# สมบัติของแผ่นสไตรีน-เมทิลเมทาคริเลตโคพอลิเมอร์ที่มียางธรรมชาติดัดแปร

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# PROPERTIES OF STYRENE-METHYL METHACRYLATE COPOLYMER SHEET CONTAINING MODIFIED NATURAL 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
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ศิริณา ถาวรวิสิทธิ์ : สมบัติของแผ่นสไตรีน-เมทิลเมทาคริเลตโคพอลิเมอร์ที่มียางธรรมชาติดัดแปร (PROPERTIES OF STYRENE-METHYLMETHACRYLATE COPOLYMER SHEET CONTAINING MODIFIED NATURAL RUBBER). อ. ที่ปรึกษา : ศ.ดร.ภัทรพรรณ ประศาสน์สารกิจ, อ. ที่ปรึกษาร่วม : อ.ดร.กิติกร จามรดุสิต, 113 หน้า.

แผ่นสไตรีน-เมทิลเมทาคริเลตโคพอลิเมอร์ที่มียางธรรมชาติดัดแปร เตรียมด้วยวิธีการบัลค์โคพอลิเมอไรเซชัน โดยใช้เบนโซอิลเปอร์ออกไซด์และสารประกอบเอโซเป็นตัวริเริ่มปฏิกิริยา ยางธรรมชาติดัดแปรที่ทำการศึกษาได้แก่ ยางธรรมชาติกราฟต์และยางธรรมชาติไฮโดรจิเนต โดยยางธรรมชาติกราฟต์เตรียมด้วยวิธีอิมัลชันโคพอลิเมอไรเซชัน พบว่า ปริมาณยางธรรมชาติกราฟต์ คือ ร้อยละ 66.1 โดยมียางที่ไม่เกิดปฏิกิริยาร้อยละ 26.9 และมอนอเมอร์ที่ไม่เกิดปฏิกิริยาร้อยละ 7.0 ส่วนยางธรรมชาติไฮโดรจิเนตเตรียมที่อุณหภูมิ 140 องศาเซลเซียส และความดัน 400 psig โดยใช้ $OsHCl(CO)(O_2)(PCy_3)$ เป็นตัวเร่งปฏิกิริยา พบว่าร้อยละของไฮโดรจิเนชันเป็น 56.5 งานวิจัยนี้ศึกษาตัวแปรที่สำคัญ คือ ปริมาณยางธรรมชาติดัดแปร และปริมาณสไตรีน ต่อสมบัติเชิงกล สมบัติทางกายภาพ และสัณฐานวิทยาของแผ่นโคพอลิเมอร์ด้วย จากการศึกษาพบว่า สมบัติเชิงกลเป็นฟังก์ชันกับปริมาณยางธรรมชาติและปริมาณสไตรีน โดยสมบัติเชิงกลที่เหมาะสมสำหรับยางธรรมชาติกราฟต์คือ ร้อยละ 2 โดยน้ำหนัก ส่วนยางธรรมชาติไฮโดรจิเนตเป็นร้อยละ 1 โดยน้ำหนัก และปริมาณสไตรีนที่เหมาะสมสำหรับการปรับปรุงสมบัติเชิงกล คือ ร้อยละ 20 โดยน้ำหนัก นอกจากนี้ยังพบว่าแผ่นโคพอลิเมอร์ที่มียางธรรมชาติไฮโดรจิเนตมีสมบัติการทนต่อความร้อนได้ดีด้วย และจากการศึกษาผิวหักโดยการดึงด้วยกล้องจุลทรรศน์อิเลกตรอนแบบส่องกราดพบว่า พื้นผิวมีความเรียบมากขึ้นและรอยแตกขนาดเล็กลง แสดงว่ายางธรรมชาติดัดแปรสามารถใช้เป็นตัวปรับปรุงสมบัติความทนแรงกระแทกของแผ่นสไตรีน-เมทิลเมทาคริเลตโคพอลิเมอร์ได้

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.. ลายมือชื่อนิสิต ศิริณา ถาวรวิสิทธิ์
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# # 4672426223 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD: ACRYLIC / / GRAFT COPOLYMERIZATION / HYDROGENATION / NATURAL RUBBER

SIRINA THAWORNWISIT : PROPERTIES OF STYRENE-METHYL METHACRYLATE COPOLYMER SHEET CONTAINING MODIFIED NATURAL RUBBER. THESIS ADVISOR : PROF. PATARAPAN PRASASSARAKICH, Ph.D., THESIS COADVISOR : KITIKORN CHARMONDUSIT, Ph.D., 113 pp.

The copolymer sheets of styrene (ST) and methyl methacrylate (MMA) containing modified natural rubber (NR) prepared by bulk copolymerization using benzoyl peroxide and 2,2'-azobis-(2,4-dimethylvaleronitrile) as initiators were studied. The modified NRs were prepared by graft copolymerization and hydrogenate reactions. The grafted NR prepared by emulsion copolymerization using redox initiator consisted of 66.1 wt% NR-g-(MMA-co-ST), 26.9 wt% free rubber and 7.0 wt% free copolymers. The hydrogenation of NR catalyzed by $OsHCl(CO)(O_2)(PCy_3)$ was carried out at 140 °C and 400 psig, the degree of hydrogenation was 56.5. The effect of styrene and rubber monomer content on the mechanical properties, physical properties and morphology of modified acrylic sheet were investigated. The results show that mechanical properties were evaluated as a function of modified NR and ST content. The appropriate mechanical properties of modified acrylic sheet were obtained at 2 wt% of grafted NR and 1 wt% of hydrogenated NR. The optimum content of ST in modified acrylic sheet for improving the mechanical properties was 20% by weight. Moreover, the HNR modified acrylic sheet present the superior thermal resistance. The tensile fracture surface examined by scanning electron microscope showed the relatively smooth surface with few relatively small cracks. It implied that the modified NR can be used as an impact modifier for acrylic cast sheet.

Field of study..Petrochemistry and Polymer Science..Student's signature..Sirina Thawornwisit
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# CONTENTS

**PAGE**

ABTRACT IN THAI ........ iv

ABTRACT IN ENGLISH ........ v

ACKNOWLEDGEMENT ........ vi

CONTENT ........ vii

LIST OF TABLES ........ xi

LIST OF FIGURES ........ xiv

LIST OF ABBREVIATIONS ........ xvii

CHAPTER I : INTRODUCTION ........ 1

- 1.1 The Purpose of the Investigation ........ 1
- 1.2 Objective ........ 2
- 1.3 Scope of the Investigation ........ 2

CHAPTER II : THEORY AND LITERATURE REVIEW ........ 4

- 2.1 Methyl Methacrylate and Poly(methyl methacrylate) ........ 4
- 2.2 Styrene and Polystyrene ........ 6
- 2.3 Chain Copolymerization ........ 10
- 2.4 Bulk Copolymerization ........ 13
- 2.5 Casting Process ........ 14
- 2.6 Natural Rubber ........ 15
  - 2.6.1 Natural Rubber Latex ........ 17
  - 2.6.2 Standard Thai Rubber ........ 18
  - 2.6.3 Modification of Natural Rubber ........ 20
- 2.7 Graft Copolymers ........ 20
- 2.8 Emulsion Polymerization ........ 21
  - 2.8.1 Ingredients and Processes ........ 22
- 2.9 Hydrogenation of Diene-Based Polymers ........ 24
  - 2.9.1 Homogeneous Hydrogenation in the Presence of 5d Metal Complexes ........ 26
  - 2.9.2 Hydrogenation of Natural Rubber ........ 28

**PAGE**

2.10 Literature Reviews ........ 29
    2.10.1 Modification of Acrylic Sheet ........ 29
    2.10.2 Graft Copolymerization on Natural Rubber ........ 31
    2.10.3 Hydrogenation in Natural Rubber ........ 33

CHAPTER III : EXPERIMENTAL ........ 35
3.1 Chemicals ........ 35
3.2 Glasswares ........ 36
3.3 Equipments ........ 36
3.4 Grafted Natural Rubber Preparation ........ 37
    3.4.1 Purification of Monomer ........ 37
    3.4.2 Preparation of Grafted Natural Rubber ........ 37
3.5 Determination of the Grafted Natural Rubber ........ 40
    3.5.1 Determination of Monomer Conversion and Grafting Efficiency ........ 40
    3.5.2 Characterization of Grafted Natural Rubber Product ........ 40
3.6 Hydrogenated Natural Rubber Preparation ........ 40
3.7 Determination of the Hydrogenated Natural Rubber ........ 41
    3.7.1 Fourier-Transform Infrared Spectroscopic Analysis ........ 41
    3.7.2 Nuclear Magnetic Resonance Spectroscopic Analysis ........ 42
3.8 Procedure of Styrene-Methyl Methacrylate Copolymer Sheet ........ 42
3.9 Characterization of Copolymer Sheet by FT-IR ........ 45
3.10 Mechanical Testing ........ 45
    3.10.1 Tensile Properties (ASTM D 638) ........ 45
    3.10.2 Impact Strength (ASTM D 6110) ........ 46
    3.10.3 Hardness (ASTM D 785) ........ 47
3.11 Physical Testing ........ 47
    3.11.1 Transparent Property ........ 47
    3.11.2 Ultraviolet Resistance ........ 47
    3.11.3 Thermal Resistance ........ 47
3.12 Scanning Electron Microscope ........ 48

**PAGE**

CHAPTER IV : RESULTS AND DISSCUSION ........ 49

- 4.1 Preparation of the Grafted Natural Rubber ........ 49
  - 4.1.1 Properties of Natural Rubber Latex ........ 49
  - 4.1.2 Properties of Grafted Natural Rubber ........ 50
  - 4.1.3 Characterization of Grafted Natural Rubber using FT-IR Spectroscopy ........ 51
- 4.2 Preparation of Hydrogenated Natural Rubber ........ 53
  - 4.2.1 Properties of Standard Thai Rubber 5L ........ 53
  - 4.2.2 Characterization of Hydrogenated Natural rubber ........ 53
    - 4.2.2.1 Characterization using FT-IR Spectroscopy ........ 53
    - 4.2.2.2 Characterization using NMR Spectroscopy ........ 55
  - 4.2.3 Degree of Hydrogenation ........ 55
- 4.3 Preparation of ST-MMA Copolymer Sheet Containing Modified Natural Rubber ........ 57
  - 4.3.1 Effect of Styrene Monomer Content on Preliminary Preparation of MMA and ST Solution with Modified Natural Rubber ........ 57
  - 4.3.2 Effect of Rubber Content on Preliminary Preparation of MMA and ST Solution with Modified Natural Rubber ........ 58
  - 4.3.3 Effect of Styrene Monomer Content on Modified ST-MMA Copolymer Sheet Preparation ........ 61
  - 4.3.4 Effect of Rubber Content on Modified ST-MMA Copolymer Sheet Preparation ........ 62
- 4.4 Characterization of Copolymer Sheet Containing Modified Natural Rubber ........ 65
- 4.5 Mechanical Properties of ST-MMA Copolymer Sheet Containing Modified Natural Rubber ........ 69
  - 4.5.1 Impact Strength ........ 71
    - 4.5.1.1 Effect of Styrene Monomer Content on Impact Strength ........ 71
    - 4.5.1.2 Effect of Rubber Content on Impact Strength ........ 72

**PAGE**

4.5.2 Tensile Properties 74

4.5.2.1 Effect of Styrene Monomer Content on Tensile Properties 74

4.5.2.2 Effect of Rubber Content on Tensile Properties 76

4.5.3 Hardness 78

4.5.3.1 Effect of Styrene Monomer Content on Hardness 78

4.5.3.2 Effect of Rubber Content on Hardness 78

4.6 Physical Properties of the ST-MMA Copolymer Sheet Containing Modified Natural Rubber 80

4.7 Morphological Study 83

CHAPTER V : CONCLUSION AND SUGGESTION 87

5.1 Conclusion 87

5.2 Suggestion for Future Work 88

REFERENCE 89

APPENDICES 93

APPENDIX A 94

APPENDIX B 95

APPENDIX C 98

APPENDIX D 101

APPENDIX E 103

APPENDIX F 104

APPENDIX G 108

VITA 113

# LIST OF TABLES

**TABLE** **PAGE**

2.1 Typical properties of poly(methyl methacrylate) 6
2.2 Typical properties of polystyrene 9
2.3 Comparative properties of typical commercial grades of ST-containing polymers 9
2.4 Monomer reactivity ratios in chain copolymerization 12
2.5 Values of $r_1r_2$ in chain copolymerization 12
2.6 Commercial polymerization systems 14
2.7 Production of natural rubber in 2006 16
2.8 Net exports of natural rubber in 2006 16
2.9 Compositions of field latex 17
2.10 Processing material of STR grades 18
2.11 Standard Thai Rubber scheme 19
2.12 Types of monomer 23
3.1 Standard recipe used for graft copolymerization 38
3.2 Standard recipe used for hydrogenation 41
3.3 Standard recipe and conditions used for bulk copolymerization of MMA and St with modified rubber 43
4.1 Typical properties of high ammonia natural rubber latex 50
4.2 Properties of grafted natural rubber 51
4.3 Typical properties of Standard Thai Rubber 5L 53
4.4 Effect of reaction time on degree of hydrogenation 55
4.5 Effect of styrene content on the preliminary preparation of MMA and ST solution with modified natural rubber 58
4.6 Effect of modified natural rubber content on the preliminary preparation of MMA and ST solution 59
4.7 Effect of styrene content on preparation of ST-MMA copolymer sheet with grafted natural rubber and hydrogenated natural rubber 61
4.8 Effect of grafted natural rubber and hydrogenated natural rubber content on preparation of ST-MMA copolymer sheet 63

**TABLE** **PAGE**

4.9 Effect of styrene content on impact strength, tensile strength (TS), elongation at break (EB) and hardness of modified ST-MMA copolymer sheet....69

4.10 Effect of modified natural rubber content on impact strength, tensile strength (TS), elongation at break (EB) and hardness of modified ST-MMA copolymer sheet....70

4.11 Mechanical properties of modified acrylic sheet....80

4.12 Physical properties of modified acrylic sheet....81

A Extraction time of the free polymer....94

B Determination of grafted natural rubber....97

F-1 Impact strength of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber....104

F-2 Tensile strength of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber....105

F-3 Elongation at break of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber....106

F-4 Hardness of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber....107

G-1 Opacity of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber....108

G-2 Thermal resistance of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber....109

**TABLE** **PAGE**

G-3 Ultraviolet resistance of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber........................................................................................111

# LIST OF FIGURES

**FIGURE** **PAGE**

2.1 Diagrams of copolymers produced by chain copolymerization (a) alternating (b) random (c) block and (d) graft copolymers ........ 10

2.2 Diagrams of polymerization setups (a) bulk (b) solution (c) suspension and (d) emulsion polymerization ........ 13

2.3 Conventional cell casting mold configuration (a) face view and (b) edge view ........ 15

2.4 Cis-1,4-polyisoprene ........ 17

2.5 Schematic diagram of emulsion polymerization ........ 22

2.6 Characterized reactions of $OsHCl(CO)(PR_3)_2$ (1a, R = Cy; 1b, R = *i*-Pr) ........ 27

2.7 General structure of natural rubber before and after hydrogenation process ........ 28

3.1 Apparatus for emulsion graft copolymerization of styrene and methyl methacrylate onto natural rubber latex ........ 39

3.2 The overall schematic experimental process ........ 44

3.3 Schematic diagram of tensile test specimen (type I) ........ 45

3.4 Dimensions of simple beam, charpy type, impact test specimen ........ 46

4.1 FT-IR spectra of (a) NR and (b) GNR ........ 52

4.2 FT-IR spectra of (a) NR and (b) HNR ........ 54

4.3 $^1$H-NMR spectra of (a) NR and (b) HNR ........ 56

4.4 Preliminary preparation of the MMA and ST solution with 2 wt% grafted natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content ........ 60

4.5 Preliminary preparation of the MMA and ST solution with 1 wt% hydrogenated natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content ........ 60

4.6 Preliminary preparation of the MMA and ST solution (ST/MMA = 20/80) with (a) 1 (b) 2 (c) 3 and (d) 4 wt% grafted natural rubber ........ 60

4.7 Preliminary preparation of the MMA and ST solution (ST/MMA = 20/80) with of (a) 0.5 (b) 1 (c) 2 and (d) 3 wt% hydrogenated natural rubber ........ 60

**FIGURE** **PAGE**

4.8 Sheet appearance of preparation of ST-MMA copolymer sheet with 2 wt% grafted natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content...64

4.9 Sheet appearance of preparation of ST-MMA copolymer sheet with 1 wt% hydrogenated natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content...64

4.10 Sheet appearance of preparation of ST-MMA copolymer sheet (ST/MMA = 20/80) with (a) 1 (b) 2 (c) 3 and (d) 4 wt% grafted natural rubber...64

4.11 Sheet appearance of preparation of ST-MMA copolymer sheet (ST/MMA = 20/80) with of (a) 0.25 (b) 0.5 (c) 1 (d) 2 and (e) 3 wt% grafted natural rubber...64

4.12 FT-IR spectra of (a) PMMA sheet, (b) ST-MMA copolymer sheet, (c) ST-MMA copolymer sheet with NR, (d) ST-MMA copolymer sheet with GNR and (e) ST-MMA copolymer sheet with HNR...66

4.13 Effect of styrene monomer content on impact strength of ST-MMA copolymer sheet : (●) No modifier, (■) 2 wt% GNR and (▲) 1 wt% HNR....73

4.14 Effect of rubber content on impact strength of ST-MMA (20/80) copolymer sheet : (●) No modifier, (◆) NR modifier, (■) GNR modifier and (▲) HNR modifier...73

4.15 Effect of styrene monomer content on (a) tensile strength and (b) elongation at break of ST-MMA copolymer sheet: (●) No modifier, (■) 2 wt% GNR and (▲) 1 wt% HNR...75

4.16 Effect of rubber content on (a) tensile strength and (b) elongation at break of ST-MMA (20/80) copolymer sheet : (●) No modifier, (◆) NR modifier, (■) GNR modifier and (▲) HNR modifier...77

4.17 Effect of styrene monomer content on hardness of ST-MMA copolymer sheet: (●) No modifier, (■) 2 wt% GNR and (▲) 1 wt% HNR...79

**FIGURE** **PAGE**

4.18 Effect of rubber content on hardness of ST-MMA (20/80) copolymer sheet : (●) No modifier, (◆) NR modifier, (■) GNR modifier and (▲) HNR modifier ........ 79

4.19 Physical properties of modified acrylic sheet: (a) opacity, (b) thermal resistance, and (c) UV resistance ........ 82

4.20 SEM photographs of modified acrylic sheet with GNR at (a) 0 (b) 1 and (c) 2 wt% ........ 84

4.21 SEM photographs of modified acrylic sheet with HNR at (a) 0 (b) 1 and (c) 2 wt% ........ 85

4.22 SEM photographs of modified acrylic sheet with (a) 2 wt% GNR (b) 1 wt% HNR and (c) 2wt% HNR ........ 86

A Extraction time of free polymer ........ 94

C-1 $^{1}$H-NMR and $^{31}$P{$^{1}$H } NMR spectra of $OsHCl(CO)(PCy_3)_2$ ........ 99

C-2 $^{1}$H-NMR, $^{31}$P{$^{1}$H } NMR and FT-IR spectra of $OsHCl(CO)(O_2)(PCy_3)_2$ ........ 100

E $^{13}$C-NMR spectra of (a) NR and (b) HNR ........ 103

G-1 Samples of thermal resistance test : (a) before test and (b) after test ........ 110

G-2 Samples of ultraviolet resistance test : (a) before test and (b) after test ........ 112

# LIST OF ABBREVIATIONS

ABVN : 2,2'-Azobis-(2,4-dimethylvaleronitrile)
b.p. : Boiling point
BPO : Benzoyl peroxide
°C : Degree Celsius
CHPO : Cumene hydroperoxide
DRC : Dry rubber content
EB : Elongation at break
FT-IR : Fourier-Transform Infrared Spectrometer
GE : Grafting efficiency
GNR : Grafted natural rubber
h : Hour (s)
HANR : High ammonia natural rubber
HNR : Hydrogenated natural rubber
LPE : Light petroleum ether
MEK : Methyl ethyl ketone
min : Minute (s)
MMA : Methyl methacrylate
NMR : Nuclear Magnetic Resonance Spectrometer
NR : Natural rubber
phr : Part per hundred
psig : Pounds-force per square inch gauge
SEM : Scanning Electron Microscope
ST : Styrene
STR 5L : Standard Thai Rubber 5L
TEPA : Tetraethylene pentamine
TS : Tensile strength
wt : Weight
wt% : % by weight

# CHAPTER I

# INTRODUCTION

## 1.1 The Purpose of the Investigation

Acrylic plastics mainly prepared from bulk polymerization of methyl methacrylate using casting process have advantages of clarity, light weight and high resistance to the outdoor environment. Consequently, it is used in a wide variety of applications such as laminated glass, laminated roof, protective coatings, aircraft window, car components, etc.

The cost of methyl methacrylate is quite high compared to styrene which gives polymer with same clarity and transparent properties [1]. Moreover, poly(methyl methacrylate) is brittle and has the high moisture uptake to cause the swelling and lower heat deflection. For purpose of cost reduction and overcome these disadvantages, styrene could be added to copolymerize with methyl methacrylate for saving cost. However, the copolymerization of methyl methacrylate with styrene has been applied, the brittleness is increased and the impact strength is decreased.

There are many attempts to improve the mechanical properties of brittle materials such as poly(vinyl chloride) and poly(methyl methacrylate) by blending with elastic polymer such as butadiene rubber, styrene-butadiene rubber, natural rubber, etc., as an impact modifier. Unfortunately, the rubber and styrene-methyl methacrylate copolymer blend components, which have good elasticity and impact strength, exhibit the poor oxidation and thermal resistance. Modifications can improve some properties of rubber. Graft copolymerization and hydrogenation are one of modification of rubber. Graft copolymer improves compatibility, impact and low temperature properties of thermoplastics. Hydrogenated natural rubber improves the oxidation and thermal resistance. Therefore, the objective of the research is to prepare the styrene-methyl methacrylate copolymer sheet using casting process by bulk copolymerization of methyl methacrylate and styrene with a small amount of modified natural rubber such as grafted and hydrogenated natural rubber. The mechanical properties, physical properties and morphology of the copolymer sheet containing modified natural rubber were investigated. For modified natural rubber, the graft copolymer of styrene and methyl methacrylate onto rubber by emulsion copolymerization was synthesized using redox initiators, cumene hydroperoxide and tetraethylene pentamine. Hydrogenated natural rubber was synthesized using $OsHCl(CO)(O_2)(PCy_3)_2$ as catalyst.

## 1.2 The Objective

The objectives of thesis can be summarized as follows:

1. To prepare the styrene-methyl methacrylate copolymer sheet containing modified natural rubber by bulk copolymerization using casting process.
2. To investigate effects of such influential parameters as the styrene monomer and modified natural rubber content.
3. To investigate the mechanical properties, physical properties, and morphology of the styrene-methyl methacrylate copolymer sheet containing modified natural rubber.

## 1.3 Scope of the Investigation

For the preparation of copolymer sheet containing modified natural rubber, the appropiate copolymerization conditions were studied. The suitable copolymer sheet containing modified natural rubber, which gave the good mechanical properties and physical properties, were prepared. The procedures are as follows:

1. Literature survey and in-depth study of this reseach work.
2. Preparation of graft copolymer of methyl methacrylate and styrene onto natural rubber by emulsion copolymerization using redox initiator.
3. Characterization of the grafted natural rubber.
4. Preparation of the hydrogenated natural rubber by using $OsHCl(CO)(O_2)(PCy_3)$ as a catalyst.
5. Characterization of the hydrogenated natural rubber.

4\. Preparation of the methyl methacrylate and styrene copolymer sheet containing modified natural rubber, such as grafted and hydrogenated natural rubber, by bulk copolymerization and study the effect of the parameters, the styrene monomer and modified natural rubber content.

5. Investigation of the mechanical properties and physical properties of the copolymer sheet containing modified natural rubber and study of the morphology of modified natural rubber dispersed in matrix.

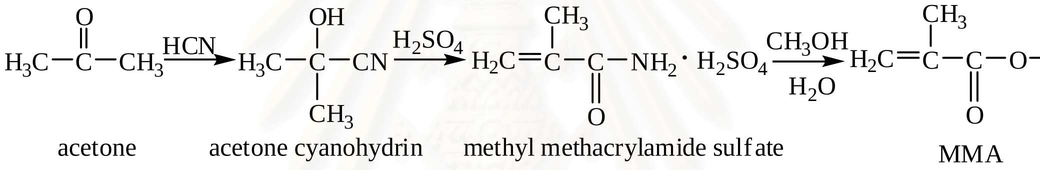
6. Summarizing the results.

# CHAPTER II

# THEORY AND LITERATURE REVIEWS

## 2.1 Methyl Methacrylate and Poly(methyl methacrylate) [2-3]

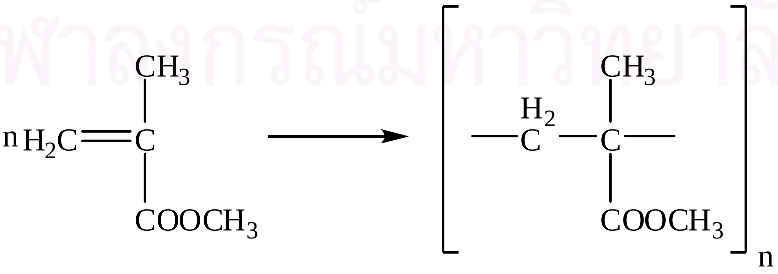
Methyl methacrylate (MMA) is a chemical compound mostly known as the monomer for the production of the transparent plastic poly(methyl methacrylate) (PMMA). In most common route for the preparation of MMA is from acetone as follows:



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{HCN} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CN \xrightarrow{H_2SO_4} H_2C=\overset{\overset{CH_3}{|}}{C}-\underset{\underset{O}{\|}}{C}-NH_2\cdot H_2SO_4 \xrightarrow[H_2O]{CH_3OH} H_2C=\overset{\overset{CH_3}{|}}{C}-\underset{\underset{O}{\|}}{C}-O-CH_3 \qquad (2.1)$$

acetone acetone cyanohydrin methyl methacrylamide sulfate MMA

In a typical process, acetone is treated with hydrogen cyanide at 40 °C in the presence of ammonia as catalyst. The acetone cyanohydrin produced is treated with concentrated sulfuric acid at 100 °C to form methyl methacrylamide sulfate which fed directly into aqueous methanol. The MMA is separated by steam distillation and purified by distillation. The MMA, known as acrylic, is colorless liquid with a characteristic sweet odor, b.p. 100.5 °C. For shipping and storage, hydroquinone or *p*-methoxyphenol are commonly added as initiators



$$n\,H_2C=\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \longrightarrow \left[ -\overset{H_2}{C}-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}- \right]_n \qquad (2.2)$$

The first acrylic polymer to be produced commercially 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 cast poly(methyl methacrylate) and found it to be a potentially useful material but high raw material cost prohibited commercial development. At this time, MMA was obtained by dehydrogenation of hydroxyisobutyric ester. In 1932, Crawford devised a synthesis based on the cheap raw materials, acetone and hydrogen cyanide. Poly(methyl methacrylate) thus became a feasible proposition and commercial production begun in 1934. Cast sheet PMMA was much used during the Second World War for aircraft glazing. Since the war, sundry other users of the sheet material have been developed; these include display signs, lighting fittings and bathroom fittings. PMMA may also be melt processed and, in fact, a recent trend has been the increasing displacement of cast sheet by material fabricated by more 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. Of these methods, bulk and suspension polymerization are mainly used for the production of the homopolymer. The production of cast sheet, rods, and tubes is carried out by bulk polymerization, starting in most cases with a syrup of partially polymerized MMA with a convenient viscosity for handling. Shrinkage and heat evolution during polymerization are reduced by the use of syrup.

Sheet of PMMA are commonly made by extrusion. Alternatively, they may be cast in cells made up of two sheets of heat-resistant glass separated by a coated rubber gasket. The cell is filled with syrup and sealed, and polymerization is carried out at 60-70 °C in an air oven or water bath, with a finishing treatment at 100 °C. Peroxide or azo initiators may be used.

PMMA is a linear, hard, polar and rigid transparent thermoplastic with a higher softening point, better impact strength, and better weatherability than polystyrene. Values for 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%.

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 hydrocarbons, chlorinated hydrocarbons, and esters but has very good resistance to water, alkalis, aqueous inorganic, and most dilute acids. PMMA has much resistance to hydrolysis than poly(methyl acrylate), probably by virtue of the shielding presented by the α-methyl group.

**Table 2.1** Typical properties of poly(methyl methacrylate) [4].

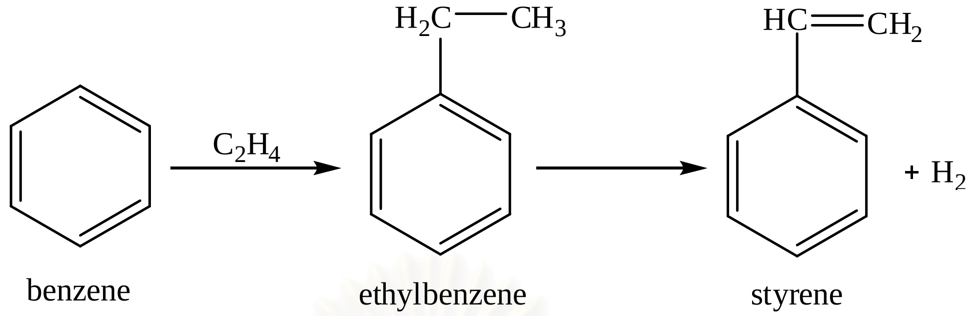
| Property | Value |
|---|---|
| Density, g/cm$^3$ | 1.15-1.19 |
| Water absorption, % | 0.3-2 |
| Hardness, Rockwell M | 63-97 |
| Young's modulus, GPa | 1.79-3.38 |
| Tensile strength, MPa | 55-85 |
| Elongation at break, % | 1-30 |
| Charpy Impact, J/cm$^2$ | 0.2-0.4 |
| Specific heat capacity, J/(g·K) | 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 |

A further outstanding property of PMMA is its good outdoor weathering. After several years under tropical conditions the color change is extremely small. The mechanical and thermal properties of the polymer, e.g. tensile strength, impact strength, etc., are good also. Electrical properties are good but not outstanding. A limitation of the optical uses of the material is its poor abrasion resistance compared to glass. Despite considerable effort, attempts to improve the scratch resistance or surface hardness of PMMA have so for been accompanied by deterioration in other properties, such as impact strength.

## 2.2 Styrene and Polystyrene [2-3, 5]

Styrene (ST), also known as 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 evaporates easily and has a sweet smell. It often contains other chemicals that can result in a sharp, unpleasant smell.

The bulk of commercial styrene is prepared from benzene by the following route:



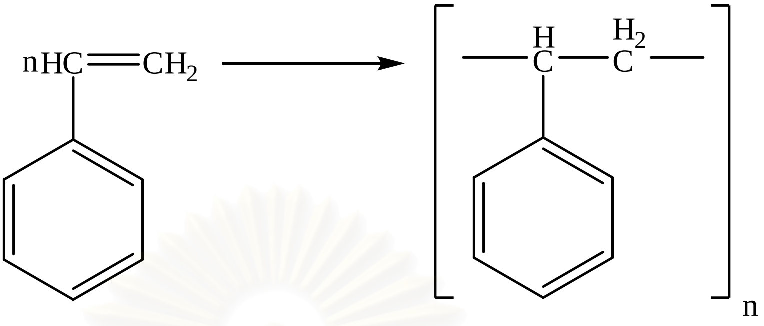
(2.3)

In the first stage, a 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). Ethylbenzene is produced in a gas phase process.

The second stage of the styrene process involves the dehydrogenation of ethylbenzene. The reaction is carried out in the vapor phase at temperatures of 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 and in order to reduce the partial pressure of the ethylbenzene the feed is mixed with superheated steam before passage over the catalyst. Styrene is a colorless liquid with a characteristic odor and refined by distillation.

Low levels of ST also occur naturally in plants as well as a variety of foods such as fruits, vegetables, nuts, beverages, and meats. The production of ST in the United States was increased dramatically during the 1940's to supply the war needs for synthetic rubber. Because the styrene molecule has a vinyl group with a double bond, it can polymerize. It is used as a monomer to make plastics such as polystyrene, 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.

Polystyrene (PS) is a polymer made from the monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum. At room temperature, polystyrene is normally a solid thermoplastic, but can be melted at higher temperature for molding or extrusion, then resolidified. Commercial interest in PS began in the 1930s when the material was found to have good electronic insulation characteristics and limited production was started by I. G. Farbenindustrie (Germany) and Dow Chemical Company (USA) shortly before the Second World War. Applications of PS were vigorously explored and the material was quickly adopted in many fields. Polystyrene is now one of the major commercial plastics, being very extensively used in such diverse applications as domestic appliances, food containers, packaging, toys, and, in expanded form, thermal insulation.



(2.4)

Styrene may be polymerized by means of all four techniques by bulk, solution, suspension, and emulsion polymerization. Although solution or emulsion polymerization may occasionally be used, most polystyrene is made either by suspension polymerization or by polymerization in bulk. The bulk polymerization of ST is begun in a prepolymerization, a stirred vessel in which inhibitor-free styrene is polymerized until the reaction mixture is as concentrated in polymer as is consistent with efficient mixing and heat transfer. The syrupy mixture from the prepolymerization then enters a cylindrical tower maintained essentially full of fluid. By cooling the upper part of the tower and heating the lower part, the polymerization is controlled to prevent runaways but to proceed to essentially pure molten polymer at the bottom.

Straight polystyrene is a hard, rigid, rather brittle material. Some properties of PS are shown in Table 2.1. It has a relatively low softening point and does not withstand the temperature of boiling water. Some comparative properties of ST-containing polymers are shown in Table 2.2. Polystyrene is a low cost material and high transparent, transmitting about 90% of visible light.

**Table 2.2** Typical properties of polystyrene [6].

| **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 |
| Transmission, % | 80-90 |
| Melting point, °C | 240 |
| Vicat Softening Point, °C | 1.03-110 |

**Table 2.3** Comparative properties of typical commercial grades of ST-containing polymers [2].

| | Polystyrene (general purpose) | Polystyrene (high impact) | SAN | ABS |
|---|---|---|---|---|
| Specific gravity | 1.04 | 1.05 | 1.08 | 1.04 |
| Yield tensile strength (MPa) | 42 | 31 | 69 | 40 |
| (lbf/in$^2$) | 6100 | 4500 | 10000 | 5800 |
| Ultimate elongation (%) | 2 | 25 | 2.5 | 25 |
| Impact strength, Izod (J/m) | 19 | 64 | 27 | 270 |
| (ft lbf/in) | 0.35 | 1.2 | 0.5 | 5 |
| Softening point, Vicat (°C) | 100 | 100 | 110 | 105 |

## 2.3 Chain Copolymerization [5]

Chain polymerization can be carried out with mixtures of two monomers to form polymeric product with two different structures in the polymer chain. This type of chain polymerization process in which two monomers are simultaneously polymerized is termed a copolymerization and the product is a copolymer, which will possess properties different to the homopolymer of either monomer. Commercially reverent copolymers include ABS plastic, SBR, styrene-isoprene-styrene (SIS), ethylene-vinyl acetate.

Chain copolymerization can be used to produce (1) alternating copolymers with regular alternating A and B unit, (2) random copolymers with random sequences of monomer A and B, (3) block copolymers comprised of two or more homopolymer subunits linked by covalent bonds, and (4) graft copolymers are a special type of branched copolymer with backbone of one monomer to which are attached one or more side chains of another monomer. Four types of copolymers are presented in Figure 2.1.

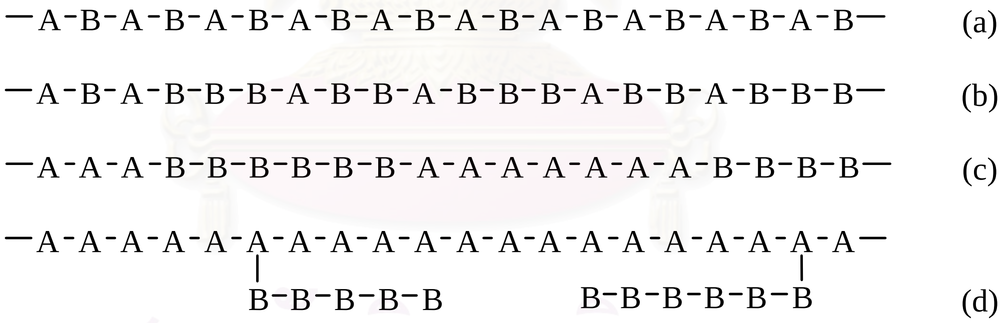


**Figure 2.1** Diagrams of copolymers produced by chain copolymerization (a) alternating (b) random (c) block and (d) graft copolymers [5].

In the copolymerization between two monomers, $M_1$ and $M_2$, the following reactions may occur:

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1M_1^* \qquad \text{homopropagation} \qquad (2.5)$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_1M_2^* \qquad \text{cross-propagation} \qquad (2.6)$$

$$M_2^* + M_1 \xrightarrow{k_{22}} M_2M_1^* \qquad \text{cross-propagation} \qquad (2.7)$$

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2M_2^* \qquad \text{homopropagation} \qquad (2.8)$$

The copolymerization equation, also called the Mayo-Lewis equation, gives the molar ratios of the two monomers in the resulting copolymer as:

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{[\mathrm{M}_1]\left(\mathrm{r}_1[\mathrm{M}_1]+[\mathrm{M}_2]\right)}{[\mathrm{M}_2]\left([\mathrm{M}_1]+\mathrm{r}_2[\mathrm{M}_2]\right)} \tag{2.9}$$

where $r_1$ and $r_2$ are termed the monomer reactivity ratios of the individual monomers, they are defined by

$$\mathrm{r}_1 = \mathrm{k}_{11}/\mathrm{k}_{12} \quad \text{and} \quad \mathrm{r}_2 = \mathrm{k}_{22}/\mathrm{k}_{21}$$

The tendency of two copolymerize is noted by r values between zero and unity. An $r_1$ value greater than unity means that $\mathrm{M}_1^*$ preferentially adds $M_1$ instead of $M_2$, while an $r_2$ value less than unity means that $\mathrm{M}_1^*$ preferentially adds $M_2$. An $r_1$ value of zero would mean that $M_1$ is incapable of undergoing homopolymer. The monomer reactivity ratios for some of common monomers in chain copolymerization are shown in Table 2.4.

One observes enhanced reactivities in certain pairs of monomers due apparently to subtle radical-monomer interactions. This effect is a very general one in chain copolymerization and corresponds to the alternating tendency of the comonomer pairs. The deviation of the $r_1r_2$ product from unity and its approach to zero is a measure of the alternating tendency. Values of $r_1r_2$ of some comonomer pairs in radical copolymerization are presented in Table 2.5. Thus acrylonitrile undergoes ideal copolymerization with methyl vinyl ketone ($r_1r_2$ = 1.1) and alternating coolymerization with butadiene ($r_1r_2$ = 0.006). For styrene-methyl meyhacrylate copolymer, $r_1r_2$ is 0.24 means that random copolymer.

**Table 2.4** Monomer reactivity ratios in chain copolymerization [5].

| $M_1$ | $r_1$ | $M_2$ | $r_2$ | T (°C) |
|---|---|---|---|---|
| Acrylonitrile | 0.046 | 1,3-Butadiene | 0.36 | 40 |
| | 0.14 | Methyl methacrylate | 1.3 | 70 |
| | 0.02 | Styrene | 0.29 | 60 |
| | 5.5 | Vinyl acetate | 0.06 | 70 |
| | 3.6 | Vinyl chloride | 0.044 | 50 |
| Ethylene | 0 | Acrylonitrile | 7 | 20 |
| | 0.38 | Tetrafluoroethylene | 0.1 | 25 |
| | 0.79 | Vinyl acetate | 1.4 | 130 |
| Methyl methacrylate | 0.36 | Acenaphthylene | 1.1 | 60 |
| | 0.46 | Styrene | 0.52 | 60 |
| | 9 | Vinyl chloride | 0.07 | 68 |
| | 2.4 | Vinylidene chloride | 0.36 | 60 |
| Styrene | 90 | Ethyl vinyl ether | 0 | 80 |
| | 42 | Vinyl acetate | 0 | 60 |
| | 15 | Vinyl chloride | 0.010 | 60 |
| | 1.8 | Vinylidene chloride | 0.087 | 60 |

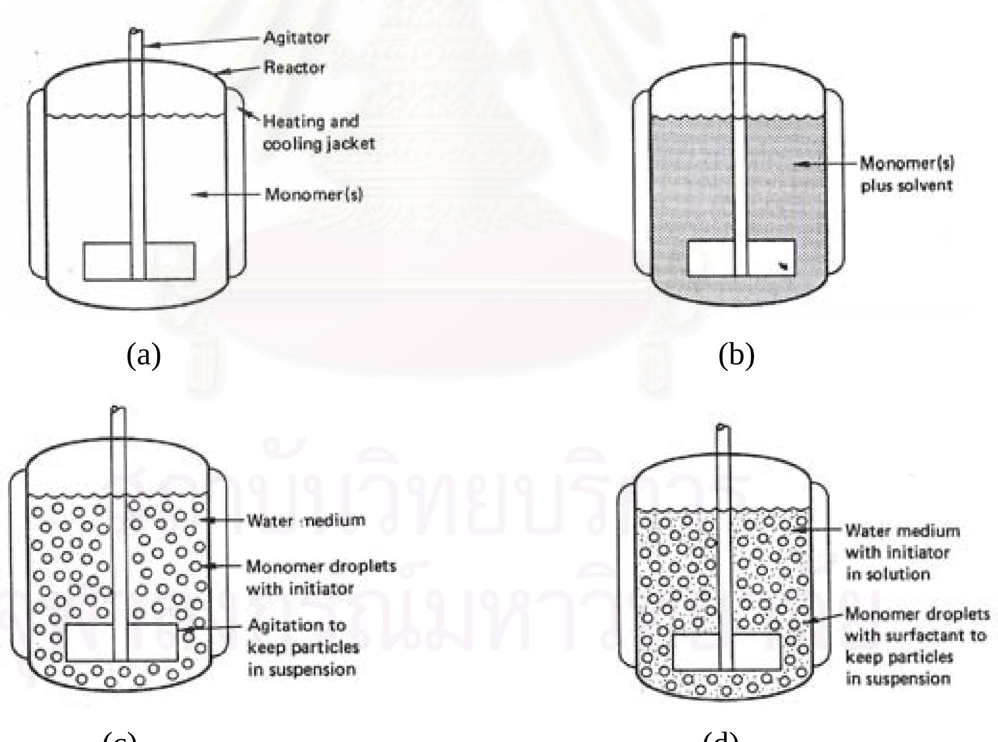
**Table 2.5** Values of $r_1r_2$ in chain copolymerization [5].

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Butadiene | | | | | | | |
| 0.78 | Styrene | | | | | | |
| | 0.55 | Vinyl acetate | | | | | |
| 0.31 | 0.34 | 0.39 | Vinyl chloride | | | | |
| 0.19 | 0.24 | 0.30 | 1.0 | Methyl methacrylate | | | |
| <0.1 | 0.16 | 0.6 | 0.96 | 0.61 | Vinylidene chloride | | |
| | 0.10 | 0.35 | 0.83 | | 0.99 | Methyl vinyl ketone | |
| 0.006 | 0.016 | 0.21 | 0.11 | 0.18 | 0.34 | 1.1 | Acrylonitrile |

## 2.4 Bulk Copolymerization [5, 7-8]

Bulk or mass polymerization of a pure monomer offers the simplest process with a minimum of contamination of product. Monomer, polymer and initiator are the only component in bulk polymerization. Polymerization setups are shown in Figure 2.2. However, bulk polymerization is difficult to control due to the characteristics of radical chain polymerization. The advantages and disadvantages of the commercial polymerization systems are shown in Table 2.6.

In the bulk copolymerization, the monomers and initiator are mixed in a reactor and heated or cooled as required. Many reactions are carried out by charging one monomer into the reactor and adding the second monomer slowly. Additional reaction is often too exothermic for the bulk process. Bulk copolymerization requires careful temperature control. It is apparent that special steps must be taken to remove heat from these reactions. Thin casting can be made by bulk polymerization.



(a) (b)

(c) (d)

**Figure 2.2** Diagrams of polymerization setups (a) bulk (b) solution (c) suspension and (d) emulsion polymerization [7].

**Table 2.6** Commercial polymerization systems [9].

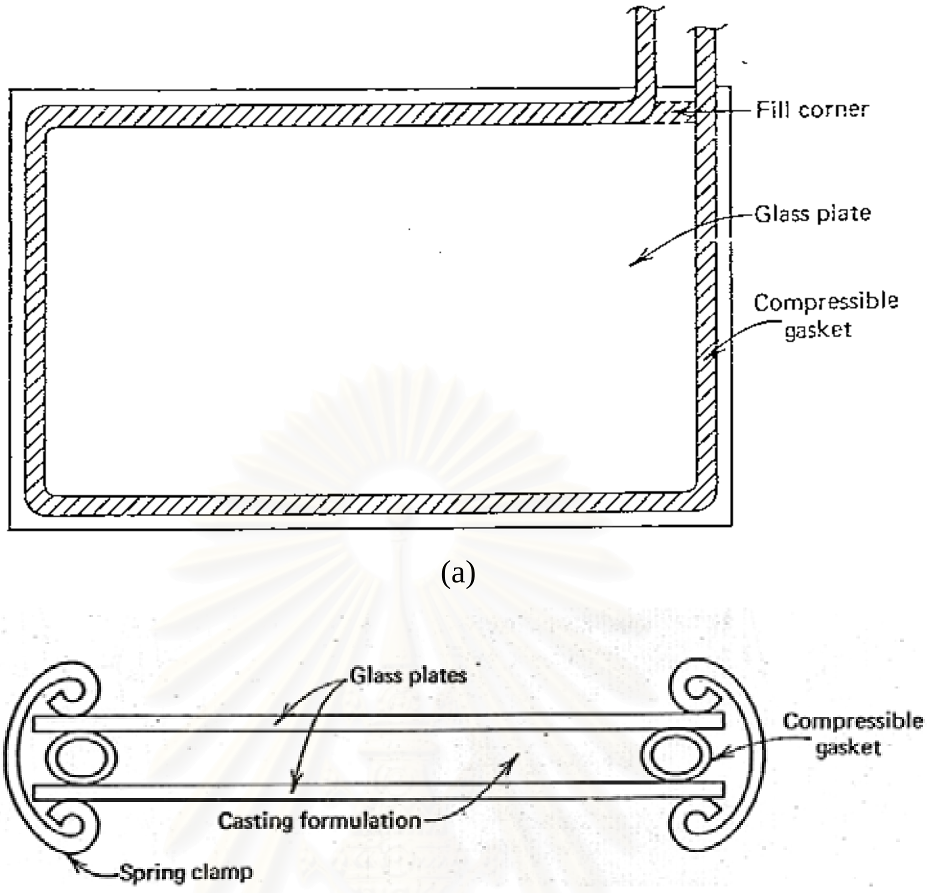
| Type | Advantage | Disadvantages |
|---|---|---|
| Bulk: batch | Simple procedure, composite lay-up and casting of unusual shapes. | Exothermic, wide molecular weight range. |
| Bulk: continuous | Temperature control, controlled MWD. | Low conversion per pass, monomer-polymer separation, high temperature, pressure may be needed. |
| Solution | Temperature control, solution form may be direct product. | Solvent may be expensive, polymer drying costly. |
| Suspension | Temperature control, dried particles may be direct product. | Agitation and scale-up difficult, additives needed. |
| Emulsion | Temperature control, fast reaction rates. | High surfactant concentrations, poor stability. |

We can differentiate between quiescent and stirred bulk polymerization. Both methods are applied to system where polymer is stable in monomer and progressively increases in viscosity with conversion. In quiescent systems, gel formation, corresponding to infinite viscosity, can occur. Because of the heat of polymerization and autoacceleration, reaction rate is difficult to control.

## 2.5 Casting Process

Casting is a manufacturing process and involves the pouring of a liquid resin into or on a form and allowing 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 [7]. Casting method is simpler machine requirements for molded part production and more economical production of small quantities. It is also lower expenses for molds [8].

Thermoplastics are used by melting or by polymerization in the mold. Figure 2.3 shows cell casting mold configuration. Acrylics and polyesters have been popular for clear decorative applications, although heat generation acrylics must be reduced by dissolving polymer in monomer. While mold casting can be accomplished with most thermoplastics, many resins are degraded by long heating cycles [7].



(a)

(b)

**Figure 2.3** Conventional cell casting mold configuration (a) face view and (b) edge view [7].

## 2.6 Natural Rubber

Natural rubber is a white milky fluid produced by specialized cells in a variety of plants, throughout the world, in totally unrelated families, including the *Compositae* and *Moraceae* as well as the *Euphorbiaceae* [10]. Although in the past many different species have been used for obtaining crops of latex the principal source of natural rubber, today, is *Hevea Brasiliensis*. *Hevea Brasiliensis* is a native of the tropical rain forest of the Amazon Basin in Brazil. Southeast Asia has become a dominant producer of natural rubber since 1913 [11]. Most of the world's natural rubber comes today from Southeast Asia, mainly Thailand, Malaysia, and Indonesia [12]. Thailand has been the world's leader in natural rubber production and exportation during the last decade followed by Indonesia and Malaysia as shown in Table 2.7 and 2.8.

**Table 2.7** Production of natural rubber in 2006 [13].

| **Country** | **January** | **February** | **March** | **April** | **Total** |
|---|---|---|---|---|---|
| Thailand | 273.5 | 243.8 | 247.7 | 195.0 | *960.0* |
| Indonesia | 194.4 | 215.1 | 179.5 | 189.5 | *778.5* |
| Malaysia | 102.9 | 121.9 | 118.7 | 80.4 | *423.9* |
| China | 39.0 | 38.0 | 40.0 | 40.0 | *157.0* |
| Vietnam | 48.0 | 47.0 | 49.0 | 44.0 | *188.0* |
| India | 93.5 | 51.5 | 48.0 | 52.5 | *245.5* |
| Others | 58.7 | 60.7 | 58.1 | 66.6 | *244.1* |
| *Total* | *810* | *778* | *741* | *668* | *2997* |

Unit : thousand tons

**Table 2.8** Net exports of natural rubber in 2006 [13].

| **Country** | **January** | **February** | **March** | **April** | **Total** |
|---|---|---|---|---|---|
| Thailand | 199.1 | 230.1 | 220.5 | 190 | *839.7* |
| Indonesia | 177.2 | 197 | 180 | 180 | *734.2* |
| Malaysia | 43.2 | 44.6 | 61.2 | 69.6 | *218.6* |
| Vietnam | 42 | 45 | 44 | 40 | *171* |
| Sri Lanka | 2.8 | 3.5 | 3 | 2 | *11.3* |
| India | 4.6 | 6 | 4.2 | 6 | *20.8* |
| Myanmar | 2 | 2 | 2 | 3 | *9* |
| Others | 44.1 | 40.8 | 40.1 | 38.4 | *163.4* |
| *Total* | *515* | *569* | *555* | *529* | *2168* |

Unit : thousand tons

*Hevea Brasiliensis*, the commercial rubber tree, is a tall tree, growing naturally up to forty meters (130 feet) and living for one hundred years or more. *Hevea Brasiliensis* requires temperature of 20-30 °C, at least 2,000 mm of rainfall per year, and high atmospheric humidity. This naturally occurring polymer is known chemically as cis-1,4-polyisoprene (see Figure 2.4).

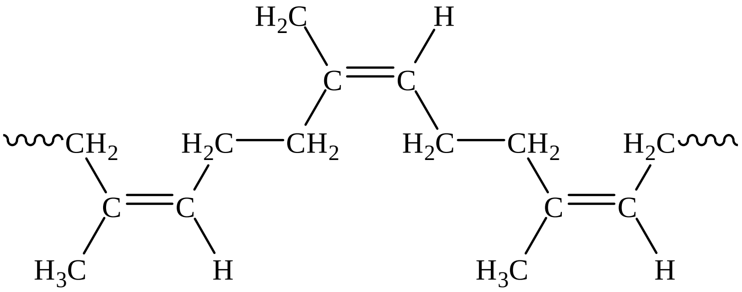


**Figure 2.4** Cis-1,4-polyisoprene [14].

### 2.6.1 Natural Rubber Latex [10]

Natural rubber latex, a milk-like liquid, comes from a layer of tiny tubes spiraling up the tree beneath the outer bark. Like milk it is an emulsion particles suspended in water. Natural latex as it comes from the tree is known as field latex. Field latex composes of only about 36% rubber and 4% non rubber substances. The non-rubber components include proteins, carbohydrates, liquids, and inorganic salts. Its composition varies according to the clones of rubber, age of rubber tree, and tapping method. The composition of typical field latex is presented in Table 2.9.

**Table 2.9** Compositions of field latex [15].

| **Composition** | **% by weight** |
|---|---|
| Water | 55 |
| Rubber hydrocarbon | 35 |
| Protein | 4.5 |
| Acetone extraction | 3.9 |
| Amino acid, etc. | 0.2 |
| Quebrachitol | 1.0 |
| Inorganic salts | 0.4 |

About 10% of natural rubber is not processed into dry rubber but sold as latex. Latex concentrate is usually made by centrifugation-spinning at high speed to separate off a cream of about 60% rubber from a liquid of about 5% rubber, from which dry skim rubber is made. A little ammonia is added to the latex, both on collection and before centrifugation, to stop it coagulating and turning into dry rubber. Another concentrate, made by evaporation, evaporated latex concentrate, has a higher rubber content and so slightly different property. Finally, there is creamed latex concentrate: the field latex is mixed with a chemical, such as ammonium alginate, which makes the rubber particles rise to the top of the liquid, like cream, when left to stand for several weeks. All latex concentrates are chemically treated to prevent coagulation.

### 2.6.2 Standard Thai Rubber [16]

STR (Standard Thai Rubber) has been proposed to replace “TTR” (Thai Test Rubber) according to the reason of international image that Thai Technically Specified Rubber attains the international standard instead of just passing the test as implicity by the name “TTR”. Furthermore, new name, STR is also followed the international style of calling this type of natural rubber.

Material to be processed for STR must be derived from *Hevea Brasiliensis* tree. The processing materials of the various STR grades for improved consistency and quality within grades are shown in Table 2.10.

**Table 2.10** Processing material of STR grades [16].

| Grade | Processing Materials |
|---|---|
| STR XL, STR 5L | Whole field latex bulked and formic acid coagulated under strictly controlled conditions. |
| STR 5 | Either whole fresh coagulum or unsmoked sheet (USS) or blend of them subjected to further crumb processing. |
| STR 10, STR 20<br>STR 10 CV, STR 20 CV | Field grade materials based on USS, lump, scrap, green crepe, or mixture. |

Lump and scrap are field grade materials derived from latex naturally coagulated in different manner such as in the tapping cup or suitable vessels, and in the trace of tapping etc. Field grade materials are USS or green crepe or cup lump of them according to the STR grade intended to process.

**Table 2.11** Standard Thai Rubber (STR) scheme [16].

| Parameter | STR XL | STR 5L | STR 5 | STR 5 CV | STR 10 | STR 10 CV | STR 20 | STR 20 CV |
|---|---|---|---|---|---|---|---|---|
| | Latex | | Latex/Sheets | | Lump/Sheet/Green Crepe | | | |
| Dirt retained on 44 μ aperture (max. %wt.) | 0.02 | 0.04 | 0.04 | 0.04 | 0.08 | 0.08 | 0.16 | 0.16 |
| Ash (max. %wt.) | 0.40 | 0.40 | 0.60 | 0.60 | 0.60 | 0.60 | 0.80 | 0.80 |
| Nitrogen (max. %wt.) | 0.50 | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 |
| Volatile Matter* (max. %wt.) | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 |
| Initial Plasticity (Po) (min) | 35 | 35 | 30 | - | 30 | - | 30 | - |
| Plasticity Retention Index (PRI) (min) | 60 | 60 | 60 | 60 | 50 | 50 | 40 | 40 |
| Colour Lovibond Scale (individual value, max.) | 4.0 | 6.0 | - | - | - | - | - | - |
| Mooney Viscosity ML (1+4) 100 °C | - | - | - | ** | - | ** | - | ** |
| Colour Coding Marker | blue | Light Green | light green | white on light green blackground | brown | white on brown blackground | red | white on red blackground |

***Note*** Provision of Rheograph with basic cure data as consumer or ACS 1 based recipe will be offered as additional test.

* Product limit is not more than 0.50% ** Product limit of 70 (+7, -5), 60 (+7, -5), and 50 (+7,-5) for STR 5 CV ; 60 (+7, -5) for STR 10 CV and 65 (+7, -5) for STR 20 CV

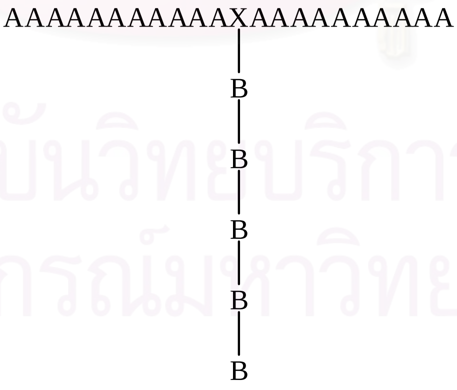
### 2.6.3 Modification of Natural Rubber

Since 1801, natural rubber has been modified in many different ways, and modified forms have been available commercially since 1915. The degree of modification can vary from a few percent to complete modification of the polymer chain. Modification highly affects its physical properties. Even thermoplastic or resinous material can be obtained by a modification of rubber [17].

The most well known types of modification are oxidation, halogenation, hydrochlorination, chlorosulphonation, hydrogenation, and free radical addition or grafting [18].

## 2.7 Graft Copolymers

A graft copolymers is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points. In a graft copolymer, the distinguishing feature of the side chains is constitutional, i.e., the side chain comprises units derived from at least one species of monomer different from those that supply the units of the main chain. The simplest case of graft copolymer can be represented by the following structure,



where a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain of graft, and X is the backbone to which the graft is attached [19].

Graft copolymers produced by causing a post polymerization of vinyl monomers such as styrene, methyl methacrylate, acrylonitrile, or vinyl acetate either independently or as a mixture of the plurality thereof to a rubber-like polymer latex have been well known.

Although graft copolymerization were widely practiced with vinyl monomer 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 properties 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 to improve compatibility, impact, and low temperature properties of thermoplastic.

## 2.8 Emulsion Polymerization [20]

The emulsion polymerization method employs various possibilities to prepare particles with controlled morphologies and surface properties. The core-shell arrangements provided by the emulsion polymerization technique. The production of two phase latex particles with defined morphology is of great technical interest. A two step procedure has emerged in which an outer layer of polymer is polymerized onto an inner core of a different polymer. According to the polymer particle morphology, there are two main kinds of core-shell copolymers: soft core-hard shell and hard core-soft shell. The core shell latex with a glassy core and rubbery shell can be used in coating and adhesive formulation; on the contrary, the latex particles with rubbery cores and glassy shells are used as impact modifiers in plastics. The rubbery particle structure could be easily made in the synthesis of core-shell particle via emulsion polymerization. The rubbery core latex particles are produced in the first stage of the polymerization. These particles are then used as a seed in a second stage emulsion polymerization, for coating with a glassy shell by grafting. By stepwise growth from a seed, the core-shell rubber particles having wide ranging sizes, composition and layer thickness could be synthesized for used as model systems in the improvement of impact modification. Schematic diagram of an emulsion polymerization system is shown in Figure 2.5. The system consists of three types of particles: monomer droplets, inactive micelles in which polymerization is not occurring, and active micelles in which polymerization is occurring.

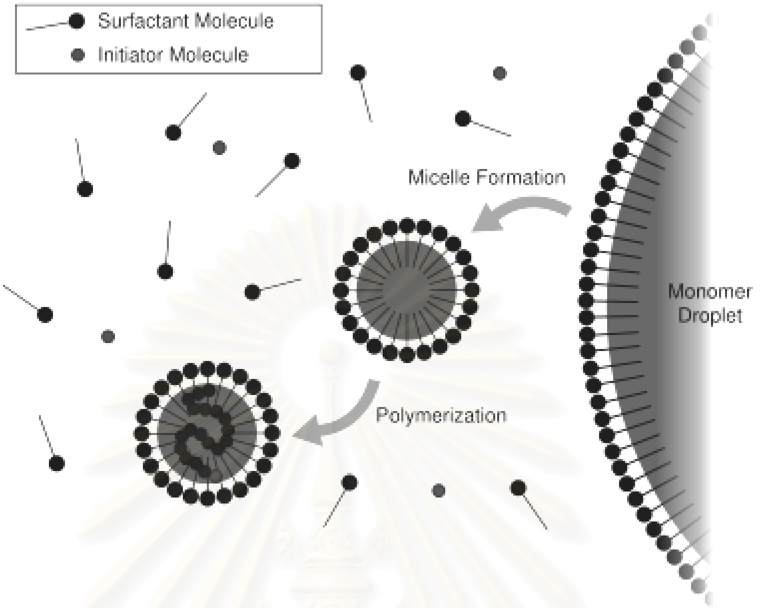


**Figure 2.5** Schematic diagram of emulsion polymerization [5].

### 2.8.1 Ingredients and Processes

An overview of the major ingredients and processes in emulsion polymerization is now present: monomer, initiator, surfactant, and other ingredients.

#### a) Monomers

The major polymerizable component of an emulsion polymerization is a monomer that is of limited solubility in water, and that swells its polymer. The monomers used in emulsion polymerization are thus often of the vinyl type, $CH_2=CHX$. X may be $C_6H_5$, CN, $O_2CCH_3$, Cl, and $CO_2R$. Some monomers that used in commonly by commercial emulsion polymerization are shown in Table 2.12.

**Table 2.12** Types of monomer [21].

| Monomer | Examples of common usage |
|---|---|
| styrene | ingredient in artificial rubber (SBR-also used in paper coating.) |
| butadiene | 1) ingredient in artificial rubber (SBR-also used in paper coating.)<br>2) impact modifier (toughen of plastic), e.g. HIPS, ABS |
| tetrafluoroethylene | 1) polytetrafluoroethylene, e.g. Teflon<br>2) ingredient influoropolymers, e.g. Viton |
| vinyl acetate | 1) polyvinyl acetate (PVA) adhesive<br>2) ingredient in paint |
| methyl methacrylate | ingredient in surface coatings |
| acrylic acid | minor ingredient in paint formulation |
| itaconic acid | minor ingredient in paint formulation |
| 2-chloro-1,3-butadiene (chloroprene) | neoprene rubber (which has sulfur as co-monomer) |
| butyl acrylate | rubber ingredient in surface coatings |
| butyl methacrylate | rubber ingredient in surface coatings |
| methyl acrylate | co-monomer in surface coatings, adhesives |
| vinyl chloride | PVC (usually produced by suspension method, sometimes by emulsion) |

### b) Initiators

A source of free radicals is needed for water-borne emulsion polymerization. The free radicals can be produced by thermal decomposition of peroxy compounds like persulfate or by redox reactions like the cumene hydroperoxide/ tetraethylene pentamine, or by γ-radiation. The free radical initiators can be either water or oil soluble, determinating the preferred phase in which the free radicals will be produced. For redox initiators, the combination of certain oxidizing and reducing agents will produce free radicals even at low temperatures. This can be particularly useful when high molecular weight polymers are sought with low levels of branching.

### c) Surfactants

Surfactants are a key formulation variable in emulsion polymerizations. They are generally categorized into four major classes: anionic, cationic, nonionic, and zwitterionic (amphoteric). The anionic and nonionic surfactants are the most widely used because of enhanced compatibility with negatively charged latex particles as compared to the cationic or zwitterionic surfactants. In addition, in many latex formulation, mixtures of surfactants are often used together in a synergistic manner to control the particle size and to impart enhanced colloidal stability to the latex with regard to mechanical shear, electrolyte, and extremes in temperatures. The most widely used anionic surfactants are sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, and sodium or potassium salts of fatty acids.

### d) Stabilizers

The dispersion stabilizers used are not confined to anionic and nonionic surfactants. Sometimes it is beneficial to add so-called protective colloids such as hydroxyethyl cellulose, polyvinyl alcohol, and resin derivatives. In emulsion polymerization, a protective colloid, which is a water soluble polymer, is usually used to increase the particle stability against coagulation.

### f) Other Ingredients

It is often to add a modifier in commercial emulsion polymerization such as chain transfer agents to control molecular weight, buffer to control pH without hydrolysis of surfactant, and electrolytes.

## 2.9 Hydrogenation of Diene-Based Polymers [22]

Hydrogenation, one type of chemical modification of unsaturated polymers, is an important method to reduce the amount of unsaturation; consequently, the structure of hydrogenation polymer has better resistance to thermal and oxidative degradation. Signification examples of hydrogenated polymer products in the commercial synthetic rubber market are hydrogenated styrene-butadiene rubber produced by Shell and hydrogenated acrylonitrile-butadiene rubber manufactured by Zeon Chemicals and Bayer Inc. Both of these hydrogenated rubbers have excellent high temperature stability and resistance to oxygen, ozone and ultraviolet radiation, which are far superior to those of the parent rubbers.

Hydrogenation of polymers can be performed by both catalytic and non-catalytic methods. There are also some reseach reports involving the non-catalytic hydrogenation by using diimide reduction. The advantage of this method over others is not to completely saturate the 1,4-double bond and it also promotes *cis-trans* isomerization of the residual 1,4 units. In addition, depolymerization and cyclization of *cis*-1,4-polyisoprene have been observed by using this method. To avoid these side reaction problems, catalytic hydrogenation, via heterogeneous and homogeneous catalysts, has been more widely studied for diene-based polymers. However, heterogeneous catalyst reaction rates are generally slower than that of homogeneous ones in solution system. Many of the new developments in the field of catalytic hydrogenation have involved the use of homogeneous catalysts because they have higher selectivity and do not have the macroscopic diffusion problems. The selection of an optimum catalyst for a given system is dependent on the selectivity of the catalyst to specific functional groups in the polymer chain, e.g., selective hydrogenation of C=C without any reduction of CN or $CO_2H$ groups. Moreover, ease of handling the catalyst and its cost are also important factors to be considered for choosing a suitable catalyst for a particular system.

There are many research reports for the hydrogenation of synthetic diene-based polymers such as polybutadiene, SBR, and acrylonitrile-butadiene rubber (NBR). Such reactions are catalyzed by homogeneous catalysts composed of transition metal complexes containing Rh, Ru, Pd or Os as well as metallocenes including Ziegler-Natta type catalysts.

The Wilkinson’s catalyst, $RhCl(PPh_3)$, has been well known to be an effective catalyst with high selectivity for hydrogenation of olefins containing other function groups such as –CN or >C=O. $RhCl(PPh_3)$ can be produced in high yield and it is easy to handle because of its excellent air stability as a dry solid.

### 2.9.1 Homogeneous Hydrogenation in the Presence of 5d Metal Complexes [22]

Generally, the groups VIII 4d transition metals in the second row of the periodic table, namely Rh, Ru and Pd, are well known to be used as catalysts for hydrogenation of unsaturated polymers. The potential reactivity of 5d transition metals in the third row of the periodic table, for homogeneous catalytic transformation has hitherto been little exploited. Presumably, the reactions typically confirming catalytic cycles such as Lewis base addition-elimination, oxidative addition-reductive elimination, insertion-deinsertion of the third row metal complexes are slower than their 4d congeners because 5d metals usually form more stable catalytic complexes. A judicious choice of the metal-ligand system may lead to highly efficient catalyst. Certain osmium complexe has been found to be high efficient catalysts for hydrogenation of alkene and alkyne substrates as well as diene-based polymers.

The square - pyramidally pentacoordinated osmium complex, $OsHCl(CO)(PR_3)_2$, has been discovered in 1971 by Moers. Figure 2.6 shows the structure of osmium complexes with the bulky phosphines *trans* positioned within a plane shared by Cl and CO. It has been shown that the osmium centre lies essentially in the basal plane of 1a and the other ligands such as $O_2$, $H_2$, olefin and –CN can coordinate to the Os metal at the vacant coordination site *trans* to the hydride to give the six-coordinate complexes. There is no evidence for the coordination of a third phosphine or a phosphite ligand to either 1a or 1b.

The osmium complex is not only active for hydrogenation of small molecule olefins, but it is also an efficient catalyst for hydrogenation of diene-based polymers such as NBR and synthetic polyisoprene.

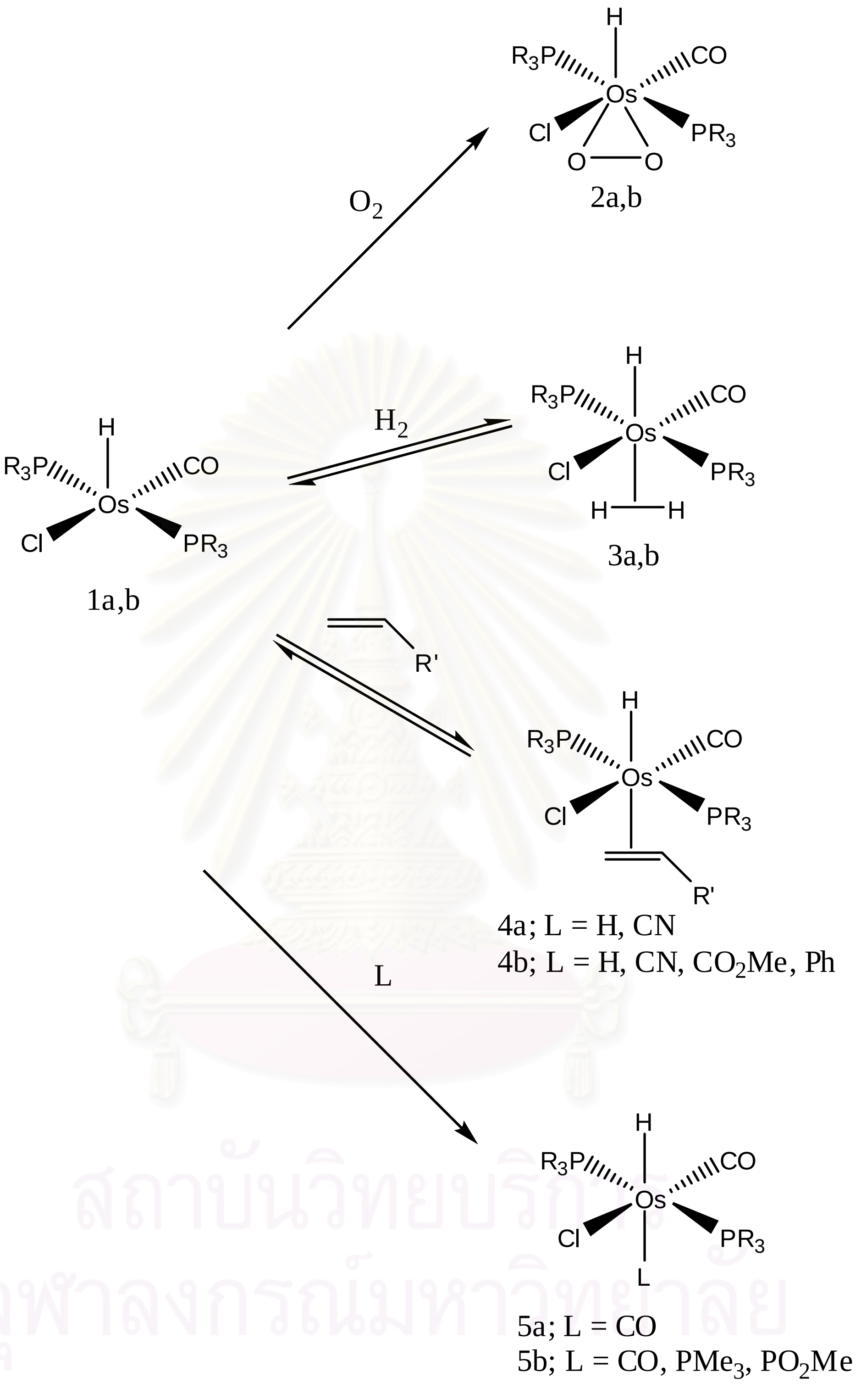


**Figure 2.6** Characterized reactions of $OsHCl(CO)(PR_3)_2$ (1a, R = Cy; 1b, R = *i*-Pr) [23].

### 2.9.2 Hydrogenation of Natural Rubber [22]

Any polymer with unsaturated hydrocarbon groups, present either in the backbone or within the side chain, can be hydrogenated. The most recent work for polymer hydrogenation has produced excellent products, such as hydrogenated NBR and hydrogenated SBR that have better resistance to thermal and oxidative degradation. In addition, hydrogenation is an alternative way to produce some polymer structures which are difficult to access via conventional polymerization, such as alternating ethylene-propylene copolymer from the hydrogenation of polyisoprene or natural rubber, and hydrogenation of block copolymers. Hydrogenation of these block copolymers forms thermoplastic elastomers with crystalline and amorphous segments is different from those of their unsaturated counterparts.

The main polymer structure within natural rubber is *cis*-1,4-polyisoprene, which is an unsaturated structure and is therefore susceptible to thermal and oxidative degradation. Hydrogenation of isoprene structure presents a rather difficult case for butadiene copolymers because the isoprenyl groups, which constitute the rubber macromolecules, are analogous to derivatives of a tri-substituted olefin; consequently, the hydrogenation rate is expected to be slower than for di- or mono- substituted olefinic units due to steric constraints. The hydrogenation process effectively changes the natural rubber structure to an alternating ethylene-propylene copolymer as shown in Figure 2.7.

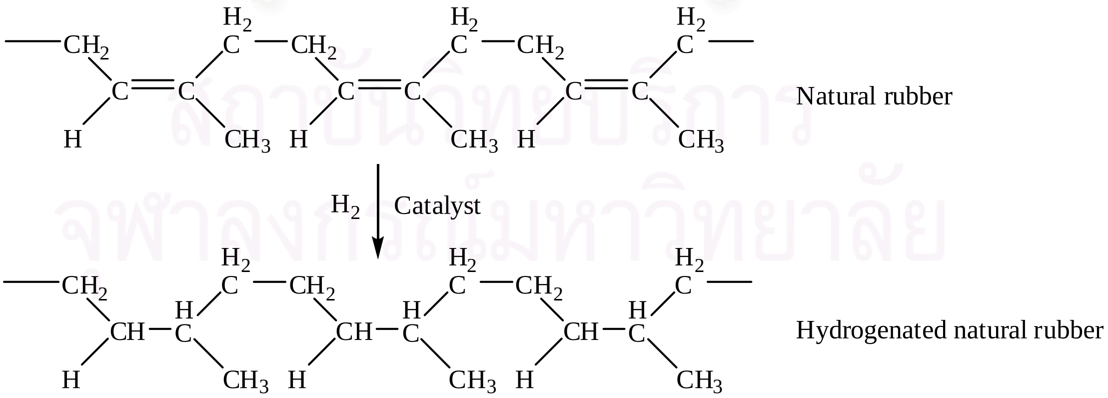


**Figure 2.7** General structure of natural rubber before and after hydrogenation process [24].

## 2.10 Literature Reviews

### 2.10.1 Modification of Acrylic sheet

Deichert et al. [25] studied the castable compositions of matter comprising (1) a monomeric mixture of methyl methacrylate and diallyl phthalate with or without comonomers copolymerizable therewith and (2) a copolymer of ethylene, castings thereof and a method for the production thereof, are disclosed. A novel group of articles of manufacture which not only possess a higher impact strength for a given content of rubber, a better transparency in regard to light transmission and good weatherability but retain these essential properties over a wide temperature range and thereby enable their usage in sections of the world where prior compositions fail in addition to those where the prior systems excel.

Graff et al. [26] studied additives for impact modified thermoplastics. Thermoplastic article having greatly reduced susceptibility to hazing was prepared from a solution of a polyurethane impact modifier in an α,β-unsaturated monomer comprising methyl methacrylate, and a haze modifier copolymer. It has been discovered that by incorporation of a small amount of a copolymer of a first member selected from the group consisting of C1 to C4 alkyl acrylates, methacrylates, and mixtures thereof, with a second member selected from the group of acrylic acid, methacrylic acid, and mixtures thereof, and an optional third member selected from the group consisting of other copolymerizable monomers, the temperature and humidity hazing are greatly and surprisingly diminished. The preferred amounts of copolymer are about 0.1 to 20 wt% based on weight of the solution, more preferably about 2 to 10 wt%, and most preferably 2.5 to 6 wt%. The copolymer has the multiple advantage of thermal and humidity haze reduction and control of mix viscosity, as well as improving weatherability. With cell casting processes, it is preferable that the copolymer be of minimum molecular weight necessary to maintain impact strength since too low molecular weight can adversely affect impact strength. A molecular weight as determined by measured intrinsic viscosity in $CH_2Cl_2$ of at least 0.10 is preferred, more preferably about 0.20. With continuous and rotational casting processes, it is preferred that the copolymer be of maximum molecular weight possible, with a molecular weight as determined by intrinsic viscosity in $CH_2Cl_2$ of at least about 0.50, with preferred viscosities about 0.90 to about 2.20.

Thiraphattaraphun et al. [27] studied the natural rubber-g-methyl methacrylate/poly(methyl methacrylate) blends by a melt mixing system. With an increase in PMMA content, the tensile strength, tear strength, and hardness increased but impact energy decreased. The mechanical properties of the blends showed considerable improvement upon the addition of the graft copolymer with a high grafting efficiency. Interfacial adhesion between the two homopolymers increased by the addition of the graft copolymer, and consequently, the mechanical properties improved. The scanning electron microscope study of the fracture surface indicated better adhesion between the components in the compatibilized system.

Nakasorn et al. [28] studied the reactive blending of maleated natural rubber (MNR) and poly(methyl methacrylate). In reactive blends of MNR/PMMA, the shear stress and shear viscosity increased until reaching the maximum at a MNR content of 60 wt%. Increasing MNRs higher than this value caused a decrease of the shear stress and viscosity. It was therefore concluded that the MNR/PMMA blends are compatible blends according to the log-additive rule. SEM micrographs were also analyzed. The decreasing sizes of dispersed PMMA domains as the maleic acid concentration increased were observed. That is, increasing levels of maleic acid caused increasing levels of chemical interaction between the MNR and PMMA phases. As a consequence, decreasing sizes of the PMMA domains dispersed in the MNR matrix were also observed.

Hinchiranan et al. [29] studied the improved properties of modified acrylic sheet via addition the grafted natural rubber. The mechanical properties of a modified acrylic sheet prepared by bulk copolymerization of methyl methacrylate and styrene were improved by the addition of a small amount of graft natural rubber (GNR). The graft copolymerization of MMA and ST onto natural rubber 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 the increase in the amount of GNR in the range of 0.5–4 parts. From the stress–strain behavior, the characteristic 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 show the relatively smooth fracture surface with relatively few small cracks. This implies that the GNR can be used as an impact modifier for acrylic plastics.

### 2.10.2 Graft Copolymerization of Natural Rubber

Arayapranee et al. [30] studied the graft copolymerization of 50/50 (w/w) styrene/methyl methacrylate mixtures onto natural rubber seed latex by using cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated $Fe^{2+}$ as a redox initiator. The effects of the process factors such as the amount of initiator, emulsifier, and chain-transfer agent, monomer-to-rubber ratio, and temperature on the grafting efficiency (GE) and grafting level (GL) are reported. Transmission electron microscopy (TEM) was used to study the morphology of the graft copolymers. It appears that the formation of graft copolymers occurs on the surface of the latex particles through a chain-transfer process.

Eawsuwan et al. [31] studied the graft copolymerization of styrene and methyl methacrylate onto natural rubber using cumene hydroperoxide and tetraethylene pentamine as a redox initiator. Statistical analysis, two-level factorial design, was used to study the influence of initiator concentration, reaction temperature, ratio of styrene to methyl methacrylate, and ratio of monomer to natural rubber on the grafting efficiency. The two-level factorial experimental design showed that initiator concentration, reaction temperature, and ratio of monomer to natural rubber had a significant effect on grafting efficiency. Reaction temperature and ratio of monomer to natural rubber had a significant effect on percentage graft copolymer. The grafted natural rubber product could be used as an impact modifier for PVC, thus, blends of the grafted natural rubber products and PVC were prepared. The mechanical properties, thermal properties, and morphology of the grafted natural rubber modified PVC were investigated as a function of grafted natural rubber content.

Suriyachai et al. [32] studied the graft copolymerization of glycidyl methacrylate and styrene onto natural rubber using cumene hydroperoxide and tetraethylene pentamine as a redox initiator. The effects of initiator and monomer concentration, reaction temperature and reaction time on grafting efficiency and monomer conversion were investigated. The optimum condition for the preparation of grafted natural rubber was found to be at the monomer concentration of 100 phr, the initiator concentration of 2.5 phr and temperature of 60°C for 10 hours. The grafted natural rubber product could be used as a compatibilizer for STR5L/PMMA blends. The mechanical properties such as tensile strength, elongation at break, tear strength, hardness and impact energy were evaluated at a function of grafted natural rubber content. The good mechanical properties of unvulcanized and vulcanized STR5L/PMMA blends were obtained at 5-10 phr of grafted natural rubber content. The mechanical properties of grafted natural rubber/PMMA blends were also studied. The tensile strength, tear strength and hardness increased with increasing of PMMA content. The tensile fracture surface examined by scanning electron microscopy showed that the grafted natural rubber acted as an interfacial agent and gave a good adhesion between the two phases of blend.

Kochthongrasamee et al. [33] studied the effects of redox initiator on graft copolymerization of methyl methacrylate onto natural rubber. Three different types of redox initiator were cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA), tert-butyl hydroperoxide (TBHPO)/TEPA, and potassium persulfate ($K_2S_2O_8$)/ sodium thiosulfate ($Na_2S_2O_3$). The optimum reaction condition for each redox initiator on grafting of natural rubber was studied. CHPO dissolved very well in the oil phase, and TBHPO dissolved moderately in the oil phase as well. Each could interact with TEPA in aqueous phase. CHPO was found to give a higher grafting efficiency. $K_2S_2O_8$ / $Na_2S_2O_3$ was water-soluble initiator. It was found that the percentages of grafting on methyl methacrylate on natural rubber latex initiated by CHPO, TBHPO, and $K_2S_2O_8$ are 84.4, 74.5, and 61.1, respectively, which are in good agreement with percentages of poly(methyl methacrylate) formed in the aqueous phase as 7.2, 12.0, and 17.9 by CHPO, TBHPO, and $K_2S_2O_8$. This research concludes that CHPO/TEPA was a good redox system for grafting of vinyl monomers onto natural rubber latex.

### 2.10.3 Hydrogenation of Natural Rubber

Charmondusit et al [34] studied the homogeneous hydrogenation of *cis*-1,4-polyisoprene catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ and $[Ir(cod)(PCy_3)(py)]PF_6$. Both catalysts were very effective for hydrogenation of isoprene rubbers leading to high level of hydrogenation ( > 95% hydrogenation) which could be obtained within 20 minutes depending on conditions. This study showed that the hydrogenation of *cis*-1,4-polyisoprene in the presence of $OsHCl(CO)(O_2)(PCy_3)_2$ had a first order dependence on the carbon-carbon double bond concentration. A second order behavior with respect to hydrogen concentration at low hydrogen concentration shifted to a zero order dependence as the hydrogen pressure was increased. The apparent activation energy over the temperature range of 115-140 °C was calculated as 109.3 kJ/mol. The kinetic study of the hydrogenation of *cis*-1, 4-polyisoprene catalyzed by $[Ir(cod)(PCy_3)(py)]PF_6$ differed from the osmium complex with respect to the effect of hydrogen pressure. The hydrogenation catalyzed by the iridium system was first order with respect to hydrogen pressure at low catalyst concentration but at high catalyst concentration tended to produce dimerization or trimerization of the catalyst, which decreased the catalytic activity. An apparent activation energy for hydrogenation in the presence of the iridium catalyst of 79.8 kJ/mol was obtained. The relative viscosity of the hydrogenated rubber catalyzed by both catalysts indicated that no side reaction such as degradation or cross linking occurred over the range of experimental conditions used. Natural rubber could be quantitatively hydrogenated using $OsHCl(CO)(O_2)(PCy_3)_2$ in the presence of acid added. It was found that the presence of a strong carboxylic acid or that of a higher coordinating power reaction solvent increased the catalytic activity for the hydrogenation process.

Hinchiranan et al. [35] studied the kinetics of natural rubber using the 5d metal catalysts, $OsHCl(CO)(O_2)(PCy_3)_2$ and $[Ir(cod)(PCy_3)(py)]PF_6$. The kinetic results indicated that the hydrogenation of NR catalyzed by both catalysts exhibited a first-order behavior with respect to catalyst concentration and an inverse behavior dependence on rubber concentration due to impurities present in the rubber. A first order behavior with respect to hydrogen concentration at low concentration shifted to a zero order dependence as the hydrogen pressure was increased for NR hydrogenation catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$. In the case of NR hydrogenation catalyzed by $[Ir(cod)(PCy_3)(py)]PF_6$, a first order behavior with respect to hydrogen concentration was reported. The apparent activation energies for NR hydrogenation catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ and $[Ir(cod)(PCy_3)(py)]PF_6$ were 122.8 and 75.6 kJ/mol, respectively. It was showed that reaction was under chemical controlled. The addition of some acids and certain nitrogen containing materials exhibited an effect on the hydrogenation range. The thermal stability of NR was improved by hydrogenation without affecting its glass transition temperature.

Mahittikul et al. [36] studied the hydrogenation of natural rubber latex (NRL) via three systems: homogenous catalytic hydrogenation, noncatalytic hydrogenation and diimide hydrogenation. For the homogenous catalytic hydrogenation, the kinetic results indicated that the hydrogenation of NRL catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ and $[Ir(cod)(PCy_3)(py)]PF_6$ exhibited a first-order behavior with respect to catalyst concentration and an inverse behavior depend on rubber concentration due to impurities present in the rubber. Noncatalytic hydrogenation using *p*-toluenesulphonylhydrazine (*p*-TSH) as reducing agent was found that the degree of hydrogenation increased with increasing ratio of p-TSH/C=C. For diimide hydrogenation, the degree of hydrogenation was increased with increasing effective diimide amount. The thermal stability of NR was improved by hydrogenation. In addition, the mechanical properties and ozone resistance of vulcanized HNR blends were also investigated.

# CHAPTER III

# EXPERIMENTAL

## 3.1 Chemicals

1. Natural rubber latex, high ammonia : Tavorn Rubber Product Industry Co., Ltd.
2. STR 5L (Standard Thai Rubber 5L) : Tavorn TTR Industry Co., Ltd.
3. Styrene monomer, commercial grade : Pan Asia Industrial Co.,Ltd.
4. Methyl methacrylate, commercial grade : Pan Asia Industrial Co.,Ltd.
5. Benzoyl peroxide : Pan Asia Industrial Co.,Ltd.
6. 2,2'-Azobis-(2,4-dimethylvaleronitrile) : Pan Asia Industrial Co.,Ltd.
7. Sodium hydroxide : Merck
8. Potassium hydroxide, AR grade : APS Ajex Finechem
9. Sodium dodecyl sulfate, AR grade : Fischer Scientific
10. Isopropanol, AR grade : Fischer Scientific
11. Cumene hydroperoxide : Fluka
12. Tetraethylene pentamine : Fluka
13. Formic acid, AR grade : Fischer Scientific
14. Light petroleum ether, AR grade : Fischer Scientific
15. Acetone, AR grade : Fischer Scientific
16. Methyl ethyl ketone, AR grade : Fischer Scientific
17. Toluene, AR grade : Fischer Scientific
18. 3-Chloropropionic acid : Aldrich
19. Nitrogen gas 99.9% : Linde

20. Hydrogen gas 99.99% : Praxair
21. Chloroform-d for NMR : Aldrich
22. Chloroform, AR grade : BHD

## 3.2 Glasswares

1. 4-Necked round bottom reactor, 500 cm$^3$ capacity
2. Condenser
3. Nitrogen gas tube
4. Soxhlet extraction apparatus
5. Iodine flask
6. Round bottom flask
7. Glass mold
8. Other general laboratory glassware

## 3.3 Equipments

1. Parr reactor : Parr 4843
2. Fourier-Transform Infrared Spectrometer : Thermo 470 FT-IR spectroscopy
3. Nuclear Magnetic Resonance Spectrometer : Bruker ACF 200 MHz
4. Scanning Electron Microscope : JEOL model JSM-5800 LV
5. Impact testing machine : Impact tester GOTECH GT 7045
6. Hardness testing machine : Rockwell Hardness Tester 4150 AR
7. Universal testing machine : LLOYD Instrument LR 10K Plus
8. Color measurement : Gretagmacbeth Instrument color i5

## 3.4 Grafted Natural Rubber Preparation

### 3.4.1 Purification of Monomer

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

The methyl methacrylate monomer (b.p. 98 °C/760 mmHg) containing a trace amount of hydroquinone as inhibitor was purified by following the above procedure as for styrene monomer purification and distilled under reduced pressure (40 °C, 20 mmHg). The purified methyl methacrylate monomer was stored in the refrigerator.

### 3.4.2 Preparation of Grafted Natural Rubber

The grafted copolymer of styrene (ST) and methyl methacrylate (MMA) onto natural rubber (NR) was prepared by emulsion copolymerization. The equipment setup is shown in Figure 3.1

The high ammonia natural rubber (HANR) latex (50 g, DRC 60%) was placed in a round bottom reactor along with 100 ml of distilled water. Potassium hydroxide (1 phr) was added a buffer, and sodium dodecyl sulfate (1 phr) as an emulsifier was then added while stirring. The mixture was deoxygenated by bubbling the nitrogen gas for approximately 15 min at room temperature. The stabilizer, isopropanol (10 phr) was added after 15 min of stirring. The monomer mixture (100 phr) of 50% styrene and 50% methyl methacrylate was then added, continually while stirring for 30 min to allow the latex particles to attain swelling. The mixture was warmed up to reaction temperature, 0.5 phr of the initiator (CHPO) was then added. After 15 min of mixing, 0.5 phr of the ammine activator (10% aqueous solution of TEPA) was added. The bipolar redox initiating system was employed at a ratio 1 : 1 (CHPO : TEPA). The reaction was then allowed to proceed for 8 h under continuous stirring to complete the polymerization and then the reaction was stopped. The product latex was discharged into boiling water containing 5% formic acid and the polymer product precipitated. The gross polymer was recovered and dried to a constant weight in vacuum pump. The standard recipe used for graft copolymerization is shown in Table 3.1

**Table 3.1** Standard recipe used for graft copolymerization.

| Ingredients | Quantities |
|---|---|
| Natural rubber latex (60% DRC) | 50 g |
| Water | 100 ml |
| Stabilizer (isopropanol) amount | 3 g |
| Buffer (potassium hydroxide) amount | 0.3 g |
| Emulsifier (sodium dodecyl sulfate) amount | 0.3 g |
| Redox initiator (CHPO : TEPA = 1:1) amount | 0.3 g |
| Styrene amount | 11.25 g |
| Methyl methacrylate amount | 11.25 g |
| Reaction temperature | 65 °C |

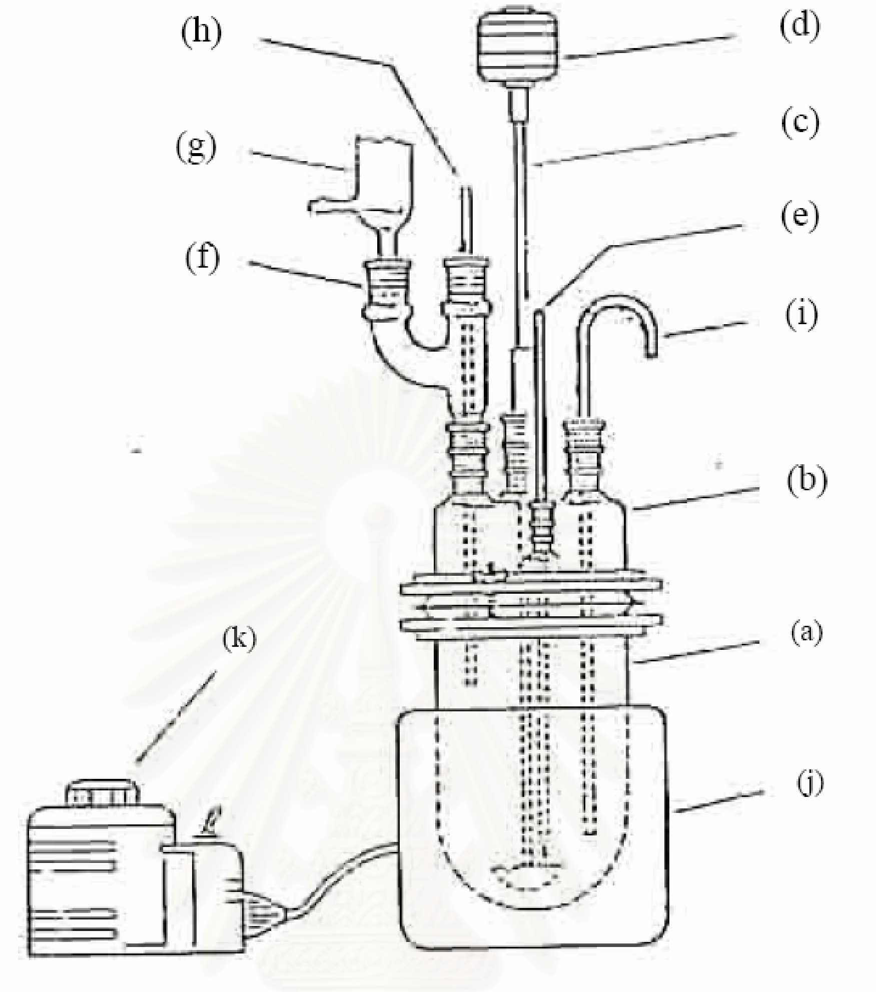


**Figure 3.1** Apparatus for emulsion graft copolymerization of styrene and methyl methacrylate onto natural rubber latex.

| | |
|---|---|
| (a) reaction kettle bottom | (g) condenser |
| (b) reaction kettle top | (h) nitrogen-inlet tube |
| (c) stainless steel stirrer | (i) sampling tube |
| (d) air motor | (j) water bath |
| (e) thermometer | (k) variable transformer |
| (f) adaptor | |

## 3.5 Determination of Properties of Grafted Natural Rubber

### 3.5.1 Determination of Monomer Conversion and Grafting Efficiency

The grafted natural rubber latex was discharged into boiling water containing 5% formic acid and the polymer product was precipitated. The gross polymer was recovered and dried to a constant weight in vacuum pump. The degree of conversion was determined by the percentage increase of rubber weight. The details of all calculations are shown in Appendix B.

The amount of grafted natural rubber, free natural rubber, free homopolymers, and free copolymer in the product could be determined by soxhlet extraction. The free natural rubber was extracted by light petroleum ether (60-80 °C) for 24 h, while free homopolymers and free copolymer was extracted in methyl ethyl ketone (MEK)/acetone (50 : 50 (v/v)) mixture for 24 h. The data obtained from all steps were used to calculate the grafted natural rubber and grafting efficiency. The details of all calculations are shown in Appendix B.

### 3.5.2 Characterization of Grafted Natural Rubber Product

After the soxhlet extraction, the grafted natural rubber (NR-g-ST/MMA) was characterized. The sample after the extraction by a MEK/acetone (50 : 50 (v/v)) mixture was analyzed by fourier-transform infrared spectroscopy (FT-IR). Spectra of grafted natural rubber were obtained by using the Thermo 470 FT-IR spectroscopy. The grafted natural rubber was dissolved in toluene (2% (w/v)) and then casted as a film on the NaCl cell

## 3.6 Hydrogenated Natural Rubber Preparation

Hydrogenation reactions were carried out in a 2 liter-Parr reactor (Parr 4843). The amount of 612.75 µM of STR5L rubber (solid rubber) was placed in flask with 1 liter of toluene, and shaken in the dark for 2 days. Then, the mixture was transferred into the reactor and the flask was rinsed with 180 ml of toluene which was also added to the reactor. The $OsHCl(CO)(O_2)(PCy_3)_2$ as a catalyst was prepared according to the method in Appendix C. The catalyst (78.74 µM) was added into a small glass bucket and placed in the catalyst addition port. 0.4822 g of 3-chloropropionic acid used to increase the rate of hydrogenation was dissolving in 20 ml of toluene and then poured into the mixture in the reactor. The reactor was then assembled. The system was degassed with hydrogen gas through the rubber solution by venting and recharging for 10 times at 200 psig without agitation. Then the mixture in the reactor was degassed by bubbling hydrogen gas through it for 45 min at 200 psig with 200 rpm agitation rate at room temperature. The reactor was then heated to 140 °C with agitation at 600 rpm. When the temperature of the reactor stabilized, the hydrogenation reaction was initiated by charging the catalyst into the mixture at 400 psig. After 15 min of reaction time, the reaction was stopped. The hydrogenated product was isolated by precipitation with ethanol, filter, and dried under vacuum. The standard recipe used for hydrogenation is shown in Table 3.2

**Table 3.2** Standard recipe used for hydrogenation.

| Ingredients | Quantities |
|---|---|
| STR5L rubber | 50 g |
| Toluene | 1200 ml |
| Catalyst ($OsHCl(CO)(O_2)(PCy_3)_2$) amount | 0.0800 g |
| Accelerator (3-chloropropionic acid) amount | 0.4822 g |
| Reaction temperature | 140 °C |
| Reaction pressure | 400 psig |
| Reaction time | 15 min |

## 3.7 Characterization of the Hydrogenated Natural Rubber

### 3.7.1 Fourier-Transform Infrared Spectroscopic Analysis

Infrared spectra were obtained on the Thermo 470 FT-IR spectroscopy. The samples were prepared by casting as a film on the NaCl cell.

### 3.7.2 Nuclear Magnetic Resonance (NMR) Spectroscopic Analysis

The final degree of olefin conversion was investigated by NMR spectroscopic analysis. The details of olefin conversion calculations are shown in Appendix D. $^1$H-NMR spectra were obtained on the Bruker ACF 200 MHz. The samples of hydrogenated natural rubber were dissolving 0.01 g of rubber in $CDCl_3$.

## 3.8 Procedure of Styrene-Methyl Methacrylate Copolymer Sheet

The copolymer sheet of methyl methacrylate (MMA) and styrene (ST) containing modified natural rubber were prepared by bulk copolymerization using casting process.

The modified natural rubber was weighed and dissolved in the mixture of ST and MMA monomer solution. The mixture was stirred overnight to obtain the homogeneous solution. 0.1 wt% benzoyl peroxide (BPO) was added as a first initiator while stirring. The mixture was heated up to 115 °C, the prepolymerization of MMA and ST with modified natural rubber was performed under continuous stirring. After the mixture was appropriately viscous, it was cooled down to room temperature. Then, 0.03 wt% 2,2'-azobis-(2,4-dimethylvaleronitrile) (ABVN) was added as a second initiator while stirring. After the bubble of the mixture was removed by vacuum pump, the mixture was filled into glass mold and cured in a water bath at 60 °C until the sheet hardened. In order to complete polymerization, the sheet was 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. The sheet was cut into the standard specimens according to the ASTM test method. The complete experiment procedure is summarized in Figure 3.2. The standard recipe and conditions used for bulk copolymerization of MMA and ST with modified rubber is shown in Table 3.3.

**Table 3.3** Standard recipe and conditions used for bulk copolymerization of MMA and ST with modified rubber.

| Ingredients | Quantities |
|---|---|
| ST/MMA ratio | 10/90, 20/80, 30/70, 40/60, 50/50 |
| Grafted natural rubber | 1, 2, 3, 4, 5 |
| Hydrogenated rubber | 0.25, 0.5, 1, 2, 3, 4 |
| Natural rubber | 0.5, 1, 2, 3, 4 |
| First initiator (BPO) amount | 0.1 g |
| Prepolymerization temperature | 115 °C |
| Second initiator (ABVN) amount | 0.03 g |
| Cured temperature | 60 °C |
| Oven temperature | 120 °C |

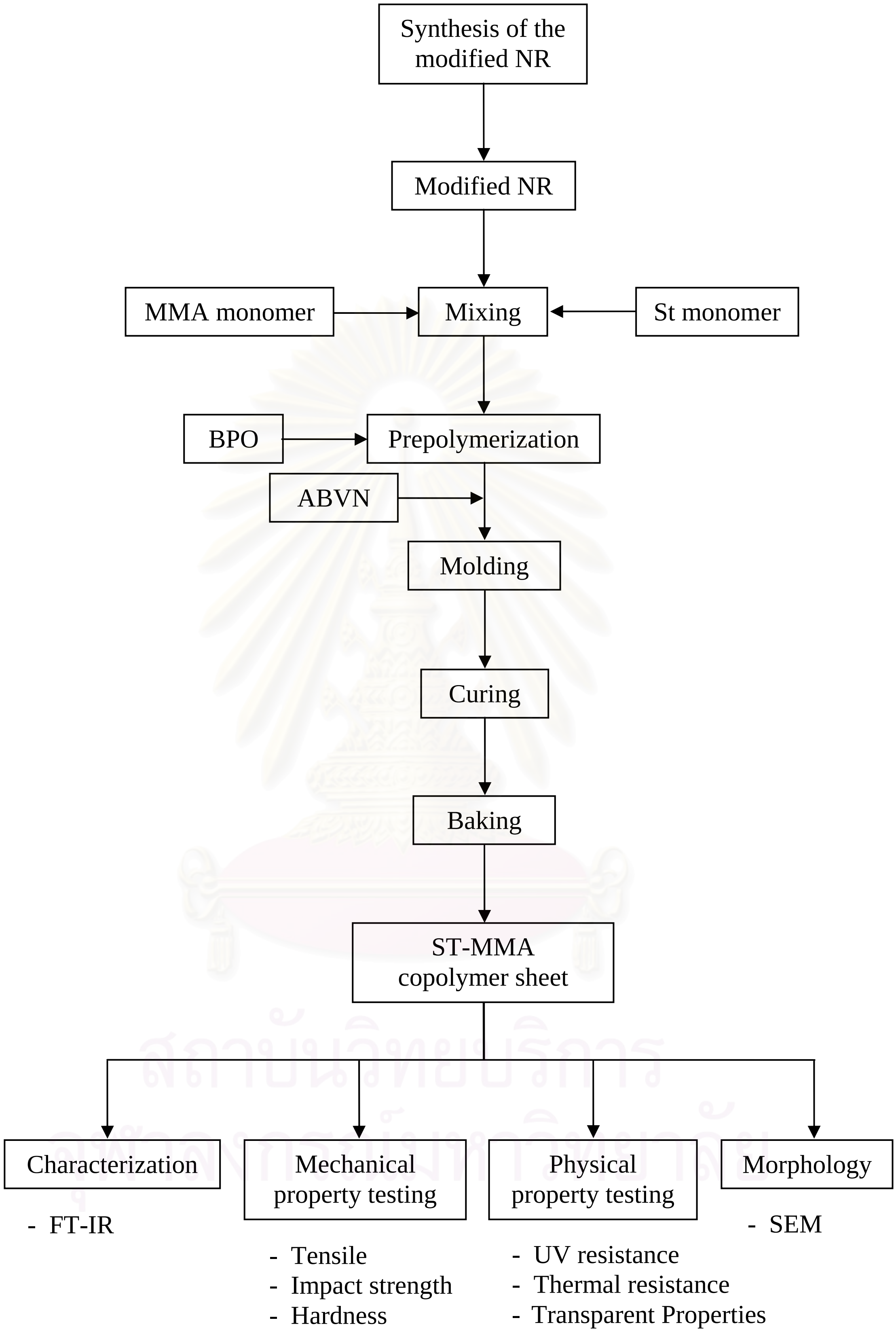


**Figure 3.2** Overall schematic experimental process.

## 3.9 Characterization of Copolymer Sheet by FT-IR

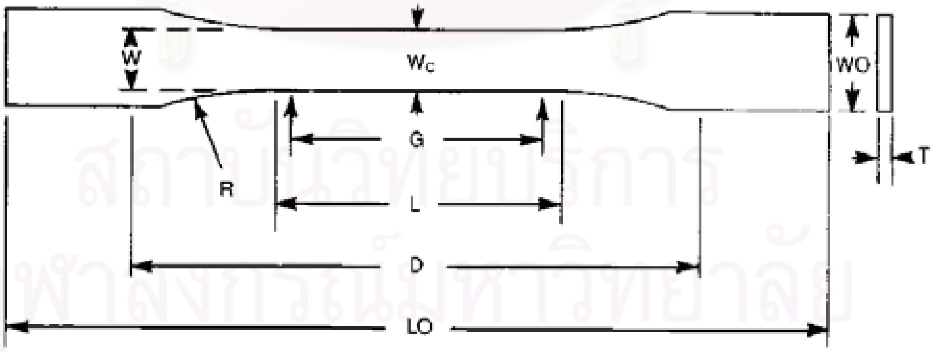
Infrared spectra were obtained on the Thermo 470 FT-IR spectroscopy. The samples of FT-IR analyses were prepared by dissolving the copolymer sheet in chloroform (2% (w/v)) and then casting as a film on the NaCl cell.

## 3.10 Mechanical Testing

The mechanical properties of the styrene-methyl methacrylate copolymer sheet, ST-MMA copolymer sheet with natural rubber, ST-MMA copolymer sheet with grafted natural rubber, and ST-MMA copolymer sheet with hydrogenated natural rubber were measured by following the ASTM test methods.

### 3.10.1 Tensile Properties (ASTM D 638) [37]

Tensile properties of the samples were measured at 25 °C and humidity of 60% using dumbbell-shaped test pieces (Type I) as illustrated in Figure 3.3. The specimens were cut from a 3.0 mm thick sheet. The testing were performed on a Universal testing machine (LLOYD Instrument LR 10K Plus) with a crosshead speed of 500 mm/min.



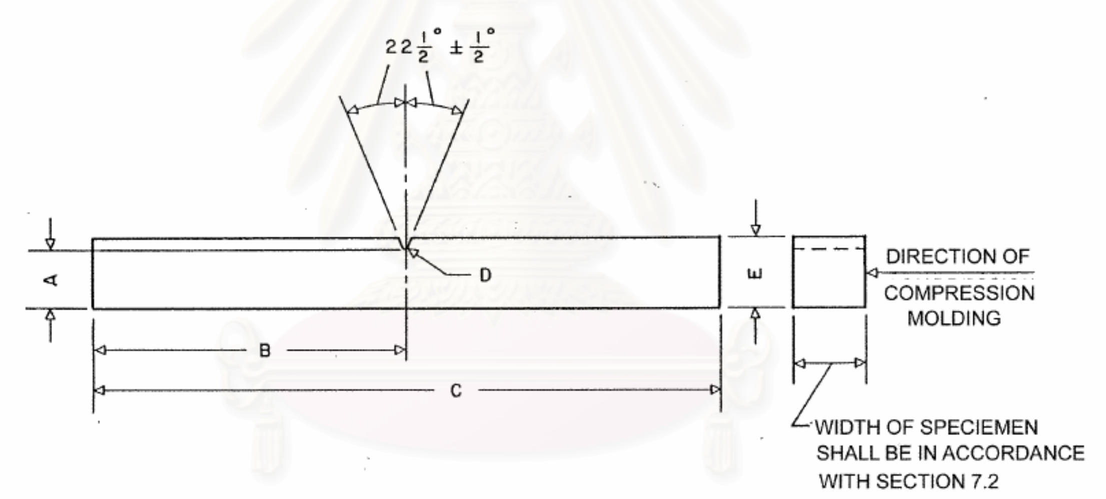
W : 13 mm WO : 19 mm G : 50 mm R : 76 mm

L : 57mm LO : 165 mm D : 1155 mm T : 4 mm or under

**Figure 3.3** Schematic diagram of tensile test specimen (type I) [37].

### 3.10.2 Impact Strength (ASTM D 6110) [38]

The test specimen conformed to the dimensions and geometry of Figure 3.4. The machine used in the present investigation was Izod-Charpy Impact Tester (Impact tester GOTECH GT 7045). The width of each specimen was measured in the region of the notch with a micrometer caliper and recorded its average width along with its identifying marking. The test specimen was put in a horizontal position so that it would be impacted edgewise at its center on the face opposite the notch for notched specimens. The breaking energy of the specimen was estimated and a pendulum of suitable energy was selected. The pendulum was released and the excess energy remaining in the pendulum was recorded after breaking the specimen, together with a description of the appearance of a broken specimen. The average impact energy was calculated in the group of specimens.



Unit : mm

A : 10.16 ± 0.05

B : 32.00 max, 31.50 min

C : 63.50 max, 63.30 min

D : 0.25 ± 0.25

E : 12.70 ± 0.05

**Figure 3.4** Dimensions of simple beam, charpy type, impact test specimen [38].

### 3.10.3 Hardness (ASTM D 785) [39]

The test specimen had a minimum thickness of 6 mm. The specimen was a piece cut from a molding or sheet. Care was taken that the test specimen had parallel flat surface to ensure good seating on the anvil and thus avoid the deflection that would be caused by poor contact. The specimen was at least 25 mm square if cut from sheet stock. The minimum width was 13 mm plus the width of the indentation resulting from the conduct of a test using the chosen indenter.

The M Rockwell scale having 10 kg of minor load and 100 kg of major load was chosen to test the acrylic. The Rockwell hardness values were reported by a letter to indicate the scale used and a number to indicate the reading. At least five hardness tests were made on isotropic materials.

## 3.11 Physical Testing

### 3.11.1 Transparent Properties

Transparent properties were obtained by using color measurement (Gretagmacbeth Instrument color i5).

### 3.11.2 Ultraviolet Resistance

The test specimens for Ultraviolet resistance had 5 cm wide and 10 cm long and were measured color by color measurement (Gretagmacbeth Instrument color i5). Then they were placed in the Ultraviolet box with the UV wavelength at 320 nm for 4 days and measured color to compare the color change with the color of specimens before treated.

### 3.11.3 Thermal Resistance

The test specimens for thermal resistance had 5 cm square and were measured color by color measurement (Gretagmacbeth Instrument color i5). Then they were placed in an oven at 165 °C for 25 min and measured color to compare the color change with the color of specimens before treated.

### 3.12 Morphological Study

The scanning electron microscope (SEM) was used to investigate the fracture surface of ST-MMA copolymer sheet, ST-MMA copolymer sheet with grafted natural rubber, and ST-MMA copolymer sheet with hydrogenated natural rubber from the tensile properties test. Samples for SEM were mounted on a SEM stub using a double-side tape and the fracture specimens were coated with gold. The SEM (JEOL model JSM-5800 LV) was operated at 15 kV.

# CHAPTER IV

# RESULTS AND DISCUSSION

The modified natural rubbers were prepared by the graft copolymerization of styrene (ST) and methyl methacrylate (MMA) onto rubber and the hydrogenation of rubber. The graft copolymer was performed by emulsion copolymerization with redox system of cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) as initiator. The grafting efficiency and percentage graft copolymer of the graft product were determined. The graft product was also characterized by Fourier-Transform Infrared Spectrometer (FT-IR). Hydrogenation of rubber catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ was performed. The hydrogenated product was used to determine the degree of hydrogenation and characterized by Nuclear Magnetic Resonance Spectrometer (NMR) and FT-IR. The modified natural rubber was added in the bulk copolymerization of methyl methacrylate and styrene using casting process. The influential factors of the ST monomer content and rubber content were investigated. The mechanical properties, physical properties and morphology were also investigated.

## 4.1 Preparation of the Graft Natural Rubber

### 4.1.1 Properties of Natural Rubber Latex

The high ammonia natural rubber (HANR) latex was obtained from Tavorn Rubber Product Industry Co., Ltd. The dry rubber content and the total solid content of latex were 61.4% and 61.7%, respectively. The typical properties of HANR are shown in Table 4.1.

**Table 4.1** Typical properties of high ammonia natural rubber latex.

| Properties | Value |
|---|---|
| Total Solids Content, % | 61.7 |
| Dry Rubber Content, % | 61.4 |
| Non Rubber Solids, % | 1.59 |
| Ammonia Content (on Total Weight), % | 0.70 |
| Ammonia Content (on Total Phase), % | 1.83 |
| pH Value | 10.4 |
| KOH Number | 0.566 |
| Volatile Fatty Acid Number (V.F.A.) | 0.0165 |
| Mechanical Stability Time @ 55 %TS (secs.) | 710 |
| Specific Gravity at 25 °C | 0.942 |
| Magnesium Content (on Solids), ppm | 33 |
| Viscosity on 60 %TS (Spindle #1 Speed 60 rpm) | 87.4 |

### 4.1.2 Properties of Grafted Natural Rubber

The grafted natural rubber (GNR) was prepared by emulsion graft copolymerization process. The optimum reaction condition was 75 phr of monomer, containing ST:MMA ratio of 1:1, 1 phr of sodium dodecyl sulfate (SDS) as an emulsifier, 10 phr of isopropanol as a stabilizer, 1 phr of potassium hydroxide as a buffer, and 1 phr of redox initiator, containing CHPO:TEPA ratio of 1:1 at 65 °C for 8 h [31]. The GNR product was extracted by light petroleum ether (LPE) for 24 h to remove free NR and then dried to constant weight. To remove free copolymer and free homopolymers, the residue was extracted in a methyl ethyl ketone (MEK)/acetone (50:50 (v/v)) mixture. The data obtained from all steps were used to calculate the GNR properties such as percentage conversion, grafting efficiency (GE), and grafting properties. The details of all calculations are shown in Appendix B. The properties of GNR are shown in Table 4.2.

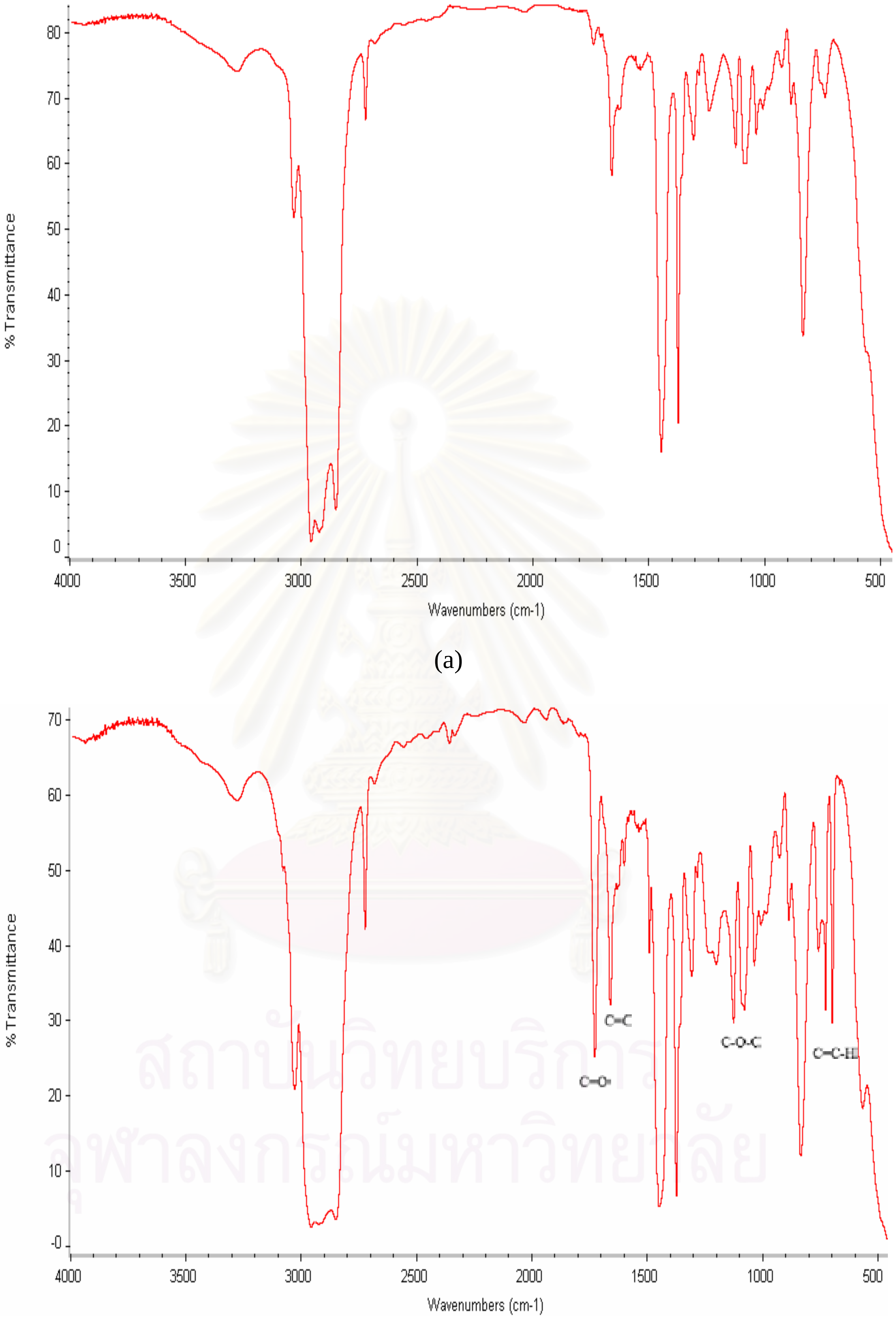
**Table 4.2** Properties of grafted natural rubber.

| **Properties** | **%** |
|---|---|
| Total conversion (%) | 25.7 |
| Grafting efficiency (%) | 59.3 |
| Grafting properties | |
| Grafted natural rubber (%) | 66.1 |
| Free natural rubber (%) | 26.9 |
| Free copolymers (%) | 7.00 |

### 4.1.3 Characterization of Grafted Natural Rubber Using FT-IR Spectroscopy

The grafted natural rubber product consisted of free NR, free copolymers and grafted copolymers. Ungrafted poly(methyl mathecrylate) (PMMA), polystyrene (PS), and Poly(styrene-*co*-methyl methacrylate) (P(ST/MMA)) are referred to as free copolymers. Grafted copolymers are referred to as NR-g-PMMA, NR-g-PS, and NR-g-P(ST/MMA).

The functional group in the natural rubber and the grafted natural rubber were indentified by FT-IR spectroscopy. Figure 4.1a and 4.1b show the FT-IR spectra in the region of 4000-500 cm$^{-1}$ for natural rubber and grafted natural rubber, respectively. The FT-IR spectrum of natural rubber exhibits the characteristic absorption band of C=C stretching vibration at 1680 cm$^{-1}$, the C–H vibration at 2997, 1473, and 1376 cm$^{-1}$, and the C=C bending vibration at 853 cm$^{-1}$. The new peaks in FT-IR spectrum of grafted natural rubber are the absorption bands of C=O stretching vibration of MMA at 1736 cm$^{-1}$, the C=C stretching of aromatic ring of ST at 1510 cm$^{-1}$, and the C=C-H bending of aromatic ring of ST at 787 and 695 cm$^{-1}$. This confirms the occurrence of grafting of MMA and ST onto natural rubber.



(a)

(b)

**Figure 4.1** FT-IR apectra of (a) NR and (b) GNR.

## 4.2 Preparation of Hydrogenated Natural Rubber

### 4.2.1 Properties of Standard Thai Rubber 5L (Solid Rubber)

The Standard Thai Rubber 5L (STL 5L) was obtained from Tavorn TTR Industry Co., Ltd. The typical properties of STR 5L are shown in Table 4.3.

**Table 4.3** Typical properties of Standard Thai Rubber 5L.

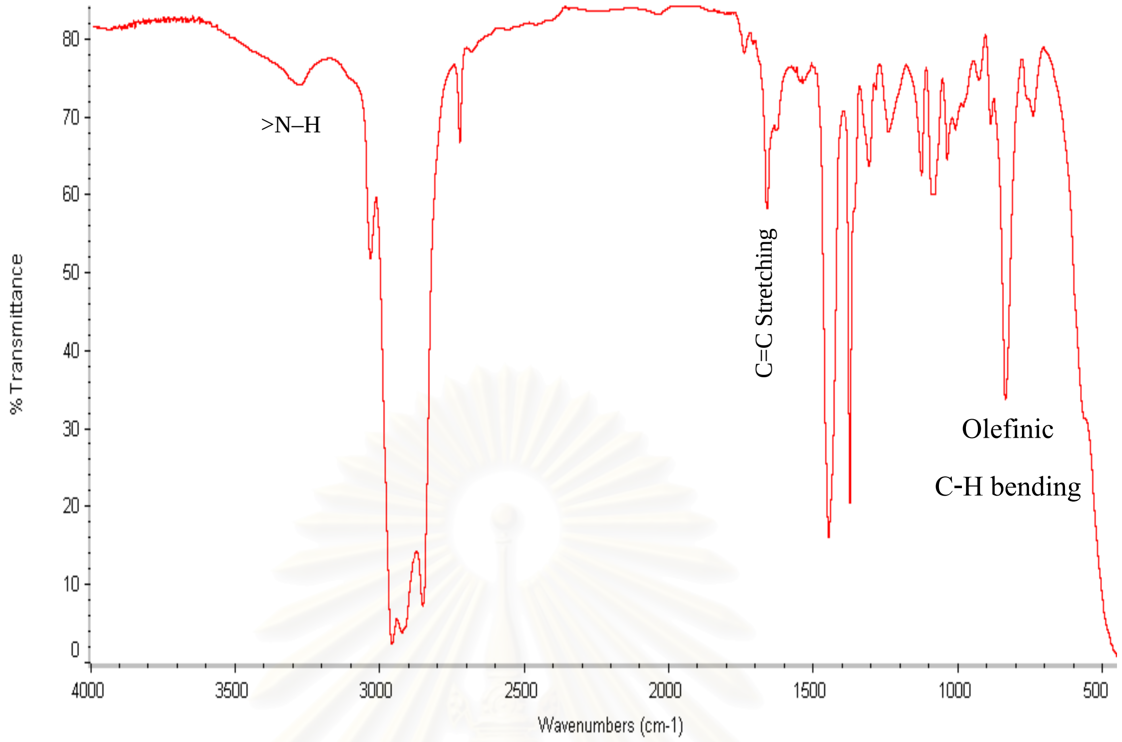
| Properties | Value |
|---|---|
| Dirt (max.) %wt. | 0.016 |
| Ash (max.) %wt. | 0.230 |
| Nitrogen (max.) %wt. | 0.420 |
| Volatile Matter (max.) %wt. | 0.625 |
| Initial Plasticity | 42.3 |
| PRI Index | 83.4 |
| Colour Lovibond Scale (indivedual value, max.) | 6.9 |
| Mooney Viscosity | 90.7 |

### 4.2.2 Characterization of Hydrogenated Natural rubber

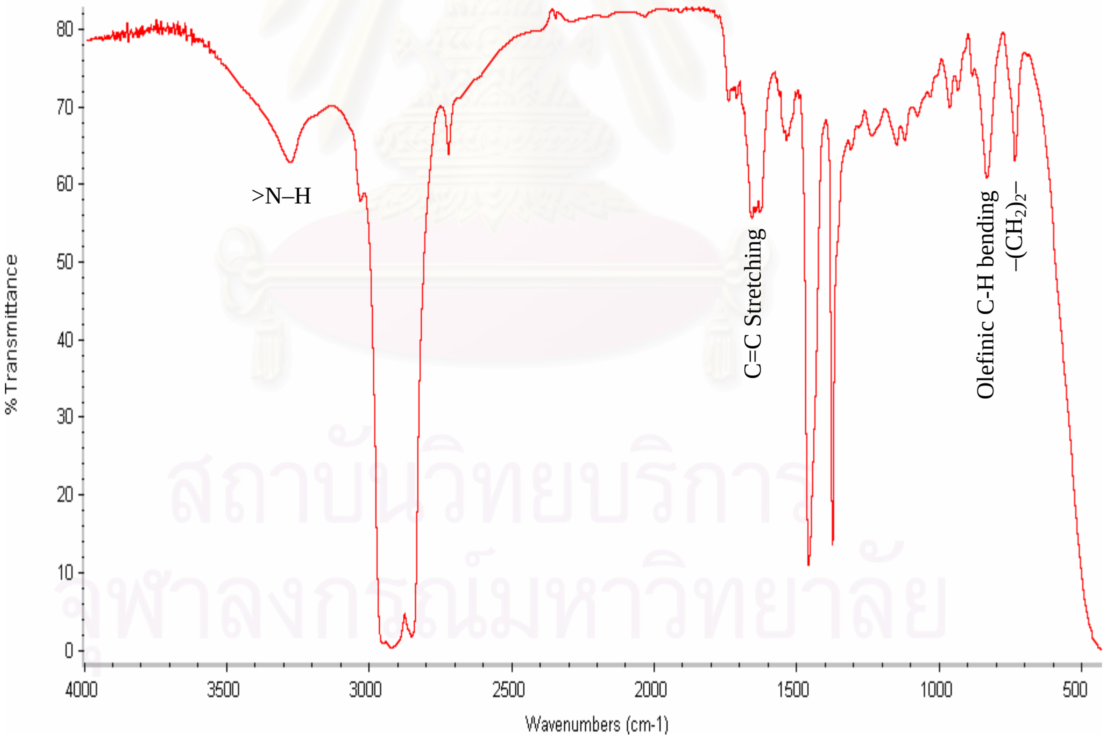
The hydrogenated natural rubber (HNR) was prepared by hydrogenation of STR 5L using $OsHCl(CO)(O_2)(PCy_3)_2$ as a catalyst. The optimum reaction condition was 612.75 mM of STR 5L, 78.74 µM of $OsHCl(CO)(O_2)(PCy_3)_2$ at 140 °C and 400 psig of $H_2$ pressure for 15 min [22]. The HNR product was analyzed by FT-IR and $^1$H-NMR.

#### 4.2.2.1 Characterization using FT-IR Spectroscopy

The structure of HNR is similar to the structure of an alternating ethylene-propylene copolymer. Figure 4.2a and 4.2b show the FT-IR spectra in the region of 4000-500 cm$^{-1}$ for NR and HNR, respectively. The FT-IR spectrum of HNR exhibited the characteristic absorption band of C=C stretching at 1660 cm$^{-1}$ and the olefinic C-H bending decreased while the intensity of the characteristic absorption band of $–(CH_2)_2–$ at 735 cm$^{-1}$ increased. For NR and HNR with impurities (amino acid), the weak transmittance bands at 3280 cm$^{-1}$ and 1530 cm$^{-1}$ which are



(a)



(b)

**Figure 4.2** FT-IR spectra of (a) NR and (b) HNR.

characteristic vibrations of >N–H and >N–C=O remained after the hydrogenation process.

#### 4.2.2.2 Characterization using NMR Spectroscopy

Figure 4.3a and 4.3b present a comparison of the $^1$H-NMR spectra of NR and HNR. The characteristic $^1$H-NMR signal of $CH_3$ at 1.7 ppm, $–CH_2–$ at 2.1 ppm, and olefinic protons at 5.1 ppm decreased and the new signals, saturated $–CH_3$ at 0.8 ppm and $–CH_2–$ at 1.3 ppm, were observed after the hydrogenation process.

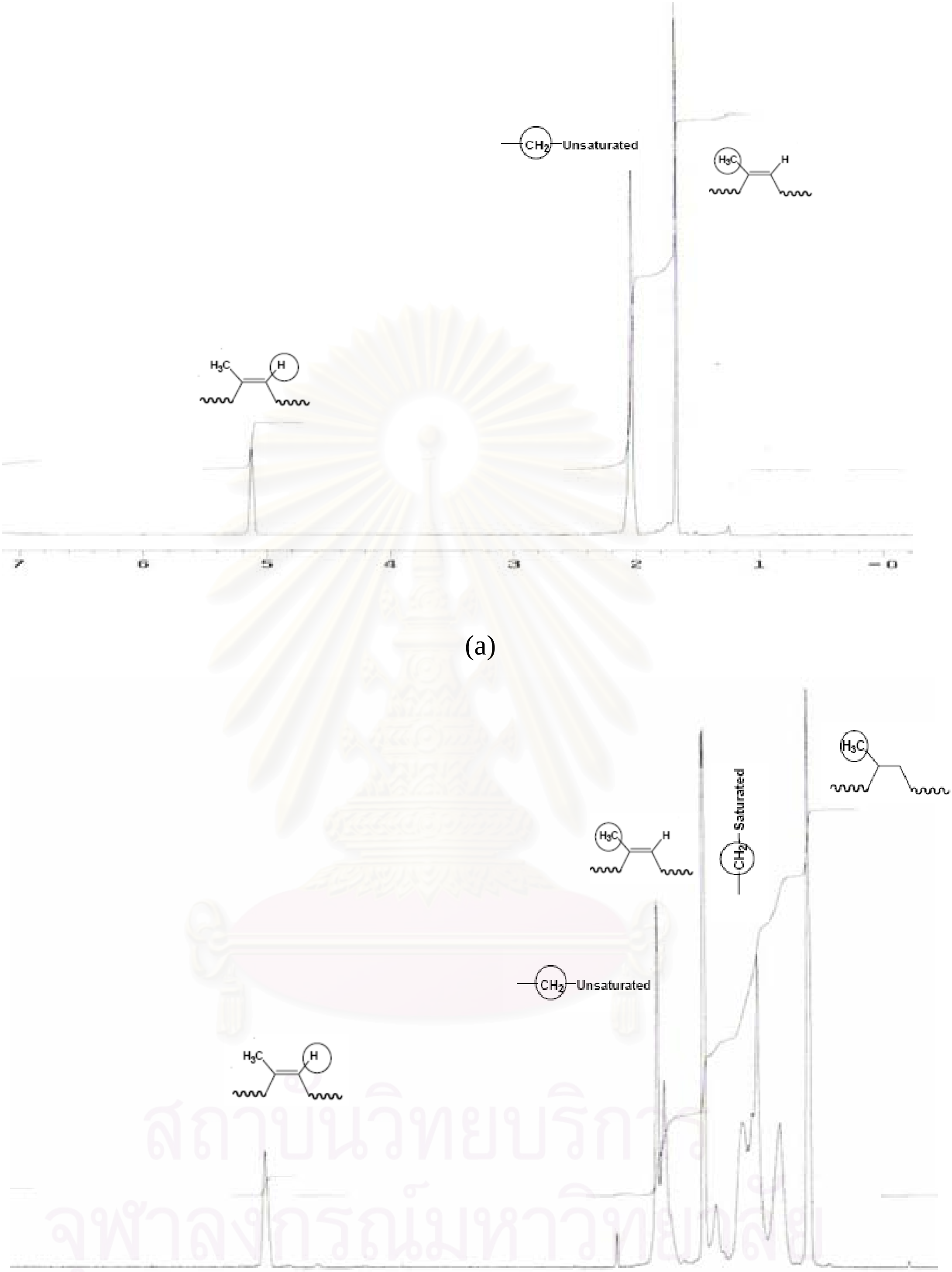
The $^{13}$C-NMR spectra of NR before and after hydrogenation process are shown in Figure E (Appendix E). The peaks at 135.3 and 125.1 ppm, which are assigned for $C_{\alpha\gamma}$, –CH–, $C_{\beta\beta}$ and $–CH_3$ carbons, respectively were observed on the HNR $C^{13}$-NMR spectrum [40].

### 4.2.3 Degree of Hydrogenation

The final degree of hydrogenation could be calculated using $^1$H-NMR spectroscopy from the peak area of olefinic protons at 5.1 ppm and the summation of peak areas of the saturated protons between 0.8-2.0 ppm as described in Appendix D. Table 4.4 shows the effect of reaction time on the hydrogenation degree of NR. The degree of hydrogenation increased with increasing reaction time.

**Table 4.4** Effect of reaction time on degree of hydrogenation (612.75 mM of STR 5L, 78.74 µM of $OsHCl(CO)(O_2)(PCy_3)_2$ at 140 °C and 400 psig of $H_2$ pressure).

| Expt. | Reaction time (min) | Degree of hydrogenation (%) |
|---|---|---|
| 1 | 15 | 56.4 |
| 2 | 30 | 70.6 |
| 3 | 60 | 85.8 |
| 4 | 120 | 93.9 |
| 5 | 180 | 97.4 |



(a)

(b)

**Figure 4.3** $^1$H-NMR spectra of (a) NR and (b) HNR.

## 4.3 Preparation of ST-MMA Copolymer Sheet Containing Modified Natural Rubber

In this section, the study of bulk copolymerization of methyl methacrylate monomer and styrene monomer containing the modified natural rubber, such as the grafted natural rubber (59.3% GE) and hydrogenated natural rubber (56.4% degree of hydrogenation), by casting process and using benzoyl peroxide (BPO) and 2,2'-azobis-(2,4-dimethylvaleronitrile) (ABVN) as initiators is described. The effect of styrene monomer content and modified NR content on the modified ST-MMA copolymer sheet preparation was investigated. The appropriate condition was found.

### 4.3.1 Effect of Styrene Monomer Content on Preliminary Preparation of MMA and ST Solution with Modified Natural Rubber

The effect of the ST monomer content on the preliminary preparation of MMA and ST monomer solution with GNR and HNR are shown in Table 4.5 and Figure 4.4-4.5. The parameters of the preliminary preparation are as follows:

ST/MMA ratio : 10/90, 20/80, 30/70, 40/60, 50/50 (wt/wt)
GNR content : 2 % by wt
HNR content : 1 % by wt

From Table 4.5 and Figure 4.4, the clear ST-MMA solution with GNR were observed when the ST content was above 20 wt%. At 10 wt% ST content, the quite clear solution were observed. It indicated that the GNR dissolved in ST monomer better than in MMA monomer. It can be explained that the GNR is almost non-polar and MMA is slightly polar compared to ST. Therefore, the appropriate condition for the preliminary preparation of MMA and ST monomer solution with GNR was at the ST content above 20 wt%. From Table 4.5 and Figure 4.5, the preliminary preparation of ST-MMA solution with HNR observed was similar to that with GNR modifier. The appropriate condition for the preliminary preparation of MMA and ST monomer solution with HNR was at the ST content above 20 wt%.

**Table 4.5** Effect of styrene content on the preliminary preparation of MMA and ST solution with modified natural rubber.

| Expt. | ST/MMA ( wt/wt) | Modified Rubber (%) | Solution Appearance |
|---|---|---|---|
| 1 | 10/90 | 2% GNR | quite clear, light yellow |
| 2 | 20/80 | 2% GNR | clear, light yellow |
| 3 | 30/70 | 2% GNR | clear, light yellow |
| 4 | 40/60 | 2% GNR | clear, light yellow |
| 5 | 50/50 | 2% GNR | clear, quite light yellow |
| 6 | 10/90 | 1% HNR | opaque, yellowish white |
| 7 | 20/80 | 1% HNR | quite clear, white |
| 8 | 30/70 | 1% HNR | quite clear, white |
| 9 | 40/60 | 1% HNR | clear, white |
| 10 | 50/50 | 1% HNR | clear, white |

### 4.3.2 Effect of Rubber Content on the Preliminary Preparation MMA and ST Solution with Modified Natural Rubber

The effect of the modified natural rubber content, GNR and HNR content, on the preliminary preparation of MMA and ST monomer solution with rubber are shown in Table 4.6 and Figure 4.6-4.7. The parameters of the preliminary preparation are as follows:

ST/MMA ratio : 20/80 (wt/wt)
GNR content : 1, 2, 3, 4 % by wt
HNR content : 0.25, 0.5, 1, 2, 3, 4 % by wt

From Table 4.6 and Figure 4.6, the opaque and brownish yellow ST-MMA solution with GNR were observed when the rubber content was above 4 wt%. Below 3 wt% GNR content, the clear and colorless solution was observed. Thus, the appropriate GNR content for the preliminary preparation of MMA and ST monomer solution was lower than 3 wt%. From Table 4.6 and Figure 4.7, the preliminary preparation of MMA and ST monomer solution with HNR observed was similar to that with GNR modifier. The appropriate HNR content for the preliminary preparation of the MMA and ST monomer solution was lower 3 wt%.

**Table 4.6** Effect of modified natural rubber content on the preliminary preparation of MMA and ST solution.

| **Expt.** | **ST/MMA (wt/wt)** | **Modified Rubber (%)** | **Solution Appearance** |
|---|---|---|---|
| 1 | 20/80 | 1% GNR | clear, light yellow |
| 2 | 20/80 | 2% GNR | clear, light yellow |
| 3 | 20/80 | 3% GNR | quite clear, yellow |
| 4 | 20/80 | 4% GNR | opaque, brownish yellow |
| 5 | 20/80 | 5% GNR | opaque, brownish yellow |
| 6 | 20/80 | 0.25% HNR | clear, colorless |
| 7 | 20/80 | 0.5% HNR | clear, white |
| 8 | 20/80 | 1% HNR | quite clear,white |
| 9 | 20/80 | 2% HNR | quite clear, yellowish white |
| 10 | 20/80 | 3% HNR | opaque, yellowish white |
| 11 | 20/80 | 4% HNR | opaque, yellowish white |

(a) (b) (c) (d)

**Figure 4.4** Preliminary preparation of the MMA and ST solution with 2 wt% grafted natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content.

(a) (b) (c) (d)

**Figure 4.5** Preliminary preparation of the MMA and ST solution with 1 wt% hydrogenated natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content.

(a) (b) (c) (d)

**Figure 4.6** Preliminary preparation of the MMA and ST solution (ST/MMA = 20/80) with (a) 1 (b) 2 (c) 3 and (d) 4 wt% grafted natural rubber.

(a) (b) (c) (d)

**Figure 4.7** Preliminary preparation of the MMA and ST solution (ST/MMA = 20/80) with (a) 0.5 (b) 1 (c) 2 and (d) 3 wt% hydrogenated natural rubber.

### 4.3.3 Effect of Styrene Monomer Content on Modified ST-MMA Copolymer Sheet Preparation

The effect of the ST monomer content on the GNR and HNR modified acrylic sheet preparation are presented in Table 4.7 and Figure 4.8-4.9. The parameters of the modified ST-MMA copolymer sheet preparation are as follows:

| | | |
|---|---|---|
| ST/MMA ratio | : | 10/90, 20/80, 30/70, 40/60, 50/50 (wt/wt) |
| GNR content | : | 2 % by wt |
| HNR content | : | 1 % by wt |

**Table 4.7** Effect of styrene content on preparation of ST-MMA copolymer sheet with grafted natural rubber and hydrogenated natural rubber.

| Expt. | ST/MMA (wt/wt) | Modified Rubber (%) | Sheet Appearance |
|---|---|---|---|
| 1 | 10/90 | 2% GNR | good, transparent |
| 2 | 20/80 | 2% GNR | good, transparent |
| 3 | 30/70 | 2% GNR | good, transparent |
| 4 | 40/60 | 2% GNR | little bubbling, transparent |
| 5 | 50/50 | 2% GNR | become bubbling while baking, transparent |
| 6 | 10/90 | 1% HNR | good, quite opaque |
| 7 | 20/80 | 1% HNR | good, quite opaque |
| 8 | 30/70 | 1% HNR | good, quite opaque |
| 9 | 40/60 | 1% HNR | good, quite opaque |
| 10 | 50/50 | 1% HNR | become bubbling while baking, quite opaque |

From Table 4.7 and Figure 4.8, The transparent ST-MMA sheet without bubbling were observed when the ST content was the range of 10-30 wt%. When the ST monomer content was above 40 wt%, the transparent sheet with bubbling were observed. It can be explained that at the condition, it was high exothermic reaction. Therefore, the appropriate ST content for the casting of ST-MMA sheet containing GNR was less than 40 wt%. From Table 4.7 and Figure 4.9, the preparation of HNR modified ST-MMA copolymer sheet observed was similar to that with GNR modifier. The appropriate ST content for the casting of ST-MMA sheet containing HNR was less than 40 wt%.

### 4.3.4 Effect of Rubber Content on Modified ST-MMA Copolymer Sheet Preparation

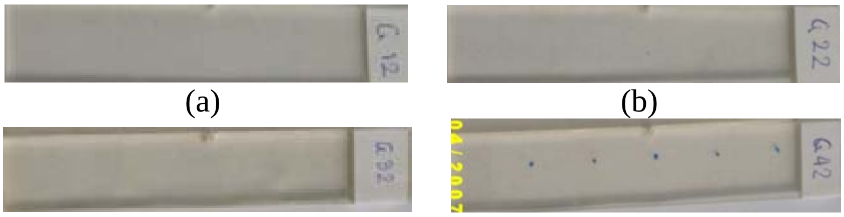
The effect of the modified natural rubber content, GNR and HNR content, on the modified ST-MMA copolymer sheet preparation are presented in Table 4.8 and Figure 4.10-4.11. The parameters of the modified ST-MMA copolymer sheet preparation are as follows:

ST/MMA ratio : 20/80 (wt/wt)
GNR content : 1, 2, 3, 4 % by wt
HNR content : 0.25, 0.5, 1, 2, 3, 4 % by wt

From Table 4.8 and Figure 4.10, the ST-MMA sheet was transparent when the GNR content was in the range of 1-3 wt%. When the GNR content was above 4 wt%, the ST-MMA sheet was opaque due to the phase separation. It might be due to the incompatibility and immiscibility of rubber with MMA and ST. Thus, the appropriate GNR content for the casting of ST-MMA sheet was less than 4 wt%. From Table 4.8 and Figure 4.11, the preparation of HNR modified ST-MMA copolymer sheet observed was similar to that with GNR modifier. The appropriate HNR content for the casting of ST-MMA sheet was less than 4 wt%.

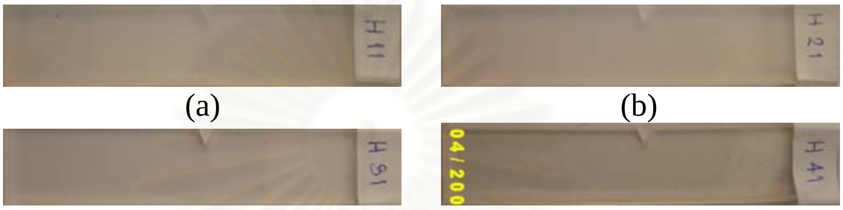
**Table 4.8** Effect of grafted natural rubber and hydrogenated natural rubber content on preparation of ST-MMA copolymer sheet.

| **Expt.** | **ST/MMA (wt/wt)** | **Modified Rubber (%)** | **Sheet Appearance** |
|---|---|---|---|
| 1 | 20/80 | 1% GNR | good, transparent |
| 2 | 20/80 | 2% GNR | good, transparent |
| 3 | 20/80 | 3% GNR | good, transparent |
| 4 | 20/80 | 4% GNR | good, quite opaque |
| 5 | 20/80 | 5% GNR | good, opaque, separated phase |
| 6 | 20/80 | 0.25% HNR | good, transparent |
| 7 | 20/80 | 0.5% HNR | good, transparent |
| 8 | 20/80 | 1% HNR | good, little opaque |
| 9 | 20/80 | 2% HNR | good, little opaque |
| 10 | 20/80 | 3% HNR | good, quite opaque |
| 11 | 20/80 | 4% HNR | good, opaque |



(a) (b) (c) (d)

**Figure 4.8** Sheet appearance of ST-MMA copolymer sheet with 2 wt% grafted natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content.

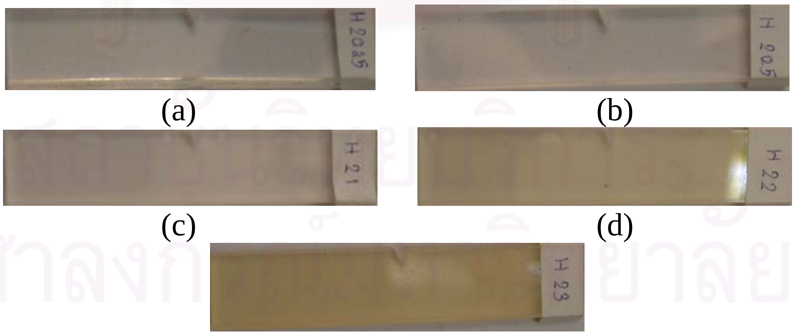


(a) (b) (c) (d)

**Figure 4.9** Sheet appearance of ST-MMA copolymer sheet with 1 wt% hydrogenated natural rubber at (a) 10 (b) 20 (c) 30 and (d) 40 wt% styrene content.

(a) (b) (c) (d)

**Figure 4.10** Sheet appearance of ST-MMA copolymer sheet (ST/MMA = 20/80) with (a) 1 (b) 2 (c) 3 and (d) 4 wt% grafted natural rubber.

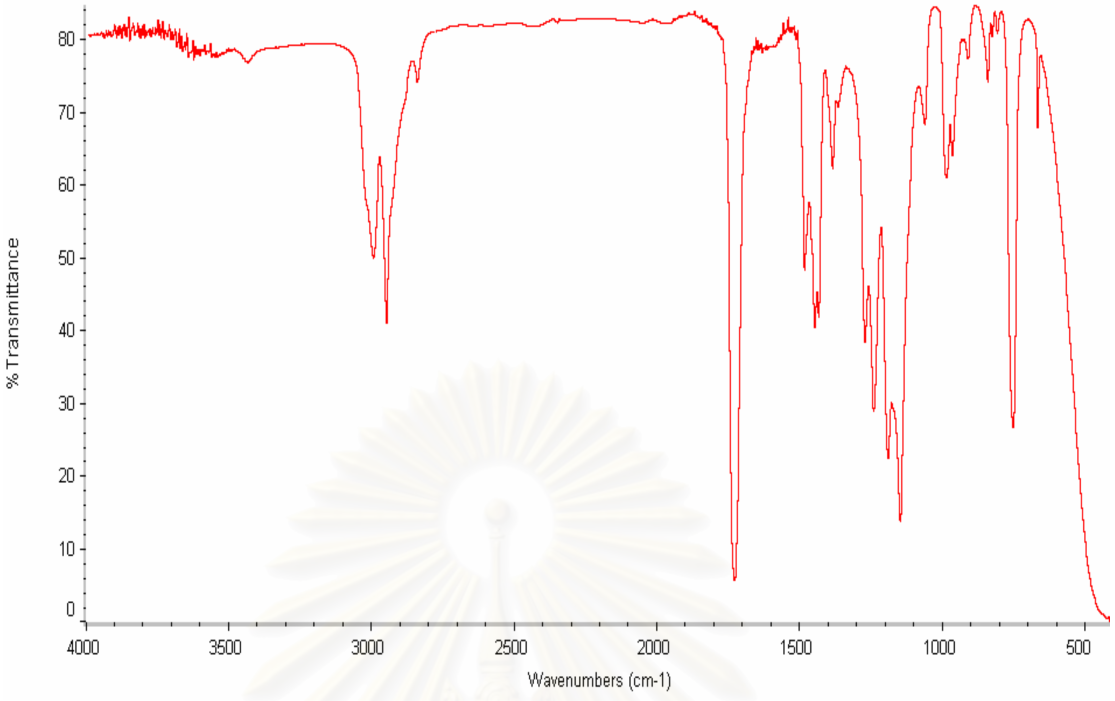


(a) (b) (c) (d) (e)

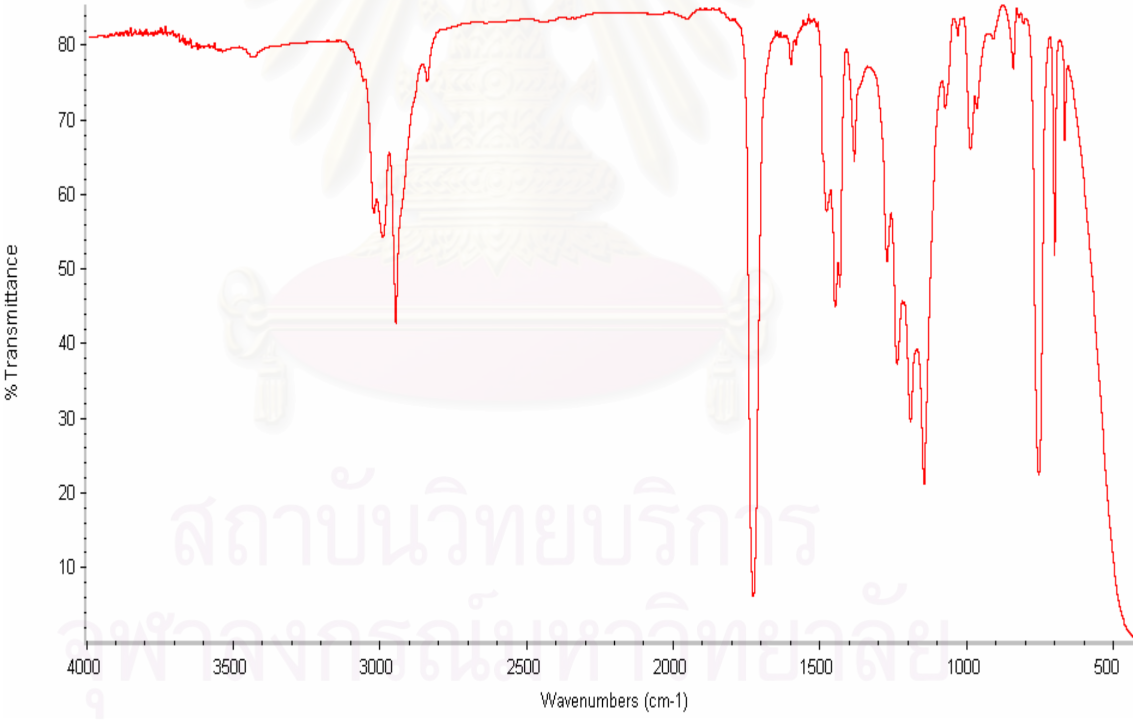
**Figure 4.11** Sheet appearance of ST-MMA copolymer sheet (ST/MMA = 20/80) with (a) 0.25 (b) 0.5 (c) 1 (d) 2 and (e) 3 wt% hydrogenated natural rubber

## 4.4 Characterization of Copolymer Sheet Containing Modified Natural Rubber

For the PMMA sheet, the ST-MMA copolymer sheet, the ST-MMA copolymer sheet with NR, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR, the functional group of polymers was determined by FT-IR spectroscopy. Figure 4.12a, 4.12b, 4.12c, 4.12d and 4.12e show the FT-IR spectra in the region of 4000-500 $cm^{-1}$ for PMMA sheet, ST-MMA copolymer sheet, ST-MMA copolymer sheet with NR, ST-MMA copolymer sheet with GNR and ST-MMA copolymer sheet with HNR, respectively. The FT-IR spectrum of PMMA sheet exhibited the characteristic absorption band of C=O stretching vibration of MMA at 1728 $cm^{-1}$. The new peaks in FT-IR spectrum of ST-MMA copolymer sheet were appeared the absorption bands of the C=C stretching of aromatic ring of ST at 1580 $cm^{-1}$, and the C=C-H bending of aromatic ring of ST at 702 $cm^{-1}$. This confirmed the occurrence of ST and MMA. The FT-IR spectra of ST-MMA copolymer sheet with NR, ST-MMA copolymer sheet with GNR and ST-MMA copolymer sheet with HNR exhibited the characteristic absorption band of C=C-H bending of aromatic ring of ST at 702 $cm^{-1}$, the C=O stretching vibration of MMA at 1728 $cm^{-1}$ and the characteristic absorption band C=C stretching and C=C bending vibration of rubber at 1680 $cm^{-1}$and 853 $cm^{-1}$, respectively. This confirmed the occurrence of ST, MMA including natural rubber and modified natural rubber.

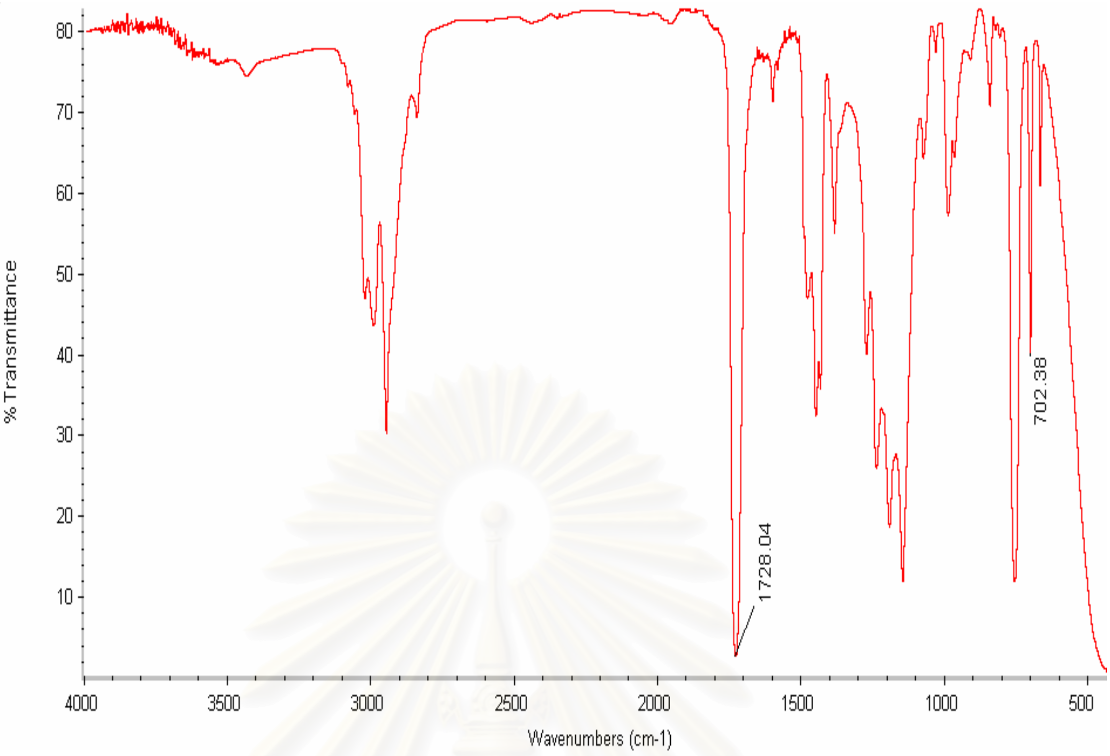


(a)

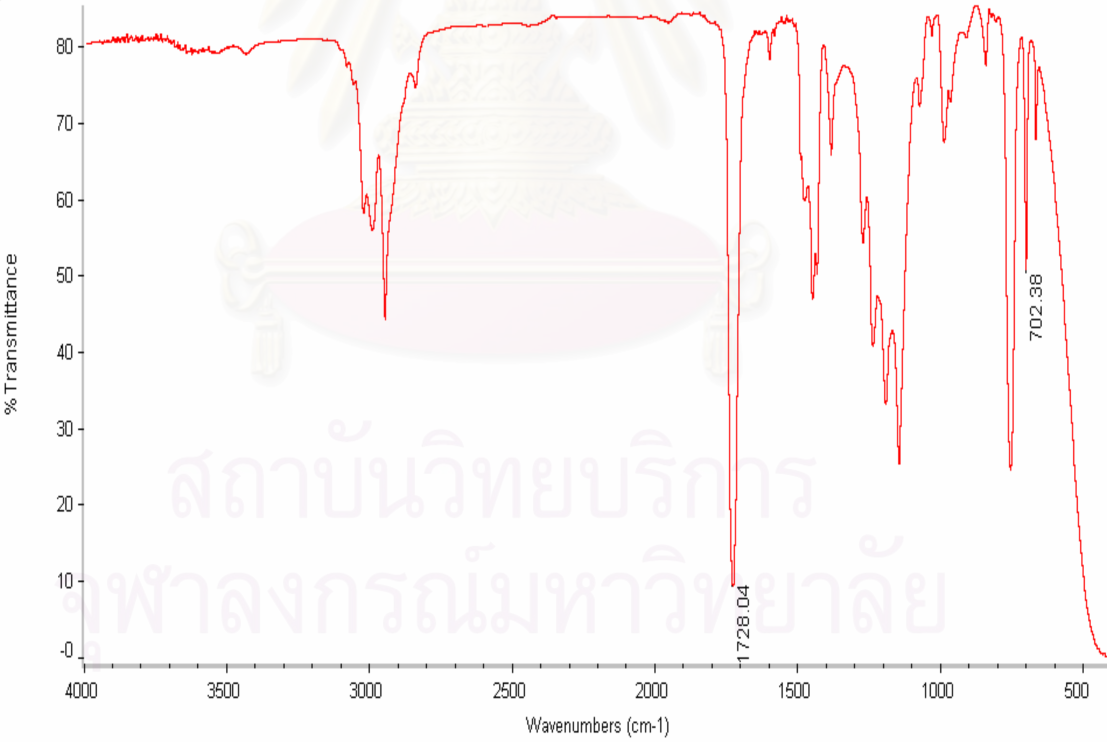


(b)

**Figure 4.12** FT-IR spectra of (a) PMMA sheet, (b) ST-MMA copolymer sheet, (c) ST-MMA copolymer sheet with NR, (d) ST-MMA copolymer sheet with GNR and (e) ST-MMA copolymer sheet with HNR.

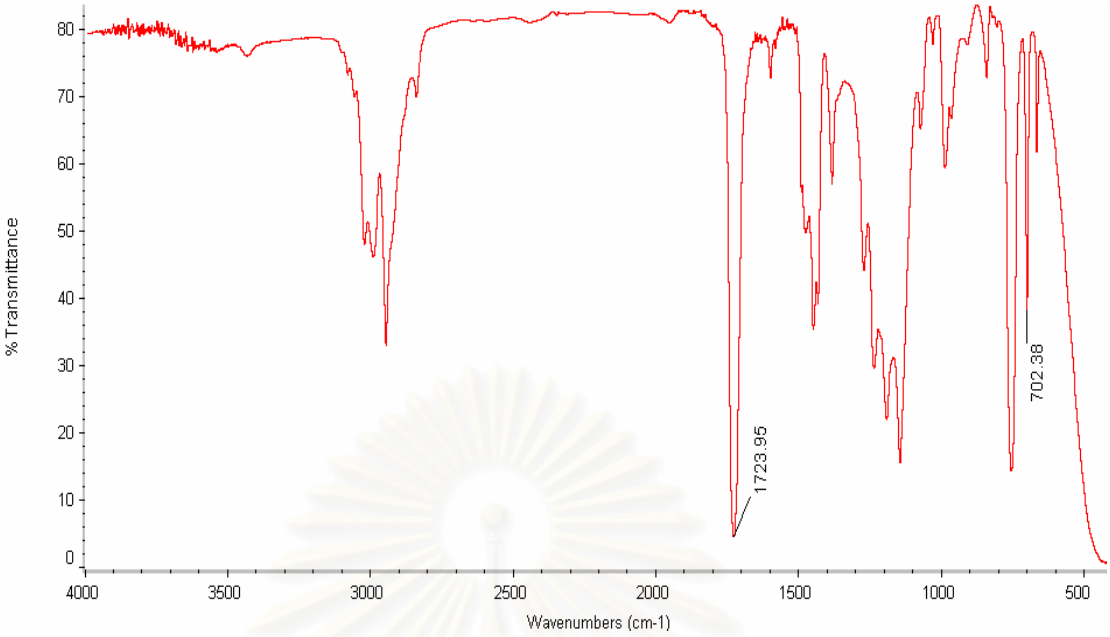


(c)



(d)

**Figure 4.12** (Continued).



(e)

**Figure 4.12** (Continued).

## 4.5 Mechanical Properties of ST-MMA Copolymer Sheet Containing Modified Natural Rubber

The ST-MMA copolymer sheets prepared by bulk copolymerization of MMA monomer and ST monomer were improved by addition of small amount of the modified NR. The mechanical properties such as impact strength, tensile properties, and hardness were investigated. The mechanical properties of the ST-MMA copolymer sheet, the ST-MMA copolymer sheet with NR, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR are presented in Table 4.9-4.10.

**Table 4.9** Effect of styrene content on impact strength, tensile strength (TS), elongation at break (EB) and hardness of modified ST-MMA copolymer sheet.

| Expt. | ST/MMA (wt/wt) | Modified Rubber (%) | Impact Strength (kJ/m$^2$) | TS (MPa) | EB (%) | Hardness (HRM) |
|---|---|---|---|---|---|---|
| 1 | 0/100 | - | 54.5 | 44.5 | 6.02 | 97.9 |
| 2 | 10/90 | - | 45.0 | 50.0 | 6.61 | 93.7 |
| 3 | 20/80 | - | 41.3 | 50.3 | 6.29 | 89.8 |
| 4 | 30/70 | - | 39.6 | 41.6 | 6.01 | 77.3 |
| 5 | 40/60 | - | 35.2 | 25.2 | 2.76 | 76.6 |
| 6 | 10/90 | 2% GNR | 73.3 | 64.3 | 7.30 | 88.4 |
| 7 | 20/80 | 2% GNR | 83.7 | 68.4 | 7.51 | 83.2 |
| 8 | 30/70 | 2% GNR | 81.9 | 64.7 | 7.30 | 75.1 |
| 9 | 40/60 | 2% GNR | 67.7 | 58.6 | 6.32 | 74.8 |
| 10 | 10/90 | 1% HNR | 60.7 | 60.9 | 8.30 | 86.4 |
| 11 | 20/80 | 1% HNR | 76.1 | 68.9 | 9.12 | 79.5 |
| 12 | 30/70 | 1% HNR | 66.6 | 55.6 | 6.86 | 75.1 |
| 13 | 40/60 | 1% HNR | 64.2 | 39.4 | 5.36 | 64.2 |

**Table 4.10** Effect of modified natural rubber content on impact strength, tensile strength (TS), elongation at break (EB) and hardness of modified ST-MMA copolymer sheet.

| Expt. | ST/MMA (wt/wt) | Modified Rubber (%) | Impact Strength (kJ/m$^2$) | TS (MPa) | EB (%) | Hardness (HRM) |
|---|---|---|---|---|---|---|
| 1 | 20/80 | - | 41.3 | 50.3 | 6.29 | 89.8 |
| 2 | 20/80 | 0.5% NR | 40.4 | 40.0 | 4.78 | 83.9 |
| 3 | 20/80 | 1% NR | 66.1 | 42.2 | 6.33 | 83.2 |
| 4 | 20/80 | 2% NR | 73.0 | 65.0 | 5.84 | 79.8 |
| 5 | 20/80 | 3% NR | 65.3 | 61.7 | 5.28 | 74.6 |
| 6 | 20/80 | 4% NR | 58.5 | 31.5 | 4.49 | 70.6 |
| 7 | 20/80 | 1% GNR | 74.8 | 66.3 | 7.16 | 87.9 |
| 8 | 20/80 | 2% GNR | 83.7 | 68.4 | 7.51 | 83.2 |
| 9 | 20/80 | 3% GNR | 70.2 | 52.1 | 7.15 | 83.7 |
| 10 | 20/80 | 4% GNR | 65.1 | 50.2 | 6.23 | 81.2 |
| 11 | 20/80 | 0.25% HNR | 40.4 | 58.8 | 6.86 | 84.2 |
| 12 | 20/80 | 0.5% HNR | 50.1 | 66.3 | 8.34 | 82.0 |
| 13 | 20/80 | 1% HNR | 76.1 | 68.9 | 11.55 | 79.5 |
| 14 | 20/80 | 2% HNR | 58.4 | 64.2 | 10.07 | 75.5 |
| 15 | 20/80 | 3% HNR | 52.2 | 61.5 | 9.43 | 74.2 |
| 16 | 20/80 | 4% HNR | 44.2 | 55.2 | 8.83 | 68.7 |

### 4.5.1 Impact Strength

#### 4.5.1.1 Effect of Styrene Monomer Content on Impact Strength

The effect of ST monomer content on the Charpy impact strength of the modified ST-MMA copolymer sheet was investigated. The impact strength of the ST-MMA copolymer sheet, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR are presented in Table 4.9 and Figure 4.13. The parameters of the modified ST-MMA copolymer sheet preparation are as follows:

ST/MMA ratio : 10/90, 20/80, 30/70, 40/60 (wt/wt)
GNR content : 2 % by wt
HNR content : 1 % by wt

From Table 4.9 and Figure 4.13, the impact strength of the copolymer sheet with modified NR was higher than that without modifier. The increase in impact strength of the modified ST-MMA copolymer sheet can be explained that the elastomeric property of the modified NR resulted in improving impact strength of the acrylic sheet [31, 41]. The impact strength of the acrylic sheet without modifier decreased with increasing ST content. For GNR and HNR modified acrylic sheet, impact strength increased and leveled off at 20 wt% ST content. The GNR modified acrylic sheet had a higher impact strength than the HNR modified specimen because the GNR with MMA and ST was more compatible with ST-MMA copolymer than the HNR [32]. At 20 wt% ST content, the impact strength of the copolymer with GNR and HNR reached maximum value of 83.7 and 76.1 kJ/m$^2$, respectively.

### 4.5.1.2 Effect of Rubber Content on Impact Strength

The effect of modified natural rubber content on the Charpy impact strength of the modified ST-MMA copolymer sheet was investigated. The impact strength of the ST-MMA copolymer sheet with NR, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR are presented in Table 4.10 and Figure 4.14. The parameters of the modified ST-MMA copolymer sheet preparation are as follows:

ST/MMA ratio : 20/80 (wt/wt)
GNR content : 1, 2, 3, 4 % by wt
HNR content : 0.25, 0.5, 1, 2, 3, 4 % by wt
NR content : 0.5, 1, 2, 3, 4 % by wt

From Table 4.10 and Figure 4.14, the impact strength of GNR and HNR modified acrylic sheet was higher than that of the specimens containing NR. The copolymer sheet with GNR had the highest impact strength. It indicates that the GNR provided the better compatibility with thermoplastics than NR and HNR because of the good miscibility of GNR in the modified acrylic solution during casting. For GNR modified sheet, the impact strength increased with increasing the GNR content and reached maximum value of 83.7 kJ/m$^2$ at 2 wt% GNR content. The copolymer sheet with NR has the similar results. For HNR modified acrylic sheet, the impact strength increased with increasing the HNR content and reached maximum value of 76.1 kJ/m$^2$ at 1 wt% HNR content. However, the high loading of modified rubber (>1 wt% HNR or >2 wt% HNR) in the ST-MMA copolymer sheet might cause the poor impact strength due to the immiscibility and incompatibility of rubber and thermoplastics.

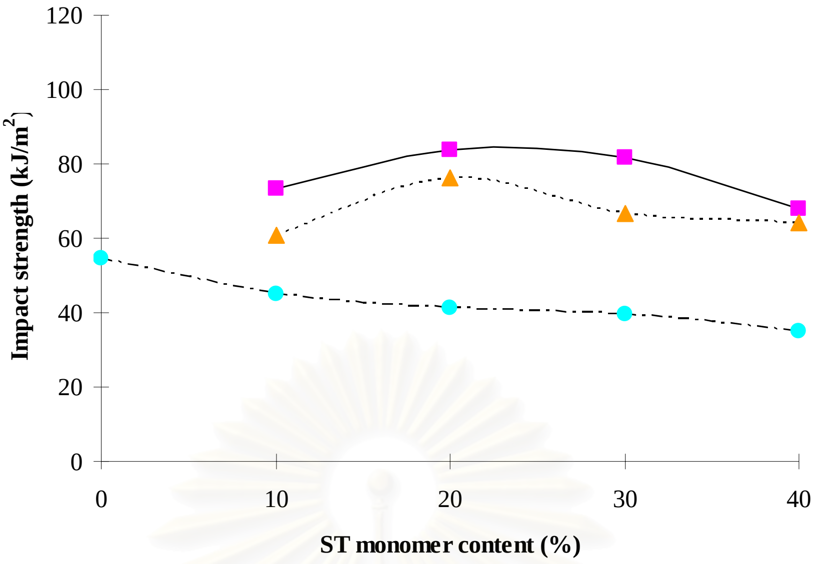


**Figure 4.13** Effect of styrene monomer content on impact strength of ST-MMA copolymer sheet : (●) No modifier, (■) 2 wt% GNR and (▲) 1 wt% HNR.

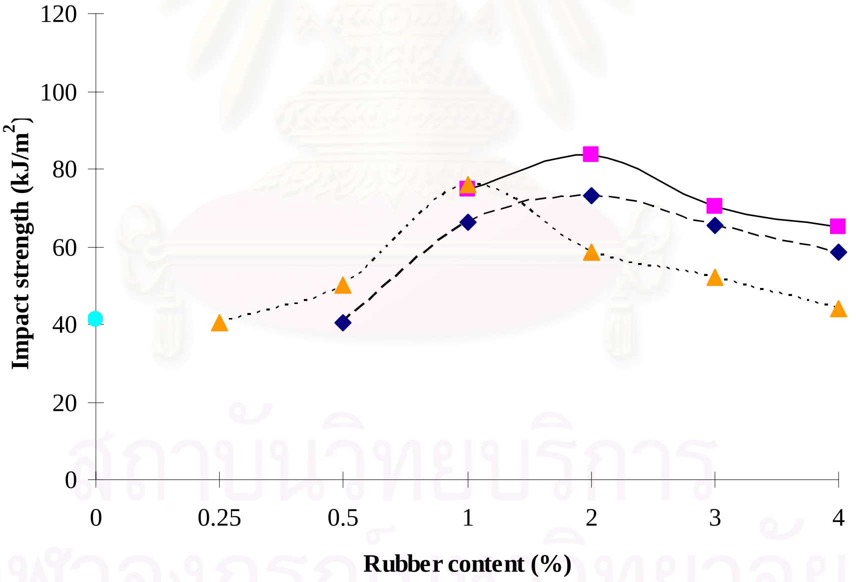


**Figure 4.14** Effect of rubber content on impact strength of ST-MMA (20/80) copolymer sheet : (●) No modifier, (◆) NR modifier, (■) GNR modifier and (▲) HNR modifier.

### 4.5.2 Tensile Properties

#### 4.5.2.1 Effect of Styrene Monomer Content on Tensile Properties

The effect of ST monomer content on tensile properties of the modified ST-MMA copolymer sheet was investigated by varying the ST monomer content of 10, 20, 30, and 40 % by wt at 2 wt% GNR and 1 wt% HNR modifier. The tensile properties of the ST-MMA copolymer sheet, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR are presented in Table 4.9 and Figure 4.15.

From Table 4.9 and Figure 4.15a, the tensile strength of copolymer sheet with modified NR was higher than that without modifier. The high toughness was obtained by the addition of an amorphous rubbery phase [41]. The tensile strength of modified acrylic sheet increased and leveled off at 20 wt% ST content. For sheet with ST content above 20 wt%, the tensile strength decreased with increasing ST content because polystyrene (PS) had less stiffness and lower tensile strength than poly(mehyl methacrylate) (PMMA).

From Table 4.9 and Figure 4.15b, the elongation at break of sheet without modifier changed slightly with increasing ST content in the range of 10-30 wt%. When the ST content was lower 20 wt%, the GNR modified sheet has lower elongation at break than the HNR modified specimen. However, the ST content did not affect the elongation at break of GNR modified sheet. It is due to the compatibility of MMA-co-ST of GNR with MMA monomer and ST monomer.

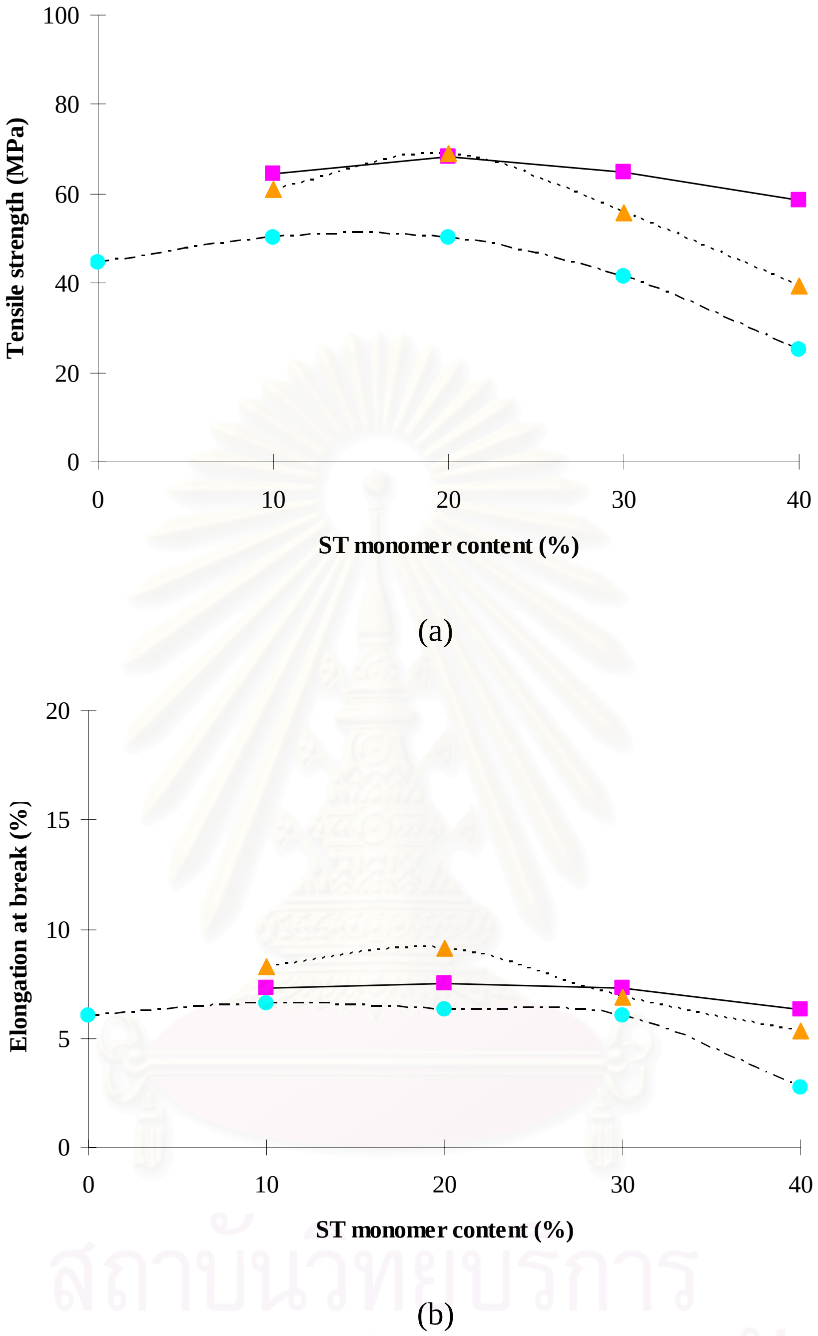


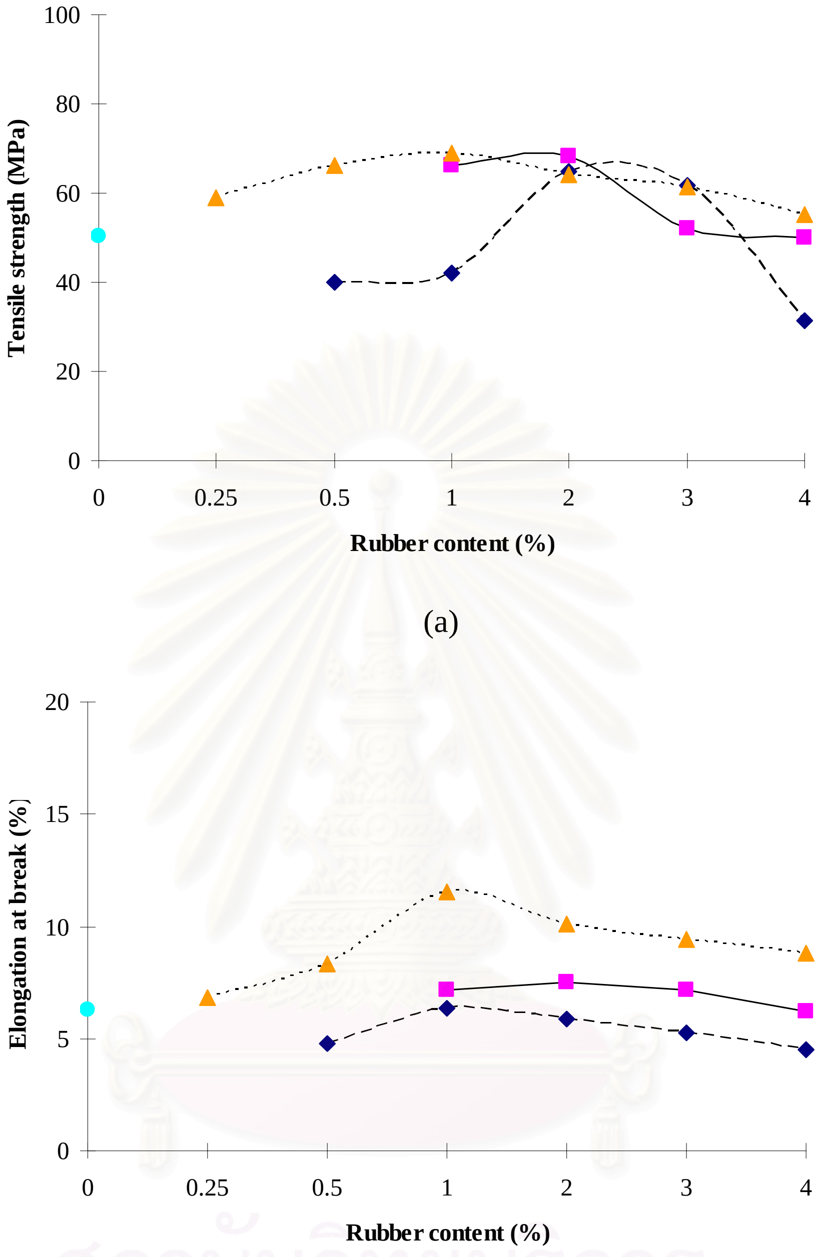
**Figure 4.15** Effect of styrene monomer content on (a) tensile strength and (b) elongation at break of ST-MMA copolymer sheet: (●) No modifier, (■) 2 wt% GNR and (▲) 1 wt% HNR.

#### 4.5.2.2 Effect of Rubber Content on Tensile Properties

The effect of modified natural rubber content on tensile properties of the modified ST-MMA (20/80) copolymer sheet was investigated by varying the GNR content of 1, 2 ,3 and 4 % by wt and the HNR content of 0.25, 0.5, 1, 2, 3, and 4 wt%. The tensile properties of the ST-MMA copolymer sheet with NR, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR are shown in Table 4.10 and Figure 4.16.

From Table 4.10 and Figure 4.16a, the modified acrylic sheet without modified NR exhibited low tensile strength. The tensile strength of modified acrylic sheet increased with increasing rubber content and reached a maximum value at the 2 wt% GNR or 2 wt% NR modifier. For HNR modified acrylic sheet, the tensile strength increased and leveled off at 1 wt% of HNR content. The NR portion of the modified NR product might promote the superior tensile strength of the modified acrylic sheet but the interfacial saturation of rubber in thermoplastic components should saturate when the rubber content is increasing. The similar behavior was also observed in the NR/PMMA blends with NR-g-GMA [32].

From Table 4.10 and Figure 4.16b, the elongation at break of the modified acrylic sheet increased with increasing rubber content and slightly decreased at rubber content above 2 wt%. The copolymer sheet with HNR had higher elongation at break than that with GNR modifier due to the influence of MMA and ST as the brittle thermoplastics in the graft product which caused the lower elongation at break.



(b)

**Figure 4.16** Effect of rubber content on (a) tensile strength and (b) elongation at break of ST-MMA (20/80) copolymer sheet : (●) No modifier, (◆) NR modifier, (■) GNR modifier and (▲) HNR modifier.

### 4.5.3 Hardness

#### 4.5.3.1 Effect of Styrene Monomer Content on Hardness

The effect of ST monomer content on hardness of the modified ST-MMA copolymer sheet was investigated by varying the ST monomer content of 10, 20, 30, and 40 % by wt at 2 wt% GNR and 1 wt% HNR modifier. The hardness of the ST-MMA copolymer sheet, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR are shown in Table 4.9 and Figure 4.17.

From Table 4.9 and Figure 4.17, the hardness of modified acrylic sheet decreased with increasing ST content due to the lower hardness of polystyrene. The hardness of the modified ST-MMA copolymer sheet was lower than that of unmodified sheet because of the rubber as elastomer which reduced the hardness of the sheet.

#### 4.5.3.2 Effect of Rubber Content on Hardness

The effect of modified natural rubber content on hardness of the modified ST-MMA (20/80) copolymer sheet was investigated by varying the GNR content of 1, 2, 3, and 4 % by wt and the HNR content of 0.25, 0.5, 1, 2, 3, 4 wt%. The hardness of the ST-MMA copolymer sheet with NR, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR are shown in Table 4.10 and Figure 4.18

From Table 4.10 and Figure 4.18, the NR, GNR, and HNR modifiers caused the reduction of hardness of the modified acrylic sheet. The hardness of modified acrylic sheet with GNR was higher than that of NR and HNR modified sheet because of the lower rubber portion and the higher MMA content in the graft product.

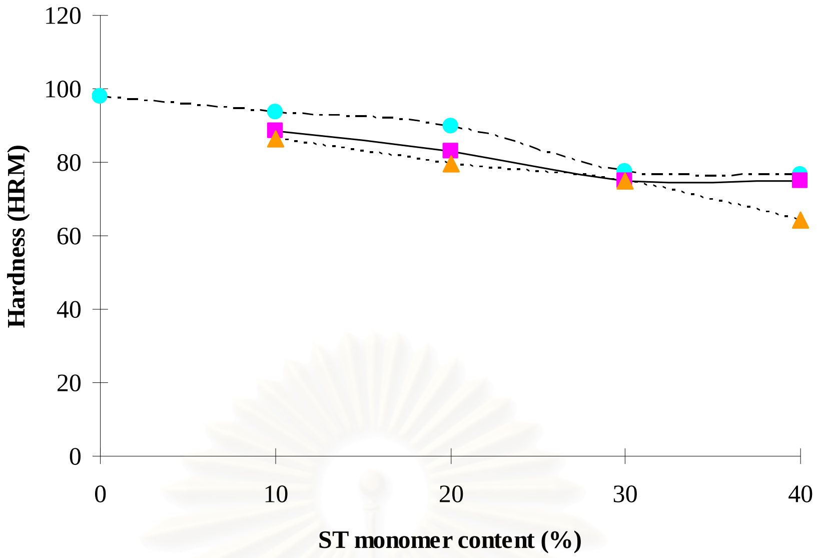


**Figure 4.17** Effect of styrene monomer content on hardness of ST-MMA copolymer sheet: (●) No modifier, (■) 2 wt% GNR and (▲) 1 wt% HNR.

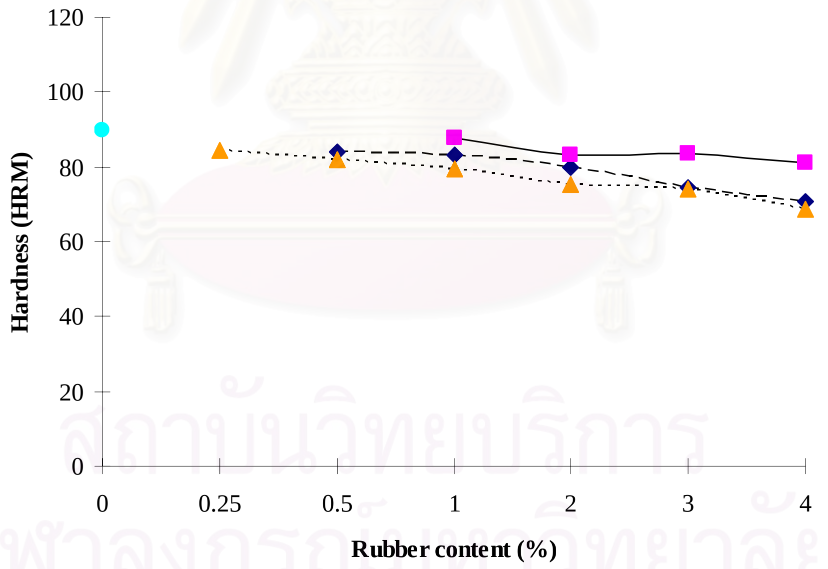


**Figure 4.18** Effect of rubber content on hardness of ST-MMA (20/80) copolymer sheet : (●) No modifier, (◆) NR modifier, (■) GNR modifier and (▲) HNR modifier.

## 4.6 Physical Properties of the ST-MMA Copolymer Sheet Containing Modified Natural Rubber

The samples of the modified ST-MMA copolymer sheet with different mechanical properties were selected. The mechanical properties of the modified ST-MMA copolymer sheet are presented in Table 4.11. The physical properties such as transparent properties, thermal resistance and ultraviolet (UV) resistance were investigated. The properties of the ST-MMA copolymer sheet, the ST-MMA copolymer sheet with NR, the ST-MMA copolymer sheet with GNR and the ST-MMA copolymer sheet with HNR were compared. The physical properties of modified acrylic sheet are shown in Table 4.12 and Figure 4.19.

The thermal and UV resistance methods were applied to investigate the weathering property of the modified ST-MMA copolymer sheet. The thermal and UV resistance were examined by monitoring the yellowness shifts of the test specimens reported in the terms of color difference (ΔE).

**Table 4.11** Mechanical properties of modified acrylic sheet.

| Expt. | Code | ST/MMA (wt/wt) | Modified Rubber (%) | Impact Strength (kJ/m2) | Tensile Strength (MPa) | Hardness (HRM) |
|---|---|---|---|---|---|---|
| 1 | B00 | 100/0 | - | 54.5 | 45.5 | 97.9 |
| 2 | B20 | 80/20 | - | 41.3 | 50.3 | 89.8 |
| 3 | NR1 | 80/20 | 1% NR | 66.1 | 42.2 | 83.2 |
| 4 | NR2 | 80/20 | 2% NR | 73.0 | 65.0 | 79.8 |
| 5 | GNR2 | 80/20 | 2% GNR | 83.7 | 68.4 | 83.2 |
| 6 | GNR3 | 80/20 | 3% GNR | 70.2 | 52.1 | 83.7 |
| 7 | GNR4 | 80/20 | 4% GNR | 65.1 | 50.2 | 81.2 |
| 8 | HNR0.25 | 80/20 | 0.25% HNR | 40.4 | 58.8 | 84.2 |
| 9 | HNR1 | 80/20 | 1% HNR | 76.1 | 68.9 | 79.5 |
| 10 | HNR2 | 80/20 | 2% HNR | 58.4 | 64.2 | 75.5 |
| 11 | HNR3 | 80/20 | 3% HNR | 52.3 | 61.5 | 74.2 |

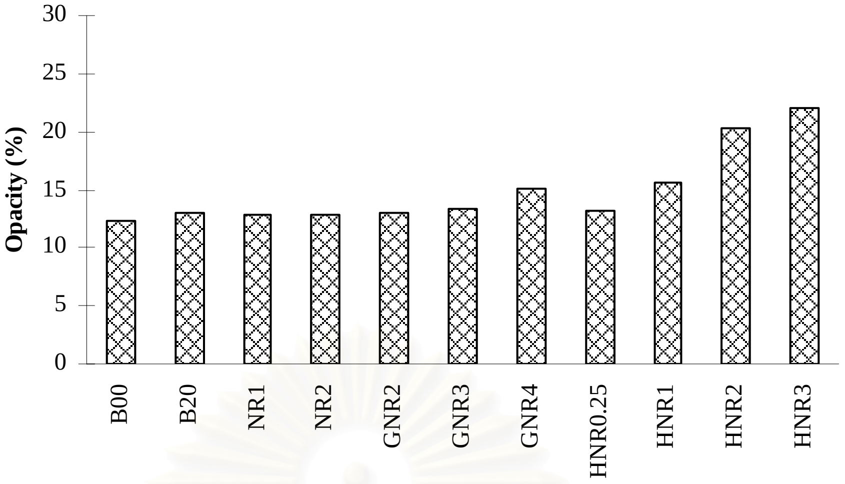
**Table 4.12** Physical properties of modified acrylic sheet.

| Expt. | Code | Opacity | ΔE of thermal resistance | ΔE of UV resistance |
|---|---|---|---|---|
| 1 | B00 | 12.3 | 0.96 | 5.35 |
| 2 | B20 | 12.9 | 10.24 | 8.90 |
| 3 | NR1 | 12.9 | 1.00 | 10.8 |
| 4 | NR2 | 12.8 | 3.44 | 10.3 |
| 5 | GNR2 | 13.1 | 15.99 | 11.3 |
| 6 | GNR3 | 13.4 | 16.22 | 8.45 |
| 7 | GNR4 | 15.1 | 22.26 | 7.76 |
| 8 | HNR0.25 | 13.2 | 2.03 | 7.99 |
| 9 | HNR1 | 15.6 | 0.66 | 8.33 |
| 10 | HNR2 | 20.3 | 0.70 | 12.6 |
| 11 | HNR3 | 22.0 | 0.57 | 13.8 |

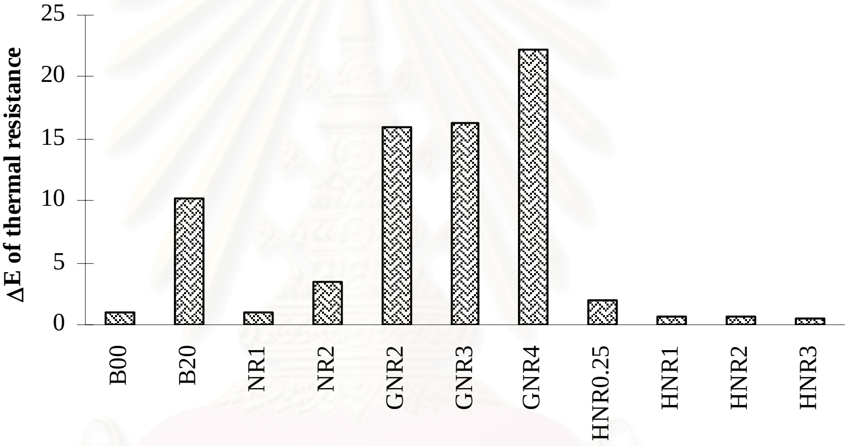
Transparency is an important property for acrylic sheet product. From Table 4.12 and Figure 4.19a, the opacity of the ST-MMA copolymer sheet, the ST-MMA copolymer sheet with NR, the ST-MMA copolymer sheet with GNR are almost the same (12.3-15.1%). The ST-MMA copolymer sheet with HNR has higher opacity (15.6-22.0%).

From Table 4.12 and Figure 4.19b, the thermal resistance of the ST-MMA copolymer sheet with HNR was the highest. It indicates that the HNR had high thermal resistance (ΔE = 0.57-2.03) due to hydrogenation which is the structure modification of natural rubber from unsaturated to saturated polymer [34-36]. The ST-MMA copolymer sheet with GNR had the lowest thermal resistance (ΔE = 15.99-22.26%). It can be explained that the GNR is unsaturated polymer due to NR, MMA and ST in graft product.

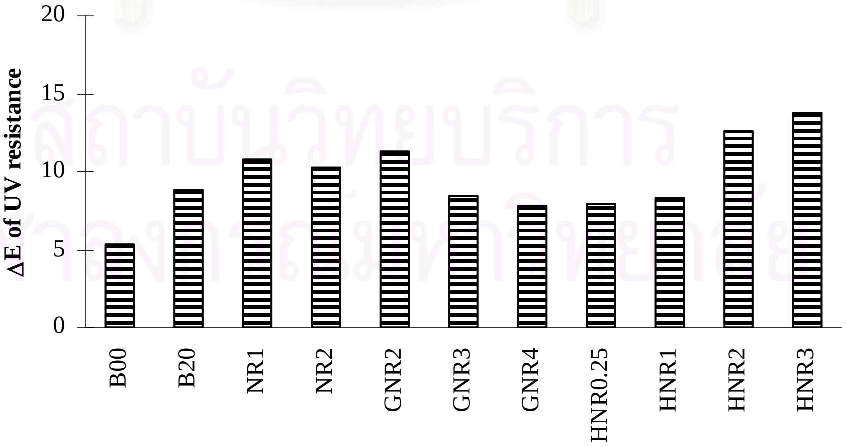
From Table 4.12 and Figure 4.19c, the UV resistance of the PMMA sheet (B00) was higher than that of the ST-MMA copolymer, the ST-MMA copolymer with NR and the ST-MMA copolymer with modified NR. It is due to the fact that the UV resistance of PMMA was higher than that of PS, NR and modified NR.



(a)



(b)



(c)

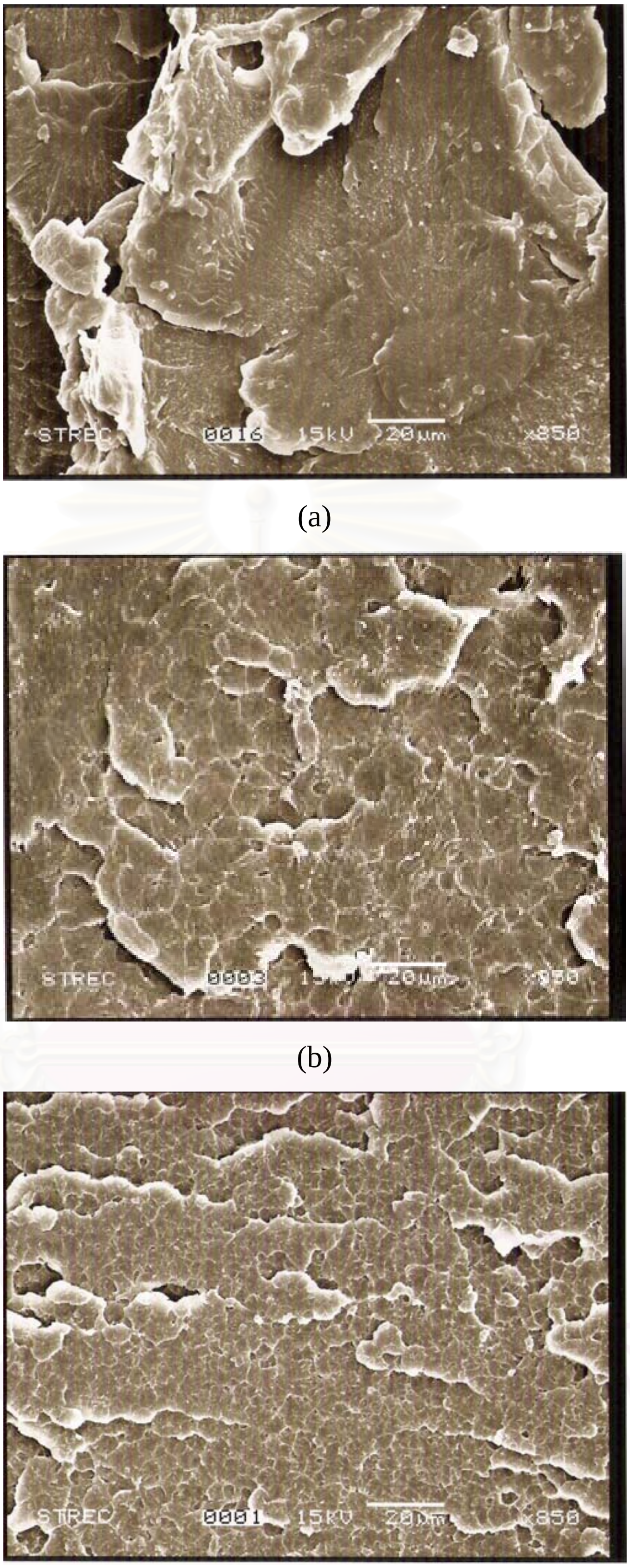
**Figure 4.19** Physical Properties of modified acrylic sheet: (a) opacity, (b) thermal resistance, and (c) UV resistance.

## 4.7 Morphological Study

The scanning electron microscope (SEM) was employed to investigate the fracture surface of the specimen from tensile properties test. Figure 4.20 and 4.21 shows the tensile fracture surface of the modified acrylic sheet (ST/MMA = 20/80) with GNR and HNR and the unmodified acrylic sheet.

For the graft copolymer of MMA and ST onto NR, NR contributed to the toughness of material, whereas the MMA-co-ST exhibited the good compatibility with thermoplastics. The increase in the impact strength of the modified acrylic sheet containing GNR was visualized using SEM technique. The result presented in Figure 4.20a indicates that the large cracking appeared on the fracture surface of the incompatible specimen. For the compatible blends with 1 and 2 wt% GNR modifier, it is observed that the fracture surfaces become smoother as shown in Figure 4.20b and 4.20c, respectively. It indicates that the GNR acted as the interfacial agent to give the compatibility with PMMA and the impact modifier to improve the impact strength of the modified acrylic sheet. The high Charpy impact strength values of the compatible blends are in agreement with this anticipation.

From Figure 4.21, it is similar to the modified acrylic sheet with GNR and the HNR acted as the interfacial agent to give the compatibility with PMMA and the impact modifier to improve the impact strength of the modified acrylic sheet. However, the GNR modifier gave higher compatibility with ST-MMA copolymer than HNR modifier as shown in Figure 4.22. This also results in the increase in opacity with increasing HNR content.

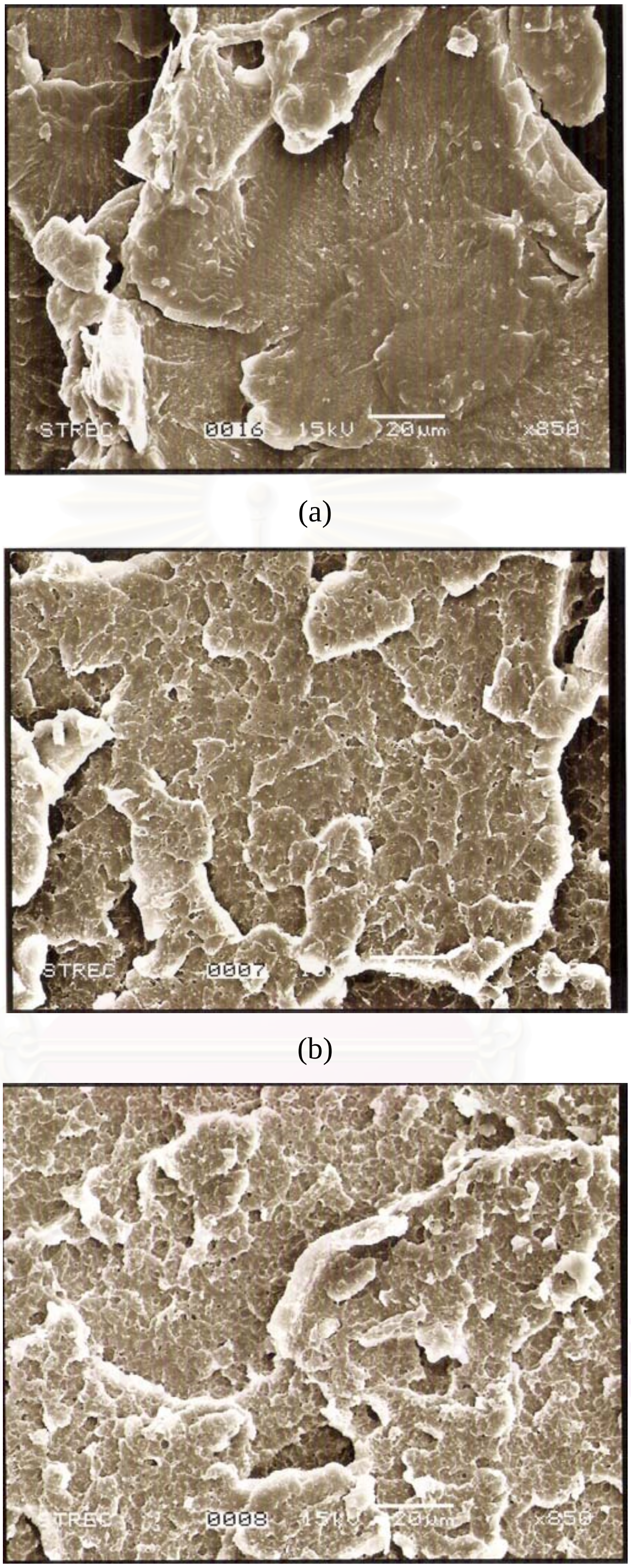


(a)

(b)

(c)

**Figure 4.20** SEM photographs of modified acrylic sheet with GNR at (a) 0 (b) 1 and (c) 2 wt%.

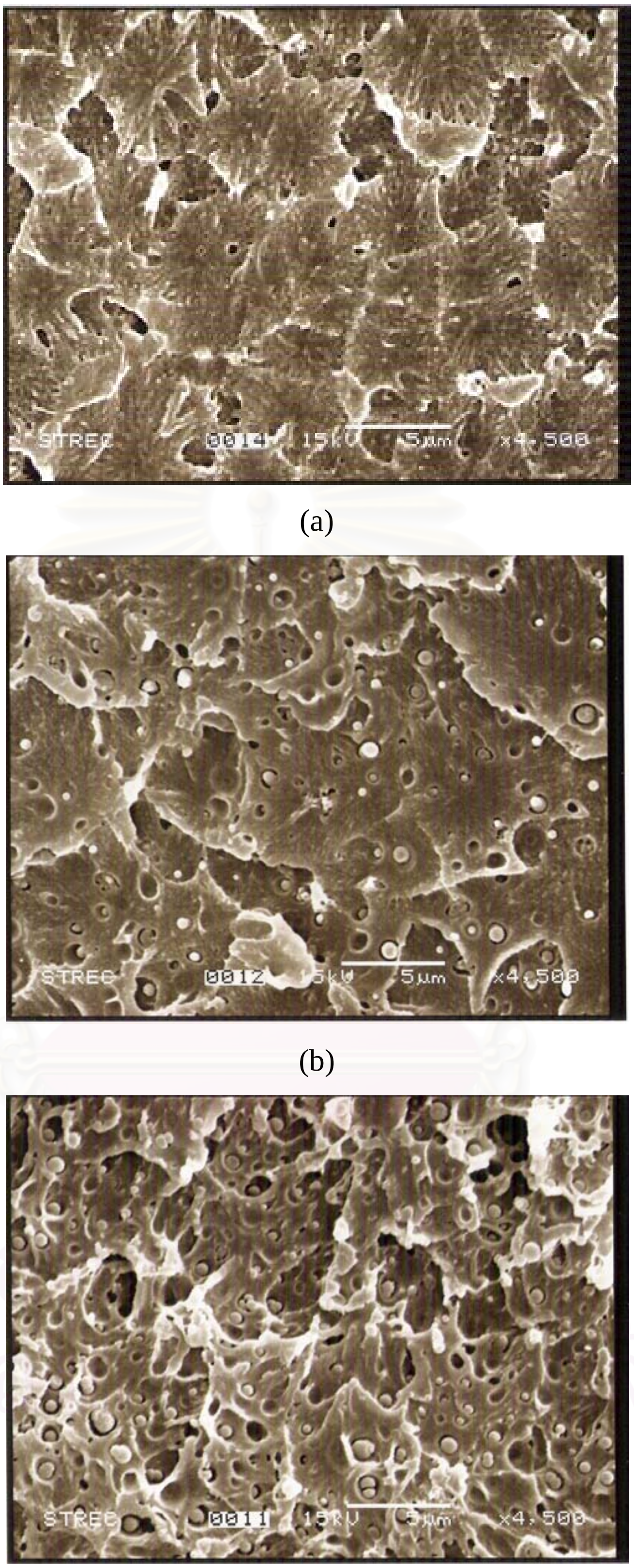


(a)

(b)

(c)

**Figure 4.21** SEM photographs of modified acrylic sheet with HNR at (a) 0 (b) 1 and (c) 2 wt%.



(a)

(b)

(c)

**Figure 4.22** SEM photographs of modified acrylic sheet with (a) 2 wt% GNR (b) 1 wt% HNR and (c) 2wt% HNR.

# CHAPTER V

# CONCLUSION AND SUGGESTION

## 5.1 Conclusion

The grafted natural rubber was prepared by emulsion graft copolymerization process. The optimum reaction condition was 75 phr of monomer containing ST:MMA ratio of 1:1, 1 phr of sodium dodecyl sulfate as an emulsifier, 10 phr of isopropanol as a stabilizer, 1 phr of potassium hydroxide as a buffer, and 1 phr of redox initiator, containing CHPO:TEPA ratio of 1:1 at 65 °C for 8 h. The grafted NR product consisted of 66.1 wt% NR-g-(MMA-co-ST), 26.9 wt% free rubber and 7.0 wt% free copolymers.

The hydrogenated natural rubber was prepared by hydrogenation of STR 5L using $OsHCl(CO)(O_2)(PCy_3)_2$ as a catalyst. The optimum reaction condition was 612.57 mM of STR 5L, 76.81 µM of $OsHCl(CO)(O_2)(PCy_3)_2$ at 140 °C and 400 psig of $H_2$ pressure for 15 min. For the hydrogenated natural rubber, the degree of hydrogenation is 56.7.

The bulk copolymerization of styrene monomer and methyl methacrylate monomer containing the modified natural rubber, such as the grafted natural rubber and hydrogenated natural rubber, were prepared by casting using benzoyl peroxide and 2,2'-azobis-(2,4-dimethylvaleronitrile) as initiators. The mechanical properties of copolymer sheet with GNR were higher than that with HNR. The ST-MMA (20/80) copolymer sheet with 2 wt% GNR exhibited the best mechanical properties: impact strength of 83.7 kJ/m$^2$, tensile strength of 68.4 MPa and hardness of 83.2 HRM. For physical properties of GNR modified sheet, the opacity is 15.99% but thermal and UV resistance are low.

The HNR modified acrylic sheet had good impact strength and tensile strength. The ST-MMA (20/80) copolymer sheet with 1 wt% HNR exhibited good mechanical properties: impact strength of 76.1 kJ/m$^2$, tensile strength of 68.9 MPa and hardness of 79.5 HRM. For physical properties of HNR modified sheet, the opacity is 15.57% and thermal resistance was high but UV resistance was low. It implies that the modified natural rubbers both GNR and HNR are good impact modifier in modified acrylic sheet. Moreover, the GNR is also a compatibilizer modifier in modified acrylic sheet. For HNR, it is a thermal resistance modifier for modified acrylic sheet.

## 5.2 Suggestion for Future Work

In area of modified acrylic sheet, it should be further studied in the following aspects:

1. To prepare the ST-MMA copolymer sheet containing the hydrogenated graft natural rubber.
2. To apply the grafted natural rubber product as impact modifier for other rigid polymer.
3. To apply the hydrogenated natural rubber as impact modifier for other outdoor weathering polymer.

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# APPENDICES

# APPENDIX A

The grafted natural rubber could be separated from the products of the emulsion copolymerization by the extraction with suitable solvent [42]. In this work, the extraction time of free polymer (e.g. free natural rubber, free homopolymers, and free copolymer) from grafted natural rubber was studied. Table A and Figure A show the time of extraction. The appropriate extraction time was 24 hrs.

**Table A** Extraction time of the free polymer.

| Time | Weight of sample (g) : extracted by LPE | | Weight of sample (g) : extracted by MEK/acetone | |
|---|---|---|---|---|
| (h) | No. 1 | No. 2 | No. 1 | No. 2 |
| 0 | 3.0011 | 3.0010 | 2.1920 | 2.0023 |
| 6 | 2.6572 | 2.5493 | 2.0511 | 1.9525 |
| 12 | 2.4116 | 2.2826 | 1.9961 | 1.8653 |
| 18 | 2.2647 | 2.0963 | 1.9852 | 1.8564 |
| 24 | 2.1932 | 2.0036 | 1.9840 | 1.8564 |
| 30 | 2.1920 | 2.0023 | 1.9830 | 1.8557 |

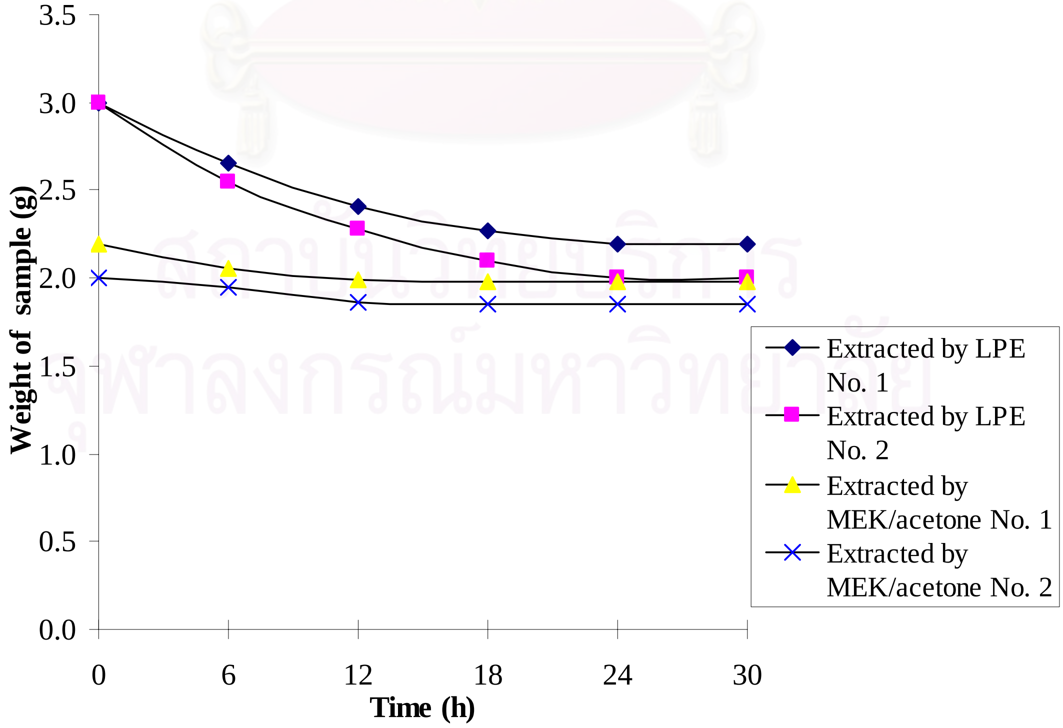


**Figure A** Extraction time of free polymer.

# APPENDIX B

## Determination of the Grafted Natural Rubber

### 1. Determination of the Conversion of Graft Copolymerization

The conversion of graft copolymerization was by the percentage increase of rubber weight. The calculations are as following equation:

$$\text{Total Conversion (\%)} = \frac{\text{Total weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \quad \text{(B-1)}$$

### 2. Determination of the Percentage Grafted Natural Rubber

The amount of grafted natural rubber, free natural rubber, free homopolymer, and free copolymer in the product could be determined by soxhlet extraction. The free natural rubber was extracted by light petroleum ether (60-80 °C) for 24 hrs. The residue was dried to constant weight in an oven at 40 °C under vacuum for 24 hrs. To remove free homopolymers and free copolymer, the residue was extracted in a methyl ethyl ketone (MEK)/acetone (50 : 50 (v/v)) mixture just as described when petroleum ether was used [28].

The products, therefore, contain three components in quantities a, b, and c respectively.

a is the weight of free rubber determined by soxhlet extraction with light petroleum ether (60-80 °C) for 24 hrs.

b is the weight of graft copolymers determined from the residual weight after extraction of free homopolymer.

c is the weight of free homopolymers and free copolymer determined by soxhlet extraction with MEK/acetone mixture for 24 hrs.

These quantities combined into a single expression are the measure of free natural rubber, free copolymers, grafted natural rubbers. All calculations are as following equations:

$$\text{Free Natural Rubber (\%)} = \frac{a}{a+b+c} \times 100 \qquad \text{(B-2)}$$

$$\text{Free Copolymers (\%)} = \frac{c}{a+b+c} \times 100 \qquad \text{(B-3)}$$

$$\text{Grafted Natural Rubbers (\%)} = \frac{b}{a+b+c} \times 100 \qquad \text{(B-4)}$$

## 3. Determination of Percentage of Grafting Efficiency

The percentage of grafting efficiency was determined by the percentage increase of grafting monomer weight. The calculations are as following equation:

$$\text{Grafting Efficiency (\%)} = \frac{\text{Total weight grafted monomer}}{\text{Total weight of monomer}} \times 100 \qquad \text{(B-5)}$$

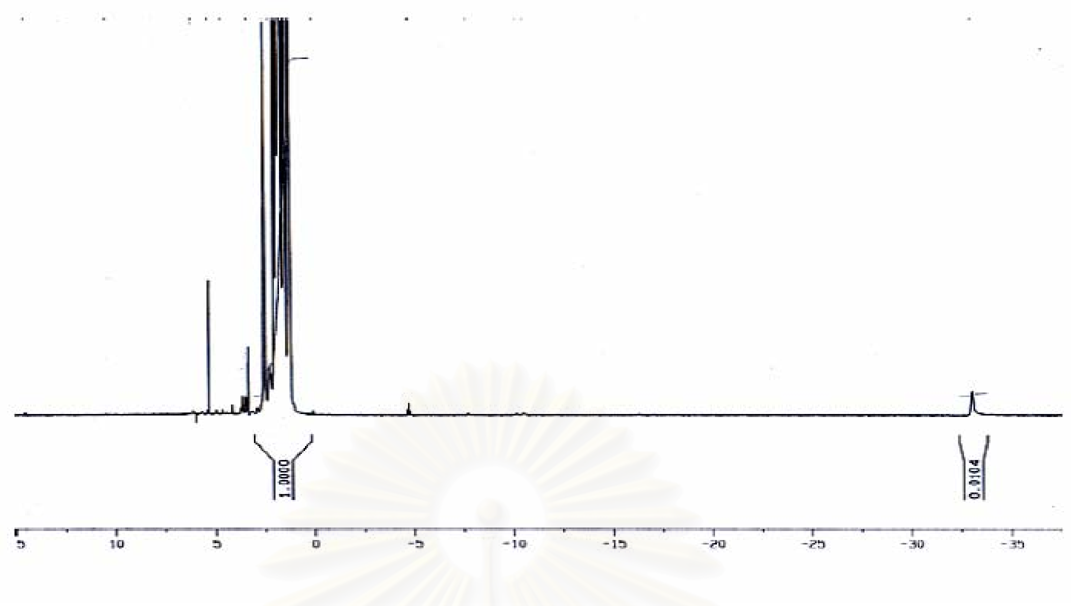
**Table B** Determination of grafted natural rubber.

| Reaction properties | GNR 01 | GNR 02 | GNR 03 |
|---|---|---|---|
| Natural rubber latex (g) | 50.60 | 50.70 | 50.10 |
| Dry rubber content (%) | 61.44 | 61.44 | 61.44 |
| Natural rubber content (g) | 31.09 | 31.15 | 30.78 |
| Graft product (g) | 37.51 | 37.21 | 36.13 |
| Total conversion (%) | 25.67 | 24.26 | 21.39 |
| Sample for soxhlet extraction (g) | 3.00 | 3.00 | 3.00 |
| Sample after extraction by LPE (g) | 2.19 | 1.89 | 2.00 |
| Sample after extraction by MEK/acetone (g) | 1.98 | 1.70 | 1.86 |
| Free natural rubber (g) | 0.81 | 1.11 | 1.00 |
| Free copolymers (g) | 0.21 | 0.18 | 0.15 |
| %Free natural rubber (%) | 26.92 | 37.05 | 33.24 |
| %Free copolymers (%) | 6.97 | 6.14 | 4.91 |
| %Grafted natural rubber (%) | 66.11 | 56.81 | 61.86 |
| Total monomer (g) | 6.42 | 6.06 | 5.35 |
| Total free monomer (g) | 2.61 | 2.29 | 1.77 |
| Total Grafted monomer (g) | 3.80 | 3.78 | 3.58 |
| Grafting efficiency (%) | 59.27 | 62.30 | 66.87 |

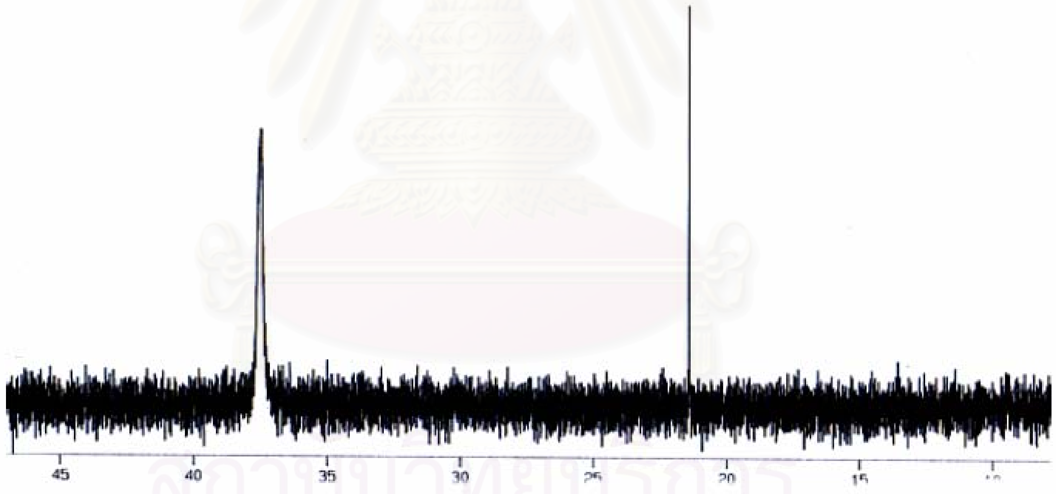
# APPENDIX C

## Preparation of $OsHCl(CO)(O_2)(PCy_3)_2$ Catalyst [22]

$OsHCl(CO)(O_2)(PCy_3)_2$ was prepared by refluxing $OsCl_3{*}H_2O$ (1 g) with tricyclohexylphosphine (5 g) in degassed 2-methoxyethanol (100 ml) in a 500 ml bottom flask with gas inlet tube under a nitrogen atmosphere for 24 hrs and then cooled down to room temperature. After that, the red-orange crystalline product, $OsHCl(CO)(PCy_3)_2$, was collected and washed with degassed methanol (15 ml) 2 times. $OsHCl(CO)(PCy_3)_2$ was kept under a nitrogen atmosphere until it was dried. $OsHCl(CO)(PCy_3)_2$ was analyzed by NMR spectroscopy and the $^1H$ and $^{31}P$ spectra obtained are shown in Figure C-1 : $^1H$-NMR ($CD_2Cl_2$): $\delta$ -33.06 (br.), $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 37.5 (s). $OsHCl(CO)(O_2)(PCy_3)_2$ was synthesized by exposing a degassed hexane (50 ml) suspension of the species $OsHCl(CO)(PCy_3)_2$ to pure oxygen gas until a while product was obtained. $OsHCl(CO)(O_2)(PCy_3)_2$ was filtered using normal filtration since the osmium complex is air-stable. The product was washed with hexane 2 times and dried in vacuum overnight. The NMR and FT-IR spectra of the final product are exhibited in Figure C-2 : $^1H$-NMR ($CD_2Cl_2$): $\delta$ -2.99 (t.), $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 16.63 (s.), IR: $\upsilon$(CO) 1945 $cm^{-1}$. The spectrum obtained from $^1H$-NMR spectroscopy showed a triplet at -2.99 ppm, attributed to the metal-hybride peaks, and peaks for various cyclohexyl protons of the complex appeared in the region from 2.5 to 0.8 ppm. The integration of the the hydride and cyclohexyl protons gave a ratio of approximately 66 to 1 which is consistent with the structural formula $OsHCl(CO)(O_2)(PCy_3)_2$

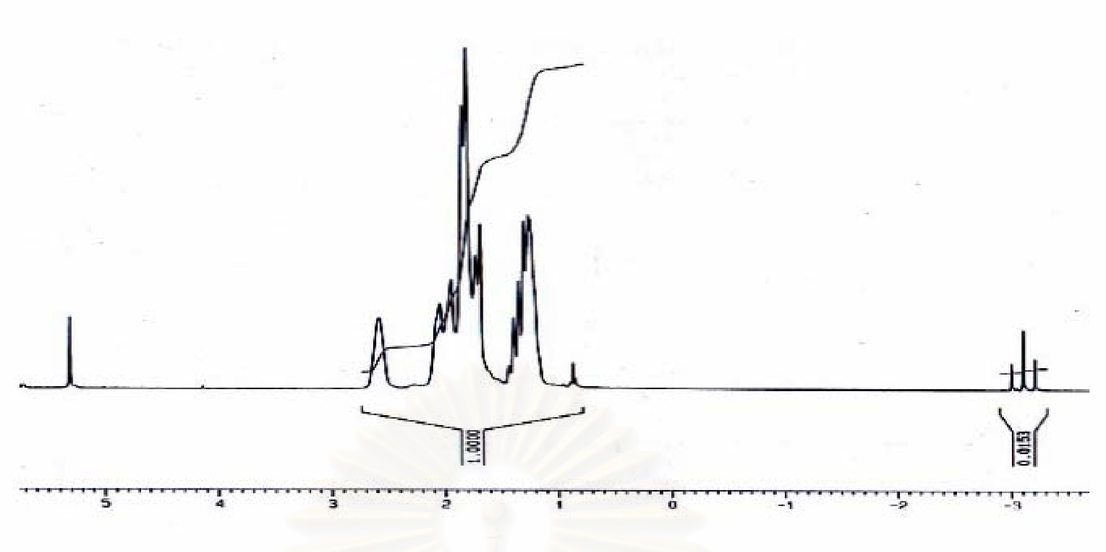


(a) $^{1}$H-NMR

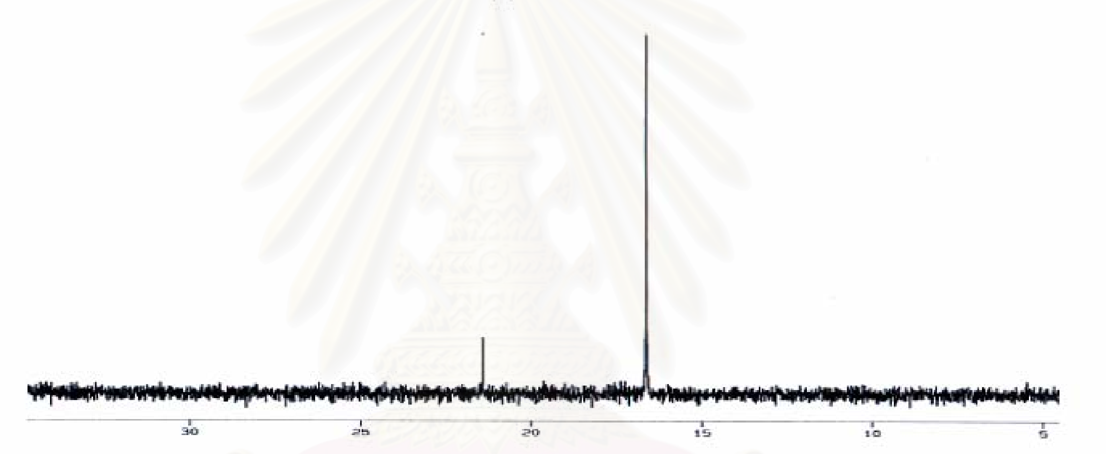


(b) $^{31}$P{$^{1}$H } NMR

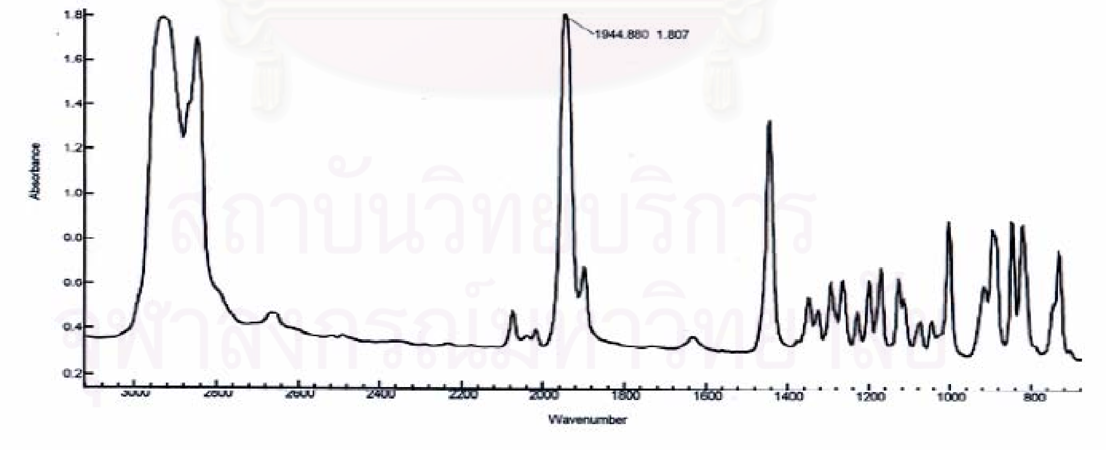
**Figure C-1** $^{1}$H-NMR and $^{31}$P{$^{1}$H } NMR spectra of $OsHCl(CO)(PCy_3)_2$ [22].



(a) $^1$H-NMR



(b) $^{31}$P{$^1$H } NMR



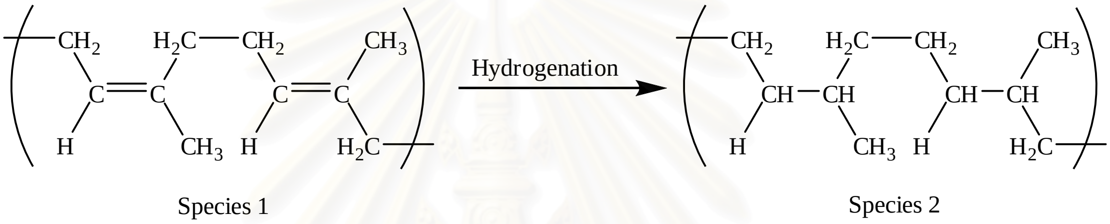
(c) FT-IR

**Figure C-2** $^1$H-NMR, $^{31}$P{$^1$H } NMR and FT-IR spectra of $OsHCl(CO)(O_2)(PCy_3)_2$ [22].

# APPENDIX D

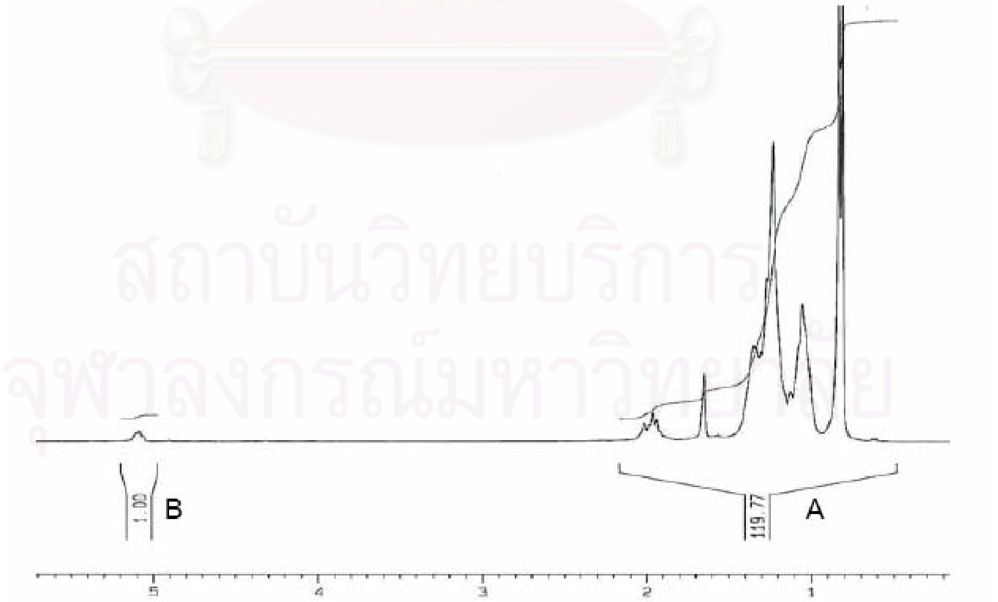
## Calculation of Degree of Hydrogenation [22]

The final degree of hydrogenation of each experiment was evaluated using $^1$H-NMR spectroscopy. The lump peak area for the saturated protons (-$CH_2$- and -$CH_3$-) in range of 0.8-2.3 ppm and unsaturated protons peak area at 5.2 ppm were measured in order to calculate the degree of hydrogenation eq. (D-1).



Protons of repeating unit except =CH in Species 1 = 7 protons

Protons of repeating unit in Species 2 = 10 protons



A = Peak area except at 5.2 ppm

B = Peak area at 5.2 ppm

C = Peak area of saturated $-CH_2-$ and $-CH_3$

$$A = 10C + 7B$$

$$C = \frac{A - 7B}{10}$$

Total peak area = Peak area of the saturated $-CH_2-$ and $-CH_3$ + Peak area at 5.2 ppm

$$= \frac{A - 7B}{10} + B$$

$$= \frac{A + 3B}{10}$$

%Hydrogenation = [(Peak are of sat. $-CH_2-$ and $-CH_3$)/(Total peak area)] × 100

$$= \frac{\left(\frac{A - 7B}{10}\right)}{\left(\frac{A + 3B}{10}\right)} \times 100$$

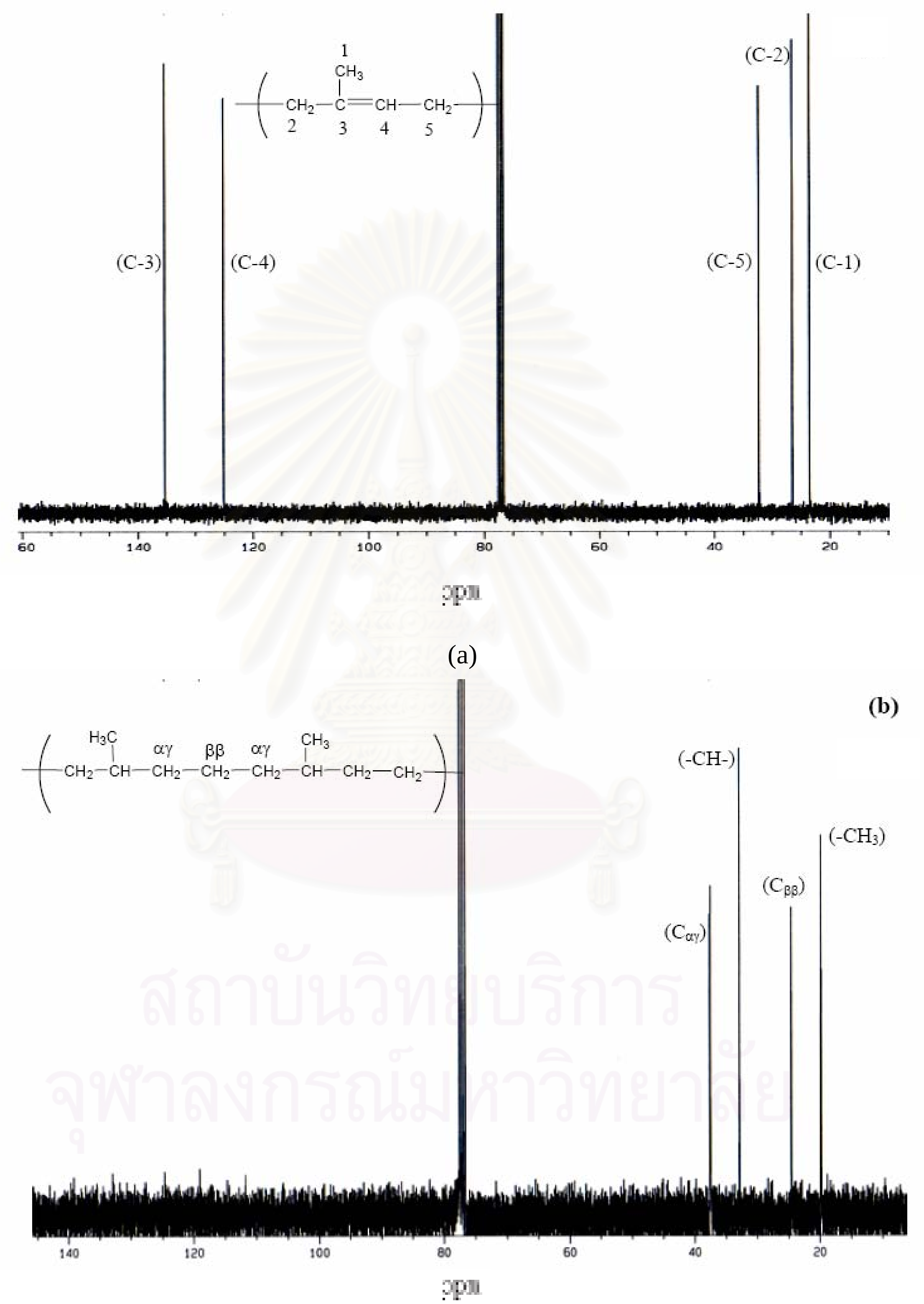
$$= \frac{A - 7B}{A + 3B} \times 100 \qquad \text{(D-1)}$$

For example : A = 119.7 and B = 1.00

$$\%\text{Hydrogenation} = \frac{119.7 - 7(1.00)}{119.7 + 3(1.00)} \times 100$$

$$= 91.85\%$$

# APPENDIX E



(a)

(b)

**Figure E** $^{13}$C-NMR spectra of (a) NR and (b) HNR [40].

# APPENDIX F

## Mechanical Properties of ST-MMA Copolymer Sheet Containing Modified Natural rubber

**Table F-1** Impact strength of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber.

| Expt. | ST/MMA (wt/wt) | Modified Rubber (%) | Impact Strength (kJ/m$^2$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 | Average | SD |
| 1 | 0/100 | - | 42.79 | 43.47 | 48.35 | 44.75 | 43.16 | 44.50 | 2.275 |
| 2 | 10/90 | - | 50.92 | 52.26 | 53.61 | 46.08 | 47.3 | 50.03 | 3.228 |
| 3 | 20/80 | - | 48.28 | 53.21 | 54.29 | 49.37 | 46.39 | 50.31 | 3.341 |
| 4 | 30/70 | - | 44.56 | 38.82 | 35.79 | 44.76 | 43.79 | 41.55 | 4.031 |
| 5 | 40/60 | - | 22.91 | 27.85 | 20.90 | 24.67 | 29.67 | 25.20 | 3.570 |
| 6 | 20/80 | 0.5% NR | 40.15 | 38.68 | 38.07 | 42.15 | 42.69 | 40.35 | 2.046 |
| 7 | 20/80 | 1% NR | 62.14 | 68.22 | 69.53 | 66.06 | 64.74 | 66.14 | 2.906 |
| 8 | 20/80 | 2% NR | 67.98 | 75.83 | 69.16 | 77.95 | 73.96 | 72.98 | 4.283 |
| 9 | 20/80 | 3% NR | 65.62 | 72.33 | 66.94 | 61.47 | 60.25 | 65.32 | 4.806 |
| 10 | 20/80 | 4% NR | 62.21 | 59.26 | 54.84 | 56.69 | 59.27 | 58.45 | 2.811 |
| 11 | 10/90 | 2% GNR | 73.82 | 69.21 | 76.96 | 71.52 | 75.15 | 73.33 | 3.042 |
| 12 | 20/80 | 2% GNR | 85.42 | 82.12 | 85.79 | 80.45 | 84.55 | 83.67 | 2.297 |
| 13 | 30/70 | 2% GNR | 80.32 | 82.62 | 79.79 | 81.85 | 84.75 | 81.87 | 1.974 |
| 14 | 40/60 | 2% GNR | 68.46 | 67.51 | 66.98 | 67.84 | 67.76 | 67.71 | 0.537 |
| 15 | 20/80 | 1% GNR | 71.86 | 79.31 | 74.32 | 72.56 | 75.93 | 74.80 | 2.978 |
| 16 | 20/80 | 2% GNR | 85.32 | 82.62 | 82.71 | 83.89 | 83.79 | 83.67 | 1.097 |
| 17 | 20/80 | 3% GNR | 70.35 | 72.46 | 68.95 | 71.52 | 67.46 | 70.15 | 1.995 |
| 18 | 20/80 | 4% GNR | 63.57 | 63.86 | 66.61 | 66.53 | 64.73 | 65.06 | 1.443 |
| 19 | 10/90 | 1% HNR | 60.62 | 60.75 | 65.53 | 57.59 | 58.93 | 60.68 | 3.006 |
| 20 | 20/80 | 1% HNR | 79.56 | 75.57 | 72.50 | 78.28 | 74.66 | 76.11 | 2.831 |
| 21 | 30/70 | 1% HNR | 67.97 | 64.40 | 66.12 | 65.25 | 69.16 | 66.58 | 1.957 |
| 22 | 40/60 | 1% HNR | 61.64 | 64.56 | 60.46 | 66.12 | 68.28 | 64.21 | 3.203 |
| 23 | 20/80 | 0.25% HNR | 45.78 | 36.63 | 39.12 | 42.68 | 37.73 | 40.39 | 3.778 |
| 24 | 20/80 | 0.5% HNR | 49.50 | 46.78 | 53.81 | 53.24 | 47.37 | 50.14 | 3.260 |
| 25 | 20/80 | 1% HNR | 79.56 | 75.57 | 72.50 | 78.28 | 74.66 | 76.11 | 2.831 |
| 26 | 20/80 | 2% HNR | 55.22 | 55.00 | 58.35 | 60.57 | 63.03 | 58.43 | 3.459 |
| 27 | 20/80 | 3% HNR | 48.83 | 53.24 | 50.09 | 57.99 | 51.07 | 52.25 | 3.592 |
| 28 | 20/80 | 4% HNR | 46.87 | 41.69 | 44.44 | 45.26 | 42.91 | 44.23 | 2.015 |

**Table F-2** Tensile strength of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber.

| **Expt.** | **ST/MMA (wt/wt)** | **Modified Rubber (%)** | **Tensile Strength (kJ/m$^2$)** | | | | |
|---|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | **Average** | **SD** |
| 1 | 0/100 | - | 43.56 | 45.50 | 44.43 | 44.50 | 0.972 |
| 2 | 10/90 | - | 52.71 | 48.03 | 49.35 | 50.03 | 2.414 |
| 3 | 20/80 | - | 50.78 | 50.53 | 49.62 | 50.31 | 0.611 |
| 4 | 30/70 | - | 41.05 | 39.33 | 44.26 | 41.55 | 2.504 |
| 5 | 40/60 | - | 26.55 | 23.80 | 25.26 | 25.20 | 1.378 |
| 6 | 20/80 | 0.5% NR | 40.01 | 41.47 | 38.43 | 39.97 | 1.520 |
| 7 | 20/80 | 1% NR | 45.21 | 43.16 | 38.35 | 42.24 | 3.521 |
| 8 | 20/80 | 2% NR | 61.75 | 63.94 | 69.23 | 64.97 | 3.846 |
| 9 | 20/80 | 3% NR | 62.71 | 60.43 | 61.92 | 61.69 | 1.158 |
| 10 | 20/80 | 4% NR | 32.29 | 30.84 | 31.31 | 31.48 | 0.740 |
| 11 | 10/90 | 2% GNR | 59.25 | 72.62 | 61.18 | 64.35 | 7.224 |
| 12 | 20/80 | 2% GNR | 72.53 | 67.99 | 64.68 | 68.40 | 3.944 |
| 13 | 30/70 | 2% GNR | 64.93 | 65.59 | 63.65 | 64.72 | 0.987 |
| 14 | 40/60 | 2% GNR | 58.28 | 58.77 | 58.69 | 58.58 | 0.261 |
| 15 | 20/80 | 1% GNR | 70.80 | 64.52 | 63.47 | 66.26 | 3.967 |
| 16 | 20/80 | 2% GNR | 72.53 | 67.99 | 64.68 | 68.40 | 3.944 |
| 17 | 20/80 | 3% GNR | 53.78 | 52.00 | 50.45 | 52.08 | 1.664 |
| 18 | 20/80 | 4% GNR | 49.27 | 50.21 | 51.03 | 50.17 | 0.881 |
| 19 | 10/90 | 1% HNR | 62.85 | 60.46 | 59.36 | 60.89 | 1.784 |
| 20 | 20/80 | 1% HNR | 69.43 | 70.16 | 67.13 | 68.91 | 1.581 |
| 21 | 30/70 | 1% HNR | 54.14 | 55.29 | 57.31 | 55.58 | 1.606 |
| 22 | 40/60 | 1% HNR | 41.62 | 38.71 | 37.83 | 39.39 | 1.982 |
| 23 | 20/80 | 0.25% HNR | 58.87 | 59.78 | 57.75 | 58.80 | 1.018 |
| 24 | 20/80 | 0.5% HNR | 67.47 | 65.63 | 65.91 | 66.34 | 0.992 |
| 25 | 20/80 | 1% HNR | 68.92 | 70.56 | 67.23 | 68.91 | 1.665 |
| 26 | 20/80 | 2% HNR | 63.36 | 64.29 | 64.93 | 64.19 | 0.790 |
| 27 | 20/80 | 3% HNR | 62.35 | 61.28 | 60.79 | 61.47 | 0.796 |
| 28 | 20/80 | 4% HNR | 55.10 | 55.34 | 55.17 | 55.20 | 0.123 |

**Table F-3** Elongation at break of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber.

| **Expt.** | **ST/MMA (wt/wt)** | **Modified Rubber (%)** | **Elongation at Break (%)** | | | | |
|---|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | **Average** | **SD** |
| 1 | 0/100 | - | 5.94 | 6.19 | 5.93 | 6.02 | 0.146 |
| 2 | 10/90 | - | 5.60 | 7.20 | 7.04 | 6.61 | 0.879 |
| 3 | 20/80 | - | 3.61 | 8.49 | 6.76 | 6.29 | 2.472 |
| 4 | 30/70 | - | 6.53 | 5.18 | 6.32 | 6.01 | 0.725 |
| 5 | 40/60 | - | 2.45 | 3.07 | 2.75 | 2.76 | 0.310 |
| 6 | 20/80 | 0.5% NR | 3.89 | 3.96 | 6.50 | 4.78 | 1.487 |
| 7 | 20/80 | 1% NR | 6.83 | 4.60 | 7.55 | 6.33 | 1.534 |
| 8 | 20/80 | 2% NR | 4.59 | 5.11 | 7.82 | 5.84 | 1.737 |
| 9 | 20/80 | 3% NR | 5.96 | 6.74 | 3.15 | 5.28 | 1.887 |
| 10 | 20/80 | 4% NR | 3.67 | 4.08 | 5.71 | 4.49 | 1.084 |
| 11 | 10/90 | 2% GNR | 7.30 | 7.51 | 7.10 | 7.30 | 0.203 |
| 12 | 20/80 | 2% GNR | 7.65 | 7.52 | 7.35 | 7.51 | 0.149 |
| 13 | 30/70 | 2% GNR | 7.76 | 7.00 | 7.15 | 7.30 | 0.402 |
| 14 | 40/60 | 2% GNR | 6.37 | 6.31 | 6.27 | 6.32 | 0.050 |
| 15 | 20/80 | 1% GNR | 6.95 | 6.99 | 7.55 | 7.16 | 0.336 |
| 16 | 20/80 | 2% GNR | 7.30 | 7.80 | 7.42 | 7.51 | 0.260 |
| 17 | 20/80 | 3% GNR | 6.90 | 7.34 | 7.21 | 7.15 | 0.229 |
| 18 | 20/80 | 4% GNR | 6.48 | 6.09 | 6.12 | 6.23 | 0.220 |
| 19 | 10/90 | 1% HNR | 8.21 | 8.17 | 8.53 | 8.30 | 0.199 |
| 20 | 20/80 | 1% HNR | 8.01 | 8.99 | 10.35 | 9.12 | 1.176 |
| 21 | 30/70 | 1% HNR | 5.06 | 8.60 | 6.92 | 6.86 | 1.774 |
| 22 | 40/60 | 1% HNR | 6.46 | 4.88 | 4.75 | 5.36 | 0.951 |
| 23 | 20/80 | 0.25% HNR | 6.74 | 6.62 | 7.23 | 6.86 | 0.324 |
| 24 | 20/80 | 0.5% HNR | 8.23 | 8.17 | 8.63 | 8.34 | 0.252 |
| 25 | 20/80 | 1% HNR | 11.86 | 11.20 | 11.61 | 11.55 | 0.332 |
| 26 | 20/80 | 2% HNR | 7.17 | 15.84 | 7.20 | 10.07 | 4.994 |
| 27 | 20/80 | 3% HNR | 9.71 | 9.12 | 9.45 | 9.43 | 0.294 |
| 28 | 20/80 | 4% HNR | 8.85 | 9.10 | 8.56 | 8.83 | 0.269 |

**Table F-4** Hardness of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber.

| **Expt.** | **ST/MMA (wt/wt)** | **Modified Rubber (%)** | **Hardness (HRM)** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | **4** | **5** | **Average** | **SD** |
| 1 | 0/100 | - | 97.5 | 97.8 | 98.3 | 97.9 | 97.9 | 97.9 | 0.275 |
| 2 | 10/90 | - | 93.9 | 93.6 | 93.7 | 93.8 | 93.7 | 93.7 | 0.103 |
| 3 | 20/80 | - | 89.8 | 89.5 | 89.4 | 89.9 | 90.2 | 89.8 | 0.322 |
| 4 | 30/70 | - | 76.8 | 77.8 | 77.2 | 77.5 | 77.1 | 77.3 | 0.383 |
| 5 | 40/60 | - | 75.9 | 76.7 | 76.9 | 76.8 | 76.5 | 76.6 | 0.397 |
| 6 | 20/80 | 0.5% NR | 84.3 | 83.8 | 83.6 | 84.1 | 83.6 | 83.9 | 0.311 |
| 7 | 20/80 | 1% NR | 82.8 | 82.9 | 83.4 | 83.4 | 83.5 | 83.2 | 0.324 |
| 8 | 20/80 | 2% NR | 80.3 | 80.0 | 79.4 | 79.5 | 79.7 | 79.8 | 0.370 |
| 9 | 20/80 | 3% NR | 74.3 | 74.8 | 74.4 | 74.9 | 74.6 | 74.6 | 0.255 |
| 10 | 20/80 | 4% NR | 70.4 | 70.5 | 70.6 | 70.6 | 70.7 | 70.6 | 0.114 |
| 11 | 10/90 | 2% GNR | 87.4 | 88.5 | 89.1 | 88.3 | 88.9 | 88.4 | 0.662 |
| 12 | 20/80 | 2% GNR | 83.9 | 83.3 | 82.8 | 83.4 | 82.7 | 83.2 | 0.487 |
| 13 | 30/70 | 2% GNR | 74.5 | 75.6 | 74.8 | 75.5 | 74.9 | 75.1 | 0.472 |
| 14 | 40/60 | 2% GNR | 75.0 | 75.7 | 74.1 | 74.1 | 75.2 | 74.8 | 0.705 |
| 15 | 20/80 | 1% GNR | 87.8 | 88.2 | 88.1 | 88.0 | 87.6 | 87.9 | 0.241 |
| 16 | 20/80 | 2% GNR | 83.9 | 83.3 | 82.8 | 83.4 | 82.7 | 83.2 | 0.487 |
| 17 | 20/80 | 3% GNR | 82.9 | 84.5 | 83.9 | 83.6 | 83.7 | 83.7 | 0.576 |
| 18 | 20/80 | 4% GNR | 81.3 | 81.6 | 80.7 | 81.1 | 80.0 | 81.2 | 0.619 |
| 19 | 10/90 | 1% HNR | 86.6 | 86.5 | 86.1 | 86.3 | 86.6 | 86.4 | 0.217 |
| 20 | 20/80 | 1% HNR | 79.6 | 78.5 | 79.5 | 78.5 | 81.4 | 79.5 | 1.185 |
| 21 | 30/70 | 1% HNR | 74.7 | 75.5 | 75.3 | 74.9 | 75.2 | 75.1 | 0.319 |
| 22 | 40/60 | 1% HNR | 63.8 | 64.4 | 63.5 | 64.8 | 64.5 | 64.2 | 0.534 |
| 23 | 20/80 | 0.25% HNR | 84.0 | 84.9 | 84.0 | 84.1 | 84.1 | 84.2 | 0.383 |
| 24 | 20/80 | 0.5% HNR | 81.9 | 82.0 | 82.0 | 82.3 | 81.9 | 82.0 | 0.164 |
| 25 | 20/80 | 1% HNR | 79.6 | 78.5 | 79.5 | 78.5 | 81.4 | 79.5 | 1.185 |
| 26 | 20/80 | 2% HNR | 75.1 | 76.5 | 75.3 | 75.0 | 75,7 | 75.5 | 0.695 |
| 27 | 20/80 | 3% HNR | 74.9 | 73.9 | 73.8 | 74.4 | 74.2 | 74.2 | 0.439 |
| 28 | 20/80 | 4% HNR | 68.2 | 69.4 | 68.9 | 68.3 | 68.5 | 68.7 | 0.493 |

# APPENDIX G

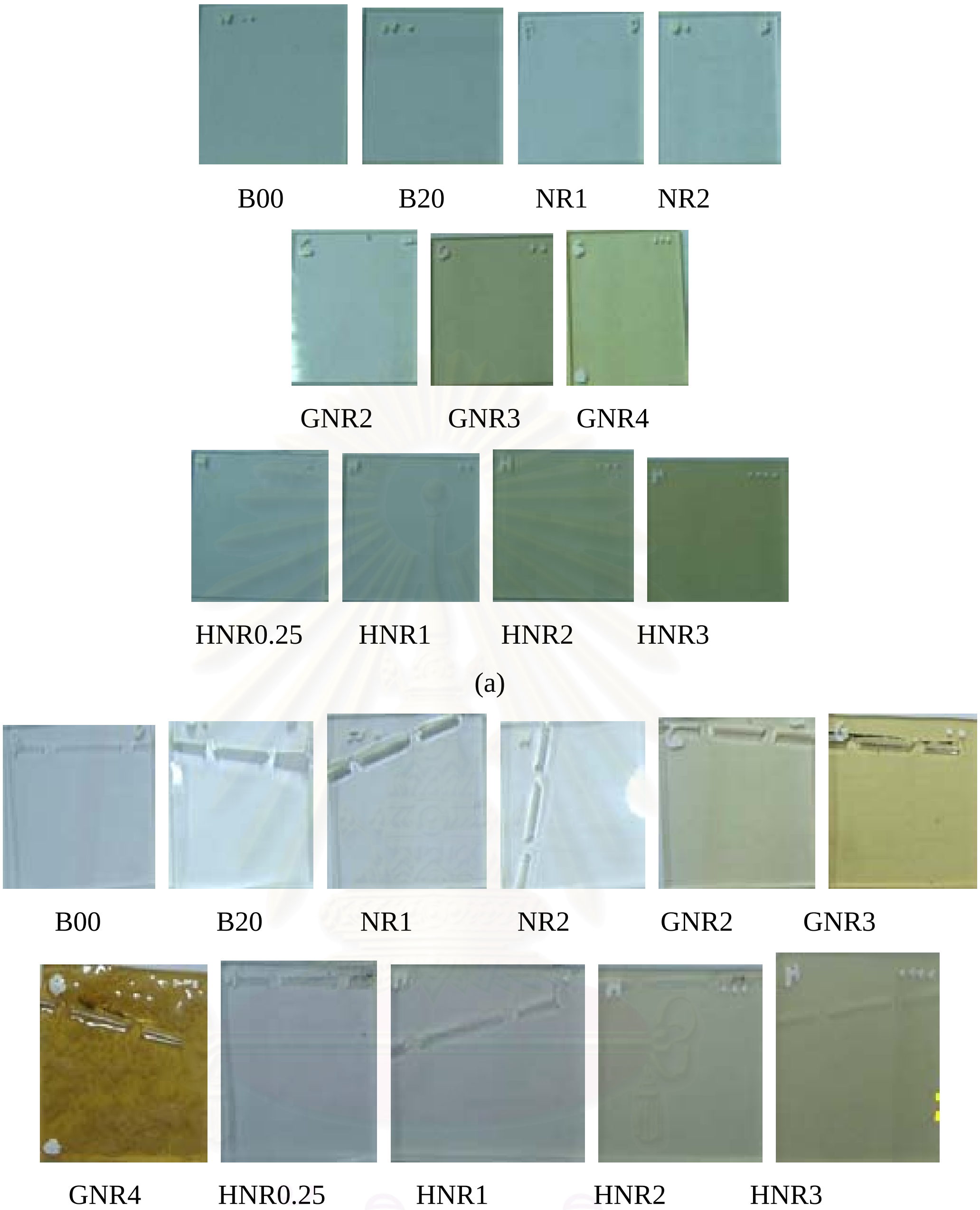
## Physical Properties of ST-MMA Copolymer Sheet Containing Modified Natural rubber

**Table G-1** Opacity of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber.

| **Expt.** | **CODE** | **ST/MMA (wt/wt)** | **Modified Rubber (%)** | **Color** | | | |
|---|---|---|---|---|---|---|---|
| | | | | **L*** | **a*** | **b*** | **Opacity** |
| 1 | *B00* | 100 | 0 | 94.40 | -0.41 | 3.08 | 12.28 |
| 2 | *B02* | 80 | 20 | 93.86 | -0.73 | 4.45 | 12.92 |
| 3 | *N21* | 80 | 20 | 94.36 | -0.65 | 4.41 | 12.86 |
| 4 | *N22* | 80 | 20 | 93.81 | -0.54 | 4.57 | 12.83 |
| 5 | *G22* | 80 | 20 | 92.91 | -0.99 | 7.25 | 13.05 |
| 6 | *G23* | 80 | 20 | 90.48 | -1.87 | 22.43 | 13.40 |
| 7 | *G24* | 80 | 20 | 87.26 | -1.01 | 22.59 | 15.10 |
| 8 | *H20.25* | 80 | 20 | 91.58 | -0.33 | 5.50 | 13.22 |
| 9 | *H21* | 80 | 20 | 87.22 | -0.01 | 8.60 | 15.57 |
| 10 | *H22* | 80 | 20 | 83.27 | -0.82 | 14.98 | 20.29 |
| 11 | *H23* | 80 | 20 | 80.52 | -0.47 | 20.31 | 22.04 |

**Table G-2** Thermal resistance of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber.

| **Expt.** | **CODE** | **ST/MMA** | **Modified Rubber** | **Opacity** | | | **Color difference (ΔE) of thermal resistance** | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **color before** | **color after test** | | | | |
| | | **(wt/wt)** | **(%)** | **test** | **1** | **2** | **1** | **2** | **Average** |
| 1 | *B00* | 100 | 0 | 12.22 | 12.69 | 12.81 | 1.05 | 0.87 | 0.96 |
| 2 | *B02* | 80 | 20 | 12.85 | 13.40 | 11.14 | 10.13 | 10.35 | 10.24 |
| 3 | *N21* | 80 | 20 | 12.63 | 12.30 | 12.51 | 0.96 | 1.04 | 1.00 |
| 4 | *N22* | 80 | 20 | 12.90 | 13.81 | 13.52 | 3.16 | 3.72 | 3.44 |
| 5 | *G22* | 80 | 20 | 13.01 | 14.02 | 13.82 | 15.94 | 16.04 | 15.99 |
| 6 | *G23* | 80 | 20 | 13.27 | 14.30 | 14.46 | 16.23 | 16.20 | 16.22 |
| 7 | *G24* | 80 | 20 | 15.11 | 33.59 | 31.81 | 22.30 | 22.21 | 22.26 |
| 8 | *H20.25* | 80 | 20 | 13.30 | 14.15 | 14.15 | 1.94 | 2.12 | 2.03 |
| 9 | *H21* | 80 | 20 | 15.80 | 15.61 | 15.88 | 0.69 | 0.62 | 0.66 |
| 10 | *H22* | 80 | 20 | 20.48 | 19.24 | 19.24 | 0.68 | 0.71 | 0.70 |
| 11 | *H23* | 80 | 20 | 22.34 | 21.23 | 21.01 | 0.53 | 0.60 | 0.57 |



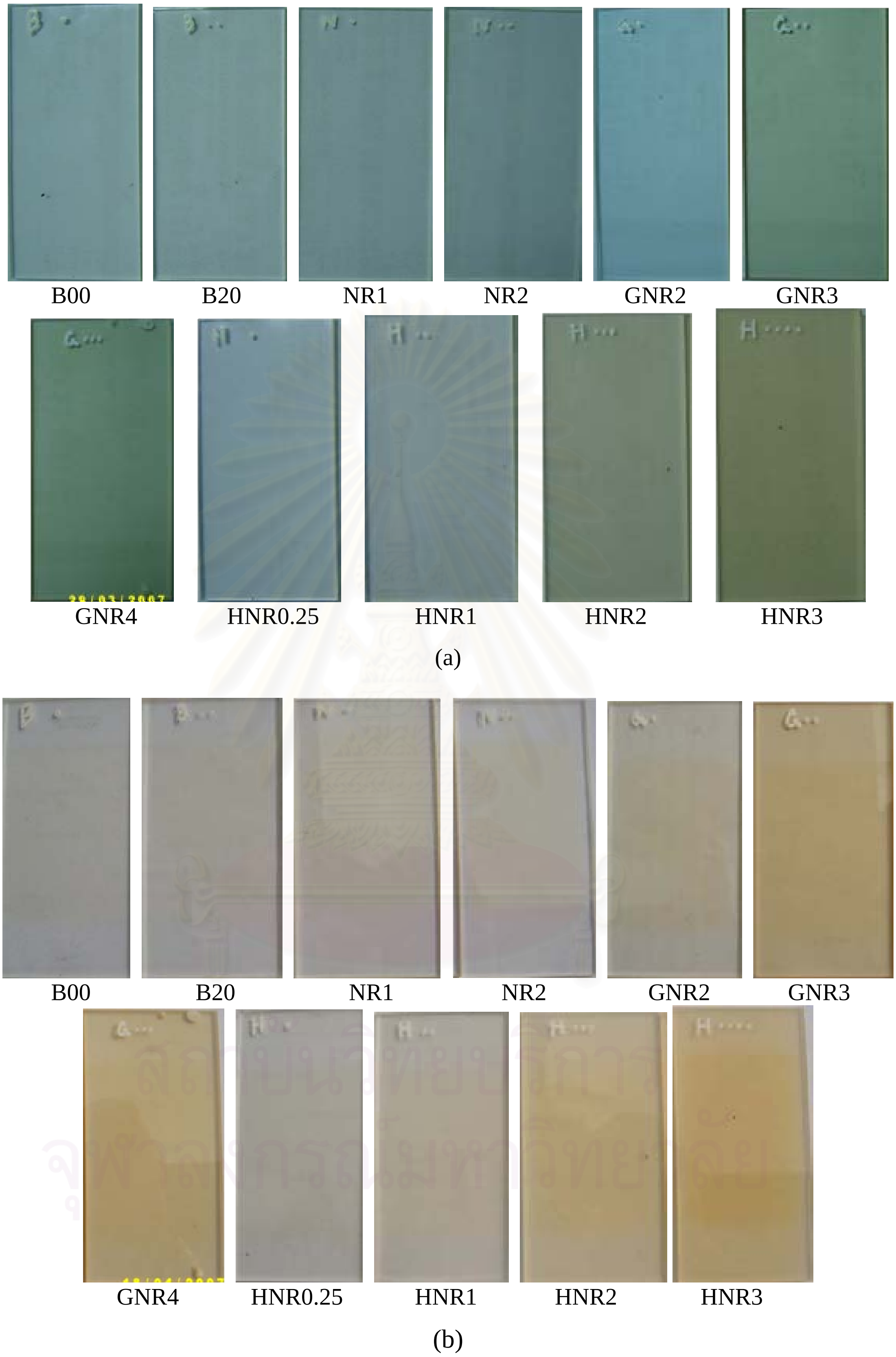
(a)

(b)

**Figure G-1** Samples of thermal resistance test : (a) before test and (b) after test.

**Table G-3** Ultraviolet resistance of ST-MMA copolymer sheet, ST-MMA copolymer sheet with natural rubber and ST-MMA copolymer sheet with modified natural rubber.

| Expt. | CODE | ST/MMA | Modified Rubber | Opacity | | | Color difference ($\Delta$E) of UV resistance | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | color before | color after test | | | | |
| | | (wt/wt) | (%) | test | 1 | 2 | 1 | 2 | Average |
| 1 | *B00* | 100 | 0 | 12.28 | 11.11 | 11.10 | 5.34 | 5.35 | 5.35 |
| 2 | *B02* | 80 | 20 | 12.92 | 11.84 | 11.84 | 8.92 | 8.87 | 8.90 |
| 3 | *N21* | 80 | 20 | 12.86 | 12.14 | 12.19 | 10.71 | 10.80 | 10.76 |
| 4 | *N22* | 80 | 20 | 12.83 | 13.39 | 13.43 | 10.39 | 10.23 | 10.31 |
| 5 | *G22* | 80 | 20 | 13.05 | 12.71 | 12.76 | 11.32 | 11.28 | 11.30 |
| 6 | *G23* | 80 | 20 | 13.40 | 12.36 | 12.35 | 8.47 | 8.43 | 8.45 |
| 7 | *G24* | 80 | 20 | 15.10 | 14.93 | 14.92 | 7.82 | 7.69 | 7.76 |
| 8 | *H20.25* | 80 | 20 | 13.22 | 11.92 | 11.81 | 8.01 | 7.96 | 7.99 |
| 9 | *H21* | 80 | 20 | 15.57 | 14.38 | 14.32 | 8.36 | 8.29 | 8.33 |
| 10 | *H22* | 80 | 20 | 20.29 | 19.2 | 19.14 | 12.65 | 12.64 | 12.65 |
| 11 | *H23* | 80 | 20 | 22.04 | 21.22 | 21.35 | 13.82 | 13.76 | 13.79 |



B00 B20 NR1 NR2 GNR2 GNR3

GNR4 HNR0.25 HNR1 HNR2 HNR3

(a)

B00 B20 NR1 NR2 GNR2 GNR3

GNR4 HNR0.25 HNR1 HNR2 HNR3

(b)

**Figure G-2** Samples of ultraviolet resistance test : (a) before test and (b) after test.

# VITA

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