7.5 wt% of 5-ethylidene 2-norbornene) was purchased from The Dow Chemical Company (Midland, USA). The properties of EPDM are shown in Appendix A. The commercial grade ST monomer and the analytical grades of toluene and acetone were supplied by SR Lab Co., Ltd (Bangkok, Thailand). The commercial grade MMA and 2,4-dimethylvaleronitrile (ABVN) were obtained from Pan Asia Industrial Co., Ltd (Bangkok, Thailand). Benzoyl peroxide (BPO) (humidified with ~25% of H₂O) from PANREAC QUIMICA (Barcelona, Spain) was used as received. Sodium hydroxide (NaOH) and anhydrous sodium sulfate (Na₂SO₄) were purchased from Merck (Bangkok, Thailand). The analytical grades of light petroleum ether (LPE) and methyl ethyl ketone (MEK) were obtained from Fisher Scientific (Leicestershire, UK). The commercial grade of methanol was the product of Reagent Chemical Industry (Bangkok, Thailand). Nitrogen gas with 99.9% purity was manufactured by Linde Co., Ltd (Bangkok, Thailand).

3.2 Experiment apparatus

- Three-neck round bottle (500 ml) equipped with condenser, nitrogen inlet and outlet tubes, overhead stirrer and thermometer for graft copolymerization step (Figure 3.1)
- Soxhlet extraction apparatus
- Glass mould for casting process
- Other general laboratory glassware
- Water bath
- Hot air oven
- UV cure apparatus



Figure 3.1 Experimental apparatus for graft copolymerization.

3.3 Analytical equipments

- Fourier- transform infrared spectrometer (FT-IR): Thermo 470 FT- IR spectroscopy
- Proton-nuclear magnetic resonance spectrometer ($^1\text{H-NMR}$): Bruker ACF 200 MHz
- Universal testing machine: LLOYD Instrument LR 10K Plus
- Hardness testing machine: Rockwell Hardness Tester 4150 AR
- Impact testing machine: Impact tester GOTECH GT 7045
- Color measurement: Gretagmacbeth Instrument color i5
- Scanning Electron Microscope: JEOL model JSM-5800 LV
- Differential Scanning Calorimeter: PerkinElmer Thermal analysis controller TAC 7/DX

3.4 Grafted ethylene propylene diene rubber preparation

3.4.1 Purification of monomer (Thawornwisit, 2006)

The ST monomer (b.p. 145.2°C/760 mmHg) contained a trace amount of hydroquinone as an inhibitor. The inhibitor was removed by washing with 10% NaOH solution and then followed by distilled water until neutral. The washed ST monomer was distilled under reduced pressure (50-60°C, 20 mmHg). The purified ST monomer was stored in the refrigerator.

For MMA purification, this monomer (b.p. 98°C/760 mmHg) also contained a small amount of hydroquinone as inhibitor. It was purified by following the above procedure similar to ST purification. The washed MMA monomer was distilled under reduced pressure at 20 mmHg and 40°C. The purified MMA monomer was also kept in the refrigerator.

3.4.2. Preparation of graft EPDM (GEPDM)

The graft copolymer of ST and MMA on EPDM was prepared by solution copolymerization performed in a three-necked round glass bottle (300 mL) equipped with a stirrer, thermometer and condenser. EPDM dissolved in toluene (8 wt%) was transferred into the glass bottle. The system was deoxygenated by purging nitrogen gas for at least 15 min. When the reaction temperature reached to 90°C, 0.1 wt% of BPO was charged into the reactor following the gradual addition of the monomer mixture (MMA/ST = 75/25 %w/w). The reaction was allowed to proceed for 4, 10 and 16 h under continuous stirring speed at 200 rpm. Then, the reaction was ceased by adding a small amount of phenol. The graft product was precipitated in the excess methanol, filtered and dried in vacuum oven at 80°C until constant weight was received. The standard recipe used for graft copolymerization is shown in Table 3.1.

Table 3.1 Recipe for preparation of GEPDM (Fu et al., 2008)

Condition	Description
Purified MMA/ST ratio (%w/w)	75/25
Rubber/monomer ratio (%w/w)	50/50
Rubber concentration (wt%)*	6, 8, 10
Initiator dosage (BPO) (wt%)**	1.0
Reaction temperature (°C)	80 - 90
Reaction time (h)	4 - 20

* The rubber concentration was based on total weight of monomer

** The initiator dosage was based on EPDM content.

3.5 Properties of GEPDM

3.5.1 Determination of monomer conversion and grafting efficiency

The gross graft EPDM (GEPDM) consisted of three parts: graft copolymer (EPDM-*g*-(MMA-*co*-ST)), free EPDM and free copolymer. The free EPDM and free copolymer were removed by using soxhlet extraction. The free rubber was extracted by light petroleum ether (60-80°C) for 24 h, while free copolymer was then extracted in MEK/ acetone at 50/50 %v/v for 24 h. The dried final product was the graft copolymer. The different weight of sample before and after soxhlet extraction in each step was defined as %free EPDM, %free copolymer and %graft copolymer, respectively (eq. 3.1-3.3) (Thawornwisit, 2006). The total conversion of monomer and percentage of grafting efficiency (%GE) were calculated from eq. 3.4 and 3.5, respectively.

$$\text{Free EPDM (\%)} = \frac{\text{weight of free rubber}}{\text{weight of gross polymer products}} \times 100 \quad (3.1)$$

$$\text{Free copolymer (\%)} = \frac{\text{weight of free homopolymer}}{\text{weight of gross polymer products}} \times 100 \quad (3.2)$$

$$\text{Graft copolymer (\%)} = \frac{\text{weight of graft copolymer}}{\text{weight of gross polymer products}} \times 100 \quad (3.3)$$

$$\text{Total conversion (\%)} = \frac{\text{weight of polymer formed} - \text{weight of GEPDM}}{\text{weight of monomer charged}} \times 100 \quad (3.4)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{weight of monomer grafted}}{\text{weight of monomer polymerized}} \times 100 \quad (3.5)$$

3.5.2 Structured characterization of GEPDM

The structures of EPDM and graft copolymer obtained after soxhlet extraction were characterized by using fourier-transform infrared spectroscopy (FT-IR) (Thermo 470 FT-IR spectroscopy). The graft product was dissolved in toluene (ca. 2 %w/v) and then casted as a film on a NaCl cell. To confirm the FT-IR results, the proton nuclear magnetic resonance spectroscopy (¹H-NMR) was also used analyse. ¹H-NMR spectra were obtained on the Bruker ACF 200 MHz. The 0.01 g of samples were dissolved in CDCl₃.

3.5.3 Preparation of modified acrylic sheet containing GEPDM

The modified acrylic sheets were prepared by dissolving EPDM (1.0 wt%) or GEPDM (1.0-4.0 wt%) in the mixture of MMA/ST solution (80/20 %w/w) in the vigorous agitation at 95°C for 0.5-3.0 h to obtain the homogeneous solution. In the pre-polymerization step, BPO (0.1 wt%) was added into the mixture as the first initiator and then heated up to 110°C for 25 min. When the mixture was viscous, it was cooled down to room temperature. Then, ABVN (0.03 wt%) was added into the mixture. The air bubble in the mixture was removed by using vacuum pump until the reaction mixture was cooled down to room temperature. The obtained syrup was filled into a glass mold and immerg in a water bath at 60°C to harden the acrylic sheet.

The acrylic sheet was further placed in an oven at 120°C for 2 h. The finished sheet was taken off from the glass mold after cooling at room temperature (Drive, 1979, Grulke, 1994 and Saechtling, 1995). The sheet was cut as a shape according to the ASTM test method. The standard recipe and conditions used for preparation of the modified acrylic sheet are shown in Table 3.2.

3.6. Testing of mechanical properties of modified acrylic sheet

The mechanical properties of the modified acrylic sheets containing various contents of EPDM or GEPDM were measured following the ASTM test methods.

3.6.1 Impact strength (ASTM D 256)

The dimension and geometry of specimens for impact strength testing are shown in Figure 3.2. The machine used to investigate the impact strength of the modified acrylic sheet was Izod Impact Tester (GOTECH GT 7045). The width of each specimen was measured in the notch with a micrometer caliper and recorded its average width.

Table 3.2 Recipe for preparation of modified acrylic sheets

Ingredient	Quantities
MMA/ST ratio (%w/w)	80/20
EPDM (wt%)	1.0
GEPDM (wt%)	1.0 - 4.0
BPO (wt%)	0.1
ABVN (wt%)	0.03
Water bath temperature (°C)	60
Oven temperature (°C)	120

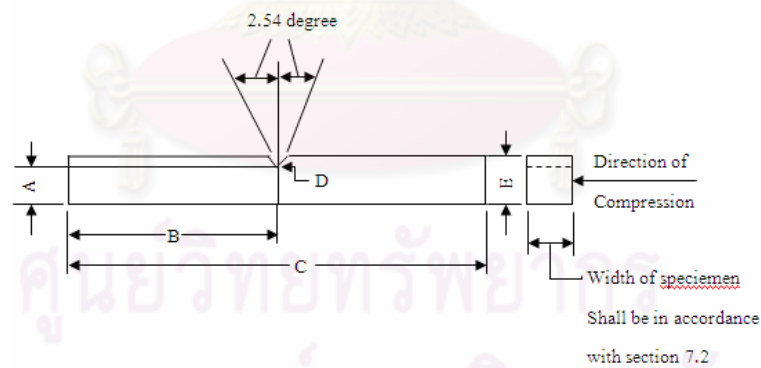
The breaking energy of specimen was estimated and the weight hammer with 2 J was applied for the specimens. The pendulum was released and an excess energy remaining in the pendulum was recorded after breaking the specimen.

3.6.2 Flexural strength (ASTM D 790)

The flexural strength of specimens was measured using a three point bending test in a universal testing machine (LLOYD Instrument LR 10K Plus) at a cross-head speed of 1 mm/min. Stress was applied until fracture by a centrally located rod connected to a 50 kgf load cell. The specimens were cut from a 3.0 mm thick sheet. The flexural strength was calculated using the eq. 3.6.

$$TS = \frac{3WL}{2bd^2} \quad (3.6)$$

where W is the maximum load before fracture, L is the distance between supports (50 mm), b is the width of specimens and d is the specimen thickness.



Unit: mm

A: 10.16 ± 0.05

D: 0.25 ± 0.05

B: 32.00 max, 31.50 min

E: 12.70 ± 0.05

C: 80 ± 0.2

Figure 3.2 Dimensions of specimens for impact strength testing (Izod type) (Shah, 2007).

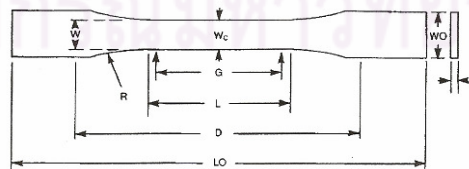
3.6.3 Tensile properties (ASTM D 638)

Tensile properties of dumbbell-shaped specimens (Type I) (Figure 3.3) were measured at 25°C and 60% of humidity. The specimens were cut from a 3.0 mm thick sheet. The testing was performed by using a universal testing machine (LLOYD Instrument LR 10K Plus) with a crosshead speed of 50 mm/min.

3.7 Properties retention after thermal and UV aging

The effect of thermal aging on the physical and mechanical properties of the modified acrylic sheets was carried out in a hot air oven at 165°C for 25 min according to Pan Asia Industrial Standard method. At the terminal of aging time interval, the specimens in the shape for each mechanical properties testing were removed from the oven and cooled down to room temperature on a flat surface for 24 h before mechanical properties determination. For the test of UV resistance, the specimens were placed in the Ultraviolet box (The Q.PANEL company model Q.U.V) with the UV wavelength at 280-320 nm and 60°C for 1 week according to Pan Asia Industrial Standard method. The impact strength, flexural strength, tensile properties and hardness of the modified acrylic sheets after thermal and UV aging were compared to untreated samples. The properties retention could be calculated following eq. 3.7.

$$\% \text{ Retention} = \frac{\text{Pr operties after ageing}}{\text{Pr operties before ageing}} \times 100 \quad (3.7)$$



W : 13 mm WO : 19 mm G : 50 mm R : 76 mm
L : 57 mm LO : 165 mm D : 1155 mm T : 4 mm or under

Figure 3.3 Dimensions of specimens for tensile testing (Shah, 2007).

3.8. Thermal properties of the modified acrylic sheets

3.8.1 Differential scanning calorimetry (DSC)

The differential scanning calorimetry (DSC) was carried out on a Perkin Elmer JSM-5800 LV to evaluate the effect of the addition of EPDM or GEPDM on the glass transition temperature (T_g) of the modified acrylic sheets. The thermogram signal was obtained from the temperature difference between the sample and the reference.

The sample of 5-10 mg was placed in a crimped aluminium pan. The differential scanning calorimetry of the modified acrylic sheets was carried out under nitrogen atmosphere at a constant heating rate of $10^\circ\text{C}/\text{min}$ from -60 - 250°C . The T_g values were calculated from the midpoint of the base-line shift of the DSC thermogram.

3.8.2 Thermogravimetric analysis (TGA) (Kissinger, 1702)

The decomposition temperature and kinetics of thermal decomposition of the modified acrylic sheets were determined by using Thermogravimetric analysis (TGA). The thermogravimetric (TG) and its derivative (DTG) curves were performed on a Seiko SSC 5000 TG/DTA. Samples (10-20 mg) were heated from room temperature to 600°C at a heating rate of 2.5, 5 and $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The flow rate of nitrogen gas was controlled at $50\text{ mL}/\text{min}$. The initial (T_{id}) and final (T_f) decomposition temperatures was obtained from the intersection of two tangents at the initial and final stage of the decomposition, respectively. The temperature at the maximum weight-loss rate (T_p) was also recorded.

To study the overall kinetics of thermal decomposition, the Kissinger method (differential method) was applied to determine the activation energy (E_a) of the solid state reaction without a precise knowledge of any mechanism of thermal decomposition. The Kissinger method proposed employs in eq. 3.8:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E_a} + \ln[\ln(1 - \alpha_p)^{n-1}] + \frac{E_a}{RT_p} \quad (3.8)$$

where β is the heating rate, T_p and α_p are the absolute decomposition temperature and weight loss at the maximum weight-loss rate $(d\alpha/dt)_p$, respectively. R is the gas constant, A is the pre-exponential factor and n is the reaction order. E_a was calculated from the slope of the straight line obtained from a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$.

3.9. Physical properties of the modified acrylic sheets

3.9.1 Change of color and transparent property

Transparent property was reported in term of opacity of specimens by using color measurement (Gretagmacbeth Instrument color i5). Thermal and UV resistance was reported in term yellow difference (ΔE) of the modified acrylic sheets after thermal and UV ageing were reported and compared to untreated sample.

3.9.2 Morphology investigation

The morphology of the fracture surface of the modified acrylic sheets was also investigated using a JEOL model JSM-6400 scanning electron microscope at 10 kV. The specimens were fractured under cryogenic condition by using liquid nitrogen. Then, the specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was sputtered with a thin gold layer.

CHAPTER IV

RESULTS AND DISCUSSION

The graft copolymers of MMA and ST onto EPDM rubber were prepared by solution polymerization using benzoyl peroxide as an initiator. The conversion, grafting efficiency, percentage of free rubber, percentage of copolymer and percentage of graft copolymer were recorded as functions of reaction temperature, rubber concentration and reaction time. The structure of graft product was also characterized by FT-IR and ¹H-NMR spectroscopy. The gross graft EPDM (GEPDM) was added into the MMA-ST syrup during the stage of bulk polymerization for preparing the acrylic sheet by casting process. The mechanical properties, optical properties and morphology of the modified acrylic sheets were investigated. The retention of mechanical properties after thermal and ultraviolet (UV) aging including the kinetics of thermal degradation of the acrylic sheets containing GEPDM was also reported.

4.1 Preparation and grafting properties of GEPDM

The GEPDM was prepared by solution graft copolymerization. The optimum reaction condition was reported by Fu et al. (2008) as shown in Table 3.1. The graft product was extracted by light petroleum ether (LPE) for 24 h by using soxhlet extraction for removing free rubber content and then dried to constant weight. To remove free copolymer, the dried residue was extracted by MEK/acetone (50/50 %v/v) for 24 h. The data obtained from all steps were used to calculate the percentage of conversion, grafting efficiency (GE) and grafting properties. The example for all calculations is shown in Appendix B. The grafting properties of GEPDM after extraction are shown in Table 4.1.

Table 4.1 Properties of graft copolymerization of MMA and ST onto EPDM

Reaction conditions			Grafting properties				
Temperature (°C)	Rubber concentration (wt%)	Time (h)	% conversion	% Free rubber	% Free copolymer	% Graft copolymer	%GE
80	8	12	33.2	78.9	10.4	10.7	57.3
90			34.1	80.0	7.98	12.0	68.7
90	6	12	24.6	78.3	11.5	10.1	41.6
	8		34.1	80.0	7.98	12.0	68.7
	10		26.6	81.0	11.4	7.52	45.5
90	8	4	20.6	80.1	15.3	4.58	10.4
		6	25.8	78.0	16.8	5.20	17.8
		8	28.6	75.3	18.1	6.65	18.7
		10	33.2	79.1	9.97	11.0	60.0
		12	34.1	80.0	7.98	12.0	68.7
		16	46.4	83.2	3.78	13.0	88.1
		20	51.8	81.0	11.5	7.53	66.4

For the effect of reaction temperature, it was found that the higher reaction temperature promoted the higher %conversion, %graft copolymer and grafting efficiency (%GE). It has been reported that both the graft polymerization rate and the copolymerization of ST and MMA increased with a rising polymerization temperature due to the enhancement of reactivity of rubber substrate, initiator and monomers and the reduction of rubber solution viscosity (Sheng et al., 1996 and Fu et al., 2008).

The effect of rubber concentration, the results showed that the %conversion, %graft copolymer and %GE increased with increasing rubber concentration from 6 wt% to 8 wt% since the chance of copolymerization between grafting sites and monomer radicals increased with increasing reactant concentration. However, overdose of rubber concentration caused the difficulty of the diffusion and mobility of monomer and free radicals of growth chains due to the higher viscosity. This decreased the rate of copolymerization and possibly promoted the formation of ungrafted copolymer (Fu et al., 2008). To obtain the highest % graft copolymer and % conversion, the suitable rubber concentration was 8 wt% of EPDM for graft copolymerization.

For the effect of reaction time, the % grafting copolymer and %GE rapidly increased with increasing reaction time to 16 h and then they tended to decrease when the reaction was leaved for 20 h. It can be explained that the ratio of the grafted monomer to copolymeric monomer increased at the initial period of reaction enough reactive sites on the EPDM chain resulting to the increase in the % graft copolymer and %GE. When the reaction time was 16 h, the EPDM chains were saturated with the grafting copolymeric chains. Above this point, the viscosity of the reaction solution increased with reaction time to obstruct the diffusion of monomer to react with EPDM (Hoang et al., 2000).

4.2 Structure characterization of GEPDM

After soxhlet extraction, GEPDM consisted of free EPDM, free copolymers and graft copolymers. Ungrafted PMMA, PS and poly(ST-*co*-MMA) are referred to as free copolymers. Grafted copolymers are referred as EPDM-*g*-PMMA, EPDM-*g*-PS, and EPDM-*g*-PMMA/ST.

4.2.1 Characterization of GEPDM using FT-IR spectroscopy

The functional groups in the EPDM rubber and its graft product were identified by FT-IR spectroscopy. Figure 4.1a and 4.1b show the FT-IR spectra in the region of 500-4000 cm^{-1} for EPDM rubber and grafted EPDM, respectively. The FT-IR spectrum of EPDM rubber exhibited the characteristic absorption band of C=C stretching vibration at 1680 cm^{-1} , the CH₂ vibration at 1449, the CH₃ vibration at 1376 cm^{-1} and the C=C bending vibration at 853 cm^{-1} . The new peaks in the FT-IR spectrum of GEPDM are the absorption bands of C=O stretching vibration of MMA at 1700 cm^{-1} . The sharp peaks at 700 and 1492 cm^{-1} are assigned to the aromatic rings. The broad peak ranging between 3100-2960 cm^{-1} is due to the presence of the stretching vibration of C-H of ethylene norbornene. The FT-IR spectrum of GEPDM after soxhlet extraction confirmed that the PMMA and PS was “grafted from” the EPDM through the double bond during free-radical copolymerization. This indicated the occurrence of grafting of MMA and ST onto EPDM rubber (Lin-vien, 1991 and Colthup, Daly and Wiberley, 1964).

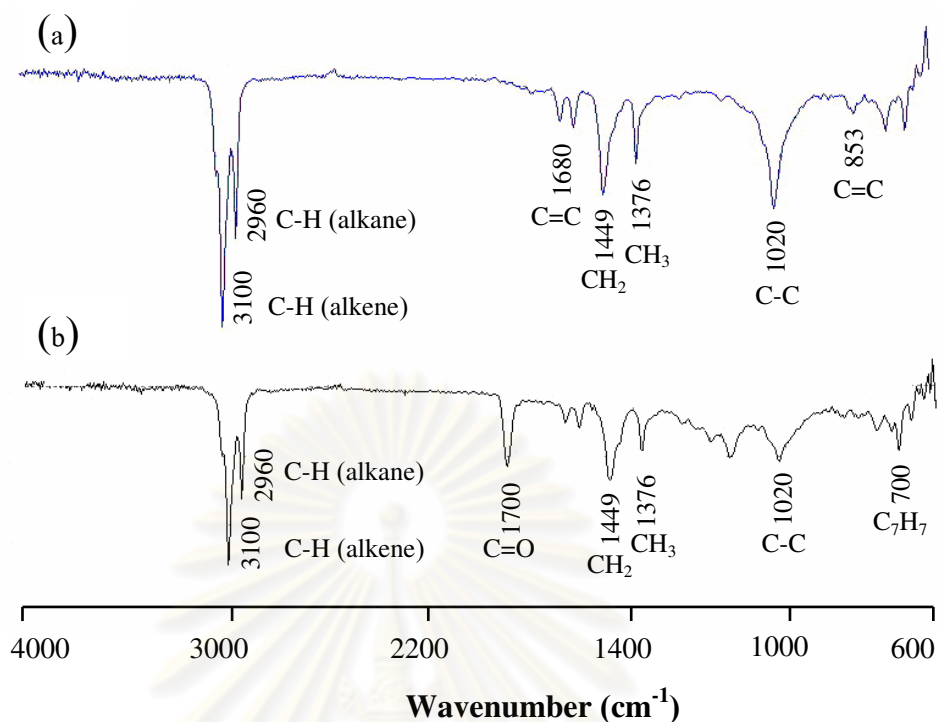


Figure 4.1 FTIR spectra of (a) EPDM and (b) GEPDM after soxhlet extraction.

4.2.2 Characterization of GEPDM using $^1\text{H-NMR}$ spectroscopy

Figures 4.2a and 4.2b present a comparison of the $^1\text{H-NMR}$ spectra of EPDM and GEPDM after soxhlet extraction. Figure 4.2 a shows the chemical shift at 5.2 ppm attributed to the olefinic proton ($=\text{CH}$) in the EPDM rubber. All EPDM protons appear at chemical shift ranging from 0.7 to 1.3 ppm to CH_3 and CH_2 in the propylene units. Figure 4.2b shows the $^1\text{H-NMR}$ spectrum of GEPDM after soxhlet extraction. The spectrum exhibits a new peak appearing at 3.40 ppm referred to the methoxyl group (CH_3O) in PMMA. The peak at 2.1 ppm is due to the methylene in EPDM. The signals at 6.9-7.1 ppm are attributed to the phenyl group of PS (Fu et al., 2008).

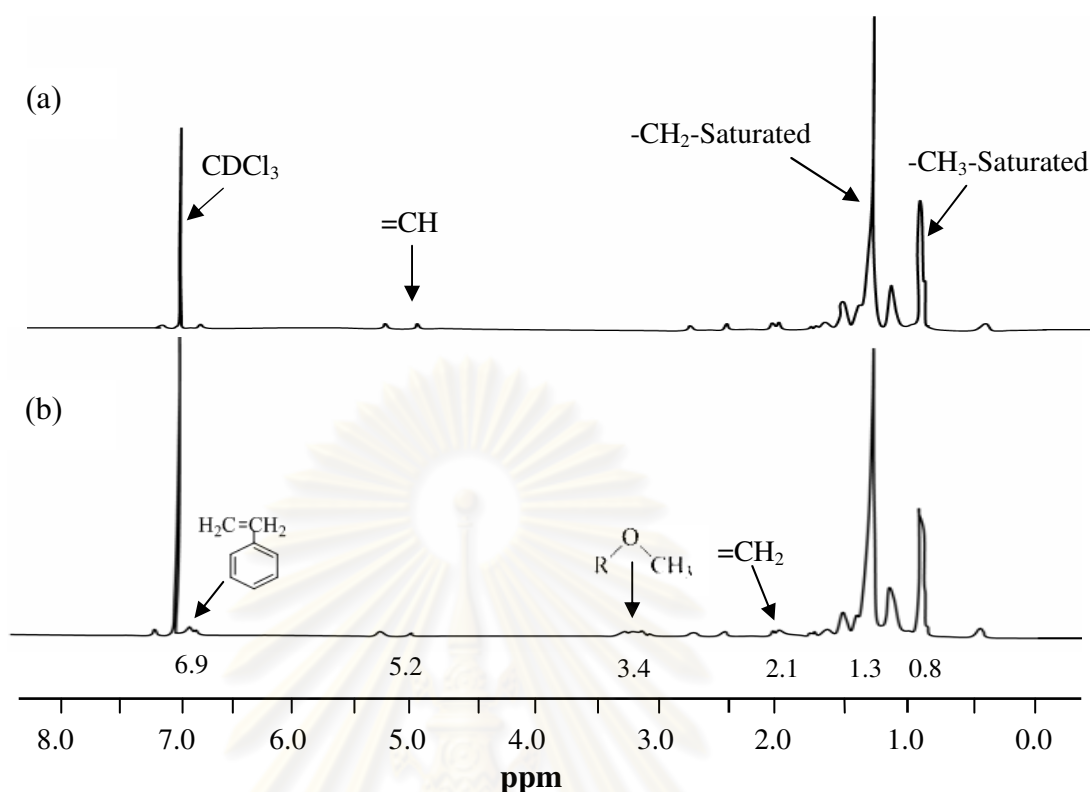


Figure 4.2 ^1H -NMR spectra of (a) EPDM and (b) GEPDM after soxhlet extraction.

4.3 Physical and mechanical properties of modified acrylic sheets containing GEPDM content

In this section, the physical and mechanical properties of the modified acrylic sheets containing GEPDM (88.1% GE) were investigated. This result was also compared to ones containing EPDM.

4.3.1 Transparency of modified acrylic sheets containing various GEPDM contents

Table 4.2 and Figure 4.3 show the appearance and color of the modified acrylic sheets containing GEPDM with various %GE and contents. For the effect of GEPDM content, it was found that the modified acrylic sheets still exhibited the transparent property when GEPDM content was in the range of 1.0–2.0 wt% (Figure 4.3c and 4.3d). Above these points, the modified acrylic sheets showed slight

opacity (Figure 4.3e and 4.3f). To compare with the modified acrylic sheet containing 1.0 wt% of EPDM (Figure 4.3b), the modified acrylic sheet was quite opaque. This indicated that the addition of EPDM and the overdose of GEPDM caused the higher opacity of the modified acrylic sheets due to the phase separation effect.

For the effect of %GE (Table 4.2) on the appearance of the modified acrylic sheets having 2.0 wt% of GEPDM, the result indicated that the increase in the %GE of GEPDM from 10.4 to 88.1% decreased the phase separation effect resulting to the reduction of opacity of the modified acrylic sheets.

Table 4.2 Appearance of modified acrylic sheets containing various rubber content and %GE.

Sample	Rubber content (wt%)	GE (%)	Sheet appearance
Acrylic sheet*	-	-	transparent
Acrylic sheet/EPDM	1.0	-	quite opaque
	1.0		transparent
	2.0		transparent
	3.0	88.1	little opaque
	4.0		little opaque
Acrylic sheet/GEPDM**	2.0	10.4	quite opaque
	2.0	17.8	quite opaque
	2.0	18.7	quite opaque
	2.0	60.0	little opaque
	2.0	68.7	little opaque
	2.0	88.1	transparent

* Acrylic sheet (MMA/ST=80/20 %w/w)

** GEPDM (88.1% GE)



(a) Acrylic sheet



(b) 1.0 wt% EPDM



(c) 1.0 wt% GEPDM

(MMA/ST=80/20 %w/w)



(d) 2.0 wt% GEPDM



(e) 3.0 wt% GEPDM



(f) 4.0 wt% GEPDM

Figure 4.3 Transparency of modified acrylic sheets containing various GEPDM rubber contents.

4.3.2 Mechanical properties of the modified acrylic sheets

The influence of the %GE and content of GEPDM on the mechanical properties of the modified acrylic sheets was shown in Figure 4.4 and Figure 4.5, respectively. The results were compared to the acrylic sheet (MMA/ST=80/20 wt%) without modification and one containing EPDM. For the addition of 1.0 wt% of EPDM, the modified acrylic sheet exhibited the significant reduction of flexural strength (Figure 4.4b), tensile strength (TS) (Figure 4.4c) and elongation at break (EB) (Figure 4.4d) possibly due to the phase separation resulting from the dissimilar polarity of EPDM and monomer mixture used for preparing the acrylic sheets. However, the addition of EPDM did not affect the impact strength of the modified acrylic sheets (Figure 4.4a). It could be explained that EPDM retained the impact strength of the modified acrylic sheet due to its good rebound property.

For the addition of GEPDM at various contents, it was found that the impact strength (Figure 4.4a), flexural strength (Figure 4.4b) and TS (Figure 4.4c) of the modified acrylic sheets were higher than those of one containing EPDM at the same content. The reduction of EB value of the modified acrylic sheet containing GEPDM also exhibited the higher crosslink density. This implied that GEPDM had the higher compatibility with MMA/ST monomer mixture resulting to the better mechanical properties of the modified acrylic sheet. The obtained experimental result were similar to the previous literature that use, the graft product-based elastomer as the compatibilizer for the blends containing constituents with different polarity (Kraus, 1978). However, Figure 4.4 shows the decrease in the flexural strength, TS and EB when the amount of GEPDM was higher than 2.0 wt%. It was due to the interfacial saturation of GEPDM in the thermoplastic components. The similar results were also observed in the natural rubber/PMMA blends compatibilized by natural rubber grafted with glycidyl methyl methacrylate (Suriyachai et al., 2004). Moreover, the overdose of GEPDM caused the high level of EPDM content in the system providing the phase separation.

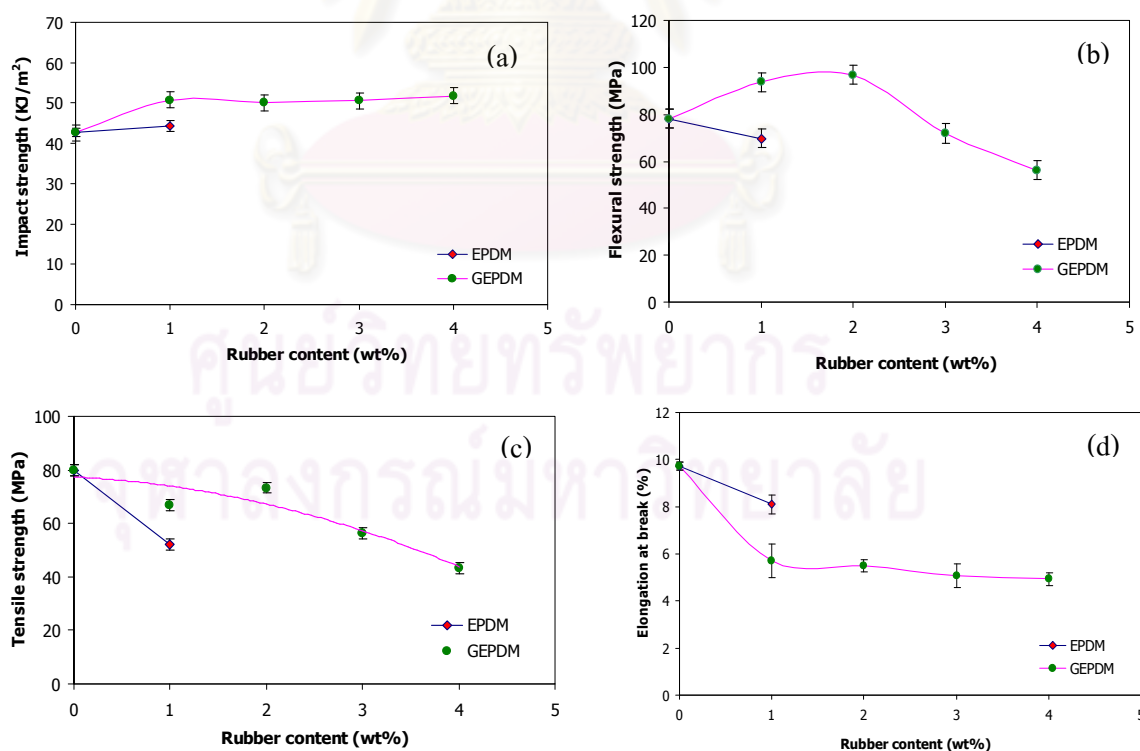


Figure 4.4 Effect of GEPDM content (%GE=88.1) on the mechanical properties of the modified acrylic sheets.

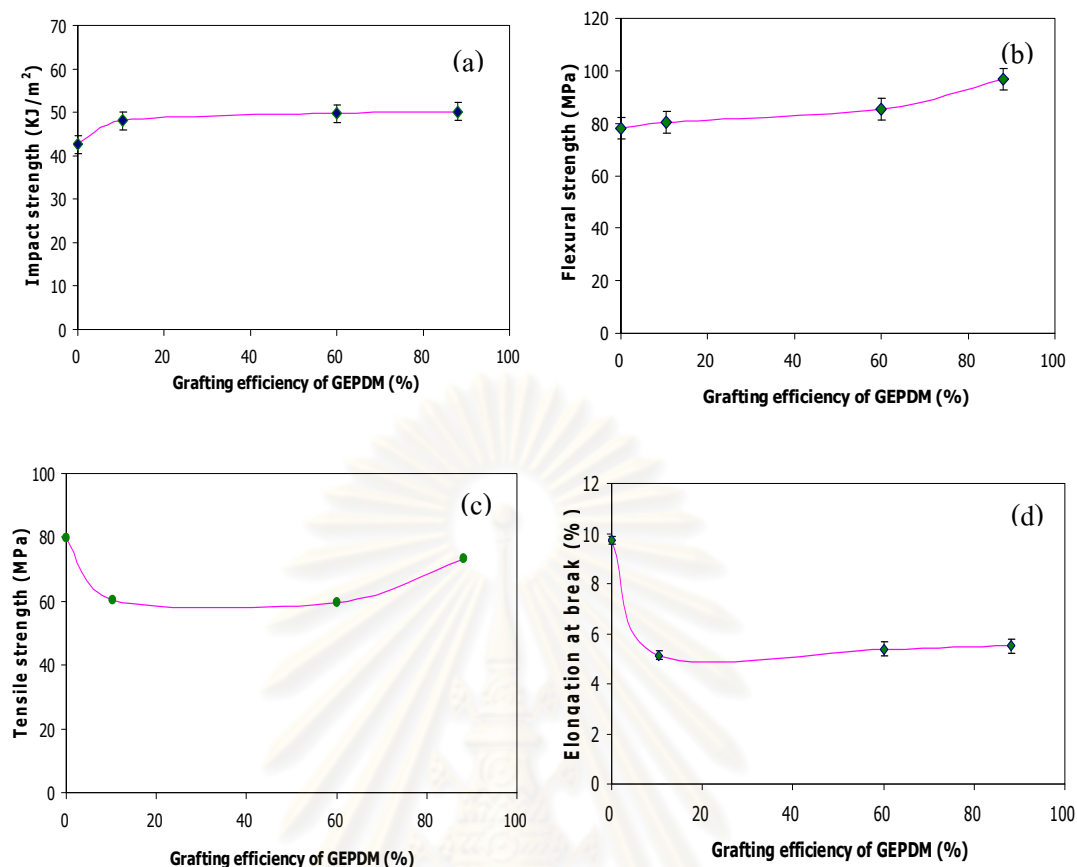


Figure 4.5 Effect of %GE on the mechanical properties of the modified acrylic sheets containing 2 wt% of GEPDM.

It was noticed that the TS and EB values of the modified acrylic sheets containing GEPDM at any content were lower than those of the acrylic sheet without the addition of GEPDM. It was due to the low tensile properties of EPDM with more brittle property after graft copolymerization of ST and MMA onto EPDM.

For the effect of %GE (Figure 4.5), it indicated that the addition of GEPDM at 2 wt% into the MMA/ST mixture gave the higher impact strength, flexural strength and tensile properties with increasing the %GE of GEPDM. This could be explained that the increase in the %GE of GEPDM promoted the higher compatibility to improve the interfacial adhesion between GEPDM and MMA/ST monomer matrix.

The stress-strain behavior of the modified acrylic sheets after tensile test is shown in Figure 4.6. The stress-strain curve of the modified acrylic sheet

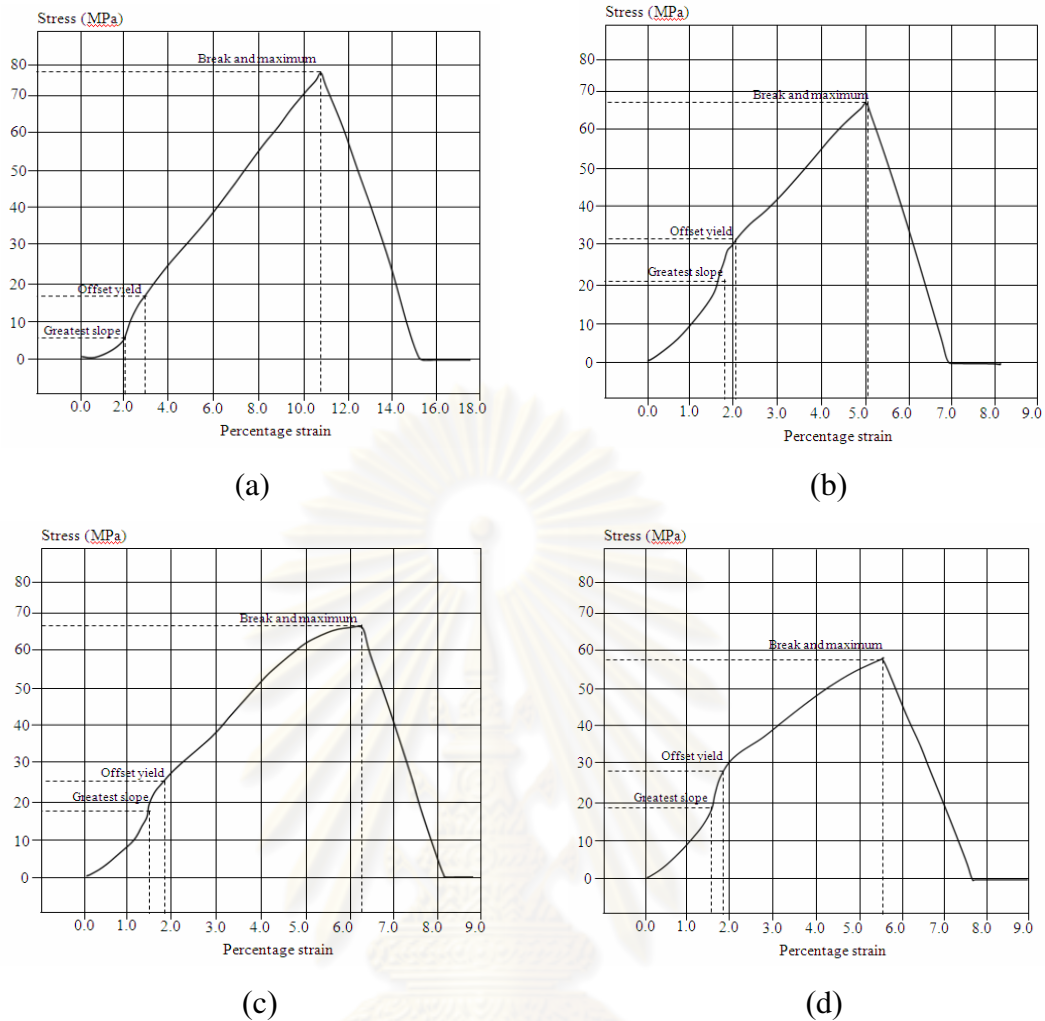


Figure 4.6 Stress-strain behavior of the acrylic sheets: (a) without GEPDM, (b) with 1 wt% of GEPDM, (c) with 2 wt% of GEPDM and (d) with 3 wt% GEPDM.

without GEPDM showed the rigid or brittle characteristics with higher elongation (Figure 4.6a). The brittle property of the modified acrylic sheet was gradually shifted to be ductile property when the amount of graft copolymer increased as shown in Figure 4.6b-d. Therefore, the modified acrylic sheets with GEPDM showed a brittle-ductile transition behavior, whereas the neat PMMA/ST was the brittle material. Similar behavior was also observed in the strain-rate effect of EVA/PMMA *in situ* polymerization blends (Cheng et al., 2004). The stress-strain curve of the modified acrylic sheet with 4 wt% of GEPDM clearly exhibited the yield point and the low percentage of strain.

4.4 Morphology of the modified acrylic sheet

The scanning electron micrographs of the fracture surface of the acrylic sheets before and after modification by addition of EPDM or GEPDM Z (%GE = 88.1%) were shown in Figure. 4.7. It was found that the uncompatibilized acrylic sheet (Figure. 4.7a) exhibited the large cracking traces indicating the brittle behavior. For the addition of EPDM at 1.0 wt% (Figure. 4.7b), the fracture surface of the modified acrylic sheet exhibited the heterogeneity with phase separation between EPDM and thermoplastic resulting to poor mechanical properties. To consider the addition of GEPDM into the MMA/ST monomer mixture, it was observed that the fracture surface of the modified acrylic sheets containing 1.0 wt% (Figure. 4.7c) and 2.0 wt% (Figure. 4.7d) became smoother which is the characteristics of the ductile materials. This implied that GEPDM could act as the interfacial agent to improve the mechanical properties of the modified acrylic sheets.

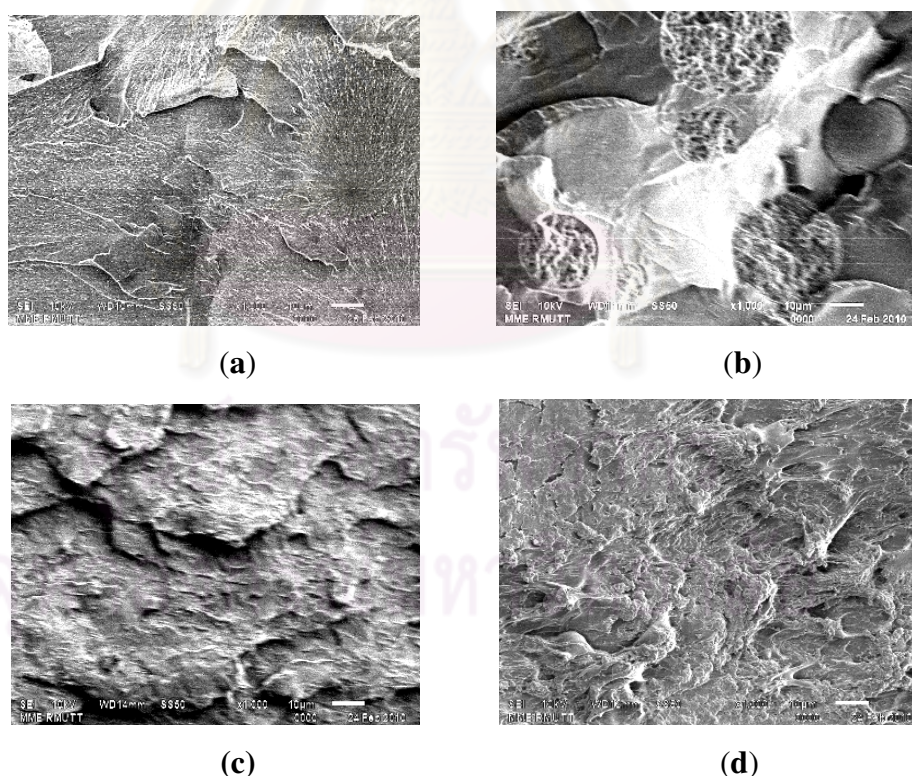


Figure 4.7 SEM micrographs of the acrylic sheets: (a) without modification, (b) addition of 1.0 wt% of EPDM, (c) addition of 1.0 wt% of GEPDM and (d) addition of 2.0 wt% of GEPDM (magnification x1000).

4.5 Thermal and UV aging of the modified acrylic sheet

In the previous section, it was found that the impact strength, flexural strength and tensile strength of the modified acrylic sheets were slightly improved by adding the small amount of GEPDM. However, it is necessary to investigate the ageing resistance of these modified acrylic sheets for outdoor application. The thermal and UV resistances of the modified acrylic sheets were examined and reported in the term of the mechanical properties retention.

4.5.1 Mechanical properties retention of modified acrylic sheets after aging

Figure 4.8 and Figure 4.9 show the effect of content and %GE of GEPDM, respectively on the retention of mechanical properties of the modified

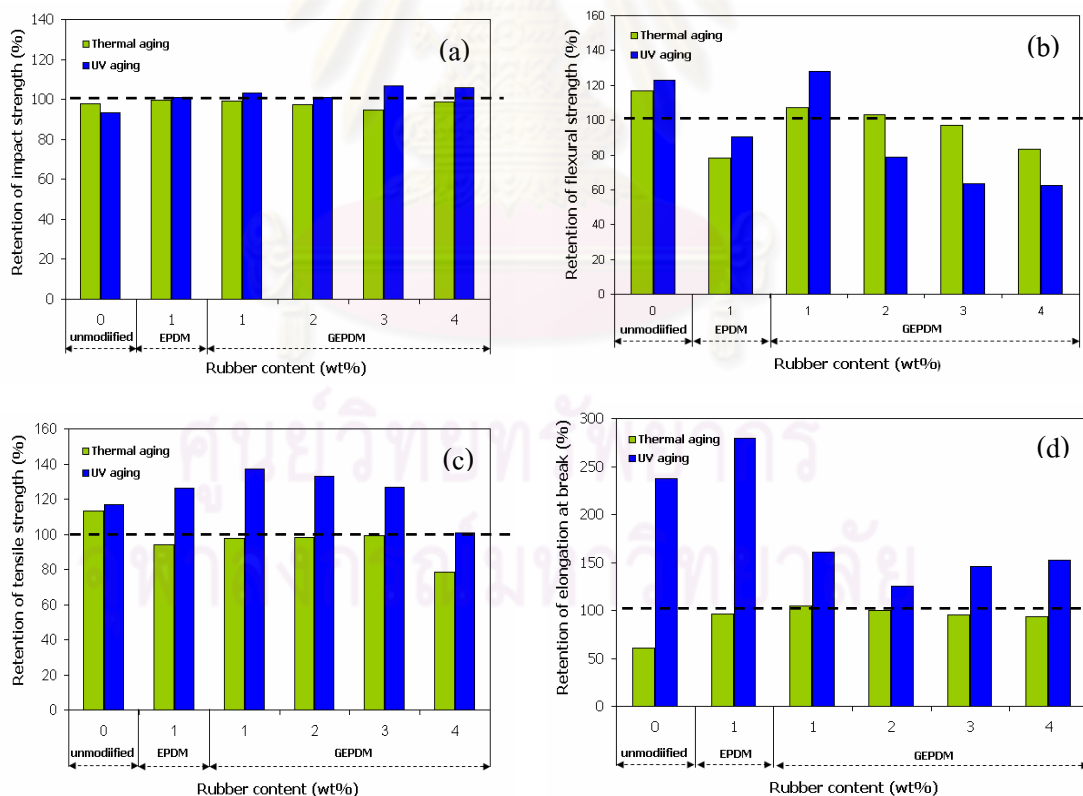


Figure 4.8 Effect of GEPDM content on the mechanical properties of the modified acrylic sheets after aging (%GE= 88.1%).

acrylic sheets after thermal and UV aging could retain and/or gave the better mechanical properties possibly due to the self polymerization during aging process. The thermal aging provided the higher flexural strength (Figure 4.8 b) and TS (Figure 4.8c) with lower EB (Figure 4.8d) resulting to the higher crosslink density. Moreover, the UV aging exhibited the good results for flexural strength, TS and EB of the acrylic sheet due to the penetration power of UV to promote the post polymerization inside the specimens. Thus, the UV aging or UV cure is generally applied for polymer used in the coating process such as polyurethane (Technical information, 2004).

For the addition of EPDM or GEPDM, the results in Figure 4.8a and 4.9a indicated that the modified acrylic sheet containing 1wt% of EPDM or GEPDM at various contents and %GEs could retained the impact strength after thermal and UV aging resulting from the EPDM segment with great thermal and UV resistance. However, at 1 wt% of rubber content, the modified acrylic sheets containing GEPDM had higher %retention of flexural strength and TS with lower EB than EPDM. It can be explained that the effect of higher compatibility was possibly promote the higher crosslink density inside the specimens. When %GE of GEPDM was kept constant at 88.1% (Figure 4.8), the increase in the GEPDM content reduced the retention of the mechanical properties of the modified acrylic sheets. This was possible that the higher rubber level promoted higher incompatibilization to inhibit the self-polymerization of MMA/ST monomer during thermal and UV aging. For the effect of %GE (Figure 4.9), it was found that the increase in the %GE of GEPDM also to decreased the thermal and UV resistance of the modified acrylic sheets due to the higher content of -C=O- functional group in GEPDM which was susceptible to heat and UV (Decker, 1996). It could be concluded that GEPDM content in the range of 1.0-2.0 wt% with 60-88.1% of %GE could retain and/or increased the mechanical properties of the modified acrylic sheet after thermal and UV aging.

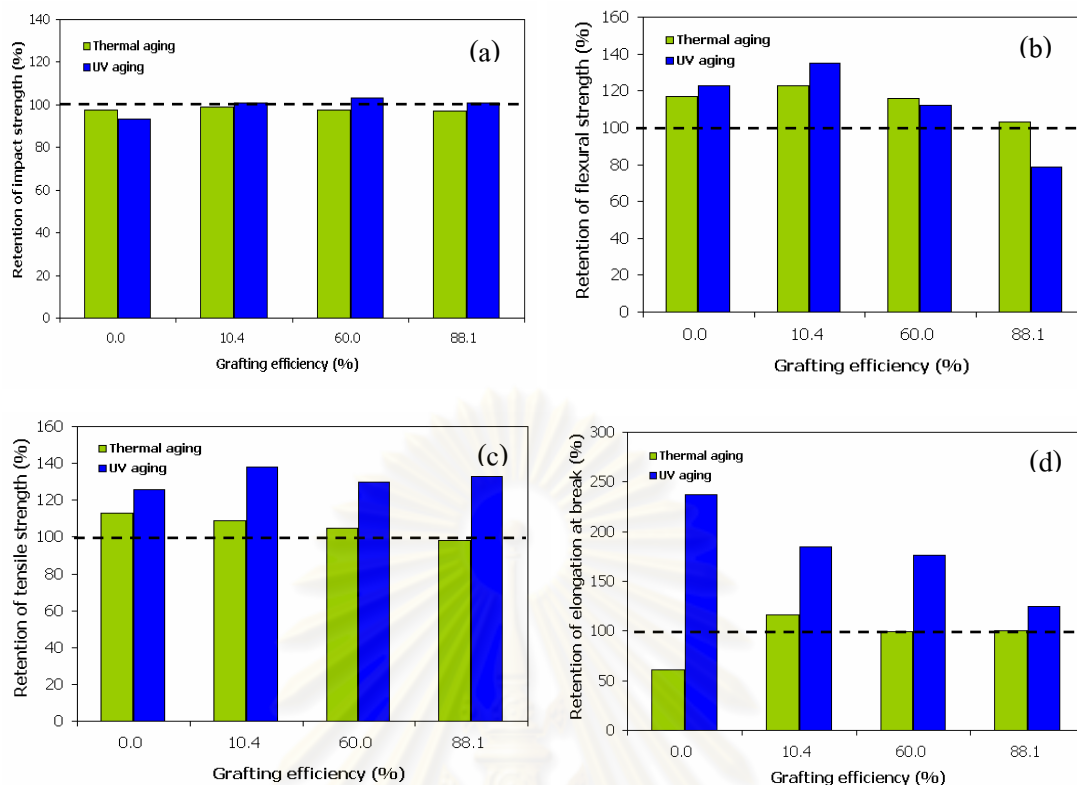


Figure 4.9 Effect of %GE of GEPDM (2 wt%) on the mechanical properties of modified acrylic sheets after aging.

4.5.2 Transparency stability of the modified acrylic sheets after aging.

Table 4.3 shows the effect of the GEPDM content and %GE of the modified acrylic sheet on the opacity value and color difference of the modified acrylic sheets after thermal and after UV aging. It can be seen that opacity of the modified acrylic sheets increased with increasing the GEPDM content. However, the opacity values of the modified acrylic sheets containing GEPDM were lower than that of one containing EPDM due to dissimilar polarity effect. This indicated the more compatibilization of GEPDM in the MMA/ST phase in the acrylic sheets.

Table 4.3 Physical properties of modified acrylic sheet

Sample	Rubber Content (wt%)	GE (%)	Opacity (%)	ΔE of thermal resistance	ΔE of UV resistance
Acrylic sheet*	-	-	12.63 \pm 0.08	0.45 \pm 0.09	10.35 \pm 0.26
Acrylic sheet/EPDM	1.0		28.30 \pm 0.45	2.56 \pm 0.16	15.61 \pm 1.40
	1.0		16.74 \pm 10.09	1.41 \pm 0.05	11.97 \pm 1.61
	2.0	88.1	18.39 \pm 0.06	2.29 \pm 0.12	12.24 \pm 0.17
	3.0		21.94 \pm 0.02	2.71 \pm 0.10	16.01 \pm 0.77
	4.0		21.74 \pm 0.25	2.96 \pm 0.23	15.82 \pm 0.46
Acrylic sheet/GEPDM**	2.0	10.4	28.72 \pm 0.07	2.93 \pm 0.18	14.55 \pm 0.77
	2.0	17.8	26.22 \pm 0.06	2.80 \pm 0.11	14.57 \pm 0.52
	2.0	18.7	23.42 \pm 0.31	2.75 \pm 0.16	14.70 \pm 0.27
	2.0	60.0	23.49 \pm 0.53	2.68 \pm 0.37	12.73 \pm 0.06
	2.0	68.7	18.67 \pm 0.19	2.52 \pm 0.15	12.44 \pm 0.18
	2.0	88.1	18.39 \pm 0.06	2.29 \pm 0.12	12.24 \pm 0.17

* Acrylic sheet (MMA/ST=80/20 %w/w)

** GEPDM (88.1% GE)

The thermal stability of the modified acrylic sheets was also examined by monitoring the yellowness of the test specimens, which can be reported in the term of ΔE . The effects of GEPDM content and %GEs on the ΔE of the specimens are shown in Table 4.3. It can be seen that ΔE of the modified acrylic sheets increased with increasing the GEPDM content possibly due to the higher incompatibilization. (Pineiro et al., 2004). The ΔE of modified acrylic decreased with increasing %GE. It was explained that the increase of %GE increased the compatibility between GEPDM and modified acrylic sheet. To compare with the modified acrylic sheet containing EPDM, the thermal resistance of one containing GEPDM was better than that of one containing EPDM. Due to the phase separation resulting from dissimilar polarity between EPDM and MMA/ST used for preparation of the acrylic sheets.

The ultraviolet stability the modified acrylic sheets was also examined by monitoring the yellowness shifts which are reported in the term of ΔE . It can be seen that the ΔE value of modified acrylic sheet with increasing the GEPDM content.

However, the increase in the %GE of GEPDM reduced the ΔE value of the modified acrylic sheets. It can be explained by the double bond in the EPDM, MMA and ST structure. Selective incorporation of UV sensitive molecular structures such as vinyl groups and non-addition of photosensitizers could promote the photodegradation. (Saechtling, 1995). It could be notice that the color stability of the modified acrylic sheets containing GEPDM after UV aging was slightly higher than that of a one containing EPDM.

4.6 Thermal properties of modified acrylic sheet

4.6.1 Differential scanning calorimetry, DSC

Differential scanning calorimetry (DSC) can be used for evaluation of the miscibility between components of copolymers. In the absence of miscibility, a polymer blend of two polymers exhibits two distinct glass transition temperature (T_g) of the pure components. Figure 4.10 shows the DSC thermograms of the EPDM, GEPDM (88.1%GE) and acrylic sheets (MMA/ST = 80/20 %w/w) with and without the addition of GEPDM (%GE = 88.1%) (1-4 wt%).

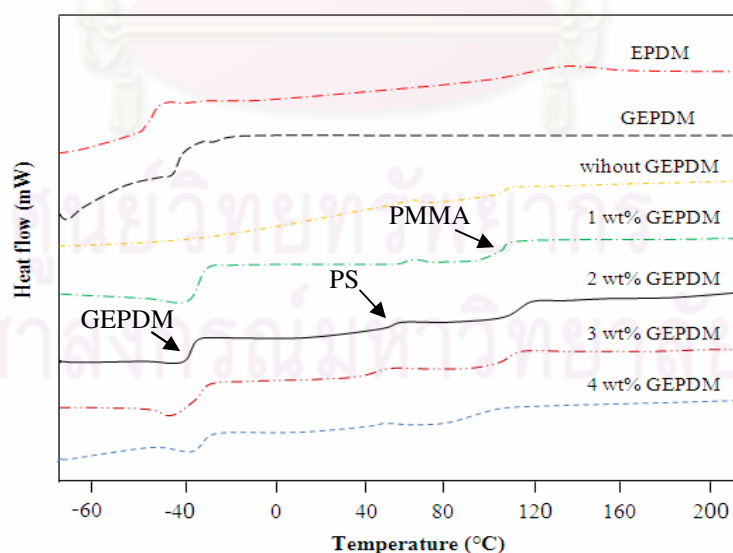


Figure 4.10 DSC thermograms of EPDM, GEPDM and acrylic sheet with and without the addition of GEPDM at various contents.

Table 4.4 summaries T_g of all samples. It was found that EPDM was shifted from -52.9°C to -40.3°C due to higher rigidity of EPDM after graft copolymerization of ST and MMA which are the monomers for producing the brittle materials. For the acrylic sheet without the addition of GEPDM, the DSC thermogram indicated two T_g values at 110°C and 73.3°C attributed to PMMA and PS phases, respectively (Silva et al., 2004). When GEPDM was added, the DSC thermograms exhibited three T_g values due to EPDM, PMMA and PS of the modified acrylic sheets. The result showed the shift of T_g values from the unmodified acrylic sheets indicating the partial compatibilization from the addition of GEPDM. It can be seen that the increase in the GEPDM content increased the T_g values of EPDM phases due to the higher rigidity resulting from the graft copolymerization as explained above. For PMMA and ST phases, the addition of 1.0-2.0 wt% of GEPDM reduced T_g from 110°C to 108°C for PMMA and 73°C to 72°C for PS resulting from the soft segment of EPDM in GEPDM. However, the increased in the GEPDM above this point increased T_g value of PMMA which was close to that of unmodified one. This result was opposited to the PS phase. This is possible that GEPDM was more compatible to PS phase than PMMA phase in the modified acrylic sheet.

Table 4.4 T_g values of modified acrylic sheet prepared by addition of GEPDM with various GEPDM contents

Sample	Rubber content in acrylic sheet (wt%)	T_g of each polymeric phases ($^\circ\text{C}$)		
		EPDM	PMMA	PS
EPDM	-	-52.9	-	-
GEPDM*	-	-40.3	-	-
Acrylic sheet**	-	-	110.0	73.3
Acrylic sheet/GEPDM	1.0	-41.5	108.2	71.0
	2.0	-41.6	108.3	71.9
	3.0	-41.0	109.3	66.4
	4.0	-39.6	111.0	65.1

* GEPDM (88.1 %GE)

** Acrylic sheet (MMA/ST=80/20 %w/w)

4.7 Kinetic study of thermal degradation

4.7.1. EPDM and GEPDM

Thermogravimetric analysis is one common technique to evaluate the thermal stability of materials, and also indicate the decomposition of polymers at various temperatures. Thermal stability can be regarded as the ability to maintain the required properties of materials at a desired temperature. Figure 4.11 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of EPDM and GEPDM (%GE = 88.1%) in the presence of a nitrogen atmosphere. The initial decomposition temperature (T_{id}), the decomposition temperature at the maximum weight loss rate (T_p) and the final decomposition temperature (T_f) are summarized in Table 4.5. It indicated that the thermal decomposition of rubbers was an overall one-step reaction because the TG curve of the samples was one-step and provided smooth weight loss curves. The initial decomposition temperature of EPDM (415.9°C) was higher than that of GEPDM (287.2°C). It indicated that GEPDM had lower thermal stability than EPDM due to the $-C=O-$ functional group in GEPDM which was susceptible to thermal degradation (Hinchiranan et al., 2009). However, it was found that the DTG curve (Figure 4.11b) of EPDM had higher maximum weight loss rate than that of GEPDM. This means that EPDM was rapidly decomposed at temperature above 496.9°C, although the saturation backbone provides the highest decomposition temperature.

The activation energy (E_a) of pure EPDM and GEPDM calculated using the Kissinger method are obtained from the slope of the plot between $\ln(\beta/T_p^2)$ versus $1/T_p$ (Kissinger, 1956) from room temperature to 600°C at 2.5, 5 and 10°C/min in nitrogen atmosphere as shown in Figure 4.12. From Table 4.5,

Table 4.5 Decomposition temperatures, maximum weight loss rate and activation energy of thermal decomposition under N₂ atmosphere of EPDM and GEPDM

Sample	Decomposition temperature (°C)*			$(d\alpha/dt)_p$ ** (%/min)	E _a (kJ/mol)
	T _{id}	T _p	T _f		
EPDM	415.9	461.6	496.9	35.17	222.5
GEPDM	287.2	459.4	493.9	23.60	274.5

* Recorded at 10 °C/min of heating rate.

** $(d\alpha/dt)_p$ = maximum weight loss rate

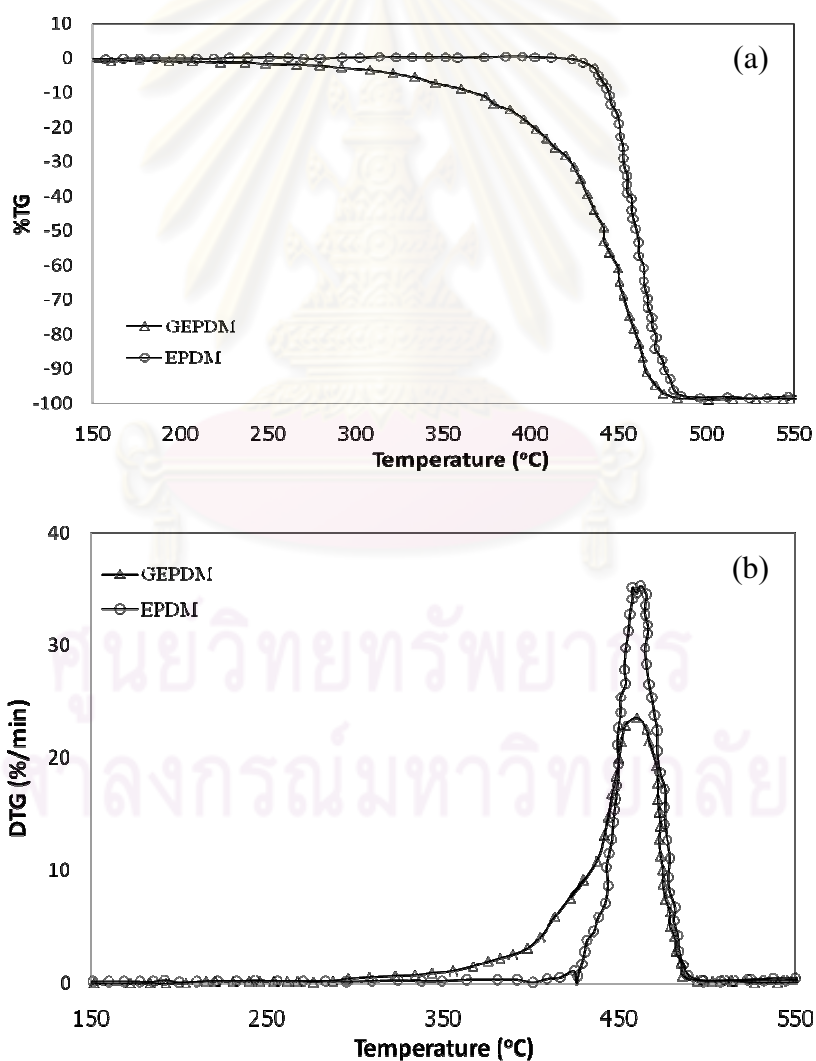


Figure 4.11 Thermogravimetric curves of GEPDM and EPDM at a heating rate of 10°C/min under nitrogen atmosphere : (a) TG and (b) DTG curves.

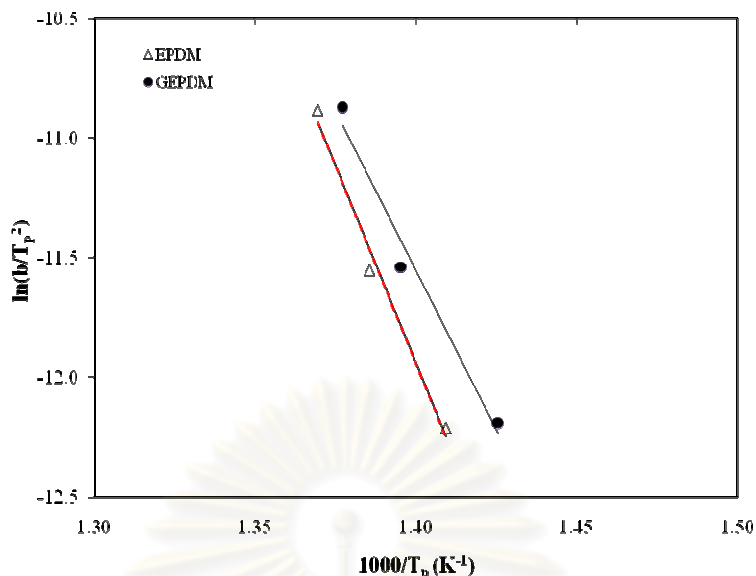


Figure 4.12 Plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ at various heating rates: (Δ) EPDM and (\bullet) GEPDM.

the E_a of GEPDM (274.5 kJ/mol) was significantly higher than that of EPDM (222.5 kJ/mol). This implies that GEPDM required more energy to break down the chemical bond due to the PS units in the GEPDM which had high thermal stability resulting from benzene ring in the structure (Kannan et al., 2009).

4.7.2. Modified acrylic sheets

Under nitrogen atmosphere, the effect of the addition of GEPDM (88.1%GE) at various contents on the decomposition temperature and activation energy of thermal decomposition of modified acrylic sheet (MMA/ST = 80/20% w/w) was presented in Figure 4.13 and Table 4.6. Figure 4.13 shows the two-stage thermal decomposition pattern of unmodified acrylic sheet and one-stage decomposition of the modified acrylic sheet with containing GEPDM. From the DTG curve (Figure. 4.13b), the one stage and two stage of the decomposition of unmodified acrylic sheet (Hu et al., 2003) were appeared at a peak temperature (T_p) around 275.9°C and of 360.3°C, respectively. The thermal decomposition referred to the decomposition of PMMA (Madras et al., 1795) and the second decomposition stage was the decomposition of PS (Silva et al., 2004, Karmore et al., 2000). The addition of GEPDM shifted the two-stage decomposition of the acrylic sheet to the one-stage decomposition. This

indicated the higher compatibility of GEPDM and the MMA/ST monomers used for preparation of the modified acrylic sheets. It was observed that the increase in the GEPDM content promoted the higher T_p due to the effect of EPDM segment in the GEPDM. This means that the modified acrylic sheets had higher thermal resistance than unmodified ones. However, the overdose of GEPDM caused the reduction of T_{id} possibly due to the higher incompatibility and GEPDM might be partially decomposed at the initial decomposition process.

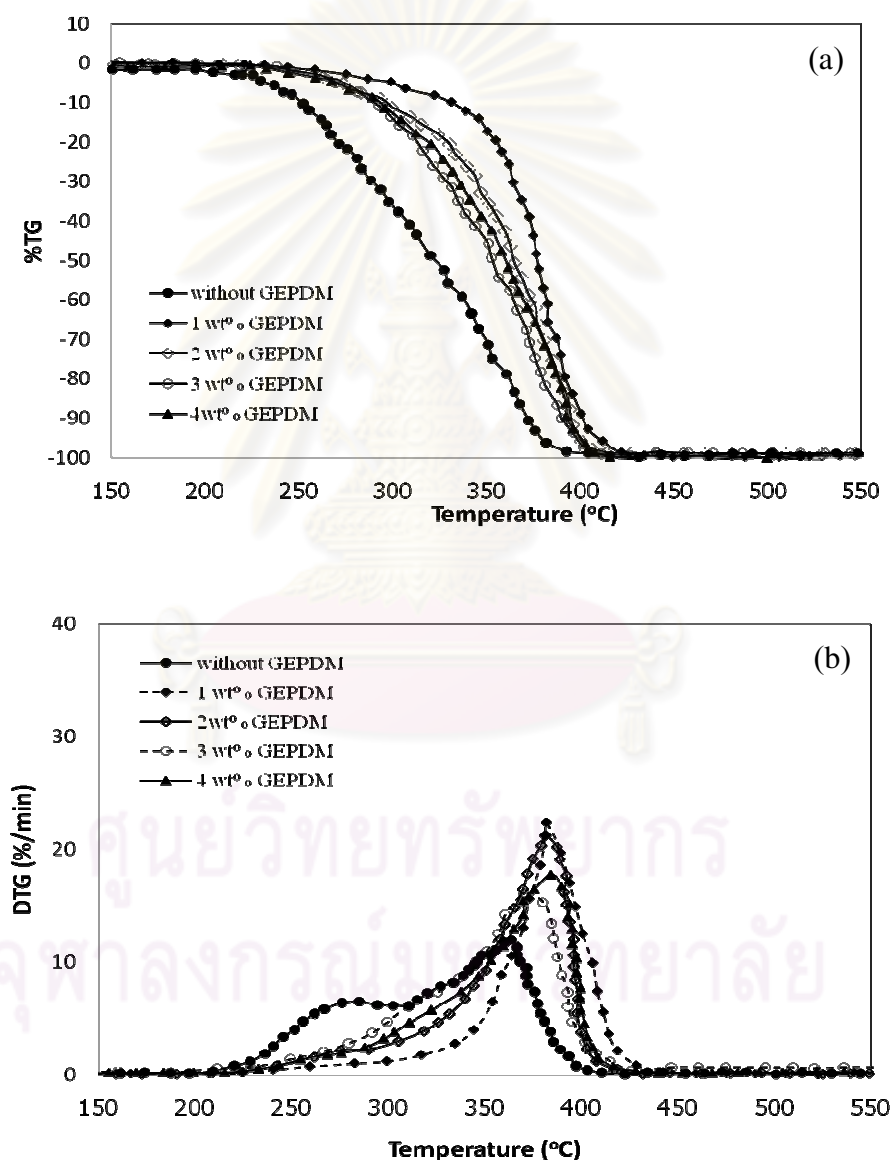


Figure 4.13 Thermogravimetric curves of the modified acrylic sheets containing various GEPDM content at heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere: (a) TG and (b) DTG curves.

Table 4.6 Decomposition temperatures, maximum weight loss rate and activation energy of thermal decomposition under N₂ atmosphere of the modified acrylic sheets with and without the addition of various GEPDM

Sample	Rubber content (wt%)	Decomposition temperature (°C) [*]			$(d\alpha/dt)_p$ ^{**} (%/min)	E _a (kJ/mol)
		T _{id}	T _p	T _f		
Acrylic sheet ^{***}						
first stage	-	209.4	275.9	310.7	6.54	183.4
second stage	-	310.7	360.3	410.6	11.78	40.8
Acrylic sheet/GEPDM ^{****}						
	1.0	240.6	382.0	439.9	22.42	210.7
	2.0	224.4	381.5	431.9	21.23	108.5

^{*} Recorded at 10 °C/ min of heating rate.

^{**} $(d\alpha/dt)_p$ = maximum weight loss rate

^{***} Acrylic sheet (MMA/ST=80/20 %w/w)

^{****} GEPDM (88.1 %GE)

The activation energy (E_a) of the modified acrylic sheets containing GEPDM (%GE = 88.1%) at various contents was also calculated using the Kissinger method at heating rate of 2.5, 5 and 10°C/min under nitrogen atmosphere as shown in Table 4.6. For the unmodified acrylic sheet, the activation energy of the first stage was higher than that of the second stage because PS is a more stable matrix which shows degradation in a single stage (Silva et al., 2004 and Madras, 1997). When 1.0 wt% of GEPDM was applied to the modified acrylic sheets, the E_a of thermal decomposition of the modified acrylic sheet was increased to 210.7 KJ/mol which was higher than that of the unmodified one. It could be explained that the EPDM segment in GEPDM enhanced the thermal resistance of the modified acrylic sheet. However, it was observed that the E_a value the modified acrylic sheets decreased with increasing the GEPDM content possibly due to the incompatibilization effect that might reduce the E_a value resulting in the ease of thermal decomposition (Awad, 1999, Nishikawa, 1999 and Srinivas, 1994).

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

In this research, an attempt was made to prepare graft copolymers of MMA and ST on EPDM by solution polymerization using benzoyl peroxide as an initiator. The conversion, grafting efficiency, percentage of free rubber, percentage of copolymer and percentage of graft copolymer was recorded as functions of reaction temperature, rubber concentration and reaction time. The graft EPDM (GEPDM) was also used as an impact modifier and stabilizer for acrylic sheets. The mechanical and physical properties including morphology of the modified acrylic sheets containing graft EPDM (GPDM) with various contents and grafting levels were investigated. The retention of mechanical and physical properties of the modified acrylic sheets containing GEPDM after thermal and UV aging was reported. The kinetics of thermal degradation and activation energy of the modified acrylic sheets were also evaluated.

5.1 Conclusions

5.1.1 Preparation and grafting properties of GEPDM

The graft copolymerization of MMA and ST onto EPDM was carried out by solution polymerization initiated by benzoyl peroxide. The appropriate condition of graft copolymerization was 1 wt% of initiator dosage 8% of rubber concentration, 50/50 %w/w of EPDM/MMA-ST ratio and 75/25 %v/v of MMA/ST ratio at 90°C for 16 h to achieve the GEPDM product consisting of 88.1% of grafting efficiency.

5.1.2 Mechanical properties of the modified acrylic sheets containing GEPDM before and after thermal and UV aging

The mechanical properties of the modified acrylic sheet containing GEPDM and %GE before and after thermal UV aging were reported. It was found

that the impact and flexural strength of the modified acrylic sheet reached to 52.08 KJ/m² and 96.75 MPa, respectively when GEPDM was applied as 2.0 wt%. For the addition of GEPDM content in the range of 1.0-2.0 wt% with 60-88.1% of %GE could retain and/or increase the mechanical properties of the modified acrylic sheet after thermal and UV aging.

5.1.3 Morphology of the modified acrylic sheet

From SEM micrographs, the addition of GEPDM into the modified acrylic sheets increased homogeneity between thermoplastic and rubber phases with increasing GEPDM content. Thus, the GEPDM could act as the interfacial agent or compatibilizer to improve the mechanical properties of the modified acrylic sheets.

5.1.4 Transparency stability of the modified acrylic sheets after aging.

The thermal and UV stability of the modified acrylic sheets was also examined by monitoring the yellowness of the test specimens, which was reported in the term of ΔE . The ΔE of the modified acrylic sheets increased with increasing the GEPDM content. The increase in the %GE of GEPDM reduced the ΔE value of the modified acrylic sheets.

5.1.5 Thermal properties of modified acrylic sheet

The DSC thermogram indicated that T_g of EPDM was shifted from -52.9°C to -40.3°C due to higher rigidity of EPDM after graft copolymerization of ST and MMA which are the monomers for producing the brittle materials. For the addition of 1.0-2.0 wt% of GEPDM reduced T_g from 110°C to 108°C for PMMA and 73°C to 72°C for PS resulting from the soft segment of EPDM in GEPDM. However, the increased in the GEPDM content above this point increased T_g value of PMMA and it was close to that of unmodified one. This result was opposite to that of PS phase. This was possible that GEPDM was more compatible to PS phase than PMMA phase in the modified acrylic sheet.

5.16 Kinetics of thermal degradation

The initial decomposition temperature of EPDM (415.9°C) was higher than that of GEPDM (287.2°C) due to the effect of brittle PMMA and PS phases inside GEPDM. The thermal decomposition of the unmodified acrylic sheet (MMA/ST = 80/20% w/w) showed the two-stage thermal decomposition. Conversely, the modified acrylic sheet with containing GEPDM exhibited the one-stage decomposition pattern due to the higher compatibility. The increase in the GEPDM content promoted the higher T_p value resulting from the effect of EPDM segment in the GEPDM. The overdose of GEPDM caused the reduction of T_{id} possibly due to the higher incompatibility and GEPDM might be partially decomposed at the initial decomposition process.

The E_a of GEPDM (274.5 kJ/mol) was significantly higher than that of EPDM (222.5 kJ/mol). The E_a of thermal decomposition of the modified acrylic sheets increased to 210.7 kJ/mol of 1.0 wt% of GEPDM which was higher than that of the unmodified one. However, it was observed that the E_a values of the modified acrylic sheets decreased with increasing the GEPDM content due to the higher incompatibilization effect.

5.2 Recommendation for the future work

1. From the result of this study, the GEPDM should be applied for the commercial production scale of the casted acrylic sheets that are used in outdoor applications.
2. The new techniques such as microwave or plasma graft copolymerization should be further studied to enhance the rate of reaction.

REFERENCES

- Asian Market Review by Clive Ong, ICIS Pricing. 2010. <http://www.icis.com/v2/Chemicals/9076471/Styrene/pricing.html> (Accessed May 21, 2010).
- Baldwin, F.B., Borzel, P., Cohen, C.A., Makowski, H.S. and Castle van de, J.F. Rubber Chemistry and Technology 43 (1970): 522.
- Bassani, A. and Pessan, L. A. Toughening of Polypropylene with Styrene/Ethylene-Butylene/Styrene Tri-block Copolymer: Effects of Reactive and Nonreactive Compatibilization, Journal of Applied Polymer Science. 86(14)(2002): 3466 – 3479.
- Bayer, A.G. Ullman's Encyclopedia of Industry Chemistry. Vol. A23: VCH Publishes, 1992.
- Bemiller, N. Encyclopedia of Polymer Science and Technology. Vol. 7, New York: John Wiley & Sons, 1976.
- Billmeyer, F.W. Textbook of Polymer Science. 3rd ed. Singapore: John Willey, 1984.
- Brinkmann, B. International Plastics Handbook: The Resource Plastics Engineers, Munich: Hanser Publishers, 2006.
- Brydson, J. A. Rubbery Material and Their Compounds. Essex, England: Elsevier Ltd., 1988.
- Charmondusit, K. and Seeluangsawat, L. Recycling of Poly (Methyl Methacrylate) Scrap in the Styrene-Methyl Methacrylate Copolymer Cast Sheet Process. Resources, Conservation and Recycling 54 (2009): 97-103.
- Chamondusit, K., Kiatkamjornwong, S. and Preasassarakich, P. Grafting of Methyl Methacrylate and Styrene onto Natural Rubber. Journal of Science Chulalongkorn University. 23(2) (1998): 167-182.
- Cheng, S.K. and Chen, C.Y. Mechanical Properties and Strain-rate Effect of EVA/PMMA *in situ* Polymerization Blends. European Polymer Journal 40 (2004): 1239-1248.
- Ciesielski, A. An Introduction to Rubber Technology. 1st ed, Rapra Technology Limited: 1999.

- Collthup, N.B., Daly, L.H. and Wiberley, S.E. Introduction to Infrared and Raman Spectroscopy. New York: Academic press, 1964.
- Collyer, A. Rubber Toughened Engineering Plastics, Chapman & Hall, London, 1994.
- Decker, C. Photoinitiated Crosslinking Polymerization. Progress in polymer science, 21 (1996): 593.
- Drive, W.E. Plastics Chemistry and Technology. New York: Van Nostrand Reinhold Company, 1979.
- Ebewele, R.O. Polymer Science and Technology. pp. 348-349, 426-427. New York: CRC Press, 2000.
- Edenbaum, Journal Plastics Additives and Modifiers Handbook. London : Chapman & Hall, 1996.
- Fred, W. Textbook of Polymer Science. 2nd ed. New York: Wiley & Sons, 1971.
- Fu, J., Wang, L. and Zhang, A. Synthesis of EPDM-graft-Methyl Methacrylate and Styrene and Its Toughening Effect on MS resin. Polymer Bulletin 60 (2008): 405-416.
- Fu, J., Wang, L. and Shang, A. Toughening Effect of EPDM-graft-Methyl Methacrylate and Styrene (EPDM-g-MMA/ST) Methyl Methacrylate-Styrene Copolymer (MS Resin). Journal of Applied Polymer Science 108 (2008): 3507-3515.
- Ghosh, P. Polymer Science and Technology of Plastics and Rubber, New Delhi: Tata McGraw Hill Publishing Company Limited, 1990.
- Grulke, E.A. Polymer Process Engineering. New Jersey : P T R Prentice Hall, 1994.
- Heim, P.H., Wrotecki, C., Avenel, M. and Gaillard, P. High Impact Cast Sheets of Poly(Methyl Methacrylate) with Low Level of Polyurethane. Polymer 34 (1993): 1653-1660.
- Hinchiranan, N., Suppaibulsuk, B., Promprayoon, S. and Prasassarakich, P. Improving Properties of Modified Acrylic Sheet via Addition of graft Natural Rubber. Materials Letters 61 (2007): 3951-3955.
- Hinchiranan, N., Lertweerasirikun, W., Poonsawad, W., Rempel G.L. and Prasassarakich, P. Hydrogenated Natural Rubber Blends: Aspect on Thermal Stability and Oxidative Behavior, Journal of Applied Polymer Science 13 (2009): 1566-1575.
- Hofmann, W. Rubber Technology handbook, p. 93. Hanser Publishers, Munich, 1989.

- Hoang, Thai., Park, Jong-Gu., Kim, GU-Kim, OH, Sang-Taek, HA, Hang-Sik., CHO, Won-JEI. Synthesis and Properties of Styrene EPDM-Vinyl Acetate Graft Polymer. Journal of Applied Polymer Science 77(2000): 2296-2304.
- Hu, Y-H., and Chen, C-Y. The Effect of End Groups on the Thermal Degradation of Poly(Methyl Methacrylate). Polymer Degradation and Stability 82 (2003): 81.
- Indian Rubber Institute. Rubber Engineering. New Delhi: Tata McGraw-Hill Publishing, 1998.
- Kannan, P., Biernacki, J. J., Visco Jr, D. P., Lambert, W. Kinetics of Thermal Decomposition of Expandable Polystyrene in Different Gaseous Environments. Journal of Analytical and Applied Pyrolysis 84 (2009): 139–144.
- Karmore, V. and Madras, G. Continuous Distribution Kinetics for the Degradation of Polystyrene in Supercritical Benzene. Industrial & Engineering Chemistry Research 39 (2000): 4020.
- Katsikis, N., Zahradnik, F., Helmschrott, A., Munstedt, H. and Vital, A. Thermal Stability of Poly(Methyl Methacrylate)/Silicanano and Microcomposites as Investigated by Dynamic-Mechanical Experiments. Polymer Degradation and Stability 92 (2007): 1966-1976.
- Kissinger, H. Reaction Kinetics in Differential Thermal Analysis. Analytical Chemistry 29 (1957): 1702.
- Kraus, S. Polymer-Polymer Compatibility in Polymer Blends Vol 1, D.R. Paul and S. Newman (eds.). pp. 35-89. Academic Press, New York,; Ch. 1, 2, 12.,1978.
- Lin-vien, Di, Colthup, N. B., Fateley, W. G., Grasselli, J.G., Handbook of Infrared and Raman Characteristics of Organic Molecules. New york, 1991.
- Lutz, Jr., and Grossman, R.F. Polymer Modifiers and Additives. New York : Marcel Dekker, 2001.
- Madras, G., Smith, J. M. and McCoy, B. J. Degradation of Poly-(Methyl Methacrylate) in Solution. Industrial & Engineering Chemistry Research 35 (1996): 1795.
- Madras, G., and McCoy, B.J. Oxidative Degradation Kinetics of Polystyrene in Solution. Chemical Engineering Science 52 (1997): 2707.
- Madras, G., Chung, G.Y., Smith, J. M. and McCoy, B.J. Molecular Weight Effect on the Dynamics of Polystyrene Degradation. Industrial & Engineering Chemistry Research 36 (1997): 2019.

- Mansour, A.F. Photostability and Optical Parameters of Copolymer Styrene/MMA as a Matrix for the Dyes used in Fluorescent Solar Collectors. Polymer Testing 23 (2004): 247-252.
- Mark, J. E., Erman, B. and Eirich, F. R. Science and Technology of Rubber. 2nd ed. London: Academic Press, 1994.
- Michaeli, W. Plastics Processing : An Introduction. Germany : Carl Hanser Verlag, 1995.
- Morton, M. Rubber Technology. 2nd ed. New York: Van Nostrand Reinhold Company, 1973.
- Nishikawa, M., Holroyd, R.A. and Itoh, K. Behavior of Excess Electrons in Supercritical Fluids. Proceedings of 13th International Conference on Dielectric Liquids (ICDL '99), Nara, Japan, July 20-25, 1999.
- Noordermeer, J.W.M. Ethylene-Propylene Elastomers, Encyclopedia of Polymer Science And Technology, 3rd Ed., Wiley & Sons, 2002.
- Odian, G. Principles of polymerization. 3rd ed. New York: John Wiley & Sons, 1991
- Oommen, Z. and Thomas, S. Interfacial Activity of Natural Rubber-g-Poly(Methyl Methacrylate) in Incompatible Natural Rubber/Poly(Methyl Methacrylate) Blends. Polymer Bulletin 31 (1993): 623-628.
- Pinheiro, L. A., Chinelatto, M.A. and Canevarolo, S.V. The Role of Chain Scission and Chain Branching in High Density Polyethylene During Thermomechanical Degradation. Polymer Degradation and Stability 86 (2004): 445-453.
- Prasertpong, P. and Charmondusit, K. Impact Modification of Styrene Methyl Methacrylate Copolymer Sheet by Using Natural Rubber via Casting Process, Proceedings of the 2nd Technology and Innovation for Sustainable Development Conference, January 28-29, Khon Kean, Thailand, 2008.
- Saechtling, H. International Plastics Handbook for the Technologist Engineer and User, 3rd ed. Munich: Wilbrand Wobcken, 1995.
- Schulz, D. N., Turner, S. R. and Golu, M. A. Recent Advances in the Chemical Modification of Unsaturated Polymers. Rubber Chemistry and Technology 55 (1982): 809-859.
- Shah, V. Handbook of Plastic Testing and Failure Analysis, 3rd ed. New Jersey: Wiley-Interscience, 2007.

- Sheng, J. and Hu, J. Graft Polymerization of Styrene onto Random Ethylene-Propylene Diene Monomer. Journal of Applied Polymer Science 60 (1996): 1499-1503.
- Silva, G.G., Rocha, P.M.F., Oliveira, P.S., and Neves, B.R.A., Domain Size Effects on the Thermal Properties of PS/PMMA Blends. Applied Surface Science 238 (2004): 64–72.
- Sriprachuabwong, C., Pongchareun, S., Rodium, S. and Charmondusit, K. Preparation of Transparent Styrene-Methyl Methacrylate Copolymer by Casting Process, Thai Patent 0601002635, June 8, 2006.
- Srinivas, P., and Mukhopadhyay, M. Influence of the Thermodynamic State on Cyclohexane Oxidation Kinetics in Carbon Dioxide Medium. Industrial & Engineering Chemistry Research 33 (1994): 3118.
- Suriyachai, P., Kiatkamjornwong, S. and Prasassarakich, P. Natural Rubber-g-Glycidyl Methacrylate/Styrene as a Compatibilizer in Natural Rubber/ PMMA Blends, Rubber Chemistry and Technology 77(5)(2004): 914-930.
- Technical Information, UV Curing Technical Principle and Mechanism, Ciba Specialty Chemical, 2004.
- Thawornwisit, S. Properties of Styrene-Methyl Methacrylate Copolymer Sheet Containing Modified Natural Rubber. Master Thesis of Science. Chulalongkorn University 2 (2006).
- Zeng, Z., Wang, L., Cai, T. and Zeng, X. Synthesis of High Rubber Styrene-EPDM-Acrylonitrile Graft Copolymer and Its Toughening Effect on SAN. Journal of Applied Polymer Science 94 (2004): 416-423.



APPINDICES

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Appendix A

The Overall Composition of Rubber

Table A-1 properties of ethylene-propylene-diene copolymer (NORDEL™ IP 5565)

Typical polymer	Value
Mooney viscosity ML (1+4) @ 125°C	65
Polymer composition (wt%)	
Ethylene	50
Propylene	42.5
Ethylidene norbornene (ENB)	7.5
Molecular weight distribution	Medium
Product density (g/cc)	0.86
Ash content (max, wt%)	0.1
Total volatiles (max, wt%)	0.4

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Reaction time (h)	11.6	20
	244.000	24.00
	335.203	36.43
	346.140	51.80
	33.005	3.04
	0.0511	0.58
	0.0340	0.23
	2.454	2.46
	0.0242	0.35
	89.00	81.00
	79.88	11.50
	1123.000	7.53
	8.1193	12.43
	2.573	4.18
	5.680	8.25
	688.667	66.40

APPENDIX B

Data of Graft Copolymerization of MMA and ST onto EPDM

Table B-1 Determination of grafting properties of GEPDM

Reaction properties	Reaction temp		Rubber concentration						
	(°C)		(wt%)						
	80	90	6	8	10	4	6	8	10
EPDM rubber content (g)	24.00	24.00	18.00	24.00	30.00	24.00	24.00	24.03	24.03
Graft Product (g)	31.98	32.20	22.43	32.20	37.98	28.94	31.28	30.90	32.01
Total Conversion	33.27	34.10	24.60	34.10	26.60	20.60	25.80	28.56	33.20
Sample for soxhlet extraction (g)	3.00	3.06	3.0	3.06	3.0	3.07	3.01	3.00	3.06
Sample after extraction by LPE (g)	0.63	0.61	0.65	0.61	0.57	0.611	0.67	0.74	0.64
Sample after extraction by MEK+ acetone/ (g)	0.32	0.37	0.30	0.37	0.23	0.14	0.09	0.20	0.33
Free ethylene propylene diene rubber (g)	2.37	2.45	2.35	2.45	2.43	2.46	2.34	2.26	2.42
Free copolymer (g)	0.31	0.24	0.35	0.24	0.34	0.47	0.58	0.54	0.30
%Free ethylene propylene diene (%wt)	78.92	80.03	78.3	80.0	81.00	80.10	77.77	75.30	79.10
%Free copolymer (%wt)	10.35	7.98	11.50	7.98	11.40	15.30	19.13	18.10	9.97
%Graft ethylene propylene diene (%wt)	10.73	12.00	10.10	12.00	7.52	4.58	3.11	6.65	11.00
Total monomer (g)	7.98	8.19	4.43	8.19	7.97	4.94	7.28	7.86	7.98
Total free monomer (g)	3.31	2.57	2.59	2.57	4.34	4.43	5.98	5.58	3.19
Total grafted monomer (g)	4.67	5.63	1.84	5.63	3.63	0.51	1.30	1.28	4.79
Grafting efficiency (%wt)	58.54	68.66	41.60	68.66	45.49	10.42	17.82	18.67	60.04

Table B-2 Repeat of grafting properties of GEPDM at 16 h

Reaction properties	Reaction time for 16 h				
	1	2	3	Mean	S.D
EPDM rubber content (g)	24.00	24.00	24.00	24.00	0.00
Graft product (g)	35.13	34.13	35.05	34.77	0.56
Total conversion (%)	46.40	46.54	46.04	44.88	2.32
Sample for soxhlet extraction (g)	3.05	3.00	3.04	3.03	0.03
Sample after extraction by LPE (g)	0.51	0.52	0.52	0.52	0.01
Sample after extraction by MEK+ acetone (g)	0.40	0.39	0.39	0.39	0.01
Free EPDM rubber (g)	2.54	2.49	2.53	2.52	0.02
Free copolymer (g)	0.11	0.10	0.11	0.11	0.00
%Free EPDM rubber (%wt)	83.23	83.03	83.22	83.16	0.10
%Free copolymer (%wt)	3.78	3.65	3.66	3.40	0.06
%Grafted EPDM rubber (%wt)	12.99	13.32	13.11	13.24	0.15
Total monomer (g)	11.13	10.13	11.05	10.77	0.56
Total free monomer (g)	1.33	1.24	1.28	1.28	0.04
Total grafted monomer (g)	9.80	8.89	9.77	9.39	0.62
Grafting efficiency (%)	88.07	87.71	88.38	88.05	0.30

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Appendix C

Data of Mechanical Properties of Modified Acrylic Sheet

Table C-1 Data of impact strength of modified acrylic sheet

Sample	Rubber Content (wt%)	GE (%)	No. of experiment of impact strength (KJ/m ²)					Mean	S.D
			1	2	3	4	5		
			Acrylic sheet	-		41.23	43.69		
Acrylic sheet /EPDM	1.0		42.62	41.28	41.22	41.09	40.16	41.27	0.88
	1.0		50.00	49.85	49.85	50.78	50.00	50.10	0.97
	2.0	88.1	50.09	51.09	53.31	52.46	52.46	52.08	0.39
	3.0		50.15	50.78	50.00	50.94	50.94	50.56	0.45
	4.0		51.54	49.23	49.03	50.19	49.0	49.80	1.09
Acrylic sheet		10.4	48.13	48.13	48.44	47.38	47.69	47.95	0.42
GEPDM		17.8	48.59	48.59	47.85	48.00	48.00	48.21	0.36
	2.0	18.7	49.38	49.53	48.77	48.77	48.92	49.07	0.36
		60.0	49.54	49.38	50.15	50.15	49.38	49.72	0.40
		68.7	50.78	50.94	50.94	50.78	50.78	50.84	0.09
		88.1	51.09	51.09	53.31	52.46	52.46	52.08	0.38

Table C-2 Data of flexural strength of modified acrylic sheet

Sample	Rubber Content (wt%)	GE (%)	No. of experiment of flexural strength (MPa)			Mean	S.D
			1	2	3		
Acrylic sheet	-		79.10	77.80	77.57	78.14	0.81
Acrylic sheet /EPDM	1.0		69.50	64.70	74.94	69.74	5.1
	1.0		96.70	92.50	92.37	93.82	2.45
	2.0	88.1	97.80	96.80	95.58	96.75	1.13
	3.0		71.50	72.90	71.47	71.94	0.81
	4.0		56.30	56.30	56.03	56.18	0.13
Acrylic sheet GEPDM		10.4	80.00	80.50	80.74	80.43	1.49
		17.8	80.40	80.90	80.23	80.49	0.33
	2.0	18.7	82.00	83.30	83.83	83.05	0.94
		60.0	85.00	85.40	85.89	85.43	0.45
		68.7	87.10	86.80	89.32	87.75	1.37
		88.1	97.80	96.80	95.58	96.75	1.13

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Table C-3 Data of tensile properties of modified acrylic sheet

Sample	Rubber content (wt%)	%GE	No. of experiment of tensile strength (MPa)			mean	S.D.	No. of experiment of elongation at break (%)			mean	S.D.
			1	2	3			1	2	3		
			Acrylic sheet					74.39	76.02	74.43		
Acrylic sheet/EPDM	1		52.41	51.98	51.66	52.02	0.38	8.39	7.65	8.25	8.10	0.39
	1		67.00	65.30	67.77	66.67	1.29	6.31	5.91	4.91	5.71	0.72
	2		74.10	72.10	73.70	73.32	1.05	5.78	5.26	5.46	5.50	0.26
	3	88.1	57.20	55.70	56.19	56.35	0.80	4.49	5.35	5.37	5.07	0.50
	4		43.40	43.20	43.33	43.31	0.09	5.13	4.63	5.04	4.93	0.27
Acrylic sheet/GEPDM		10.4	60.10	59.20	61.3	60.19	1.06	5.24	5.23	4.93	5.13	0.17
		17.8	56.20	57.50	57.79	57.16	0.84	5.25	4.85	4.59	4.89	0.33
		18.7	58.40	57.80	57.69	57.97	0.41	4.85	4.79	5.08	4.91	0.16
	2	60.0	59.30	59.20	59.99	59.51	0.42	5.24	5.24	5.69	5.39	0.26
		69.7	67.40	65.10	65.21	65.90	1.26	5.22	5.21	5.47	5.30	0.15
		88.1	74.10	72.10	73.74	73.32	1.05	5.78	5.26	5.46	5.49	0.26

Table C-4 Data of opacity of modified acrylic sheet

Sample	Rubber Content (wt%)	GE (%)	No. of experiment of opacity (%)			Mean	S.D
			1	2	3		
Acrylic sheet	-		12.56	12.71	12.62	12.63	0.08
Acrylic sheet /EPDM	1.0		28.00	28.08	28.82	28.30	0.45
	1.0	88.1	16.66	16.83	16.74	16.74	0.09
	2.0		18.32	18.44	18.40	18.39	0.06
	3.0		21.93	21.93	21.96	21.94	0.02
	4.0		21.72	22.00	21.50	21.74	0.25
Acrylic sheet GEPDM		10.4	28.73	28.78	28.64	28.72	0.07
		17.8	26.16	26.28	26.22	26.22	0.06
	2.0	18.7	23.70	23.47	23.09	23.42	0.31
		60.0	23.72	23.43	23.33	23.49	0.20
		68.7	18.77	18.46	18.79	18.67	0.19
		88.1	18.32	18.44	18.40	18.39	0.06

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Appendix D

Data of Mechanical Properties of Modified Acrylic Sheet after Thermal Aging

Table D-1 Data of impact strength of modified acrylic sheet after thermal aging

Sample	Rubber content (wt%)	%GE	No. of experiment of impact strength (KJ/m ²)					Mean	S.D
			1	2	3	4	5		
			Acrylic sheet	-		43.69	43.69		
Acrylic sheet/ EPDM	1.00		43.08	43.23	45.23	43.75	45.23	44.10	1.06
	1		51.54	50.93	51.54	51.72	51.54	51.49	1.10
	2		52.41	52.41	53.62	52.92	52.92	52.26	0.31
	3	88.1	52.15	52.81	52.0	55.31	54.22	53.30	1.43
	4		51.69	52.0	50.44	51.19	51.92	52.05	0.82
Acrylic sheet/ GEPDM		10.4	48.88	48.28	47.81	47.08	47.54	48.50	0.66
		17.8	49.22	49.22	48.62	48.62	48.46	48.83	0.36
		18.7	50.47	50.63	49.85	49.69	50.54	52.24	1.48
	2	60.0	50.46	51.38	50.31	51.38	50.46	50.80	0.53
		68.7	50.94	51.56	50.94	52.19	51.56	51.44	0.52
		88.1	52.41	51.41	53.62	52.92	50.92	52.26	1.10
		66.4	50.77	50.77	50.94	50.46	50.46	50.68	0.21

Table D-2 Data of flexural strength of modified acrylic sheet after thermal aging

Sample	Rubber Content (wt%)	GE (%)	No. of experiment of flexural strength (MPa)			Mean	S.D
			1	2	3		
			Acrylic sheet	-			
Acrylic sheet/ EPDM	1.0		80.20	81.00	80.97	80.71	0.13
	1.0		92.50	89.90	92.37	91.57	1.45
	2.0	88.1	89.10	91.90	89.73	90.25	1.45
	3.0		72.50	73.80	76.19	74.17	1.87
	4.0		69.30	64.00	69.54	67.60	3.12
Acrylic sheet/ GEPDM		10.4	71.80	73.40	70.02	71.73	1.70
		17.8	72.50	76.40	72.96	73.95	2.11
	2.0	18.7	74.40	75.10	74.73	74.73	0.36
		60.0	77.20	70.80	73.8	73.95	3.18
		68.7	75.70	81.50	76.73	77.95	3.08
		88.1	89.10	91.90	89.73	90.25	1.45

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Table D-3 Data of tensile properties of modified acrylic sheet after thermal aging

Sample	Rubber Content (wt%)	%GE	No. of experiment of tensile strength (MPa)			mean	S.D.	No. of experiment of elongation at break (%)			mean	S.D.
			1	2	3			1	2	3		
			Acrylic sheet					68.35	62.80	68.36		
Acrylic sheet/EPDM	1.0		54.53	54.65	57.13	55.43	1.47	7.49	8.99	9.12	8.53	0.91
	1.0		70.10	68.01	69.33	68.15	0.44	5.33	6.41	4.66	5.47	0.88
	2.0		75.42	74.14	74.0	74.52	0.78	5.03	5.88	5.64	5.52	0.44
	3.0	88.1	55.43	56.15	58.73	56.77	1.74	5.48	5.22	5.30	5.33	0.14
	4.0		55.08	56.17	54.24	55.16	0.97	5.28	5.30	5.30	5.29	0.01
		10.4	55.03	55.07	55.24	55.11	0.11	4.45	4.54	4.31	4.43	0.12
		17.8	57.38	57.40	57.30	57.36	0.05	4.26	4.47	4.38	4.37	0.11
Acrylic sheet/GEPM	2.0	18.7	58.29	56.33	58.48	57.70	1.19	4.40	4.19	4.91	4.50	0.37
		60.0	59.14	58.93	59.61	59.23	0.35	5.66	5.36	5.24	5.42	0.22
		68.7	65.13	65.31	65.23	65.23	0.09	5.11	5.73	5.55	5.46	0.32
		88.1	75.42	74.14	74.00	74.52	0.78	5.03	5.88	5.64	5.52	0.44

Table D-4 Data of opacity and ΔE of modified acrylic sheet after thermal aging

Sample	Rubber Content (wt%)	%GE	No. of experiment of opacity (%)				mean	S.D.	No. of experiment of ΔE			mean	S.D.
			1	2	3	1			2	3			
			Acrylic sheet			7.24			7.65	7.48	7.46		
Acrylic sheet/ EPDM	1.0		23.68	23.45	21.78	22.97	1.04	2.74	2.46	2.47	2.56	0.16	
	1		11.70	11.56	11.66	11.64	0.07	1.42	1.45	1.35	1.41	0.05	
	2		14.50	14.46	14.25	14.40	0.13	2.34	2.37	2.15	2.29	0.12	
	3	88.1	16.00	16.19	16.12	16.10	0.10	2.72	2.60	2.80	2.71	0.10	
	4		20.42	20.80	20.78	20.67	0.21	3.23	2.83	2.83	2.96	0.23	
Acrylic sheet/ GEPDM		10.4	20.04	20.08	20.02	20.05	0.03	3.00	2.86	2.93	2.93	0.07	
		17.8	16.53	16.36	16.78	16.56	0.21	2.92	2.65	2.83	2.80	0.14	
		18.7	15.84	15.76	15.90	15.83	0.07	2.88	2.70	2.76	2.78	0.09	
	2	60.0	16.84	16.73	16.76	16.78	0.06	2.51	2.68	2.85	2.68	0.17	
		68.7	14.78	14.86	14.85	14.83	0.04	2.66	2.53	2.37	2.52	0.15	
		88.1	14.50	14.46	14.25	14.40	0.13	2.24	2.37	2.14	2.25	0.12	

Appendix E

Data of Mechanical Properties of Modified Acrylic Sheet after UV Ageing

Table E-1 Data of impact strength of modified acrylic sheet after UV aging

Sample	Rubber Content (wt%)	%GE	No. of experiment of impact strength (KJ/m ²)					Mean	S.D
			1	2	3	4	5		
Acrylic sheet	-		48.31	48.31	42.15	45.85	44.06	45.74	2.69
Acrylic sheet/ GEPDM	1.0		52.81	49.31	50.31	50.31	51.06	49.80	1.23
	1.0		48.31	49.77	50.85	49.54	50.54	49.80	0.72
	2.0		51.31	50.77	52.38	51.94	50.74	51.43	1.87
	3.0	88.1	45.85	48.31	46.56	45.85	50.77	47.47	2.10
	4.0		48.31	48.31	49.54	50.00	50.00	49.25	0.88
Acrylic sheet/ GEPDM		10.4	47.31	43.94	49.54	50.16	47.54	47.70	2.44
		17.8	47.38	50.49	47.54	43.94	48.31	47.53	2.36
	2.0	18.7	47.08	48.31	47.08	48.31	47.08	47.57	0.67
		60.0	47.81	48.31	48.31	48.31	49.54	48.46	0.64
		68.7	48.31	50.77	59.54	50.77	48.31	51.54	4.64
		88.1	51.31	50.77	52.38	51.94	50.74	51.43	0.72

Table E-2 Data of flexural strength of modified acrylic sheet after UV aging

Sample	Rubber Content (wt%)	%GE	No. of experiment of flexural strength (MPa)			Mean	S.D
			1	2	3		
Acrylic sheet	-		65.95	58.06	68	64.00	5.25
Acrylic sheet /EPDM	1		85.87	79.19	69.42	78.16	8.27
	1		73.28	76.17	69.97	73.14	3.10
	2	88.1	115.9	125.1	128	123.0	6.32
	3		113.9	107.4	120.3	113.87	6.45
	4		84.98	95.91	89.53	90.14	5.49
Acrylic sheet/ GEPDM		10.4	66.76	82.87	72.47	74.03	8.17
		17.8	80.11	63.78	76.09	73.33	8.51
	2	18.7	75.7	72.46	67.68	71.95	4.03
		60.0	73.97	75.25	80.25	76.49	3.32
		68.7	112.3	93.75	98.86	101.64	9.58
		88.1	115.9	125.1	128	123	6.32

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Table E-3 Data of tensile properties of modified acrylic sheet after UV aging

Rubber type	Rubber Content (wt%)	%GE	No. of experiment of Tensile strength (MPa)				No. of experiment of elongation at break (%)				mean	S.D.		
						mean	S.D.						mean	S.D.
			1	2	3			1	2	3				
Acrylic sheet			62.48	67.13	62.93	64.18	2.57	4.26	3.68	4.45	4.13	0.40		
Acrylic sheet/ EPDM	1.0	1.0	44.60	40.24	39.02	41.29	2.93	3.30	2.94	2.57	2.94	0.37		
	1	88.1	47.24	49.58	49.13	48.65	1.24	3.61	3.60	3.41	3.54	0.11		
	2		55.94	54.72	54.84	55.17	0.67	4.81	4.21	4.19	4.40	0.35		
	3		44.69	44.16	44.42	44.42	0.27	3.43	3.29	3.70	3.47	0.21		
	4		42.96	44.11	41.87	42.98	1.12	3.17	3.46	3.12	3.25	0.18		
Acrylic sheet/ GEPDM		10.4	44.62	43.04	43.11	43.59	0.90	2.62	2.87	2.47	2.78	0.28		
		17.8	45.72	43.72	44.48	44.64	1.01	2.84	2.91	2.93	2.89	0.05		
	2	18.7	46.88	44.80	45.17	45.62	1.11	3.02	2.95	2.85	2.94	0.08		
		60.0	44.72	45.26	45.96	45.64	1.17	3.22	3.44	2.69	3.12	0.38		
		68.7	50.18	46.97	45.80	47.65	2.27	3.28	3.21	3.34	3.28	0.07		
		88.1	55.94	54.72	54.84	55.17	0.67	4.81	4.21	4.19	4.40	0.35		

Table E-4 Data of opacity and ΔE of modified acrylic sheet after UV aging

Sample	Rubber Content (wt%)	%GE	No. of experiment of opacity (%)				mean	S.D.	No. of experiment of ΔE			mean	S.D.
			1	2	3	1			2	3			
Acrylic sheet			8.25	8.26	8.24	8.25	0.01	10.05	10.47	10.52	10.35	0.26	
Acrylic sheet	1.0		21.94	24.87	24.49	23.77	1.59	17.12	14.36	15.36	15.61	1.40	
	1	88.1	11.12	11.06	11.04	11.07	0.04	13.69	11.74	10.49	11.97	1.61	
	2		14.54	15.06	14.07	14.56	0.50	12.06	12.26	12.40	12.24	0.17	
	3		20.36	19.94	20.32	20.21	0.23	15.52	15.60	16.90	16.01	0.77	
	4		21.31	19.31	18.36	19.68	1.53	16.26	15.85	15.34	15.82	0.46	
Acrylic sheet/ GEPDM		10.4	13.37	13.23	13.26	13.29	0.07	14.64	14.74	14.28	14.55	0.24	
		17.8	16.54	15.88	16.53	16.32	0.38	14.83	14.92	13.97	14.57	0.52	
	2	18.7	16.34	16.74	16.21	16.43	0.28	14.87	14.83	14.39	14.70	0.27	
		60.0	17.26	16.88	17.04	17.06	0.19	12.75	12.78	12.66	12.73	0.06	
		68.7	13.51	13.74	13.83	13.69	0.17	13.08	13.43	13.20	12.44	0.18	
		88.1	14.54	15.06	14.97	14.86	0.28	12.06	12.26	12.40	12.24	0.17	

Appendix F

Data of Thermal Properties of Unmodified and Modified Acrylic Sheet

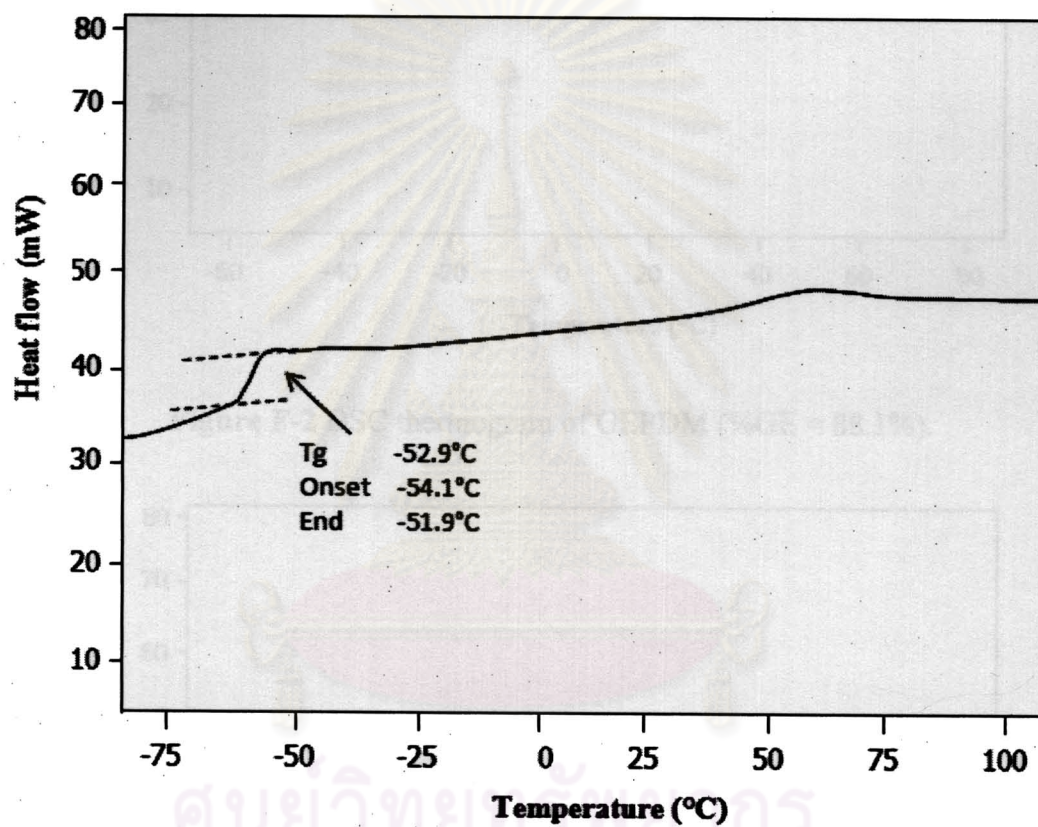


Figure F-1 DSC thermogram of EPDM.

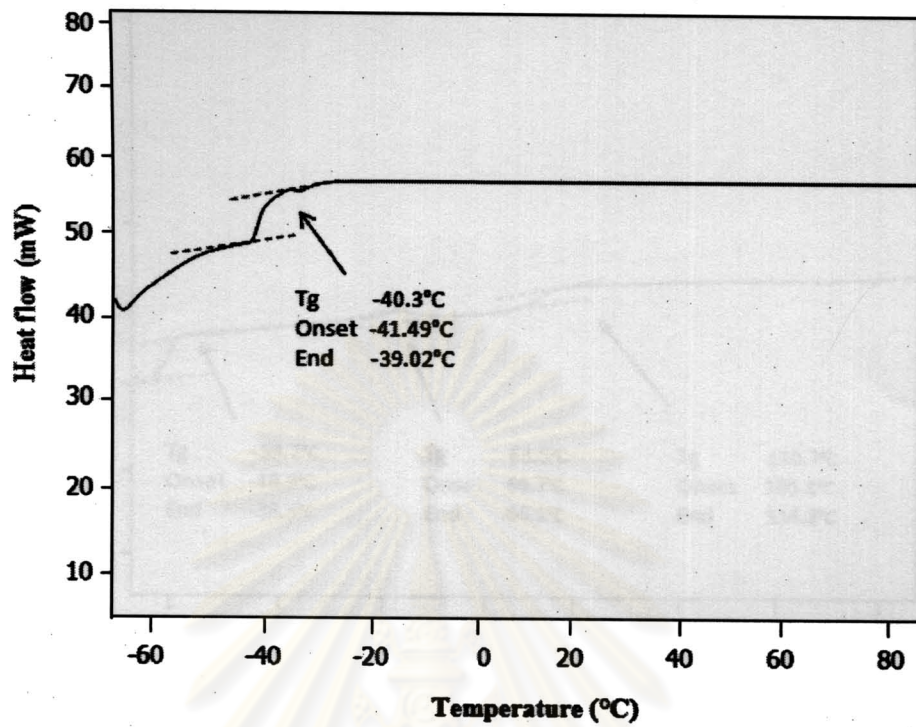


Figure F-2 DSC thermogram of GEPDM (%GE = 88.1%).

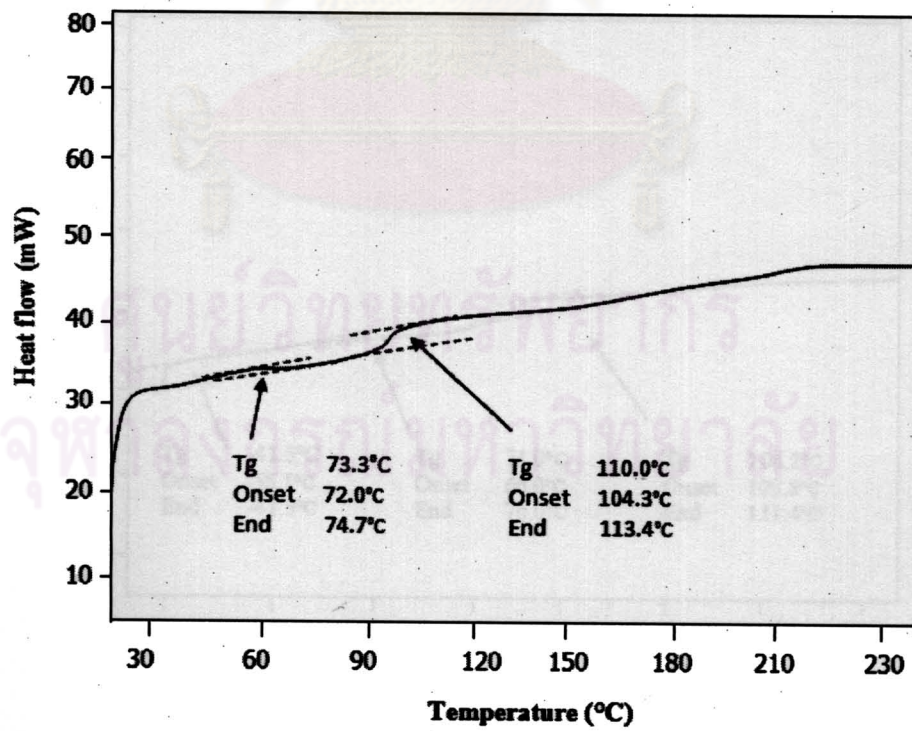


Figure F-3 DSC thermogram of acrylic sheet (MMA/ST = 80/20 % w/w).

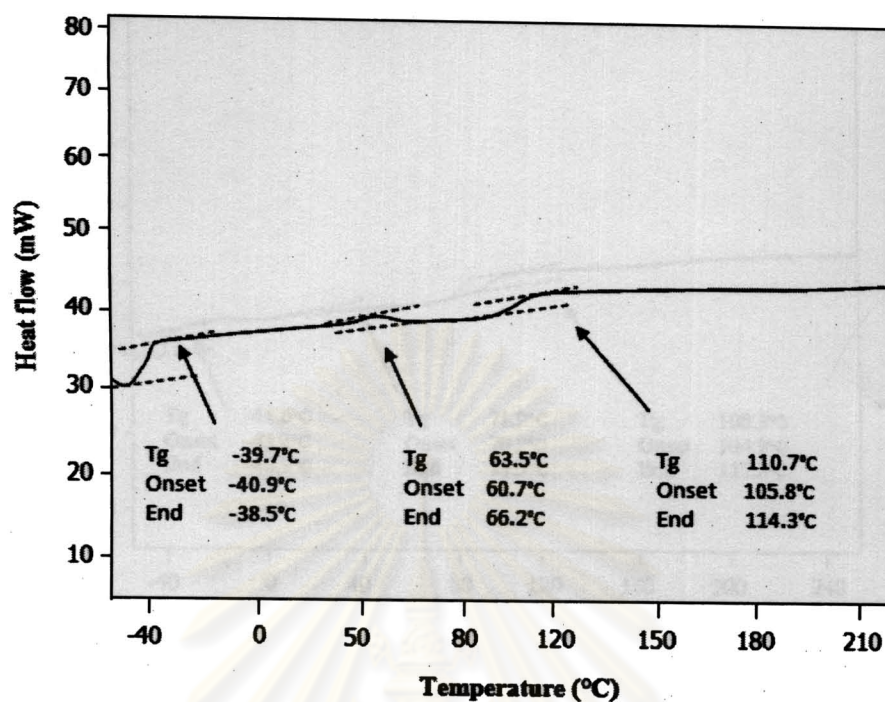


Figure F-4 DSC thermogram of acrylic sheet containing 1.0 wt% of EPDM.

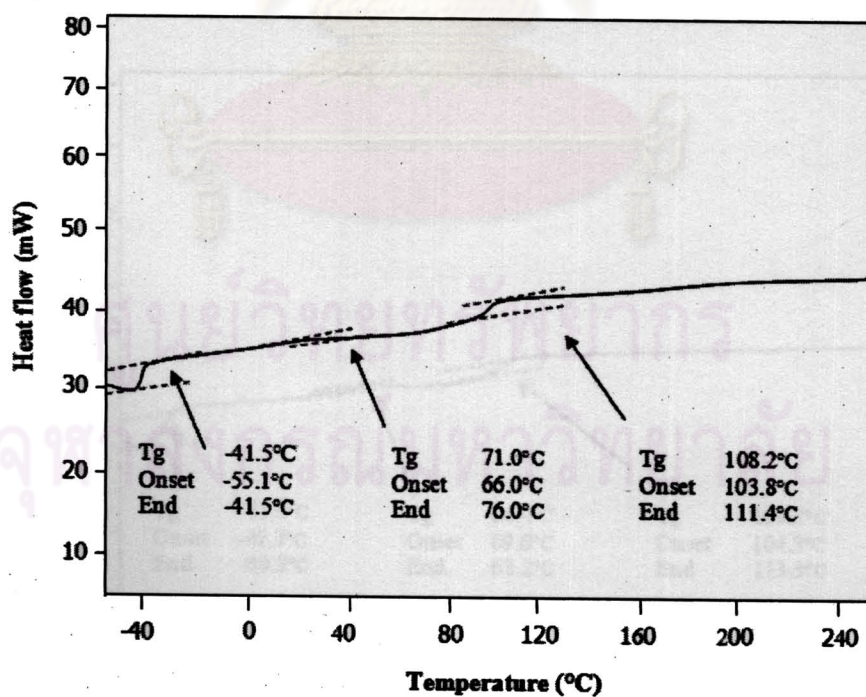


Figure F-5 DSC thermogram of acrylic sheet containing 1.0 wt% of GEPDM (%GE = 88.1%).

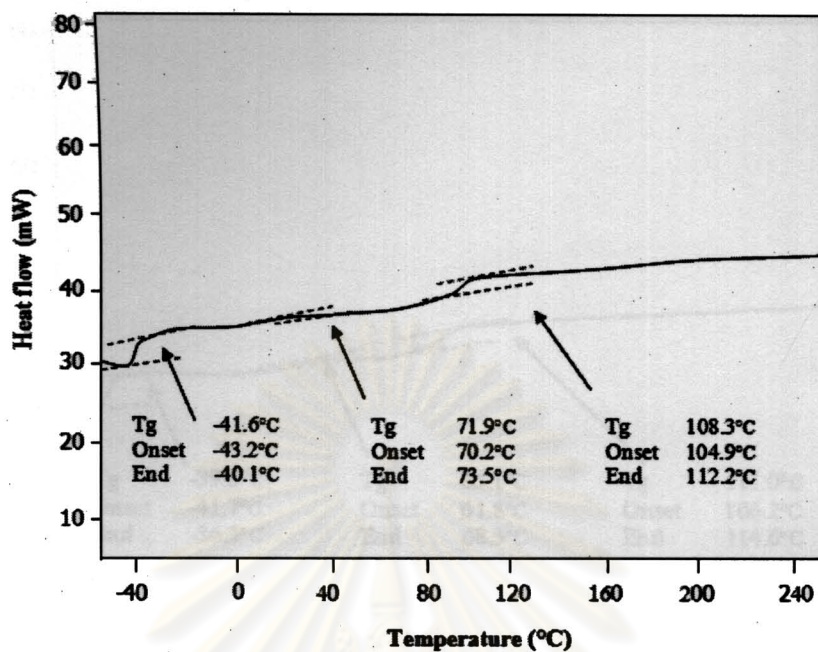


Figure F-6 DSC thermogram of acrylic sheet containing 2.0 wt% of GEPDM (%GE = 88.1%).

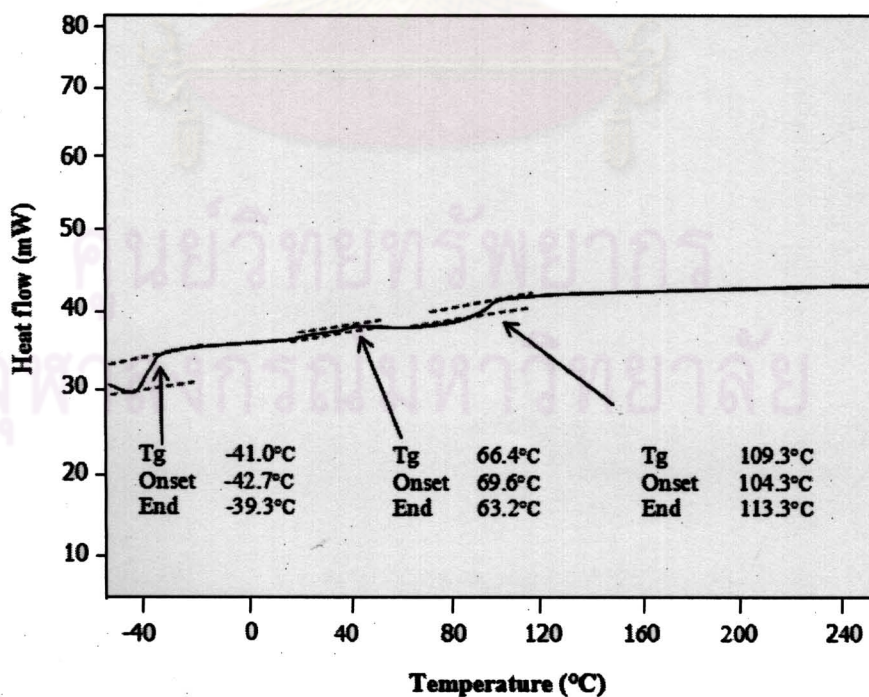


Figure F-7 DSC thermogram of acrylic sheet containing 3.0 wt% of GEPDM (%GE = 88.1%).

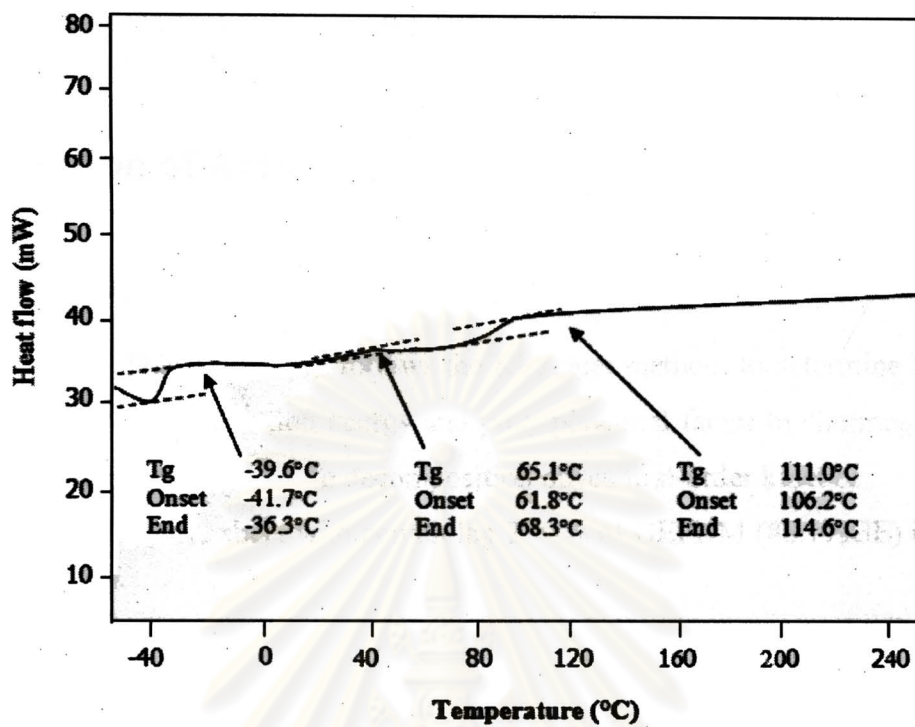


Figure F-8 DSC thermogram of acrylic sheet containing 4.0 wt% of GEPDM (%GE = 88.1%).

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Appendix G

Calculation of Activation Energy of Thermal Decomposition of Modified Acrylic Sheets

This calculation follows the Kissinger method to determine the kinetic parameters such as activation energy and preexponential factor by thermogravimetry, based on the assumption that the decomposition obeys first-order kinetics.

The modified acrylic sheet with containing 2 wt% of GEPDM (88.1%GE) is used for an example.

- (1) Record the degradation temperatures at different heating rate as showed in figure G-1 and Table G-1

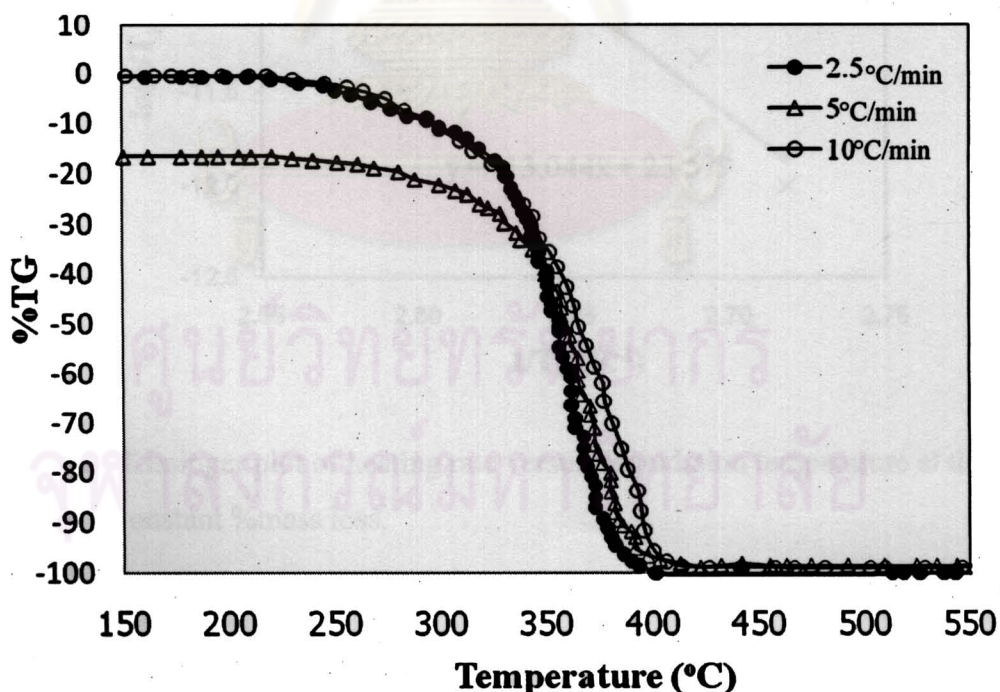


Figure G-1 Mass loss curves of modified acrylic sheet with containing 2 wt% of GEPDM (%GE = 88.1%) at various heating rates.

Table G-1 Degradation temperature of modified acrylic sheet with containing 2 wt% of GEPDM (%GE = 88.1%) at various heating rate

Heating rate (°C/min)	2.5	5	10
Degradation temperature (°C)	367.89	371.67	381.49

(2) Plot the logarithm of the heating rate expressed as kelvin per min versus the reciprocal of the absolute degradation temperature (1) at which the conversation level was reached. A straight line as shown in Figure G-2 show result.

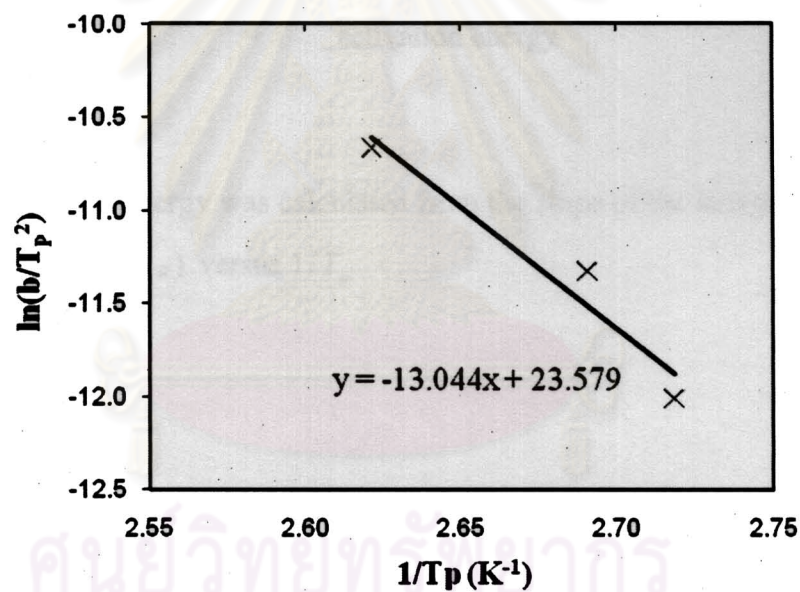


Figure G-2 Kissinger plot of heating rate versus degradation temperature at the constant %mass loss.

(3) Calculate an estimation of the activation energy (E_a) as shown in eq (D-1), use of the value of slope obtained from

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_a} + \ln[n(1-\alpha_p)^{n-1}] - \frac{E_a}{RT_p} \quad (\text{D-1})$$

Where β	=	heating rate,
T_p and α_p	=	absolute decomposition temperature
$(d\alpha/dt)_p$	=	weight loss at the maximum weight-loss rate, R
	=	gas constant, 8.314 J/(mol*K)
A	=	pre-exponential factor
n	=	reaction order
E_a	=	activation energy

Remark:

The activation energy was calculated from the slope of the straight line obtained from a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$

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Table G-2 Activation energy of modified acrylic sheet at various of GEPDM content

Sample	Heating rate (°C/min)	t_p (°C)	T_p (K)	$1/T_p$ (K ⁻¹)	$\ln(b/T_p^2)$	Slope	Intercept	E_a (KJ/mol)
EPDM	2.5	436.58	709.58	1.41	-12.21	-26.76	25.90	222.44
	5	448.69	721.69	1.39	-11.55			
	10	457.18	730.18	1.37	-10.88			
GEPDM	2.5	428.57	701.57	1.43	-12.19	-33.02	34.28	274.49
	5	443.73	716.73	1.39	-11.54			
	10	453.11	726.11	1.38	-10.87			
without GEPDM first stage	2.5	259.20	532.20	1.88	-11.64	-22.06	29.83	183.41
	5.0	264.31	537.31	1.86	-10.96			
	10.0	275.95	548.95	1.82	-10.31			
without GEPDM second stage	2.5	290.85	563.85	1.77	-11.75	-4.91	3.08	40.83
	5.0	349.20	622.20	1.61	-11.26			
	10.0	360.30	633.30	1.58	-10.60			
1 wt% GEPDM	2.5	362.50	635.50	2.76	-11.99	-25.34	13.70	210.68
	5.0	372.70	645.70	2.68	-11.33			
	10.0	381.95	654.95	2.62	-10.67			
2 wt% GEPDM	2.5	367.89	640.89	2.72	-12.01	-13.04	23.58	108.45
	5.0	371.67	644.67	2.69	-11.33			
	10.0	381.49	654.49	2.62	-10.67			
3 wt% GEPDM	2.5	359.60	632.60	2.78	-11.98	-11.85	20.98	98.50
	5.0	370.87	643.87	2.70	-11.33			
	10.0	370.24	643.24	2.70	-10.63			
4 wt% GEPDM	2.5	365.05	638.05	2.74	-12.00	-9.02	12.87	75.00
	5.0	369.68	642.68	2.71	-11.32			
	10.0	384.06	657.06	2.60	-10.67			

VITA

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