การเตรียมอินซิทูซิลิกาที่มีหลายหมู่ฟังก์ชันในยางธรรมชาติผ่านกระบวนการโซล-เจล

นางสาวทวินันท์ เทพประดิษฐ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2555

PREPARATION OF IN SITU SILICA WITH MULTI-FUNCTIONAL GROUPS IN NATURAL RUBBER VIA SOL-GEL PROCESS

Miss Thawinan Theppradit

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2012

Thesis Title	PREPARATION OF IN SITU SILICA WITH MULTI-FUNCTIONAL GROUPS IN NATURAL RUBBER VIA SOL-GEL PROCESS
By	Miss Thawinan Theppradit
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Assistant Professor Sirilux Poompradub, Ph.D.
Thesis Co-Advisor	Professor Pattarapan Prasassarakich, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………. Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

……………………………………. Chairman
(Associate Professor Tharapong Vitidsant, Ph.D.)

……………………………………. Thesis Advisor
(Assistant Professor Sirilux Poompradub, Ph.D.)

……………………………………. Thesis Co-advisor
(Professor Pattarapan Prasassarakich, Ph.D.)

……………………………………. Examiner
(Assistant Professor Varawut Tangpasuthadol, Ph.D.)

……………………………………. External Examiner
(Assistant Professor Chanchai Thongpin, Ph.D.)

ทวินันท์ เทพประดิษฐ : การเตรียมอินซิทูซิลิกาที่มีหลายหมู่ฟังก์ชันในยางธรรมชาติผ่านกระบวนการโซล-เจล (PREPARATION OF IN SITU SILICA WITH MULTI FUNCTIONAL GROUPS IN NATURAL RUBBER VIA SOL-GEL PROCESS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.ศิริลักษณ์ พุ่มประดับ, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ.ดร.ภัทรพรรณ ประศาสน์สารกิจ, 102 หน้า.

งานวิจัยนี้มุ่งเน้นที่จะปรับปรุงความเข้ากันได้ระหว่างอนุภาคซิลิกากับยางธรรมชาติ โดยการดัดแปรพื้นผิวของอนุภาคซิลิกาด้วยโมดิฟายเออร์ 3 ชนิดได้แก่ เมทิลไตรเอทอกซีไซเลน ไวนิลไตรเอทอกซีไซเลนและอะมิโนโพรพิลไตรเมทอกซีไซเลน การเตรียมยางธรรมชาติผสมอนุภาคซิลิกาดัดแปรผิวมี 2 กระบวนการคือ การผสมทางตรงและการผสมทางอ้อม สำหรับการผสมทางตรงเตรียมได้โดยการนำองค์ประกอบทั้งหมดผสมลงในน้ำยางธรรมชาติเพื่อให้เกิดอินซิทูซิลิกาพร้อมกับการดัดแปรผิวในเนื้อยางธรรมชาติในเวลาเดียวกัน ส่วนการผสมทางอ้อมจะเริ่มจากการสังเคราะห์อนุภาคซิลิกาดัดแปรผิวแล้วจึงนำไปผสมกับน้ำยางธรรมชาติ สภาวะที่เหมาะสมในการเตรียมยางธรรมชาติผสมอนุภาคซิลิกาดัดแปรผิวของทั้งสองกระบวนการคือ ใช้เวลาในการทำปฏิกิริยาเพื่อเกิดอนุภาคซิลิกาดัดแปรผิว 24 ชั่วโมงที่อุณหภูมิห้อง โดยใช้อัตราส่วนของโมดิฟายเออร์ 0.1 โมลต่อโมลของเตตระเอทอกซีไซเลน อนุภาคซิลิกาที่ผ่านการดัดแปรผิวจะถูกนำไปวิเคราะห์ด้วยเทคนิคต่าง ๆ เพื่อยืนยันถึงความสำเร็จในการสังเคราะห์อนุภาคซิลิกาดัดแปรผิว ส่วนผลจากการทดสอบสมบัติของยางวัลคาไนเซตพบว่า วิธีการผสมทางตรงจะให้สมบัติเชิงกล สมบัติทางความร้อนและสมบัติเชิงพลวัตของยางวัลคาไนเซตที่สูงกว่าการเตรียมโดยวิธีทางอ้อมเล็กน้อย แต่อย่างไรก็ตามยางธรรมชาติที่ผสมซิลิกาที่ผ่านการดัดแปรผิวจากทั้งสองวิธีให้สมบัติของยางวัลคาไนเซตที่ดีกว่ากว่ายางธรรมชาติที่ผสมซิลิกาที่ไม่ผ่านการดัดแปรผิว

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อนิสิต…………………………………...….

ปีการศึกษา…………...2555…………….………ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก………..….

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม…...………

5372492623: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: NATURAL RUBBER / *IN SITU* SILICA / SOL-GEL PROCESS / SURFACE MODIFICATION

THAWINAN THEPPRADIT: PREPARATION OF IN SITU SILICA WITH MULTI-FUNCTIONAL GROUPS IN NATURAL RUBBER VIA SOL-GEL PROCESS. ADVISOR: ASST. PROF. SIRILUX POOMPRADUB, Ph.D., CO-ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, PH.D., 102 pp.

This research focuses on the improvement of compatibility between silica particles and NR matrix by modification of silica surface particles. The modifier containing MTES, VTES and APTMS were selected for investigation in this study. The preparations of modified silica filled NR compounds used two methods, i.e. direct and indirect methods. For direct method, all ingredients were mixed together with NR latex for silica particle generation and modification of their surface. For indirect method, the modified silica particles were first prepared and then directly mixed with NR latex. The optimum condition for both methods was carried out at 24 h under room temperature and the mole ratio of modifier to TEOS of 0.1. The modified silica particles were confirmed by using various techniques such as fourier transform infrared spectroscopy (FTIR), CHN analyzer and hydrophobic tester. The mechanical, thermal and dynamic properties of modified silica filled NR prepared by direct method were slightly enhanced when compared with indirect method. In addition, it is interesting to note that the modified silica filled NR vulcanizates of both direct and indirect methods were improved when compared with unmodified silica filled NR vulcanizates.

Field of Study:..Petrochemistry and Polymer Science….Student’s Signature…………………….
Academic Year:......................2012..............................Advisor’s Signature…………………
Co-advisor’s Signature……………….

ACKNOWLEDGEMENTS

The author would like to express his sincerest appreciation and deepest thankfulness to my advisor, Asst. Prof. Dr. Sirilux Poompradub for her discerning suggestion encouragement, sacrifice, and forbearance through his course of study. Thanks are also extended to Prof. Dr. Pattarapan Prasassarakich, Assist. Prof. Dr. Varawut Tangpasuthadol and Assist. Prof. Dr.Chanchai Thongpin from Silpakorn University for being members of the thesis committee and for their worthy comments and suggestions.

The author acknowledges the funding support from Toyo Tire & Rubber Co. Ltd., (Japan). Many thanks are going to the Program of Petrochemistry and Polymer Science and the Department of Chemical Technology, Faculty of Science, Chulalongkorn University for providing research facilities throughout the research work.

Finally, the author would like to express his gratitude to family members for their love, understanding and great support throughout his study. Also, special thanks are expanded to his friends for friendship, encouragements and cheerful moral support.

CONTENTS

Page

ABSTRACT IN THAI.......... iv
ABSTRACT IN ENGLISH.......... v
ACKNOWLEDGEMENTS.......... vi
CONTENTS.......... vii
LIST OF TABLES.......... xi
LIST OF FIGURES.......... xiii
LIST OF SCHEMES.......... xv
LIST OF ABBREVIATIONS.......... xvi

CHAPTER I: INTRODUCTION.......... 1
  1.1 Introduction.......... 3
  1.2 Objectives.......... 3
  1.3 Scope of the Investigation.......... 3

CHAPTER II: THEORY AND LITERATURE REVIEWS.......... 5
  2.1 Natural Rubber.......... 5
    2.1.1 General Introduction.......... 5
    2.1.2 NR Latex.......... 6
    2.1.3 Properties of NR.......... 8
    2.1.4 Improvement for NR.......... 9
  2.2 Fillers.......... 10
    2.2.1 Reinforcement of Rubber with Particulate Fillers.......... 10
      2.2.1.1 Reinforcing Fillers.......... 11
      2.2.1.2 Semi-Reinforcing Fillers.......... 11
      2.2.1.3 Diluent Fillers.......... 11

Page

2.2.2 The Factors of Reinforcement.. 11
    2.2.2.1 Fillers Content... 12
    2.2.2.2 The Particle Size.. 12
    2.2.2.3 Specific Surface Area... 13
    2.2.2.4 Particle Shape... 14
    2.2.2.5 Specific Surface Activity/Chemical Composition............. 15
2.3 Silica Material... 15
  2.3.1 Silica Classification.. 16
  2.3.2 Chemistry of Silica.. 17
  2.3.3 Silica-Rubber Interaction... 19
2.4 Improvement of Reinforced Ability... 21
  2.4.1 Coupling Agent.. 21
  2.4.2 Sol-gel Method... 22
    2.4.2.1 The Sol-Gel Chemistry of Silica....................................... 25
    2.4.2.2 Influence of Parameters in Sol-Gel Process...................... 28
      2.4.2.2.1 The Precursors.. 28
      2.4.2.2.2 pH/Catalysts.. 29
      2.4.2.2.3 Water: TEOS Molar Ratio... 29
      2.4.2.2.4 The Temperature, Aging and Drying............................ 30
  2.4.3 Silica - Surface Modification... 31
    2.4.3.1 Heat Treatment.. 31
    2.4.3.2 Organoalkoxysilane Modification. 31
    2.4.3.3 Polymer Grafting.. 33
2.5 Applications of Modified Silica Nanoparticles....................... 36
2.6 Literature Reviews... 37

Page
CHAPTER III: EXPERIMENTALS 41
3.1 Chemicals 41
3.2 Equipments 41
3.3 Procedure 42
3.4 Preparation of silica particles for indirect method 42
3.5 Characterization 44
3.5.1 Fourier transform infrared spectroscopy (FTIR) 44
3.5.2 CHN analyzer 45
3.5.3 Scanning electron microscopy (SEM) 45
3.5.4 Water contact angle measurement 46
3.5.5 Thermogravimetric analysis (TGA) 47
3.6 Preparation of rubber compound 47
3.6.1 Rubber compound prepared by direct method 47
3.6.2 Rubber compound prepared by indirect method 47
3.7 Preparation of NR vulcanizates 48
3.8 Properties of NR vulcanizates 49
3.8.1 Morphology of NR vulcanizates 49
3.8.2 Measurement of swelling behavior 49
3.8.3 Mechanical properties 50
3.8.3.1 Tensile properties 50
3.8.3.2 Hardness 50
3.8.3.3 Tear resistance 51
3.8.3.4 Abrasion resistance 52
3.8.3.5 Compression set 52
3.8.4 Thermal properties 53
3.8.5 Dynamic mechanical analysis (DMA) 53

Page
CHAPTER IV: RESULTS AND DISCUSSION.. 54
4.1 Synthesis of silica particles.. 54
4.1.1 Effect of reaction time and temperature....................................... 54
4.1.2 The modification reaction... 55
4.1.3 Characterization.. 56
4.1.3.1 FTIR.. 56
4.1.3.2 CHN analysis.. 59
4.1.3.3 SEM analysis.. 60
4.1.3.4 The hydrophobicity.. 62
4.1.3.5 The thermal analysis.. 63
4.1.4 Effect of mole ratio of modifier to TEOS..................................... 64
4.2 Properties of NR vulcanizates.. 70
4.2.1 Morphology... 70
4.2.2 Cure characteristics... 72
4.2.3 Mechanical properties.. 74
4.2.4 Thermal properties... 76
4.2.5 Dynamic mechanical analysis... 79

CHAPTER V: CONCLUSION AND FUTURE DIRECTION....................... 83
5.1 Conclusion.. 84
5.2 Future Direction.. 84
REFERENCES... 85
APPENDICES.. 89
APPENDIX A.. 90
APPENDIX B.. 92

VITAE.. 102

LIST OF TABLES

Table Page

2.1 The compositions of the total content in NR latex.. 6

2.2 The general properties of NR.. 8

2.3 Forms and properties of silica used in rubber compounding........................... 17

2.4 The solubility parameters of common compounding ingredients................... 19

3.1 Formulations in parts by weight per hundred parts of rubber (phr) for rubber compound.. 47

4.1 CHN analyses of U-Si, M-Si, V-Si and A-Si particles.................................... 58

4.2 Average particle sizes of U-Si, M-Si, V-Si and A-Si particles....................... 59

4.3 The contact angle of U-Si, M-Si, V-Si and A-Si particles.............................. 61

4.4 The peak area of Si–OH groups (A.cm^{-1}) and contact angle of U-Si, M-Si, V-Si and A-Si particles which using the difference of mole ratios of modifier to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0.................................... 69

4.5 Cure properties of rubber vulcanizates.. 73

4.6 Properties of NR vulcanizates.. 76

B.1 CHN analysis of U-Si, M-Si, and A-Si particles, respectively....................... 91

B.2 Silica particle size (nm) determined by SEM (50 particles)........................... 92

B.3 The contact angle (°) of M-Si, V-Si and A-Si particles.................................. 94

B.4 Effect of reaction time and temperature on % yield of U-Si particles............ 95

B.5 100% modulus of NR vulcanizates.. 96

B.6 300% modulus of NR vulcanizates.. 96

B.7 500% modulus of NR vulcanizates.. 97

B.8 Tensile strength of NR vulcanizates.. 97

B.9 Elongation at break of NR vulcanizates.. 98

B.10 Hardness of NR vulcanizates compounding... 98

B.11 Tear resistance of NR vulcanizates.. 99

Table Page

B.12 Volume loss of NR vulcanizates.. 99
B.13 Compression set (%) of NR vulcanizates... 100
B.14 Compression set (%) of NR vulcanizates... 100

LIST OF FIGURES

Figure Page

2.1 Natural rubber or *c*is-1, 4 polyisoprene.......... 4
2.2 Tapping latex from a rubber tree.......... 5
2.3 Model of rubber particle in NR latex.......... 6
2.4 Filler classification class.......... 13
2.5 Idealized shapes of typical filler.......... 14
2.6 Types of silica surface silanols.......... 18
2.7 The chemical structure of Si-69 and Si-264.......... 21
2.8 The reaction of silica particle with coupling agent (TESPT) and formation of rubber-to-filler bonds.......... 23
2.9 The sol-gel technologies and their products.......... 24
2.10 The sol-gel reaction.......... 26
2.11 Surface modifications of silica particles.......... 32
2.12 “Grafting to” approach of surface modification.......... 34
2.13 “Grafting from” approach for surface modification.......... 34
3.1 Overview procedure.......... 42
3.2 Fourier transform infrared spectrometer and CHN analyzer.......... 44
3.3 Scanning electron microscope and water contact angle measurement.......... 45
3.4 Thermogravimetric analyzer.......... 47
3.5 Rubber "dumbbell" tensile test sample.......... 48
3.6 Shore hardness test.......... 50
3.7 The specimens of standard tear test by using die C.......... 50
3.8 Compression set device.......... 52
4.1 Effect of reaction time and temperature on % yield of U-Si particles.......... 53
4.2 The suspension of U-Si, M-Si, V-Si and A-Si particles in ethanol.......... 55

Figure Page

4.3 FTIR spectra of (a) U-Si (b) M-Si, (c) V-Si and (d) A-Si particles................ 56
4.4 SEM micrographs of (a) U-Si (b) M-Si, (c) V-Si and (d) A-Si particles......... 60
4.5 TGA curves U-Si, M-Si, V-Si and A-Si particles.. 63
4.6 FTIR spectra of M-Si which using the difference of mole ratios of MTES to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0.. 66
4.7 FTIR spectra of V-Si which using the difference of mole ratios of VTES to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0…... 67
4.8 FTIR spectra of A-Si which using the difference of mole ratios of APTMS to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0.. 68
4.9 TEM micrographs of NR vulcanizates with silica content of 10 phr by direct method of (a) U-Si (b) M-Si and (c) V-Si and by indirect method of (d) U-Si (e) M-Si, (f) V-Si and (g) A-Si... 70
4.10 The thermal properties of NR vulcanizates with silica content of 10 phr by (a) direct method and (b) indirect method of unmodified silica and modified silica particle... 77
4.11 Dynamic mechanical properties of NR vulcanizates with silica content of 10 phr by direct method of unmodified silica and modified silica particles as described by (a) the storage modulus (E') and (b) tan δ.................................. 80
4.12 Dynamic mechanical properties of NR vulcanizates with silica content of 10 phr by indirect method of unmodified silica and modified silica particles as described by (a) the storage modulus (E') and (b) tan δ.............................. 81

LIST OF SCHEMES

Scheme Page
3.1 The reaction for conversion of TEOS to silica particles by sol-gel process..... 43
4.1 Mechanism for modification of silica particles... 55
4.2 The route for preparation of (a) U-Si (b) M-Si, (c) V-Si and (d) A-Si particles.. 57

LIST OF ABBREVIATIONS

APTMS : Aminopropyltrimethoxysilane
A-Si : modified silica particles by APTMS
ASTM : American Society for Testing and Materials
CA : Contact angle
°C : Degree celsius
DMA : Dynamic mechanical properties
DRC : Dry rubber content
EA : Elemental analyzer
FTIR : Fourier transform infrared spectroscopy
MBTS : Mercaptobenzothiazole disulfide
MDR : Moving Die Rheometer
mm : Millimeter
M-Si : modified silica particles by MTES
MTES : Methyltriethoxysilane
nm : Nanometer
NR : Natural rubber
NR-V : unfilled NR vulcanizate
phr : Part per hundred part of rubber
PEG : Polyethylene glycol
SEM : Scanning electron microscopy
TEM : Transmission electron microscopy
TEOS : Tetraethoxysilane
TGA : Thermal gravimetric analysis
U-Si : unmodified silica particles
V-Si : modified silica particles by VTES
VTES : Vinyltriethoxysilane
ZnO : Zinc oxide

CHAPTER I

INTRODUCTION

1.1 Introduction

One of the major achievements of the rubber industry is to use reinforcing filler to improve desired properties rubber product for the extensive use in many applications. Silica has been used as an important reinforcing filler in the rubber industry for a long time ago. This is because it provides good mechanical properties for rubber products such as the tensile strength, tear resistance and abrasion resistance [1-2]. Silica is a non-black filler, thus it can add color to the rubber products. However, it cannot fully perform as a reinforcement in the NR matrix. This is because silica is classified as a polar filler due to the presence of more silanol groups on the silica surface. The hydrophilicity of silica surfaces leads to a strong silica-silica interaction. Silica particles tend to be aggregated resulting in poor dispersion inside the rubbery matrix [3]. This is the cause of low efficiency of silica particles for reinforcement in rubber materials.

These problems can be overcome or minimized by adding coupling agents, synthesizing the silica particle inside the rubbery matrix via a sol-gel process, and modifying the silica surface. Rubber industry often requires the use of silane coupling agents to improve the performance of silica filler. Silane coupling agent is a bifunctional compound that react with silica particles and rubber molecules via chemical linkages. The result is the enhancing of rubber-silica interaction and consequently the reinforcing efficiency of the silica is enhanced [4]. However, there was another method for improving reinforcement effects of silica. The sol-gel process of tetraethoxysilane (TEOS) as a precursor was developed to generate in-situ silica inside the rubbery matrix. In this silica particles were dispersed homogeneously in rubbery matrix both before and after curing [5]. Finally, the modification of the silica surface is an alternative method for enhancing compatibility between silica particles and rubber molecules. The functionalization of silica surfaces can be used to enhance and control the overall properties of silica particles. Generally, the functional groups on the particle surface usually play a critical role in the surface properties of particles such as hydrophobicity and the chemical reactivity that depends on substituted organic groups of modifier. The modified silica particle was carried out by several methods, however the most convenient technique for silica surface tailoring is using the reaction of silanol groups with suitable organoalkoxysilane reagents [6-7].

This work is focused on the modification of silica surface in order to enhance the compatibility between silica particles and NR molecules. Three kinds of organoalkoxysilane were used as modifier, i.e., methyltriethoxysilane (MTES), vinyltriethoxysilane (VTES) and aminopropyltrimethoxysilane (APTMS), respectively. Although, among three kinds of organoalkoxysilane had been used to modify the silica surface for various applications such as catalysts, electronics and sensor industries [8], there have not yet been applied on the reinforcement in NR vulcanizates.

By using modified silica surface with MTES and VTES, the hydrophobicity of the silica surface became increased [9-10]. Therefore, it was easily compatible with NR matrix which contained long chain hydrophobic molecules. Furthermore, the general silica surface was acidic and highly reactive. The silanol groups could react quickly with the curing agents, i.e. accelerator or activator. The efficiency of the curing agent was reduced leading to an increase in the scorch time and curing time of NR vulcanizates [11]. Therefore, the modifier as a basicity was interestingly used to enhance curing rate of NR compounding. Based on this idea, APTMS was also selected for modification of silica surface.

The preparation of rubber compounding was divided into two methods, i.e. indirect and direct methods. For indirect method, the modified silica particles were first prepared via sol-gel reaction of TEOS and then directly mixed with NR latex. Otherwise, a direct method was prepared by mixing all ingredients together in the same time for in-situ silica particles generated and modification of their surface inside NR matrix. The morphology of modified silica particles filled NR vulcanizates and their properties, i.e. cure characteristic, thermal, mechanical and dynamic mechanical properties were investigated and then compared with NR vulcanizates reinforced by unmodified silica particles.

1.2 Objectives

1.2.1 Prepare the modified silica particles by using organoalkoxysilanes containing MTES, VTES and APTMS

1.2.2 Characterize and analyze the modified silica particles

1.2.3 Study the effect of modified silica particles on the cure characteristic, mechanical properties and thermal properties of rubber vulcanizate compared with unmodified silica particles

1.3 Scope of the Investigation

1.3.1 Survey the previous literatures and related research works

1.3.2 Prepare the silica particles via a sol-gel reaction under a base catalyst as follows:

- 1.3.2.1 Unmodified silica
- 1.3.2.2 Modified silica by using three kinds of organoalkoxysilane containing MTES, VTES and APTMS, respectively

1.3.3 Characterize the unmodified and modified silica particles by using various techniques as follows:

- 1.3.3.1 Functional groups by fourier transform infrared spectroscopy (FTIR)
- 1.3.3.2 The content of carbon, hydrogen and nitrogen by CHN analysis
- 1.3.3.3 Morphology by scanning electron microscopy (SEM)
- 1.3.3.4 Hydrophobicity by water contact angle measurement
- 1.3.3.5 Thermal stability by thermogravimetric analysis (TGA)

1.3.4 Study the effect of the synthesis silica particles by varying parameters as follows:

- 1.3.4.1 Reaction time (12, 24, 48 hours)
- 1.3.4.2 Reaction temperature (30, 40, 50 ºC)
- 1.3.4.3 Types of modifiers (MTES, VTES, APTMS)
- 1.3.4.4 Mole ratio of modifier to TEOS

1.3.5 Prepare the rubber compounding by 2 methods as follows:

    - 1.3.5.1 Direct method: all ingredients including NR latex, TEOS, water, catalysts and modifier were mixed together in the same time to generate modified silica in NR matrix
    - 1.3.5.2 Indirect method: the modified silica particles were first prepared and then they were directly mixed with NR latex
- 1.3.6 Prepare the NR vulcanizates by a conventional mixing on a two-roll mill and prepared into sheets by compression molding
- 1.3.7 Study of the properties as follows:
    - 1.3.7.1 Morphology by TEM
    - 1.3.7.2 Cure characteristics by moving die rheometer (MDR)
    - 1.3.7.3 Mechanical properties as follows:
        - 1.3.7.3.1.1 Tensile strength (ASTM D412)
        - 1.3.7.3.1.2 Tear resistance (ASTM D624)
        - 1.3.7.3.1.3 Compression set (ASTM D 395)
        - 1.3.7.3.1.4 Hardness (ASTM 2240)
        - 1.3.7.3.1.5 Abrasion resistance (DIN 53516)
    - 1.3.7.4 Thermal property by TGA
    - 1.3.7.5 Dynamic mechanical properties (DMA) by a dynamic mechanical analyzer
- 1.3.8 Summarize and conclude the results

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber

2.1.1 General Introduction [12]

NR is one of the most important biosynthesized polymers. It is obtained from various plants. The only important commercial source of NR (sometimes called Para rubber) is from the *Hevea brasiliensis* tree; which is a native plant of Brazil. Hevea rubber was introduced to tropical Asia in 1876, by Sir Henry Wickman H.N. Ridley (Matthan, 1998). In 1899, Hevea rubber was first cultivated in Trang province, in the south of Thailand by Khosimby Na Ranong. The chemical structure of NR is comprised of more than 98% *cis*-1, 4-polyisoprene (Figure 2.1), which is unable to crystallize under normal conditions. NR is a high molecular weight polymeric substance with viscoelastic properties. The molecular weight distribution of NR is in the range of 200,000- 400,000. Its density is about 0.93 grams/cubic centimeter at a temperature of 20 degrees celsius, and its glass transition temperature is at about -72 degrees celsius.

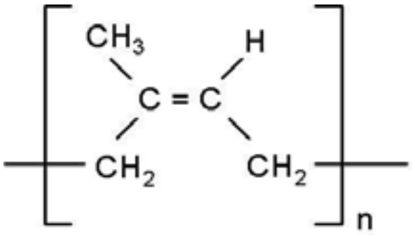


Figure 2.1 Natural rubber or *c*is-1, 4-polyisoprene (Morton, 1973)

2.1.2 NR Latex [13]

NR is extracted in the form of latex from the rubber tree as shown in Figure 2.2. The freshly tapped NR latex is of approximately 25-45% dry rubber content (DRC). NR latex contains not only rubber particles but also non-rubber particles dispersed in an aqueous serum as shown in Table 2.1. The ratio of rubber to non-rubber components varies from source to source.

The NR particles are covered by phospholipids and protein at the outermost layer, and may contain some metals such as magnesium, potassium and copper, at about 0.5%. Generally, NR latex exists in a form of a colloid of rubber particles in a spherical shape, with a size in the range of 0.004-4 micrometers (μm) as shown in Figure 2.3.

Figure 2.2 Tapping latex from a rubber tree (Andrew, 1999)

Table 2.1 The compositions of the total content in NR latex (Blackley, 1997)

Component	%(by weight)
Total solid content	27-48
Dry rubber content	25-45
Protein	1-1.5
Resin	1-1.25
Ash	≤ 1
Sugar	1
Water	52-73

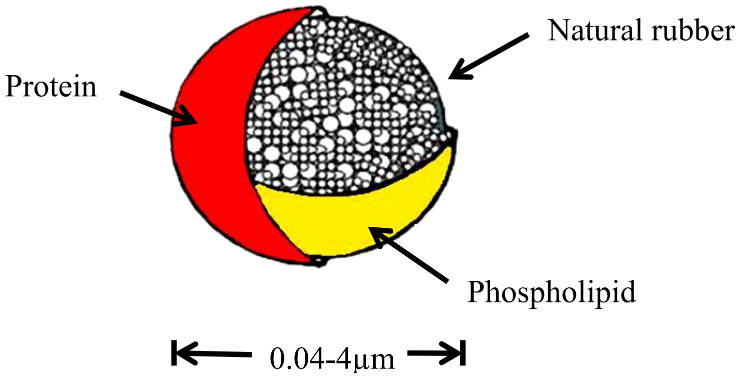


Figure 2.3 Model of rubber particle in NR latex (Wirach, 2549)

2.1.3 Properties of NR [14]

NR vulcanizate has excellent elasticity, in which the NR can return quickly to its original state when taking it out of loading, which is applied from an external force. NR without curing has excellent tacking. This is an important property for rubber production, which needs an assembly of each part. However, NR vulcanizate has a high tensile strength because NR can induce spontaneous crystallization at low temperatures or when stretched. The crystallization at low temperatures leads to enhanced stiffness of the NR matrix, although this crystalline polymer can easily be reversed by warming. The spontaneous crystallization causes the NR to have good properties, such as tensile strength, resistance to cuts, tearing resistance, and abrasion resistance. Additionally, NR has high dynamic properties, low energy loss, high fatigue resistance and high abrasion resistance.

The main component of NR is a non-polar hydrocarbon, so it can dissolve in non-polar solvents such as benzene, hexane or toluene etc. Its ability to dissolve tends to decrease when it is put through the curing process. The crosslinking of NR molecules brings a three dimensional network, resulting in the enhancive prevention of inserting solvents between NR molecules. NR has a number of double bonds in its structure, which leads it to be easily degraded by oxygen (oxidation) and ozone (ozonation) with catalyst by sunlight or heat. NR can be used in a range of temperatures from -55 to 70 degrees celsius. Its usage over 70 degrees celsius leads to the deterioration of NR chains, which brings a decrease in its mechanical properties. Table 2.2 summarizes some physical properties of NR. Notwithstanding, even after the curing process, NR still has carbon-carbon double bonds of rubber chain. Thus, it is weakened by oxygen, ozone and weather, which degrades the rubber chains. Apart from that, the mechanical properties of NR vulcanizates are not adequate for use in many applications. For these reasons, many efforts have been applied to improve the properties of NR to be used in wider applications.

2.1.4 Improvement for NR

There are various methods to improve the properties of NR materials. NR materials with a number of other components called compounding ingredients offer an alternative way to improve the processability, performance properties and life of the final product. Fillers are also used to enhance the performance related properties of rubbers. Commonly used reinforcing fillers for blending with NR are carbon black, calcium carbonate and silica. The fillers are classified by their reinforcing effects, as inactive, semi active to very active fillers.

Table 2.2 The general properties of NR (Blackley, 1997)

Properties	Value
Specific gravity	0.92
Refractive index (20 °C)	1.52
Coefficient of cubical expansion	0.00062/°C
Cohesive energy density	63.7 Cal/cc.
Heat of combustion	10547.084 Cal/g
Thermal conductivity	0.00032 Cal/sec/cm/°C
Dielectric constant	2.37
Power factor (at 1000 cycles)	0.15-0.2
Volume resistivity	1015 ohm.cm
Dielectric strength	3937 V/mm

2.2 Fillers [15]

The reinforcing fillers were used in rubber industry about 2.1 million tons per year that containing carbon black was 70%, kaolin clay was 15%, calcium carbonate was 8%, precipitated silica and silicates 4% and the varieties of miscellaneous mineral. The objective of reinforcing fillers is expected to improve the physical and mechanical properties of NR products. However, the efficiency of reinforcing fillers is depending on the filler types.

2.2.1 Reinforcement of Rubber with Particulate Fillers [16]

Another classification of fillers on the basis of physical nature groups are containing continuous and discontinuous in form. Continuous fillers have long aspect ratios, while discontinuous fillers have short aspect ratios and continuous fillers composites normally have a preferred orientation, while discontinuous fillers generally have a random orientation. Examples of continuous reinforcements include fibre, filament or tape, while examples of discontinuous reinforcements are whisker, flakes or particle. The elastomers reinforced with particulate fillers can maintain almost the same flexibility as that of the unfilled. The improvement in modulus and other physical properties achieved for elastomeric vulcanizates through particulate fillers is more pronounced with non-crystallising rubbers. The interaction of particulate fillers is dependent on a number of factors. The particulated fillers can be classified into three types.

2.2.1.1 Reinforcing Fillers

Reinforcing fillers, or very active fillers, can improve the physical and mechanical properties of rubber products, such as the enhancement of tensile strength, tear resistance and abrasion resistance, when using an appropriate amount; but using an excessive amount causes a decrease in resiliency properties. The main particle size of reinforcing fillers is in the range of 180 – 600 Å, with the example of carbon black and silica.

2.2.1.2 Semi-Reinforcing Fillers

Semi-reinforcing fillers, or semi active fillers, can improve some properties of rubber products. The main particle size of these fillers is in the medium size range, such as aluminum silicates, calcium silicates and kaolin.

2.2.1.3 Diluent Fillers

Diluent fillers or inactive fillers are not reinforcing fillers. They do not improve the properties of rubber products, but have a low cost, and the main particle size is larger than 10,000 Å, such as calcium carbonate, talcum and barium sulfates. Furthermore, these fillers can decrease the effects of some properties, such as tensile strength, tear resistance and abrasion resistance, and can improve some properties, such as its hardness, and it is easy to process and reduces production costs.

2.2.2 The Factors of Reinforcement [17]

The characteristics of fillers influence for reinforcement in rubber composite containing the amount, particle size, specific surface area, shape and surface activity of fillers.

2.2.2.1 Filler Content

The formulation of rubber vulcanization in order to acquire certain properties must use an appropriate content of filler. This is due to an excessive use of filler, which causes a loss in the natural properties of the rubber. Apart from that, an excess of filler contents tends to increase aggregation. This results in the properties of the rubber to decrease in quality, rather than be improved. The appropriate content of filler depends on various factors, such as method of mixing, the condition of mixing, and the usage of a coupling agent.

2.2.2.2 The Particle Size

The effect of reinforcement is mainly influenced by the size of the filler particles. Generally, a small particle size of filler brings a high efficiency of reinforcement. This is due to the small particle size of filler leading to an increase of specific surface area. The high specific surface area of filler brings a high interaction between filler particles and rubber chains (when compared with equal weights of filler). Accordingly, the usage of reinforcing filler with a small particle size can improve the properties of rubber vulcanizates such as tensile strength, tear resistance and abrasion resistance. If the particle size of filler were larger than that of polymer inter-chain distance, it introduced to localized stress area. This can contribute to the rupture of rubber chain on flexing or stretching. Fillers with particle size more than 10,000 nm (10 μm) are therefore avoid due to its can reduce performance rather than reinforce. The fillers with particle size in the range of 1,000-10,000 nm (1-10 μm) are used mainly as diluents and usually have no significant effect on rubber properties. Semi-reinforce fillers within the range of 100-1,000 nm (0.1-1 μm) can improve the strength and modulus properties. The really reinforcing fillers within the range of 10-100 nm (0.01-1μm) significantly enhance the properties of rubber product.

The example of various types of fillers, most talc and dry-ground calcium carbonate are not reinforcing filler because of their large particle size, although the planar shape of the talc particle contributes some improvement in reinforcement potential. The soft clay would fall into a class of diluent fillers that do not contributes reinforcement, yet are not so large that they degrade properties. The hard clay contributes some reinforcement to rubber compound, primarily because of their smaller particle size and is normally classified as semi-reinforcing filler. Ultra-fine precipitated calcium carbonate also fit into the semi-reinforcing class. The carbon black and precipitated silicates and silica are available in various particle sizes that range from semi-reinforcing to highly reinforcing. They generally exists as structure agglomerates or aggregates rather than that individual spherical particles. The example for filler classification class is shown in Figure 2.4.

2.2.2.3 Specific Surface Area [18]

Specific surface area (SSA) is the area of surface present in unit weight of filler and frequency used as a measurement of filler particle size. In some case this information is calculated from the particle size information, assuming a particular particle shape (usually spherical), but now a day it is usually measured by technique such as gas adsorption or dye adsorption. The most rigorous method is BET procedure, using nitrogen as the adsorbing molecule. As nitrogen is a very small molecule, it can insert in small pores and crevices that larger molecules may not be accessible. Thus it may give an overestimates of the area more than that using polymer. This is where larger molecules, such as dye, adsorbed from solution can be more useful. The specific surface area is obviously related to the particle size distribution of the filler and with materials of the same density and shape, a higher specific surface area means a smaller particles size.

2.2.2.4 Particle Shape

The shape of filler is an important factor in the use of fillers in polymers, affecting processing and composite properties. Typical particulate filler shapes are illustrated in Figure. 2.5. Anisotropy or aspect ratio is particularly important, being valuable in improving factor such as stiffness and heat distortion temperature. Despite this, shape is poorly described in the literature and specification. This is due to the difficulty of carrying out meaningful measurements, especially as aspect ratio is often significantly affected (reduced) by processing conditions. The difference in the measured SSA from that calculated from the size distribution, assuming a spherical shape, can sometimes be used as an indication of anisotropy. It is reported that some light scattering methods currently used for particle size measurement can be adapted to give shape information directly. The use of fractal analysis is now beginning to be explored by the filler industry, especially for carbon blacks and may ultimately allow particle shape to be measured and specified in a more useful way.

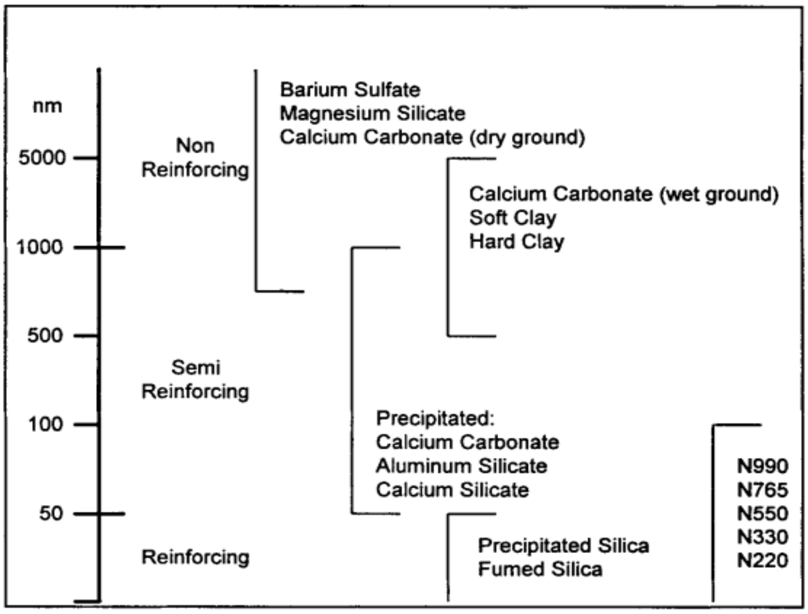


Figure 2.4 Filler classification class [17]

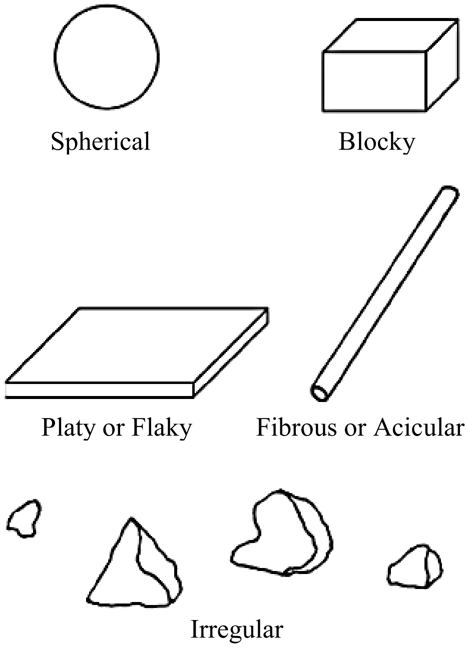


Figure 2.5 Idealized shapes of typical filler [18]

2.2.2.5 Specific Surface Activity/ Chemical Composition

The specific surface activity denotes the chemical composition of the filler surface. The nature of the filler surface may be varying in a chemical sense, having different chemical groups, e.g., hydroxyl or metal oxide in white fillers and carbonyl, quinone, lactone etc in carbon black. In a physical sense they may be different in adsorptive capacity and in energy of adsorption, e.g., polar rubbers showing dipole interaction with filler surface groups. Chemical surface groups on fillers play an important role in their effect on rate of cure, with many vulcanizing systems. Physical adsorption activity of the filler surface is of greater importance than its chemical nature. Carbon black, which loses the active sites on heat treatment, exhibits poor mechanical properties. Strong chemical bonding between filler and polymer does not lead to desirable vulcanizate strength properties, but causes high moduli.

2.3 Silica Material [19]

It is well known that carbon black and silica are important reinforcing fillers in the rubber industry. This is because the adding of these fillers in rubber can improve the mechanical properties of rubber vulcanizates, in particular, the hardness, modulus, tensile strength, tear strength and abrasion resistance etc. Nowadays, carbon black is used as a reinforcing filler in most industries. This is because carbon black is good as a reinforcing filler for rubber, has a low cost and is easily mixed with rubber. However, carbon black is limit in some applications, as the color of the product which uses carbon black as a filler is black. For this reason, carbon black is not suitable to be used as a filler for some products which combine good properties with a colorful product. For this case, using silica as a filler instead of carbon black is inevitable.

2.3.1 Silica Classification [20]

The two major classes, based on origin, are natural and synthetic. This distinction translates to a division between crystalline and amorphous forms, and equal importance, to a substantial division between coarse and fine primary particles. Among the natural, non-reinforcing materials, the term "ground quartz" includes a number of variously named grades which are defined in respect to their geographic origin. Among the synthetic group, rubber reinforcement, in terms of enhanced abrasion resistance and tear and tensile strengths, is supplied only by those precipitated and fumed silica. Forms and properties of silica used in rubber compounding are shown in Table 2.3.

There are two categories of commercially available synthetic silicas which are precipitated and fumed silica. The precipitated silica is by far the most common variety for general rubber usage. Precipitated silica is made by acid precipitation of alkali silicate solutions under controlled conditions. The sodium silicate solution is usually produced by combining high purity sand in a high temperature furnace, then dissolving the molten „glass" in water, the reaction is shown in equation 2.1. Precipitated silica is silicon dioxide containing about 10-14% water, with particle size in the range 1-40 nm. They are reinforcing fillers giving composites of high tensile strength, tear resistance, abrasion resistance and hardness. It is being used in the manufacture of translucent and coloured products, shoe soling, tyres and other mechanical rubber goods.

$$Na_2Si0_3 + HCl \rightarrow 2NaCl + H_20 + SiO_2 \qquad (2.1)$$

Fumed or pyrogenic silica is produced by high temperature gaseous process, a process which results in a pure silica with low silanol and water content and is more expensive. Fumed silica is silicon dioxide containing less than 2% combined water, the reaction is shown in equation 2.2. These silicas are highly reinforcing fillers of very small particle size, giving high tensile strength, tear resistance and abrasion resistance particularly to silicone rubbers.

$$nSiH_4 + 2nO_2 \rightarrow nSiO_2 + 2nH_2O \qquad (2.2)$$

Table 2.3 Forms and properties of silica used in rubber compounding [20]

	Primary size (µm)	Function in rubber
Natural (crystalline):		
Ground quartz	1-10	Extending
Diatomite	1-5	Processing; Extending
Neuberg silica	1-5	Extending
Synthetic (amorphous):		
Fumed	0.005-0.02	Reinforcing
Precipitated	0.01-0.03	Reinforcing
Precipitated	0.04	Semi-reinforcing
Precipitated	0.08	Processing; color
Ferro-silicon by-product	0.10	Extending

2.3.2 Chemistry of Silica [21]

Silica is an inorganic compound with the general formula SiO_2. In silicon dioxide, silicon atom uses *d* orbitals for bonding and hence SiO_2 exists as infinite three-dimensional structures and it is a high melting solid. Silica which is amorphous contains about 4% water and can be represented as $SiO_2.nH_2O$. It consists of silicon and oxygen arranged in a tetrahedral structure with particle size usually ranging from 1-30 nm and the surface area from 20-300 m^2/ g. Surface silanol concentration (Silanol groups -Si-OH) influences the degree of hydration. Water content can affect processing and vulcanization. Silanol types fall into three categories - isolated, geminal (two-OH groups on the same silicon atom) and vicinal (-OH on adjacent silicon atoms) were depicted in Figure 2.6.

Isolated hydroxyls exist predominantly on dehydrated silicas, pyrogenic silica and to a lesser extent on precipitated silica. Vicinal hydroxyls are stronger adsorption sites and hence, have stronger reinforcement effect than the isolated hydroxyls. The hydroxyl groups on the surface of the silica control surface acidity. This intrinsic acidity can influence vulcanization. These sites affect the rubber filler interaction.

The polar hydroxyl groups on the silica surface lead to the adsorption of foreign substances. So moisture is absorbed by silica. The higher moisture content increases the dispersion time of silica into the rubber. The filler also adsorbs organic compounds. Therefore, a larger amount of the same has to be added to compensate for the loss due to adsorption by silica. Accelerator adsorption by the filler will be lower, if it already contains water.

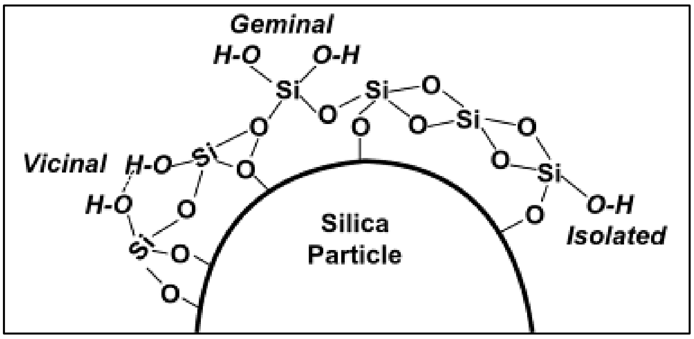


Figure 2.6 Types of silica surface silanols [21]

2.3.3 Silica-Rubber Interaction

One of the models for the adsorption of polymers on the surface of carbon black is based on the uncoiling of the polymeric chains and multiple adsorptions of these chains onto the surface of the filler. The released adsorption enthalpy is partly changing the chain conformation entropy, enabling the chains to abandon their coiled conformation and to take the form of extension. With several contacts per polymer chain the bonding strength of a polymer molecule is in the range of a chemisorptive interaction.

The intensity of wetting of the filler by a polymer depends on the difference of the solubility parameters. The surface concentration of adsorbed trains is inversely proportional to the difference of the solubility parameters between the polymer and the filler. The solubility parameters for some polymers and fillers are given in Table 2.4. For the silica polymer system, the difference of the solubility parameters is significant, with the effect that the two materials are difficult to blend. When a coupling agent is used, a hydrophobic shell is formed around the filler particle and the solubility parameter of the filler is reduced, the difference in the solubility parameters decreases and the compatibility of the two materials increases.

Table 2.4 The solubility parameters of common compounding ingredients

Material	Hildebrand Solubility parameter
FKM, silicones	7-7.5
PE, EPM, EPDM	8
NR, BR,IR	8
SBR, low molecular weight resins	8.5 - 9
CR, CSM, some NBR	9-9.5
Typical lubricants and process aids	8.5 - 9.5
PVC, ECO, ACM, some NBR	9.5 -10
Carbon black	12 -15
Clay, whiting, talk	13-14
Silica (untreated)	14-18

2.4 Improvement of Reinforced Ability

There are three important methods to improve or enhance the reinforcing efficiency of silica particles on rubber, including the usage of a coupling agent, the synthesis of silica inside the NR matrix via sol-gel method, and the modification of the silica surface.

2.4.1 Coupling Agent [22]

The silane coupling agent is a bifunctional compound widely used to improve reinforcing efficiency of silica by enhancing the rubber–filler interaction via chemical linkage. It possesses two functionally active end groups which can chemically react with both silica and rubber. The readily hydrolyzable alkoxy group will react with silanols on the silica surface to form stable siloxane linkages. The other end group, namely the organo-functional group, can participate in sulfur vulcanization leading to chemical linkage with the rubber. The reaction between silica and silane coupling agent is now well studied and reported in many published works. Nowadays, various types of silane coupling agent have been commercially developed. Extensive work has therefore been carried out to study their role in improving processability and properties of silica-filled rubbers. Recently, it was reported that the reinforcing action of the two well-known silane coupling agents, i.e. bis-(3-triethoxysilylpropyl) tetrasulfane (Si-69) and 3-thiocyanatopropyl triethoxy silane (Si-264) as shown in Figure 2.7 depends greatly on the curing system, i.e. Si-264 gave better reinforcement than Si-69 in the conventional vulcanization (CV) system whereas different results were found in the efficient vulcanization (EV) system. The chemical structures of both Si-69 and Si-264 are given in Figure 2.8 and the reaction of silica particle with coupling agent was shown in Figure 2.8.

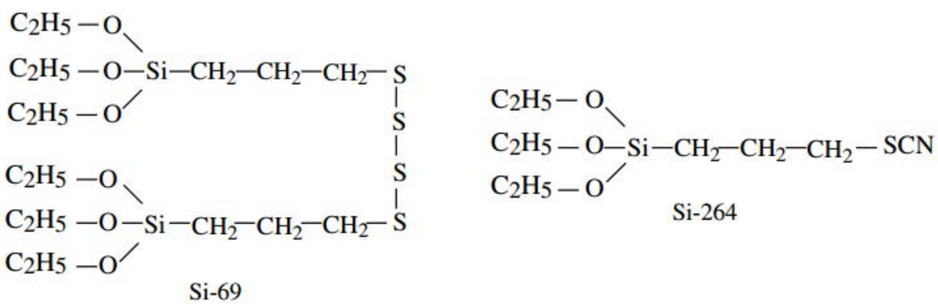


Figure 2.7 The chemical structure of Si-69 and Si-264, respectively, as a commonly used for coupling agent [22]

2.4.2 Sol-gel Method [23]

The sol-gel technique has been used for reproduce new porous nanomaterials, with well-defined structures and complex shapes, which used in numerous applications, such as coatings and thin films in electronic or optical components and devices. The process has been used to produce amorphous materials in various forms, such as powders, fibers, coatings and thin films, monoliths and porous membranes as shown in Figure2.9. It is known that the sol-gel technology is relatively simple and allows the control of the distribution of the components in molecules, through a pre-orientation of the network. Thus, the potential applications of the materials synthesized by this method can be competitive (also in terms of production costs). Sol-gel is a very flexible route for the synthesis of inorganic, organic-inorganic networks such as glasses, ceramics, films or powders.

The sol-gel process involves the formation of mineral phases starting from soluble molecular precursors, following an inorganic polymerization reaction. The reaction is at room temperature, in water or organic solvents and in a wide range of pH/ionic strength conditions. The transition from a liquid (solution or colloidal solution) into a solid (di- or multiphase gel) explains the name of the “sol-gel process”. The first step in the sol-gel process of silica consists of hydrolyses of silicon alkoxides through condensation, forming the silica nanoparticles. Depending on the reaction conditions, these particles can further grow and form a sol. The nature of precursors, the molar ratios between the reactants, the nature of the solvent, the use of modifying agents, pH, the synthesis temperature, influence the microstructure and thus the properties of the resulting material

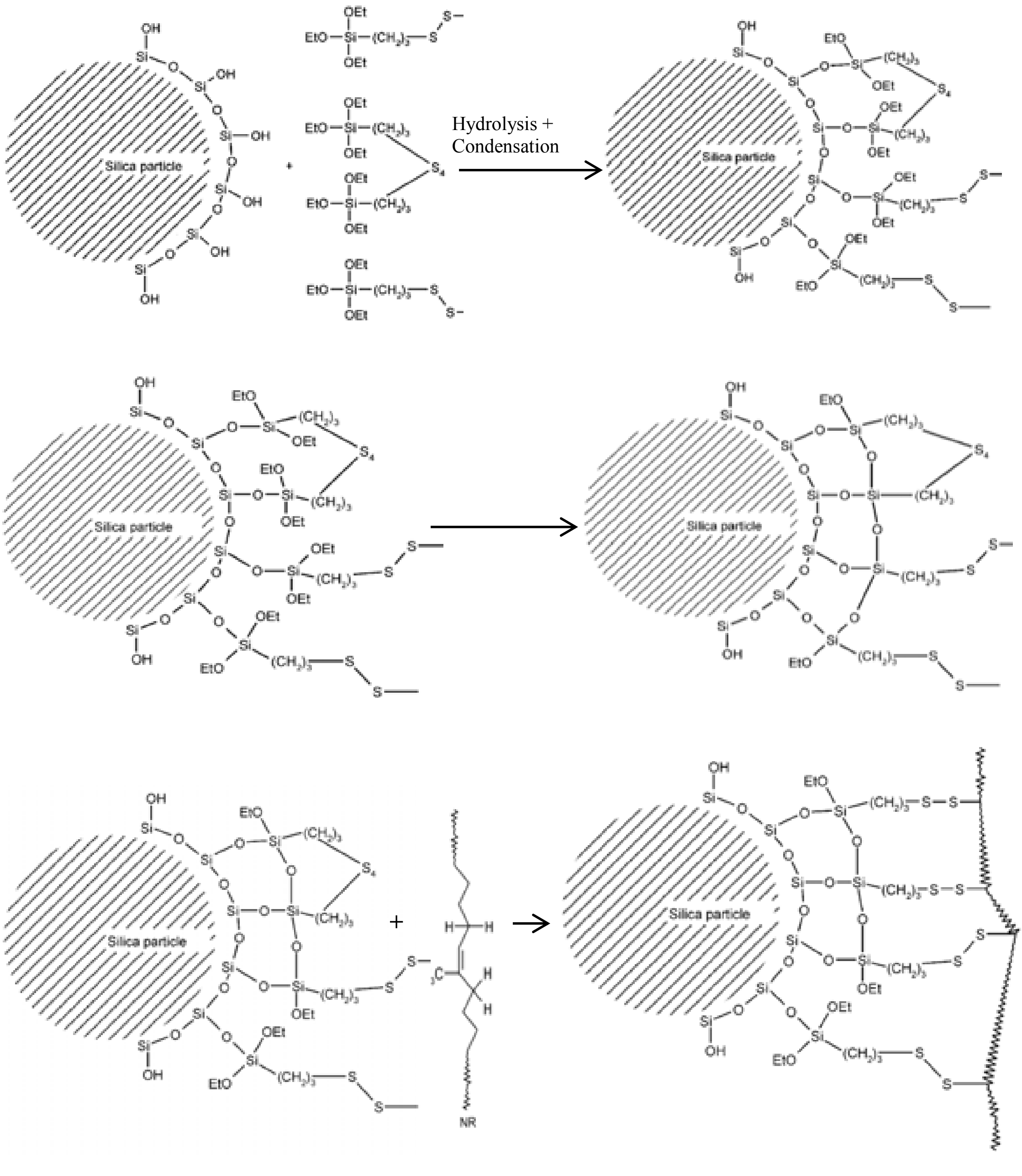


Figure 2.8 The reaction of silica particle with coupling agent (TESPT) and formation of rubber-to-filler bonds [22]

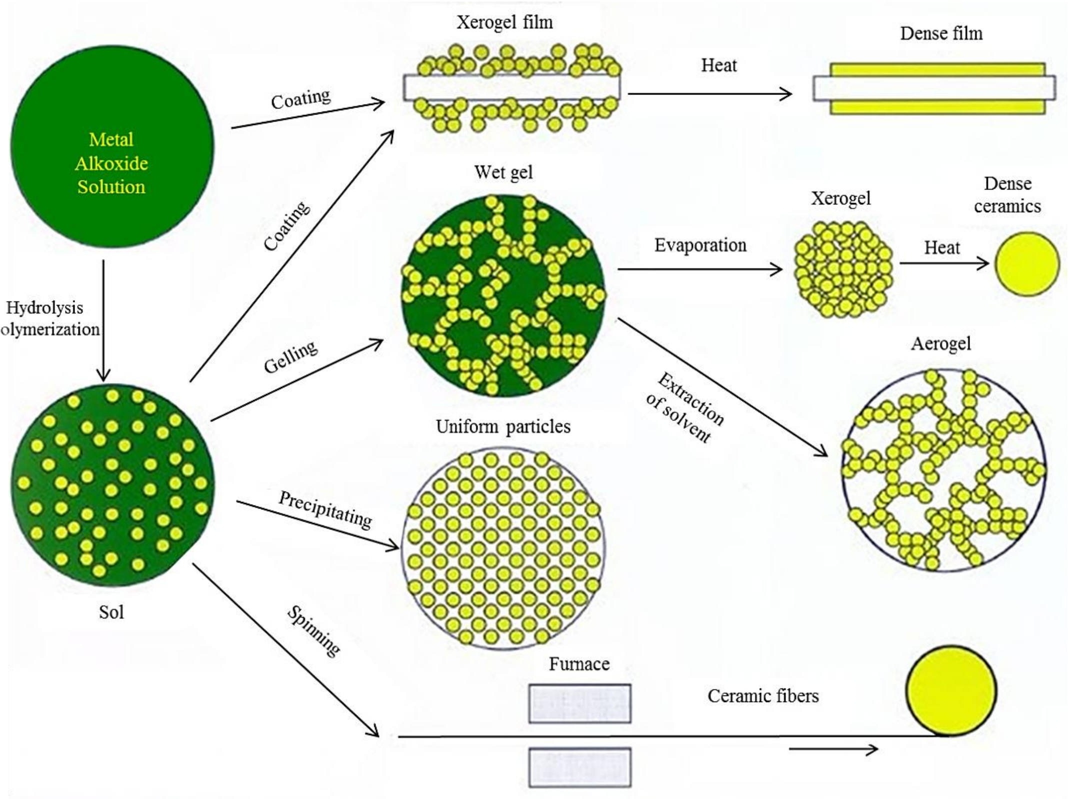


Figure 2.9 The sol-gel technologies and their products [23]

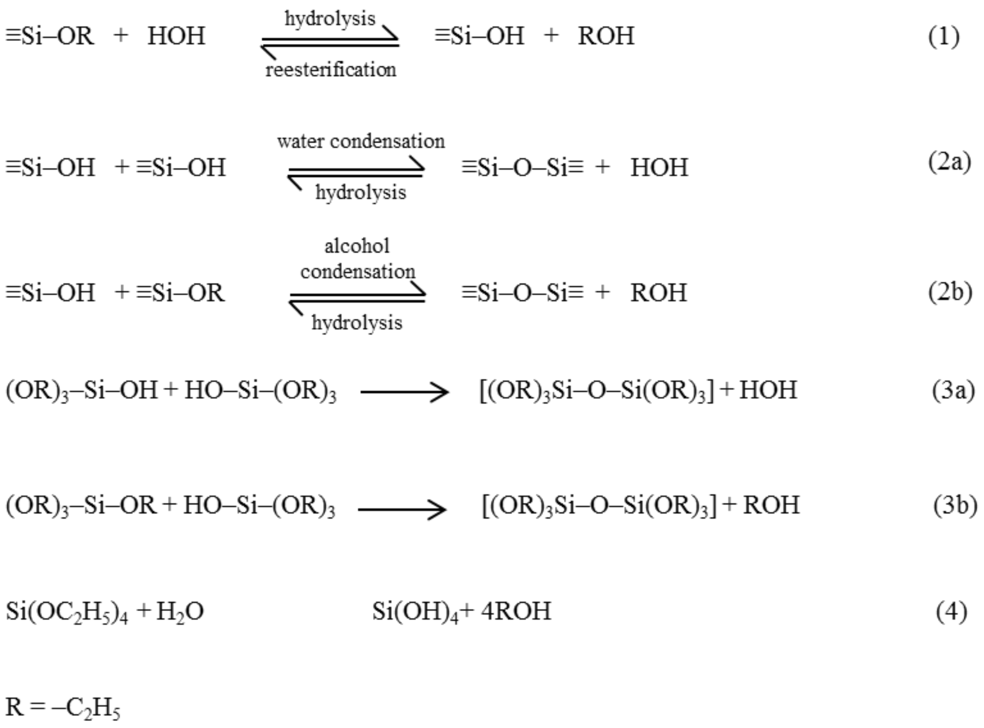
2.4.2.1 The Sol-Gel Chemistry of Silica [24]

Basically, the sol-gel process means the synthesis of an inorganic network by a chemical reaction produced in solution at low temperature. The major advantage of the method - widely accepted - is that it offers the possibility to obtain hyaloids solids, which are very difficult to be obtained by conventional techniques of burning at high temperatures and offers the possibility to obtain materials with predetermined structure, depending on experimental conditions. The advantages of the sol-gel process for material synthesis containing it provides high purity homogeneous materials, offers an easy way for the introduction of trace elements.

The sol-gel process allows the use of chemical techniques for the reaction control, allows the formation of a “pre”-inorganic network in solution and allows the densification to inorganic solids at comparatively low temperatures (due to the “pre”-inorganic network). It allows the introduction of permanent organic groups in solution (thus leading to inorganic-organic hybrid materials), allows the synthesis of special materials such as films, reactive ceramic powders, fibres and allows formation of new crystalline phases from the non-crystalline solids. Additionally, the sol-gel process allows the preparation of new glass composition with superior properties determined by the specific properties of gel and low processing temperatures allow energy saving, minimizes the evaporation losses, ensures purity by avoiding contamination with the containers during heat treatment, and avoids undesirable separation and crystallization of microphases.

Most work in the sol-gel field was done by using metal alkoxides and metal chlorides as precursors that in most cases form monomers which are soluble in common organic solvents especially alcohols. The development of silica sol-gel process in materials science starts with a solution of silicon alkoxide precursor $Si(OR)_n$ in an alcohol or other low-molecular weight organic solvent, were R is an alkyl group (C_xH_{2x+1}). Compared with colloid chemistry, the alkoxide route can be more easily controlled by controlling hydrolysis (1) and condensation reactions (2a-water condensation, 2b-alcohol condensation):

Generally speaking, the hydrolysis reaction (1-4) as shown in Figure 2.10, consists in replacing of the alkoxide groups (-OR) with hydroxyl groups (-OH) and releasing of the corresponding ROH alcohol molecules. A complete hydrolysis (4) is obtained when the stoichiometric molar ratio water:$Si(OR)_n$ is 4. Any intermediate species $[(OR)_2\text{-}Si\text{-}(OH)_2]$ or $[(OR)_3\text{-}Si\text{-}(OH)]$ would be considered the result of partial hydrolysis (3a, 3b). A small amount of water leads to a slow hydrolysis due to the reduced reactant concentration. A large amount of water gives a slow hydrolysis due to the increased reactant dilution. Subsequent condensation reactions involve the silanol groups (Si-OH), produce siloxane bonds (Si-O-Si) and as by-products water and alcohol:



$$\equiv\text{Si–OR} + \text{HOH} \underset{\text{reesterification}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} \equiv\text{Si–OH} + \text{ROH} \quad (1)$$

$$\equiv\text{Si–OH} + \equiv\text{Si–OH} \underset{\text{hydrolysis}}{\overset{\text{water condensation}}{\rightleftharpoons}} \equiv\text{Si–O–Si}\equiv + \text{HOH} \quad (2a)$$

$$\equiv\text{Si–OH} + \equiv\text{Si–OR} \underset{\text{hydrolysis}}{\overset{\text{alcohol condensation}}{\rightleftharpoons}} \equiv\text{Si–O–Si}\equiv + \text{ROH} \quad (2b)$$

$$(\text{OR})_3\text{–Si–OH} + \text{HO–Si–(OR)}_3 \longrightarrow [(\text{OR})_3\text{Si–O–Si(OR)}_3] + \text{HOH} \quad (3a)$$

$$(\text{OR})_3\text{–Si–OR} + \text{HO–Si–(OR)}_3 \longrightarrow [(\text{OR})_3\text{Si–O–Si(OR)}_3] + \text{ROH} \quad (3b)$$

$$\text{Si(OC}_2\text{H}_5)_4 + \text{H}_2\text{O} \qquad \text{Si(OH)}_4 + 4\text{ROH} \quad (4)$$

$$\text{R} = \text{–C}_2\text{H}_5$$

Figure 2.10 The sol-gel reaction [24]

Under most conditions, condensation can start before a complete hydrolysis. Conditions such as pH, H_2O/Si molar ratio (R) and catalyst can force complete hydrolysis before condensation begins. Due to the immiscibility of the alkoxide and water, a mutual solvent-an alcohol is used as homogenizing agent to facilitate the hydrolysis process. The condensation reaction is followed by an inorganic polymerization process with SiO_2 nanoparticles formation. This process is strongly pH dependent. Thus, acidic conditions lead to dense microporous (pore size < 2 nm) networks and in alkaline conditions mesoporous (2 nm < pore size < 50 nm) gels are obtained.

2.4.2.2 Influence of Parameters in Sol-Gel Process

There are numerous parameters involved in the sol-gel technique with an important influence on textural and structural properties of the synthesized material. The process is basically affected by the initial reaction conditions, such as precursors, pH, and temperature, molar ratios (R) of reactants, solvent composition and by the aging and drying conditions.

2.4.2.2.1 The Precursors

There are two general requirements for sol-gel precursors include (1) they have to be soluble in the reaction media and (2) they have to be reactive enough to participate at the gel formation. The most common precursors that can be used belong to one of the following categories: salts, oxides, hydroxides, complexes, alkoxides, acylates, and amines. The reaction between alkoxysilanes and water is quite gentle avoiding phase separation and leading to good homogeneity. That makes the SiO_2 formation the most investigated system in the sol-gel literature.

The concentration and the type of silicon alkoxides influences the rates of the both hydrolysis and condensation, and thus reactive monomers are produced at different rates. The synthesis of SiO_2 nanomaterials is usually based on TEOS as precursor. An increase in the TEOS concentration leads to an increase in the solution‟s viscosity but also in the polymer‟s concentration, without significant variations in their size or shape. The alkoxide concentration has no impact on the density of the final material and no significant effects on the mechanical properties were observed. Another recent study in sol-gel chemistry is based on aqueous precursors of silica such as silicates, which are low cost, non-toxic species, but are more difficult to control than alkoxides due to their reactivity:

$$Si(OCH_3)_4 > Si(OC_2H_5)_4 > Si(OC_3H_7)_4 > Si(OC_3H_7)_4 > Si(OC_4H_9)_4 > Si(OC_6H_{13})_4$$

2.4.2.2.2 pH/Catalysts

The microstructure of the metal oxide obtained by sol-gel process depends on the hydrolysis and condensation reactions that are generally controlled by the solution"s pH. Under acid-catalyzed conditions, the hydrolysis kinetic is favoured instead of the condensation, which generally starts when hydrolysis is completed. In alkali-catalyzed reactions, condensation is faster than hydrolysis, resulting in a highly condensed species that may agglomerate into fine particles. Compared to the transition metal alkoxides, TEOS is known to be less sensitive to hydrolysis, due to Si which is less electropositive. Thus, in the case of silicon alkoxides, a change of surface charge can be easily carried out by changing pH using acid or alkaline catalysts to enhance the hydrolysis and condensation reactions.

The rate of silicon alkoxides hydrolysis exhibits a minimum at pH = 7 and increases exponentially at both lower and higher pH. That is in contrast with the rate of condensation, which exhibits a minimum at pH = 2 and a maximum around pH = 7.

2.4.2.2.3 Water: TEOS Molar Ratio

As expected from Eqs. (1), (2a) and (2b) the quantity of water in the sol-gel solution strongly influences the hydrolysis and condensation kinetics. At fixed TEOS concentration, an increase in water content leads to a corresponding increase in hydrolysis and condensation rate. When involving $Si(OR)_4$ as precursors it is preferable to use a water: alkoxide ratio of at least 4, with acid catalysis. A low water content or high dilution with alcohols (solvents) can lead to a high content of oligomers (soluble or volatile) and a decrease in the yield of SiO_2. The time of gelation and the pore size are influenced by the molar ratio of hydrolysis. The time of gelation decreases for low water: TEOS molar ratio and showed that pore size decreased with increasing ethanol: TEOS molar ratio and pH.

2.4.2.2.4 The Temperature, Aging and Drying

The role of chemistry for the steps after gelation may not look very important, but there are some interesting aspects especially with respect to homogeneity, purity and porosity of the silica gels. Under atmospheric conditions, drying involves the loss of water, alcohol and other volatile components. This leads to gel shrinkage, and as consequence to high stresses in the structure. If the strains cannot be stopped by relaxation, the monoliths obtaining will be difficult due to the cracks appearing. This may create additional random porosity, deformation and breaking of the structures. In order to reduce this stress, drying additives, such as non-hydrolyzing organic groups (methyl or phenyl), can be used. They allow structural relaxation during the drying stage, decreasing the risk of cracking. The addition of water to the alkoxide solution leads to the formation of polymeric species, whose size increases with aging time. Because both hydrolysis and condensation are not completed after gel formation, reactive silanols are still in the system. Heating at relatively high temperatures (100-500 °C) is carried out to accelerate this phase, removes the organic species and leads to formation of covalent Si-O-Si bonds. Many of these Si-O-Si bonds are not stable at temperature below 450 °C and typically, temperatures higher than 1000 °C are needed to achieve bonding energy close to bulk fracture energy. Increasing thermal treatment temperature leads to an increase in the porosity, the porosity of the xerogel film can reach 78% when the thermal temperature is 350 °C.

2.4.3 Silica - Surface Modification [25]

The chemical properties of the silica surface are mainly determined by the various silanol and siloxane groups that are present on the external as well as the internal structure, their distribution and also the conformation of the surface siloxanes depend on the method of preparation and thermal treatment. The distribution and also the close proximity of the hydroxyl groups have an influence on the adsorption and reinforcing properties. Various modifications have been done to improve the reinforcing ability of the silica, which include heat treatment and modification of silica surface.

2.4.3.1 Heat Treatment

Heat treatment is the simplest way of modifying the silica surface. The surface hydroxyl groups remain constant up to a temperature of 300 °C. At this temperature the adsorbed water molecules are removed and then thermal condensation begins. At temperatures beyond 600-700 °C, only 1.5 -OH per nm^2 is left over and used Inverse Gas Chromatography (IGC) for characterizing the heat treated silica surface. At infinite dilution, IGC is an ideal tool to characterize the changes in the surface of the silica due to heat treatment.

2.4.3.2 Organoalkoxysilane Modification

The hydroxyl groups on the surface of silica particles can be easily tailored with organic compounds or polymers. Silanol groups can be easily functionalized by different chemical procedures. The most convenient technique for silica surface functionalization is the use of the reaction of silanol groups with suitable silane reagents, a possible mechanism of the surface modification of silica particles as shown in Figure 2.11.

The alkoxy molecules are hydrolyzed in contact with water. This is followed by self-condensation reactions between the hydrolyzed silanes. Then, the silane molecules are deposited on the silica surface through formation of siloxane bonds between the silanol groups and hydrolyzed silanes with the release of water molecules.

The organoalkoxysilane are used to modify the silica surface by chemical reaction with the silanol groups. Varieties of organoalkoxysilanes are being used for improving the interfacial adhesion or bonding of silica with the polymers. The chemical modification of silica surface with organofunctional groups is an important step towards the preparation of silica-polymer nanocomposites. More precisely, the surface modifications have been reported to enhance the affinity between the organic and inorganic phases and at the same time improve the dispersion of silica nanoparticles within the polymer matrix. Modification of silica surface with organofunctional groups is alternative way for improvement of reinforcement efficiency. The modified silica surface has the ability to bond inorganic materials such as silica nanoparticles to organic resins, the $Si(OR)_3$ portion of the silica reacts with the inorganic reinforcement, while the organofunctional group (R) reacts with the resin.

Surface modification of silica nanoparticles can be carried out by using various types of silane coupling agents such as aminopropylmethydiethoxy silane (APMDS) and methacryloxypropyltriethoxysilane (MPTS) via nonaqueous and aqueous route. A slight increase in the particle size (~25%) after the surface modification was observed. The treatment of nanosilica by epoxy silane with a longer reaction time and lower silane concentrations assisted with pretreatment by sonication can achieve monodispersed silica in polar medium.

2.4.3.3 Polymer Grafting

Polymer grafting on silica surface for improve the performance properties of rubber compounds. Surface modification of silica so as to increase the silica rubber bonding is a method used for the better reinforcement. Silica surface modification by grafting of alkyl chains through esterification has been reported by several workers. Grafting of methyl and hexadecyl chains on the surface of silica has been found to decrease the thermodynamic parameters. The esterification results in the reduction of the dispersive component of the surface energy, the surface heterogeneity of the modified silica reduces and hence the filler-filler inter-aggregations diminish.

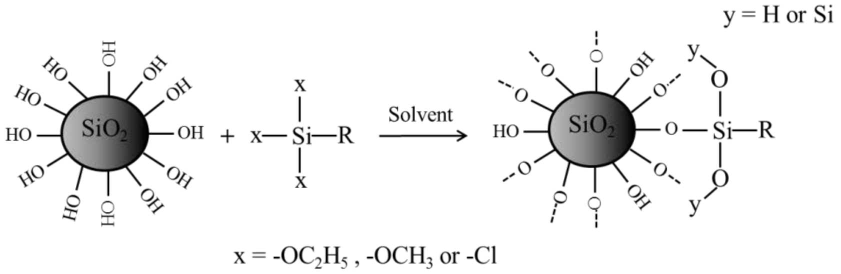


Figure 2.11 Surface modifications of silica particles [25]

Generally the surfaces of inorganic materials are functionalized with polymer chains either chemically (through covalent bonding) or physically (by physisorption). Physisorption involves adsorption of polymers with sticky segments. The noncovalent adsorption makes the adsorption reversible, especially during processing, and is not a favored technique. Covalent grafting techniques are preferred to maximize a stable interfacial compatibility between the two phases. There are two methods for chemically attaching polymer chains to a solid substrate: the “grafting to” and “grafting from” techniques. Polymer films anchored in this manner are inherently more thermally stable.

In the "grafting to" method, pre-formed, end-functionalized polymer chains are reacted with a chemically activated substrate (Figure 2.13). One advantage of this method is that polymer chains can be characterized before being attached to the substrate. The drawback, however, is that only relatively low grafting densities are obtained due to steric crowding of already attached chains on the surface, which hinder diffusion of additional chains to reactive sites. Reactive end groups must diffuse through a barrier of existing polymer film to couple with functional groups on the surface and this diffusion barrier becomes more pronounced as more chains are attached and the number of grafted chains decreased as the molecular weight of the chains increased. Though brushes have been prepared *via* the "grafting to" method, more densely grafted brushes may be prepared by using the "grafting from" method to circumvent the diffusion barrier problem.

The "grafting from" method involves formation of an initiator layer (I) on the surface of the silica followed by polymerization of monomer (M) (Figure 2.13). Different polymerization techniques can be used to modify the surface of silica. Thick brushes with a high graft density can be formed because monomer can easily diffuse to reactive sites of the growing polymer chains. In this method, the steric barrier to incoming polymers imposed by the *in situ* grafted chains does not limit the access of smaller monomer molecules to the active initiation sites. This polymerization technique is also commonly referred to as surface-initiated polymerization. Preparation of polymer brushes via the "grafting from" technique on silica nanoparticles can be accomplished by conventional free radical, controlled free radical, cationic, anionic and ring-opening metathesis polymerization techniques.

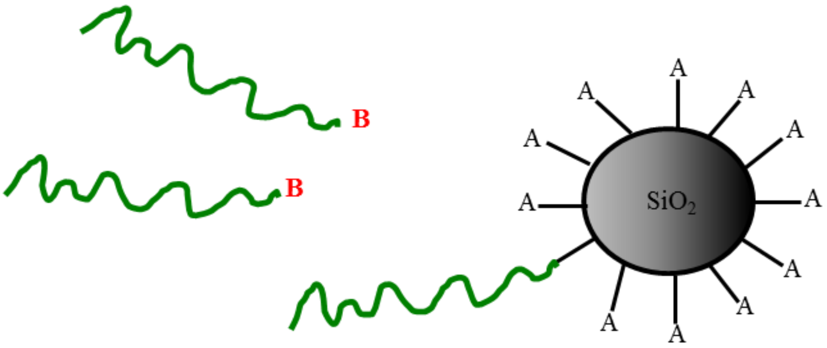


Figure 2.12 “Grafting to” approach of surface modification [25]

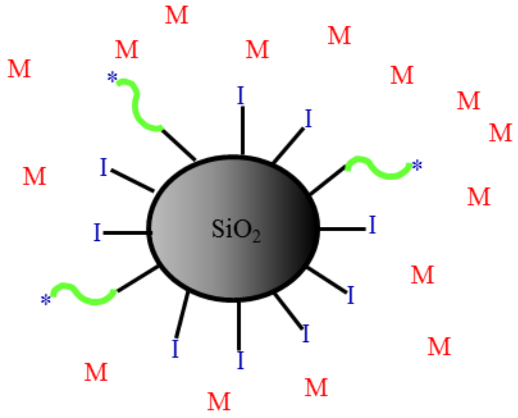


Figure 2.13 “Grafting from” approach for surface modification [25]

2.5 Applications of Modified Silica Nanoparticles

The main challenge in dispersing silica particles lies in controlling the interparticle aggregation. It is necessary to stabilize these particles to prevent aggregation, which is done by grafting polymer chains using the different methods mentioned above. These long polymer chains control the nanoparticle aggregation by steric repulsions. Another advantage of grafted polymer chains is that they can improve the compatibility of the matrix with the particle surface. It has been reported that controlling the aggregation improves the mechanical properties of the composite. The formation of stable dispersions in solvents or polymer matrices is an important variable affecting the final properties of formulations and coatings. Smart surfaces that respond to external stimuli are important for changing wettability and adhesion properties. Brushes of molecularly imprinted polymers on silica particles have been used for chromatographic supports. They have been used as a stationary phases for separation of triazinic herbicides. Synthesis of hollow polymeric nanocapsules using silica nanoparticles were developed by Blomberg and co-workers. These materials have potential applications for the encapsulation of active substances such as drugs and dyes. Silica/polymer hybrids are important candidates for environmental pollution control processes. The application of silica/polymer hybrid systems for removal of heavy metal ions such as cobalt and copper salts from waste water has been studied by Meyer and co-workers86. The large surface area, well-defined pore size and pore shape of the silica particles, and the specific binding sites of the polymer help removal of these metals.

2.6 Literature Reviews

Wu *et al.* [26] studied the surface modification of silica particles with aminopropyl groups (APTES) and phenyl groups (PhTES) through a one-step process, by using TEOS as a silica precursor in a base catalyst. SEM results showed that the modified silica particles were spherical with uniform size and shape. The modified silica particles with the phenyl groups (PhTES particles) exhibited lowest water adsorption because their surfaces were more hydrophobic than that of TEOS and APTES particles. Regarding dye adsorption after acidification, it was found that APTES showed the highest dye adsorption due to the hydrophobic attraction and enhanced electrostatic attraction from the aminopropyl groups.

Xue *et al.* [10] studied the super- hydrophobicity of modified silica surface particles with vinyl groups (V-SiO_x-NPs) of vinyltriethoxysilane (VTEOS). The wettability of silica surface particles depends on the chemical composition and the geometrical shape of the micro-structure. Materials experienced super-hydrophobicity when the contact angle was more than 150 degrees, which was achieved by two main approaches, thereby resulting in surface roughness and surface modification. The study of the surface structure of V-SiOx-NPs compared with unmodified silica particles by using field emission scanning electron microscopy (FESEM) showed that the unmodified silica particles were orderly arranged with close particles, differentiating with the surface roughness of V-SiO_x-NPs. The study of wettability showed that the unmodified silica had high hydrophilicity, with a contact angle in the range of 17 to 42 degrees, while V-SiOx-NPs with a contact angle of approximately 166 degrees represented a super-hydrophobicity of V-SiOx-NPs.

Siramanont *et al.* [27] studied the formation of alkylated silica particles inside the NR matrix via sol-gel reaction by using three types of alkyltriethoxysilane that contained vinyltriethoxysilane (VTOS), ethyltriethoxysilane (ETOS) and i-butyltriethoxysilane (BTOS) combined with TEOS. The conversion to silica in the NR matrix of silane was almost complete for TEOS, but decreased when the size of the alkyl groups of alkyltriethoxysilane were increased. TEM showed that the in situ silicas were fine and well dispersed in the NR matrix more than that with mixing with the commercial silica. The tensile and tear properties of the in situ silica filled NR vulcanizates were higher than those of the vulcanizate prepared by conventional mixed method. In addition, it was found that the tensile strength and tear strength of NR vulcanizates increased when using VTOS as a mixture with TEOS.

Jeon *et al.* [28] studied the modification of silica surface particles by using organoalkoxysilane, such as MTMS, MTES, VTMS and VTES. The relative hydrolysis and condensation rates of organoalkoxysilane can be considered from kinetic data that were measured with the mixing time (hydrolysis) and turbid time (condensation) within this system. The hydrolysis rates related to the structure or the size groups of silane, the small size showing higher hydrolysis rates than that of the larger size, and the condensation rates related to the polarity of silane, with the silane showing similar polarity with TEOS at high condensation rates. The structure of the silica particles, analyzed by SEM and TEM, showed that the size of the silica particles depended on the types and the ratio of silane/TEOS. It was found that the sizes of the pure and modified silica with MTMS and VTMS were 300, 430 and 430 nm, respectively, and the size of the particles increased with the increase of organoalkoxysilane. The roughness of surface related to the size of the alkyl groups, and the large size of the alkyl groups showed high roughness.

Chaichua *et al.* [29] studied the formation of in situ silica inside the NR matrix via sol-gel reaction by using TEOS as a precursor. The dispersion of silica inside the NR matrix were investigated by TEM analysis, compared with the commercial silica filled NR. The in situ silicas were well dispersed inside the NR matrix more than that of the commercial silica filled NR. The properties of the in situ silica filled NR vulcanizates were investigated in comparison to that of a commercial silica preparation. The Mooney viscosity and curing time of the in situ silica filled NR vulcanizates increased with the increase of silica content and both showed lower values compared with that of the commercial silica filled NR vulcanizates. The mechanical and thermal properties of the in situ silica filled NR vulcanizates were improved compared with the commercial silica filled NR vulcanizates.

Yang *et al.* [9] studied the hydrothermal stability and the influence of surface functional groups on the surface wettability of methyl-modified silica films by FTIR and Raman spectroscopy. The free energy parameters of the silica surface were determined by using the Lifshitz-van der Waals/acid–base approach. The results show that the surface free energy and surface wettability of the silica films decreased greatly with the increase of the MTES/TEOS ratio. This is mainly because the contribution of the acid–base term and the intensity of the Si–CH_3 groups increase at the expense of the intensity of the O–H groups in the samples. The contact angle on the silica film surface rises with the increase of the mole ratio of the MTES/TEOS ratio and reaches its maximum value when calcination is performed at 350 °C.

Chonkaew *et al.* [30] studied the modification of nanosilica surface by using two silane coupling agents that contained 3-methacryloxypropyl trimethoxysilane (MPTMS) and 3-mercaptopropyl trimethoxysilane (MPS). The surface characteristics were analyzed using FTIR. The vulcanization kinetics of silica filled NR composites was studied and compared to behavior of neat NR using differential scanning calorimetry (DSC) in the dynamic scan mode. DMA was performed to evaluate the effects of the surface modification. Activation energy (E_a) values for the reaction are obtained. The neat silica containing system has the lowest cure rate index and the highest activation energy for the vulcanization reaction. The modifier with longer chains cause more swelling and move the glass transition temperature (T_g) downwards.

Xu *et al.* [31] studied the modification of nanocrystalline cellulose by 3-aminopropyl-triethoxysilane (KH550). The modified nanocrystalline cellulose (MNCC) was further investigated to partially replace silica in NR composites via coagulation. NR/MNCC/silica and NR/nanocrystalline cellulose (NCC)/silica nanocomposites were prepared. Through the comparison of vulcanization characteristics, processing properties of compounds and mechanical properties, compression fatigue properties, dynamic mechanical performance of NR/MNCC/silica and NR/NCC/silica nanocomposites, MNCC was proved to be more efficient than NCC. MNCC could activate the vulcanization process, suppress Payne effect, increase 300% modulus, tear strength and hardness, and reduce the heat build-up and compression set. Moreover, fine MNCC dispersion and strong interfacial interaction were achieved in NR/MNCC/silica nanocomposites. The observed reinforcement effects were evaluated based on the results of apparent crosslinking density (*V*r), TGA and SEM analyses of NR/MNCC/silica in comparison with NR/NCC/silica nanocomposites.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The high ammonia NR latex containing ca. 60% DRC manufactured by Thai Rubber Latex Co., Ltd. (Thailand) was used as a raw rubber. TEOS from Sigma-Aldrich was used as a precursor for silica generation. Absolute ethanol as a medium of synthesis silica particles and ammonia solution (28 wt% ammonia) as a base catalysts for sol-gel reaction were purchased from Qrec Chemicals Ltd. (Thailand). Acetone obtained from Qrec Chemmical (Thailand) acetone was used to precipitate NR latex compound. MTES, VTES and APTMS obtained from Sigma-Aldrich (Singapore) were used as a modifier. Active zinc oxide (ZnO), stearic acid, mercaptobenzothiazole disulfide (MBTS), polyethylene glycol (PEG) and sulfur were used as a curing agent and purchased from PI Industry Ltd.

3.2 Equipments

1. Beaker, 50, 100, 250, 600 ml
2. Dropper
3. Erlenmeyer flask, 250 ml
4. Suction flask
5. Buchner funnel
6. Glass funnel
7. Graduated cylinder, 10, 25 ml
8. Round-bottomed flask, 250 ml
9. Pipette, 1, 10 ml
10. Watch glass
11. Metal stand and Clamp
12. Hotplate and magnetic stirrer
13. Overhead stirrer
14. Magnetic bar
15. Stirring rod
16. Aluminium foil
17. Duran bottle, 500, 1000 ml
18. Parafilm
19. Filter Papers no. 5

3.3 Procedure

In this work, the silica filled NR compounds were prepared by using 2 methods, "direct method" and "indirect method". For direct method, all ingredients including NR latex, TEOS, water, catalysts and modifier were mixed together in the same time to generate modified silica in NR matrix. For indirect method, the modified silica particles were first prepared and then modified silica particles were directly mixed with NR latex. The modified silica particles filled NR were subsequently mixed with curing agent. The NR compound was then vulcanized. Finally, the morphology, mechanical, thermal and dynamic properties of NR vulcanizates were investigated. The overall procedures used in this study are showed in Figure 3.1

3.4 Preparation of silica particles for indirect method [26]

Two solutions were rapidly mixed at room temperature. The first solution was the mixture of 3.0 ml TEOS and 23.0 mL ethanol, and the second solution was the mixture of 1.0 ml 28 wt% ammonia, 7.0 ml deionized water, and 18.0 mL ethanol. After 4 h of reaction, 0.1 mole ratio of modifier (MTES, VTES or APTMS) to TEOS was added into the stirred solution, and the reaction was allowed to continue for 20 h with stirring. For the preparation of pure silica particles (unmodified silica particles), the total reaction time was 24 h without the addition of modifier. After that, the silica particles were separated by filtrating, washing and drying under vacuum at 40 °C until the weight of samples became constant. The conversion of TEOS to silica particles was calculated by using equation (3.1)

$$\text{Percent yield} = (\text{actual yield} / \text{theoretical yield}) \times 100 \qquad (3.1)$$

where theoretical yield was the amount of silica being generated assuming quantitative conversation of TEOS to silica as shown in Scheme 1. The results reported were averaged from five times.

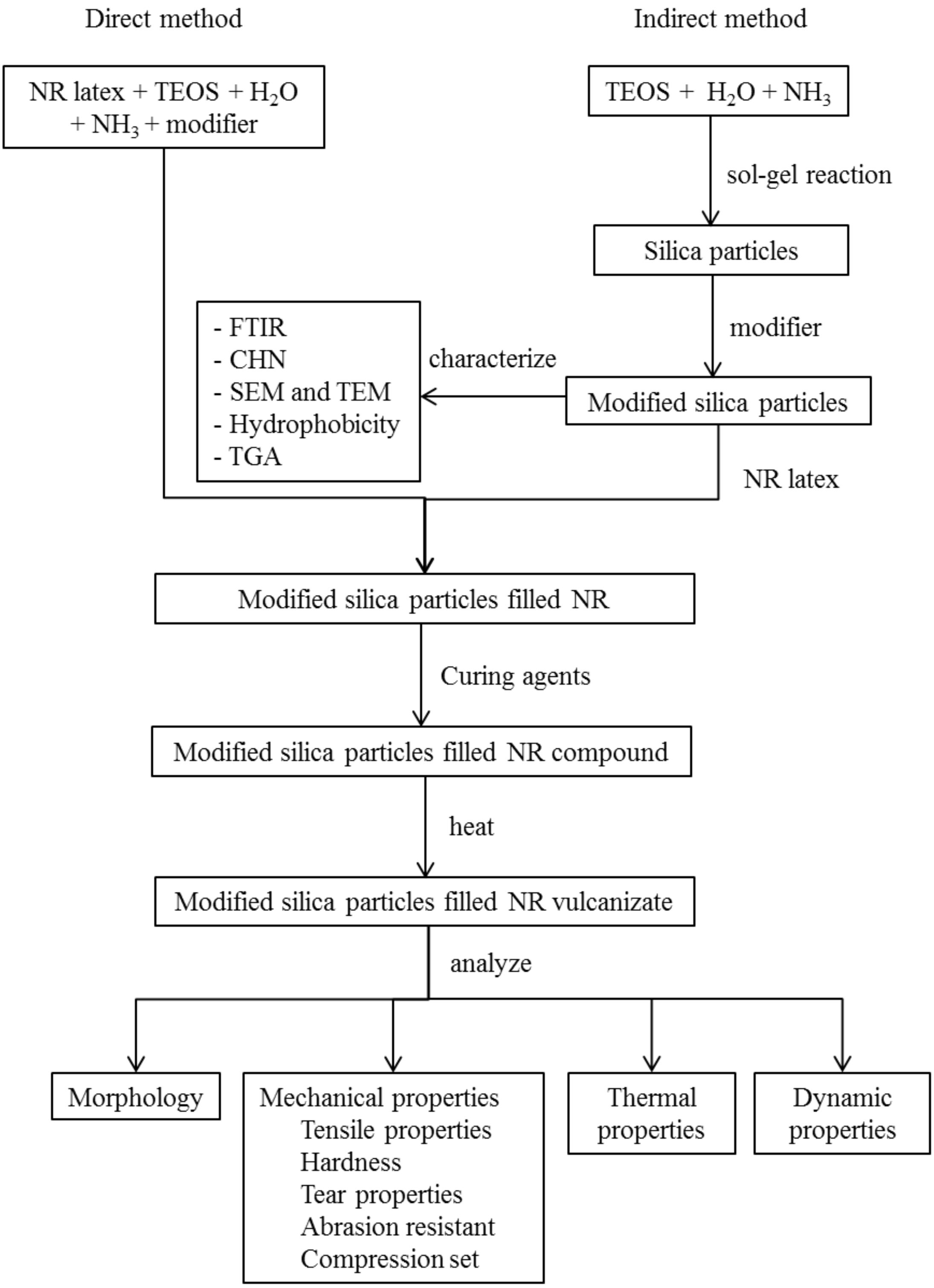
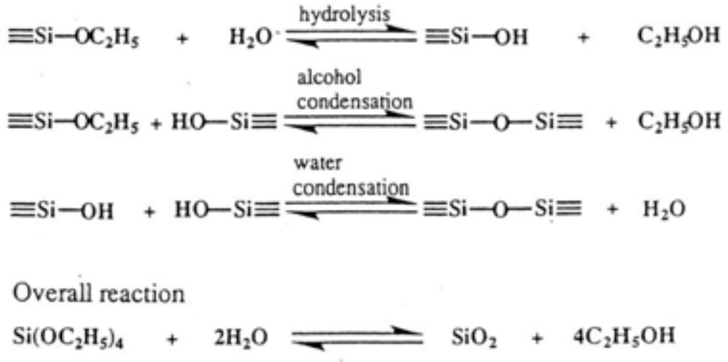


Figure 3.1 Overview procedure



Scheme 3.1 The reaction for conversion of TEOS to silica by sol-gel process [24]

The effects of reaction temperature (30, 40, and 50 ºC) and reaction time (12, 24 and 48 hours) on the percent yield of silica were investigated. Furthermore, types of modifiers (MTES, VTES, and APTMS) and the effects of mole ratio of modifier to TEOS (0.1, 0.5, 1.0, and 2.0) on the properties of modified silica particles were also investigated.

3.5 Characterization of unmodified and modified silica particles

The obtained unmodified and modified silica particles were characterization by using various techniques as follows:

3.5.1 Fourier transform infrared spectroscopy (FTIR)

The unmodified and modified silica particles were characterized by FTIR (Figure 3.2 (a)) in order to confirm the functional groups of modifier. FTIR spectra were recorded on a PerkinElmer spectrum One Transform Infrared Spectroscopy, USA. The samples were prepared in a thin KBr disk under high pressure and determined in ranges of 4000 to 400 cm^{-1} with resolution of 4 cm^{-1}.

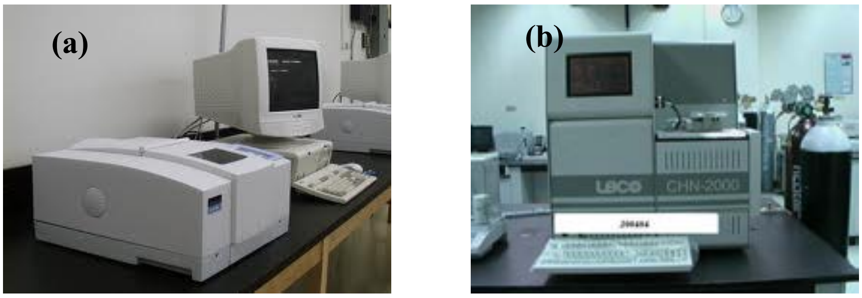


Figure 3.2 Fourier transform infrared spectrometer (a) and CHN analyzer (b), respectively

3.5.2 CHN analyzer

Elemental analyzer (EA) (CHNS/O Analyzer) was carried out by Perkin Elmer (PE-2400) (Figure 3.2 (b)) to determine the content of carbon, hydrogen and nitrogen that coated on silica surface particles. The sample was weighed (ca. 2-3 mg) in tin capsules and then these capsules are introduced into a pyrolysis reactor at a temperature of 1000 °C with a constant flow of helium stream. A few second before introduction the helium stream was enriched with high purity oxygen. The combustion mixtures were separated in a chromatographic column and detected by thermo conductivity detector.

3.5.3 Scanning electron microscopy (SEM)

The morphology of unmodified and modified silica particles was observed by using a JEOL (JSM-5410LV, Japan) SEM instrument (Figure 3.3 (a)) operating at 15 kV. The sample was prepared by dispensing drops of an ethanol suspension of silica particles onto a glass plate. It was allowed to dry at room temperature and was then coated with thin Au film.

Figure 3.3 Scanning electron microscope (a) and water CA measurement (b), respectively

3.5.4 Water contact angle measurement

The hydrophobicity of modified silica surface particles was observed by using water contact angle measurement. A contact angle was measured by producing a drop of liquid on a solid. The angle formed between the solid/liquid interfaces is referred to as the contact angle (CA). A drop with a contact angle over 90° is hydrophobic. This condition is exemplified by poor wetting, poor adhesiveness and the solid surface free energy is low. A drop with a small contact angle is hydrophilic. This condition reflects better wetting, better adhesiveness, and higher surface energy. The CA were determined by a ramé-hart instrument, USA, (Figure 3.3 (b)), at an ambient temperature. The samples were prepared by coating the silica particles on the glass plate with adhesive tape. The droplet volume of deionized water was 3 μl were placed on the surface of the silica sample. The average CA value was obtained by measuring the same sample at 5 different positions.

3.5.5 Thermogravimetric analysis (TGA)

TGA was carried out by a TG/DTA PerkinElmer Pyris Diamond (Figure 3.4) to analyze the thermal stability and amount of modifier substituted on silica surface. A sample (ca. 10 mg) was placed in a platinum pan and heated from room temperature up to 1000 °C under nitrogen at a heating rate of 10°C/min.

3.6 Preparation of rubber compound

3.6.1 Rubber compound prepared by direct method

NR latex 167 g were mixed with 200 g of distilled water. After that, TEOS solution 38 ml, 28%Ammonia solution 10 ml and modifier with 0.1 mole ratio of modifier to TEOS were slowly dropped in to NR latex, respectively. The reaction was allowed to continue for 24 h with stirring at room temperature. Then, the NR compound was separated by coagulation with acetone and drying under vacuum at 40 °C until the weight of samples became constant.

3.6.2 Rubber compound prepared by indirect method

In the case of the preparation of NR compound by indirect method, the modified silica particles were first prepared and then it was directly mixed with NR latex. NR latex 167 g were mixed with appropriate amount of distilled water for reduced the viscosity. After that, 10 g of silica powder was slowly added in to NR latex and then stirring until all ingredients were homogeneous. NR compound was separated by coagulation with acetone and drying under vacuum at 40 °C until the weight of samples became constant.

Figure 3.4 Thermogravimetric analyzer

3.7 Preparation of NR vulcanizates

The rubber vulcanizates were prepared by a conventional mixing on a two-roll mill. The formulations of rubber compound are presented in Table 3.1. The rubber compound was prepared into sheets by compression molding at 150 °C under the pressure of 150 kg/m^2. In this work, unfilled NR vulcanizate was designated by “NR-V” and modified silica particles with prepared by direct and indirect methods were specified by alphabet “D” and “I”, respectively. The silica particles filled NR vulcanizates containing unmodified silica and modified silica by MTES, VTES and APTMS were designated by alphabet “USi”, “MSi”, “VSi” and “ASi”, respectively

Table 3.1 Formulations in parts by weight per hundred parts of rubber (phr) for rubber compound

Ingredients (phr)	Direct method				Indirect method			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
NR with D-Si	-	110	110	110	-	-	-	-
NR with I-Si	-	-	-	-	110	110	110	110
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
MBTS[a]	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
PEG[b]	-	0.33	0.33	0.33	0.33	0.33	0.33	0.33

[a] Mercaptobenzothiazole disulfide

[b] Polyethylene glycol

3.8 Properties of NR vulcanizates

3.8.1 Morphology of NR vulcanizates

The morphology of unmodified and modified silica filled NR vulcanizates was investigated by using a STEM (ZEISS ULTRA plus, Germany). Ultra-thin films of the vulcanized rubber samples were prepared using a microtome (Leica EM FC6, Germany).

3.8.2 Measurement of swelling behavior

The swelling ratio of the rubber vulcanizates was determined according to ASTM D471. The vulcanized rubber sample was cut to 20×20×2 mm sized pieces and immersed in toluene until they reached equilibrium (within 7 days) at room temperature. Then, the test piece was taken out and surface liquid was rapidly removed by blotting with filter paper. The swelling ratio of the polymer (Q) was calculated using Equation (3.2).

$$Q = \frac{W_2 - W_1}{W_1} \tag{3.2}$$

where W_1 and W_2 are the weights of the test piece before swelling and after immersion, respectively.

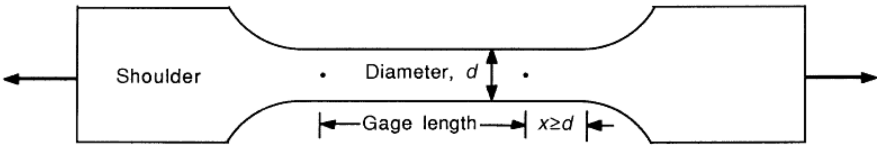


Figure 3.5 Rubber "dumbbell" tensile test sample

3.8.3 Mechanical properties

3.8.3.1 Tensile properties

A tensile test involves mounting the specimen in a machine and subjecting it to tension. The tensile force is recorded as a function of the increase in gage length. The samples of NR vulcanizates were prepared by cut as dumbbell-shaped pieces (Figure 3.5). The thickness of the test specimens was 2.0 mm. The tensile properties of NR vulcanizates were performed on a universal testing machine (LLOYD LR 10 K) according to ASTM D412 with a cross-head speed of 500 mm/min and a load cell of 5 kN. The reported values were an average of five specimens.

3.8.3.2 Hardness

Shore hardness is a measure of the resistance of a material to penetration of a spring loaded needle-like indenter. Elastomers (rubbers) and other soft polymers are usually measured with either a Shore A Scale Durometer. The method for hardness testing followed ASTM D 2240. The hardness of specimens was measured using a Durometer Hardness System Model 716 (Figure 3.8) shore A. To perform a test, the specimen is first placed on a hard flat surface. The spring pushes the indenter into the sample and the indicator displays the depth of penetration. The hardness values were averaged from the contacting of specimen after one and five second of test. The reported values were an average of five different points distributed over the specimen.

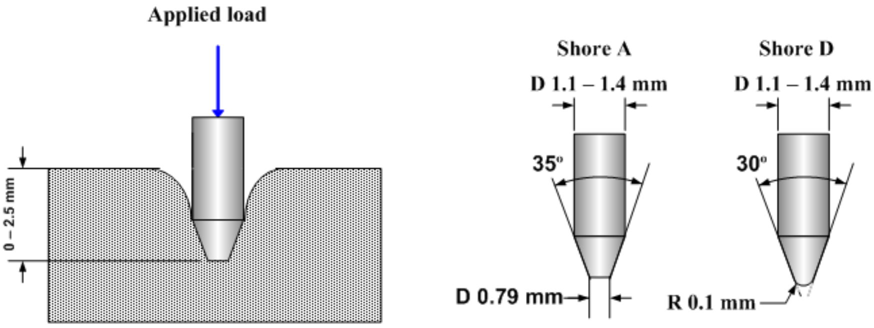


Figure 3.6 Shore hardness test

3.8.3.3 Tear resistance

Tear resistant is applied to a test specimen by means of a tensile testing machine operated without interruption at a constant rate of crosshead traverse until the specimen is completely torn. This test method measures the force per unit thickness required to rupture, initiate, or propagate a tear through a sheet of rubber in the form of one of several test piece geometries. In this study, tear properties were measured using LLOYD Instruments LS 500. The specimens were cut using die C (Figure 3.9) according to ASTM D624 at a crosshead speed of 500 mm/min. The values reported for each sample were averaged from five specimens.

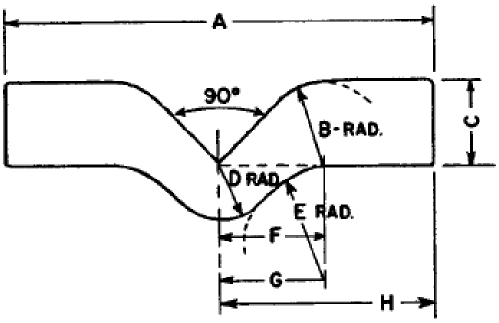


Figure 3.7 The specimens of standard tear test by using die C

3.8.3.4 Abrasion resistance

The abrasion resistance is measured by moving a test piece across the surface of an abrasive sheet mounted to a revolving drum, and is expressed as volume loss in cubic millimeters or abrasion resistance index in percent. For volume loss, a smaller number indicates better abrasion resistance, while for the abrasion resistance index, a smaller number denotes poorer abrasion resistance. In this study, abrasion resistance was measured by using Happen Abrasion testing machine, according to DIN 53516 (ZWICK), England at room temperature upon cylindrical in shape of samples used was 16 mm diameter and a minimum thickness of 6 mm.

3.8.3.5 Compression set

Compression set testing measures the ability of rubber to return to its original thickness after prolonged compressive stresses at a given temperature. As a rubber material is compressed over time, it loses its ability to return to its original thickness. Compressions set results for a material are expressed as a percentage maximum figure. The lower the percentage figure, the better the material resists permanent deformation under a given temperature range. In this study, the method for compression set testing was determined followed ASTM D395 (Figure 3.10). The thickness and diameter of the original sample were determined. The sample was placed in an oven and compressed to 25% strain at 70 °C for 22 h. Then, the sample was removed from the oven and allowed to cool for 30 min before measuring the final thickness.

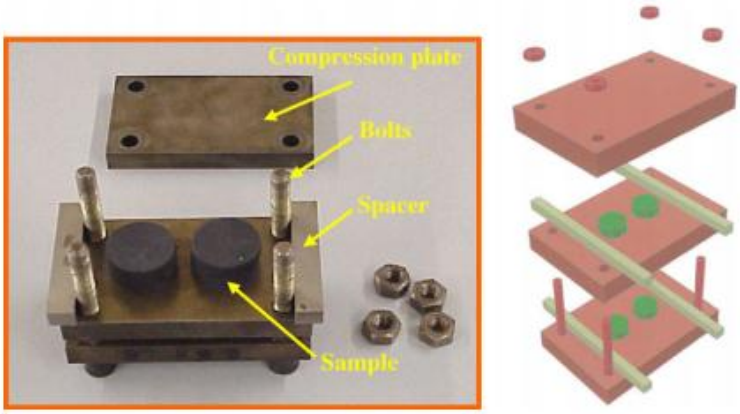


Figure 3.8 Compression set device

3.8.4 Thermal properties

The thermal stability of NR vulcanizates was analyzed by using a Perkin Elmer Pyris Diamond TG/DTA, USA. The NR vulcanizates samples (ca.10 mg) was placed in a platinum pan and heated from room temperature up to 1000 °C under nitrogen at a heating rate of 10 °C/min.

3.8.5 Dynamic mechanical analysis (DMA)

DMA of NR vulcanizates in a rectangular shape (3x10x2 mm) was investigated using a dynamic mechanical analyzer (Mettler Toledo DMA/SDTA 816^e). The range of testing temperature was -130 to100 ^{o}C with 5 ^{o}C min^{-1} of heating rate under nitrogen atmosphere. The tension mode was applied with a constant frequency and amplitude at 1 Hz and 1 μm, respectively. The storage modulus (E'), loss modulus (E'') and the mechanical loss factor ($\tan \delta = E''/E'$) were reported.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of silica particles

4.1.1 Effect of reaction time and temperature

Figure 4.1 shows the effect of time and temperature of sol-gel reaction on synthesis unmodified silica particles (U-Si). The results show that the reaction rate increased with the increase of temperature. As a rule, the higher the reaction temperature, the higher the yield of silica was obtained. However, for all temperature reactions (30, 40 and 50 °C), silica had nearly 100 % yield at reaction time for 24 h. Therefore, the reaction temperature for synthesis silica particles in this study was used at 30 °C to have mild conditions and to save energy. According to this result, the optimum condition for synthesis silica particles used ammonia solution as a base catalyst at 30 °C for 24 h. Under this condition, the unmodified silica particles produced 98 % yield.

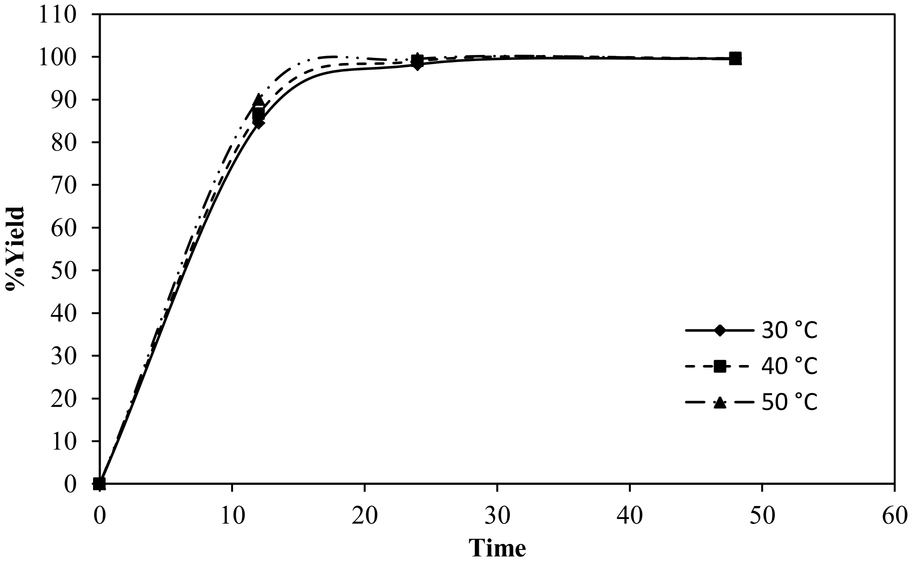
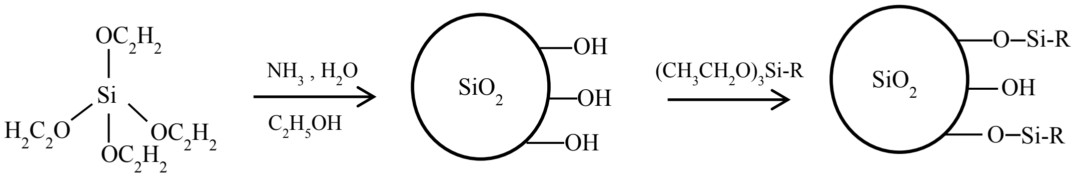


Figure 4.1 Effect of reaction time and temperature on % yield of U-Si particles

4.1.2 The modification reaction

A possible mechanism for modification of silica surface particles by MTES, VTES and APTMS is shown in Scheme 4.1. A typical reaction was consisted of the following steps: (1) the base-hydrolysis of TEOS to generate the silica particles with the –OH groups on the surface, (2) the condensation reaction of silica particles with modifier to form modified silica particles.

The suspension of U-Si and modified silica particles with MTES, VTES and APTMS, respectively (M-Si, V-Si and A-Si) in ethanol after synthesis for 1 week is shown in Figure 4.2. The U-Si particles were suspended in ethanol without sedimentation. This is because all the types of silica particles were suspended into a polar solvent. Thus, the U-Si, having polar particles, was compatible with the ethanol solvent, so the solvent could be well enclosed with these particles. Therefore, the U-Si particles could be stably suspended in the ethanol solution. In contrast, the modified silica particles were obviously settled. In the case of M-Si and V-Si, the methyl and vinyl groups decreased the polarity of the silica surface particles. Consequently, the solvent was difficult to enclose with the modified silica particles as it tended to aggregate. Additionally, in the case of the A-Si particles, it showed a more evident settlement than those of all silica types. This may be due to the large size of substituted groups of APTMS, leading to enhance aggregation. The aminopropyl groups of APTMS brought high entanglement, and amino groups on the surface were supplemented to enhance aggregation as well. Furthermore, the increased size of modified silica particles after modification could be contributed to precipitate more than that of U-Si particles.



Scheme 4.1 Mechanism for modification of silica particles by R = methyl, vinyl or aminopropyl groups

Figure 4.2 The suspension of U-Si, M-Si, V-Si and A-Si particles, respectively in ethanol (after synthesis for 1 week)

4.1.3 Characterization

4.1.3.1 FTIR

Figure 4.3 shows the FTIR spectrum of U-Si, M-Si, V-Si and A-Si. The spectra of U-Si particles appeared at 3435 and 1631 cm^{-1} (Figure 4.3 (a)) were attributed to the vibration of O–H groups (stretching and bending vibrations, respectively) which arise from the water adsorption by Si–OH groups. The bands at 1104, 948, 802 and 471 cm^{-1} were associated with Si–O asymmetric stretching, O-H stretching of Si-OH , Si-O symmetric stretching and Si-O-Si bending, respectively [9].

After modification with MTES, the additional absorption peaks of M-Si particles at 2973, 1402 and 1272 cm^{-1} (Figure 4.3 (b)) were corresponding to the C-H stretching of -CH_3 groups, C-H bending of -CH_3 groups and Si–CH_3 vibration, respectively [9].

For the modification with VTES, the additional absorption peaks of V-Si particles at 1620 cm^{-1} (Figure 4.3 (c)) were corresponding to the C=C stretching of -CH=CH_2 groups [10]. Additionally, the O-H stretching of Si-OH (around 948 cm^{-1}) seemed to be weaken after modification of silica surface with MTES and VTES because the Si-OH groups on silica surface were substituted by the organic groups of modifier (methyl and vinyl groups) as related to Scheme 4.2.

By using APTMS as a modifier, the asymmetric and symmetric stretching vibrations of the –NH_2 groups appear at 3300-3400 cm^{-1}. However, the same absorption peak of adsorbed water molecule was in the same range as the -NH_2 group [32-34]. The O–H absorption peaks around 952 cm^{-1} also seemed to be weakened.

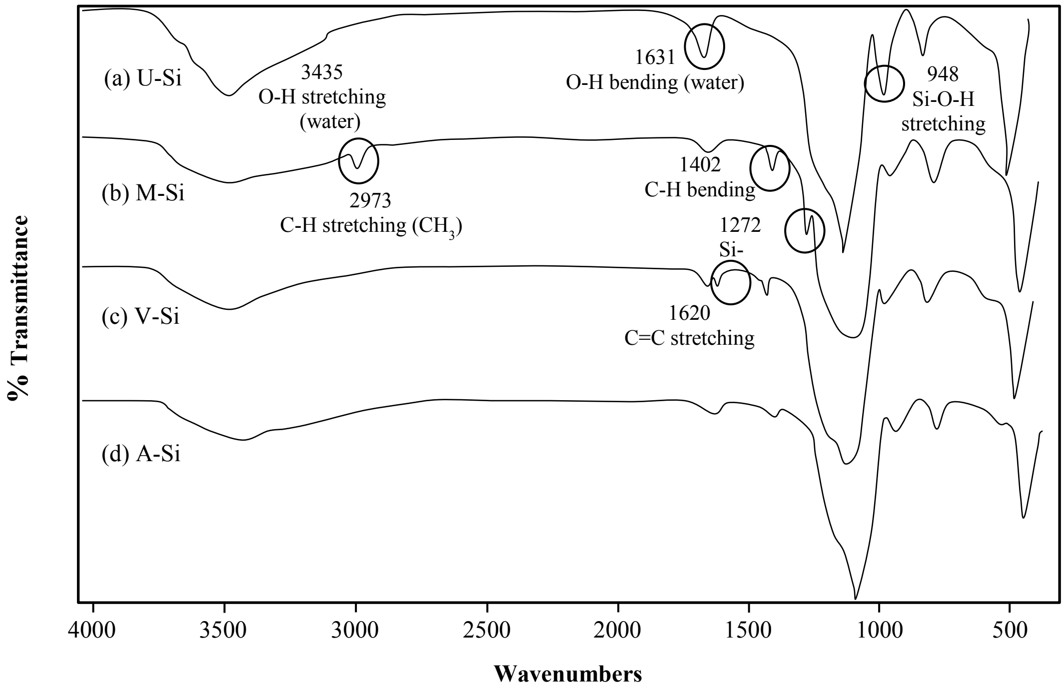
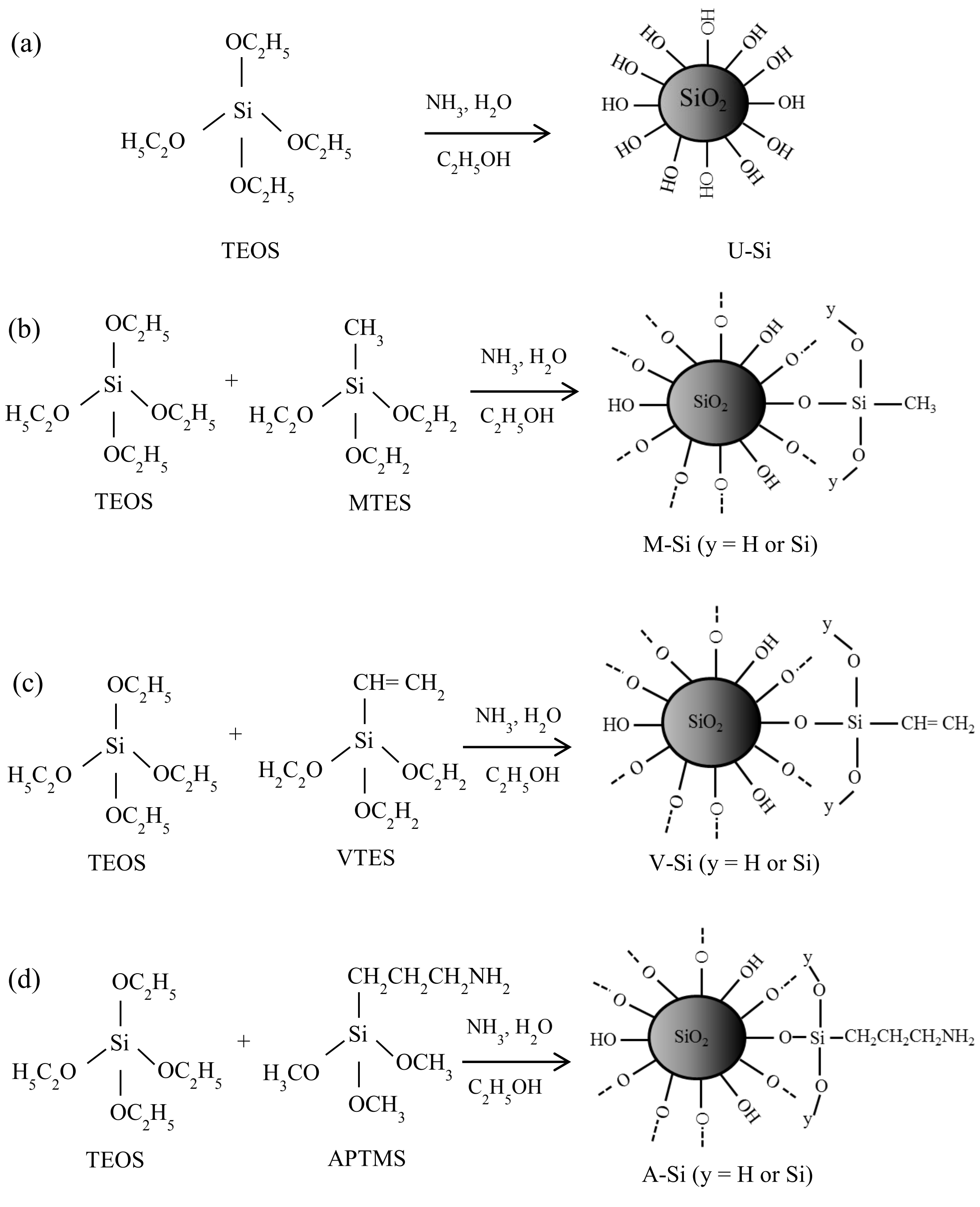


Figure 4.3 FTIR spectra of (a) U-Si (b) M-Si, (c) V-Si and (d) A-Si particles, respectively



Scheme 4.2 The route for preparation of (a) U-Si (b) M-Si, (c) V-Si and (d) A-Si particles, respectively

4.1.3.2 CHN analysis

Table 4.1 shows CHN contents of unmodified and modified silica particles. The CHN contents of the unmodified silica particles showed only hydrogen content of 1.46 %weight. After modification with MTES, VTES and APTMS showed a content of carbon and hydrogen, with addition of nitrogen in the case of modification with APTMS. According to these results, it can be seen that the modified silica with APTMS appeared to be of a nitrogen element. It was confirmed to successfully react on the surface of silica particles.

In addition, the percent weight of organic groups coated on silica surface could be calculated. The organic groups of MTES, VTES and APTMS, coated on the silica surface had about 7.84, 8.08 and 4.96 %weight, respectively (see the calculation in Appendix No. A.2). These results confirmed that the content of organic groups on silica surface decreased by increasing the size of substituted groups of a modifier due to the steric effect.

Table 4.1 CHN analyses of U-Si, M-Si, V-Si and A-Si particles, respectively

Sample	%C	%H	%N
U-Si	0.00 ± 0.00	1.46 ± 0.04	0.00 ± 0.00
M-Si	6.27 ± 0.06	2.15 ± 0.05	0.00 ± 0.00
V-Si	7.18 ± 0.03	1.48 ± 0.03	0.00 ± 0.00
A-Si	3.08 ± 0.09	2.05 ± 0.04	1.24 ± 0.02

4.1.3.3 SEM analysis

The SEM micrographs of the silica particles are shown in Figure 4.4. The U-Si, M-Si, V-Si and A-Si particles were in a spherical shape with uniform size and shape. The average sizes of all silica particle types are shown in Table 4.2. The average particle size of U-Si, M-Si, V-Si and A-Si was 133, 151, 152 and 154 nm, respectively with the narrow size distribution. The particle size of modified silica increased with the increase in molecular weight of substituted groups for each modifier: molecular weight of substituted groups for MTES ($-CH_3$ = 15 g/mole), VTES ($-CH=CH_2$ = 27 g/mole), APTMS ($-CH_2CH_2CH_2NH_2$ = 58 g/mole).

According to the obtained result, the M-Si, V-Si and A-S were successfully prepared by sol-gel reaction. The particle sizes of modified silica are depending on the molecular weight or the size of substituted group of each modifier. Finally, the modified silica particles prepared by using sol-gel technique are expected to be well dispersed in the rubbery matrix and the improvement of mechanical properties of NR vulcanizates could be achieved.

Table 4.2 Average particle sizes of U-Si, M-Si, V-Si and A-Si particles, respectively

Sample	Particle size of silica (nm)
U-Si	133 ± 0.06
M-Si	151 ± 0.06
V-Si	152 ± 0.06
A-Si	154 ± 0.07

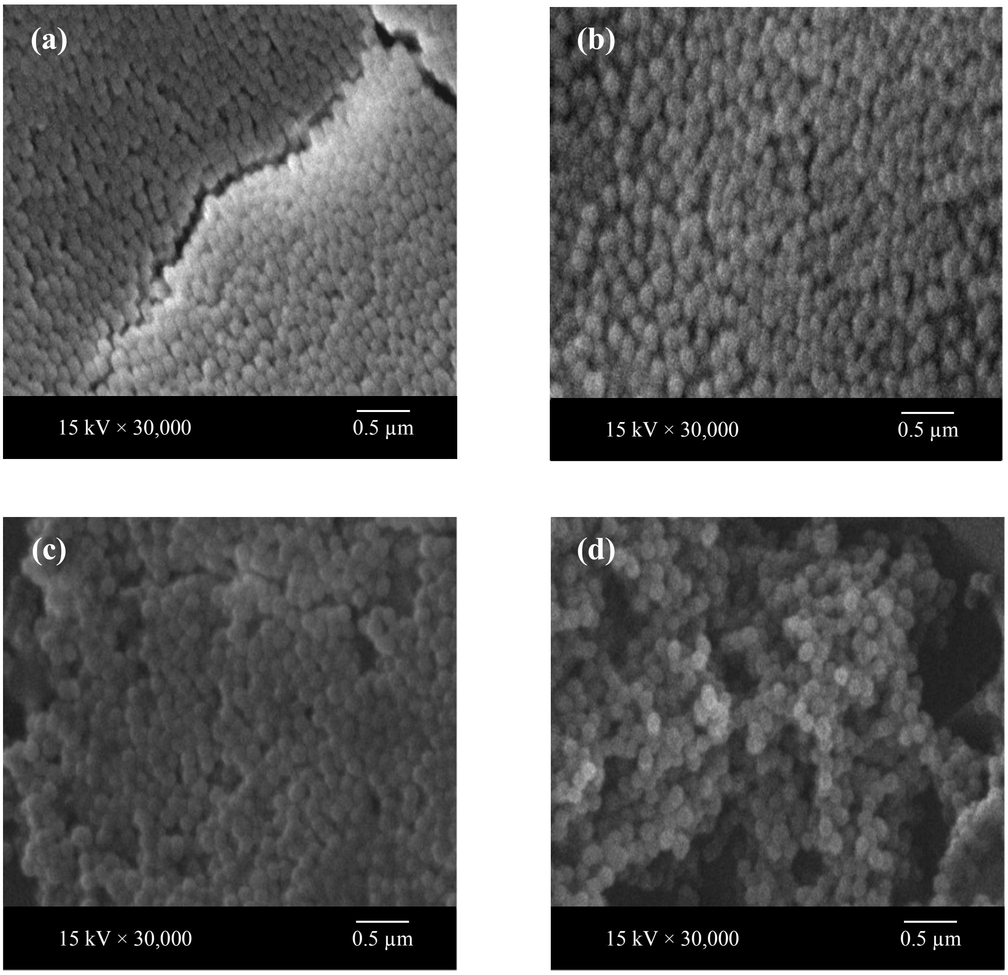


Figure 4.4 SEM micrographs of (a) U-Si (b) M-Si, (c) V-Si and (d) A-Si particles, respectively

4.1.3.4 The hydrophobicity

The hydrophobicity of silica surface particles was investigated with the consideration of water contact angle measurement are summarized in Table 4.3. Unfortunately, the contact angle of U-Si particles could not be determined due to the presence of high polarity of silanol groups on the silica surface.

The contact angles of M-Si and V-Si became increased. This is because the methyl and vinyl groups as hydrophobicity molecules substituted on silica surface particles lead to the enhancement of the hydrophobicity of the silica particles. In addition, the contact angle of V-Si slightly escalated more than that of M-Si. In the case of A-Si, the contact angle was less than that of M-Si and V-Si, because of the presence of amino groups as a polar group. However, the hydrophobicity of A-Si was higher than that of U-Si particles. This may be attributed to that the part of propyl groups of APTMS which bring a decrease in the polarity of modified silica particles when compared with the U-Si particles.

Table 4.3 The contact angle of U-Si, M-Si, V-Si and A-Si particles, respectively

Silica particles	Contact angle (°)
U-Si	could not determine
M-Si	140 ± 1.15
V-Si	141 ± 1.23
A-Si	67 ± 1.06

4.1.3.5 The thermal analysis

Figure 4.5 shows the thermogravimetric analysis curves of U-Si, M-Si, V-Si and A-Si particles, respectively. The same behaviors of TGA curve for all silica particles types were observed. The weight loss below 180 °C was due to ethanol and water evaporation. The U-Si, M-Si, V-Si and A-Si particles were released ethanol and water in the amount of 3.1, 2.2, 2.1 and 2.6 %weight, respectively. The U-Si and A-Si exhibited a higher weight loss at 180 °C more than V-Si and M-Si due to the presence of silanol groups and amino groups of U-Si and A-Si, respectively, resulting in the quick absorption water and ethanol.

A further weight decrease between 180-800 °C was related to organic group's decomposition and silanol group's condensation (dehydroxylation). The weight decrease between 180-800 °C of U-Si, M-Si, V-Si and A-Si particles was about 1.9, 6.7, 6.9 and 5.9 %weight, respectively. According to the results of the CHN analysis, the organic groups coated on M-Si, V-Si and A-Si particles had a value of 7.84, 8.08 and 4.96 %weight, respectively. Additionally, the TGA results were used to calculate the mole of organic groups which were coated on silica surface. The organic groups of M-Si, V-Si and A-Si particles which could be coated on silica surface had values of 0.45, 0.26 and 0.10 % mole, respectively (see the calculation in Appendix No. A.3). These results showed the modification decreased with an increase in the size of substituted groups of modifier, due to the steric effect of reaction.

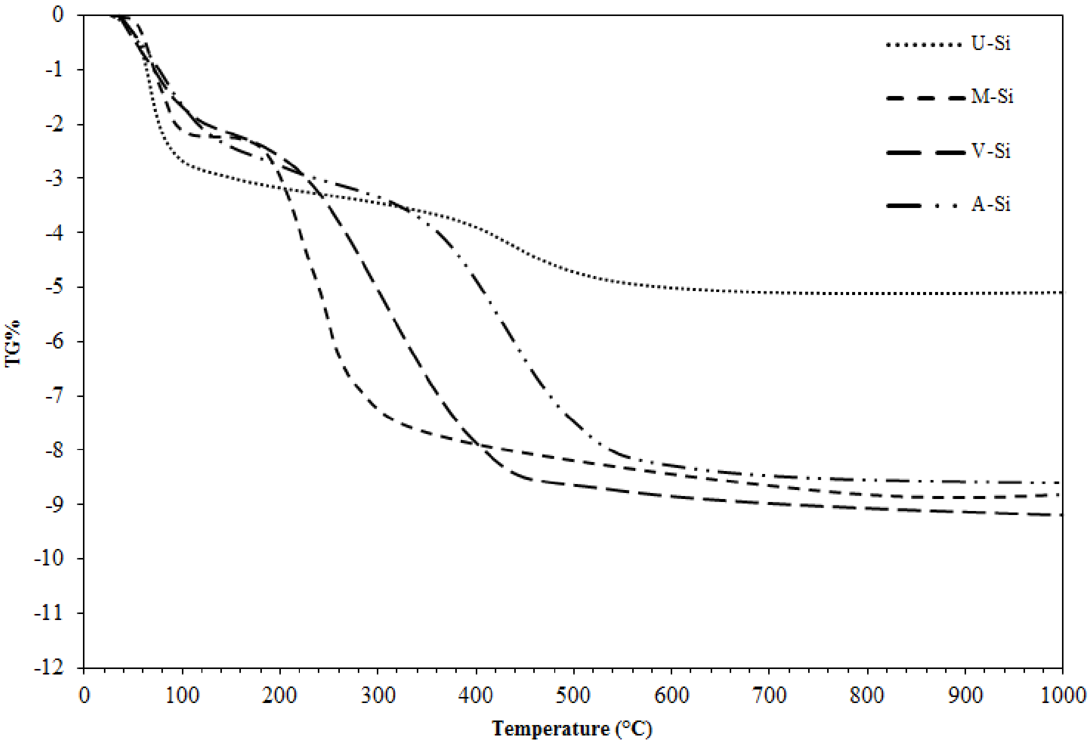


Figure 4.5 TGA curves U-Si, M-Si, V-Si and A-Si particles, respectively

4.1.4 Effect of mole ratio of modifier to TEOS

Figure 4.6, 4.7 and 4.8 shows the FTIR spectra of M-Si, V-Si and A-Si particles, respectively, at various mole ratios of modifier to TEOS. The differences of mole ratio of modifier to TEOS were varied as follows: 0.1, 0.5, 1.0 and 2.0.

With the FTIR spectra of M-Si particles experiencing an increase of mole ratios of MTES to TEOS, the absorption peak of C-H stretching of $–CH_3$ groups, C-H bending of $–CH_3$ groups and $Si–CH_3$ vibration peak at 2973, 1428 and 1273 cm^{-1} were enhanced. In the case of using VTES as a modifier, the absorption peaks of C=C stretching bond of $CH=CH_2$ groups at 1620 cm^{-1}, C-H bending of $CH=CH_2$ groups and Si–C vibration peak at 1402 and 1272 cm^{-1} were increased. According with the case of modification by APTMS, the FTIR spectra of the absorption peak around 1457 cm^{-1}(–CH bending of $CH_2CH_2CH_2NH_2$) also increased.

In addition, the O-H absorption peaks of Si-OH groups at 946 cm^{-1} seemed to be weakened after modification, and it decreased with the increasing of the mole ratio of modifier to TEOS, as shown in Table 4.4. This is because the Si-OH groups on silica surface were substituted by organic groups of modifier, the substitution could be increased with increasing the amount of modifiers. The FTIR results accorded with the contact angle measurements. The contact angle of modified silica surface particles increased with the rise in the mole ratio of modifiers (MTES, VTES and APTMS) to TEOS, as shown in Table 4.4. These results show that the increasing of modifier to TEOS enhanced the hydrophobicity of surfaces due to the modifications on the silica surface being more complete. For this work, a mole ratio of modifier to TEOS of 0.1 was chosen to study the effect of modified silica surface for the reinforcement of NR vulcanizates. Because this condition at least amount of modifier were used and could observe that the hydrophobicity of modified silica particles was clearly enhanced when compared with U-Si. So, the mole ratio of modifier to TEOS of 0.1 may be able to improve the compatibility between modified silica and NR matrix.

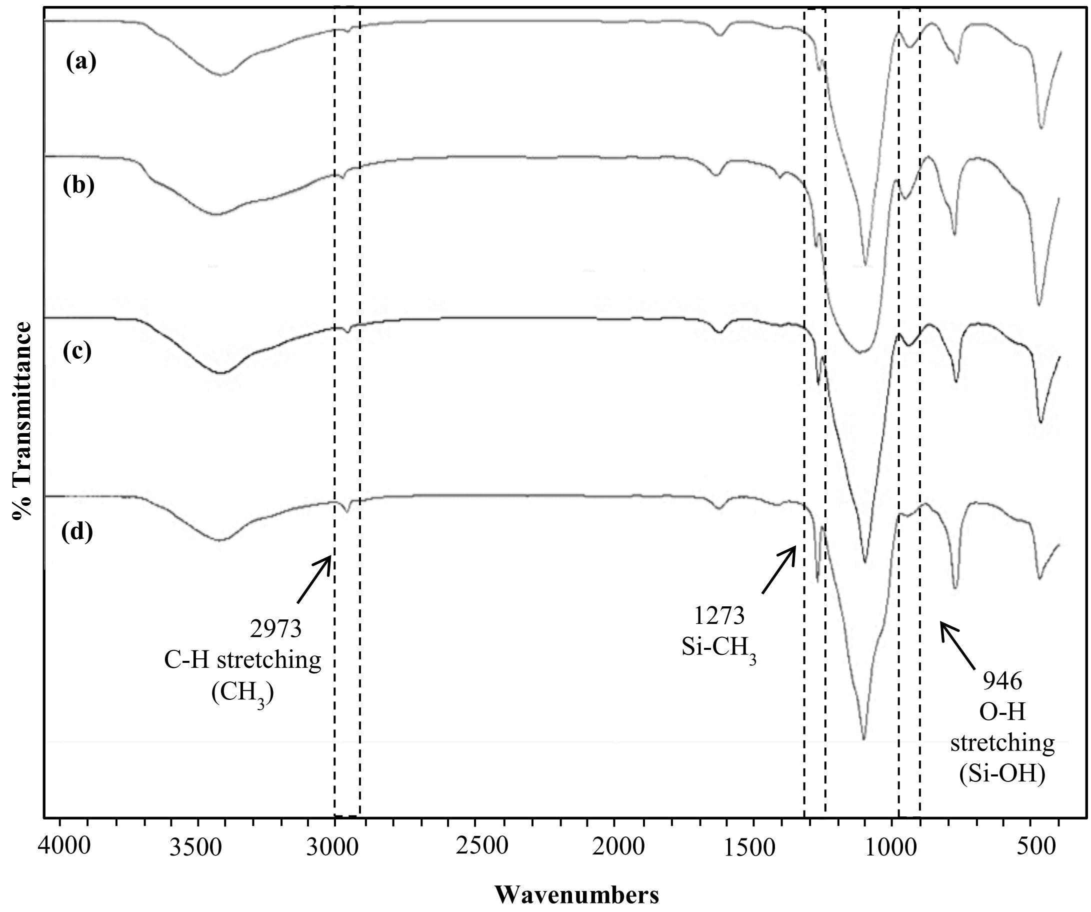


Figure 4.6 FTIR spectra of M-Si which using the difference of mole ratios of MTES to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0

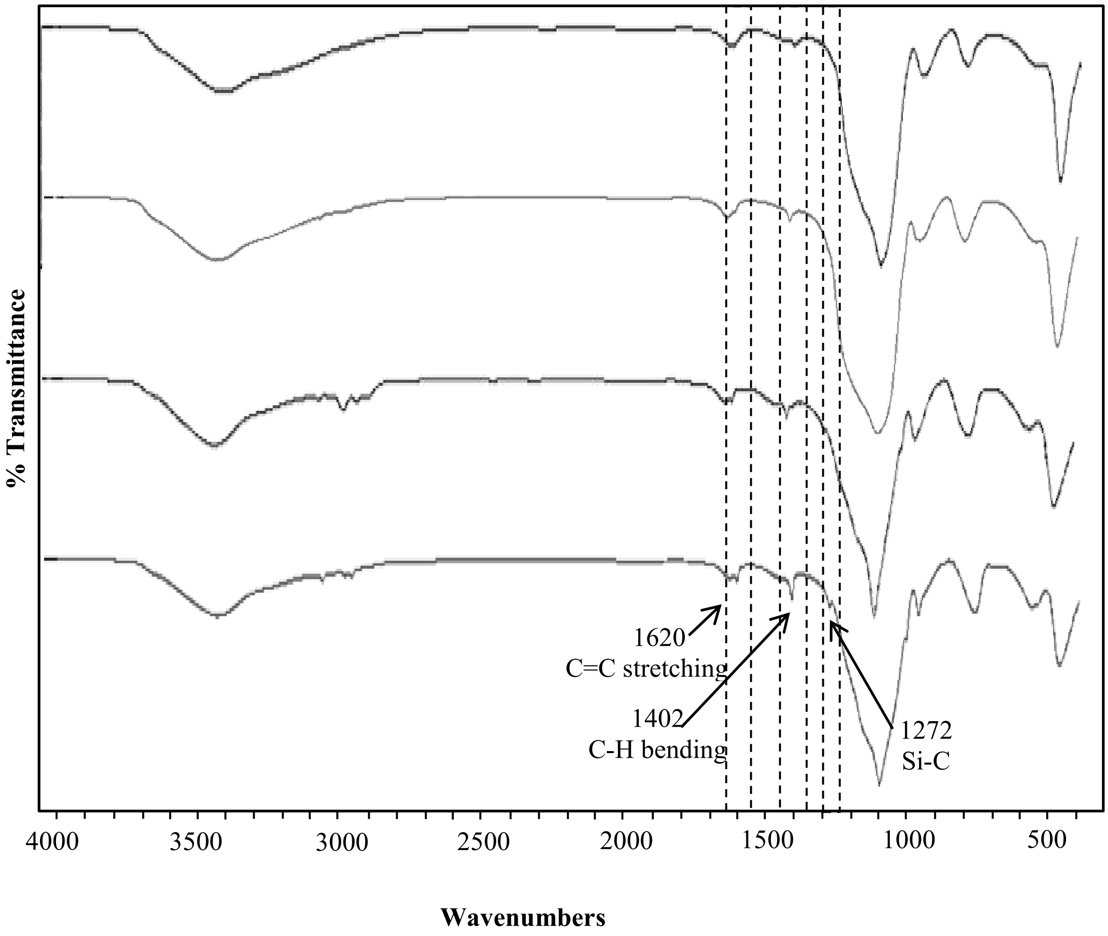


Figure 4.7 FTIR spectra of V-Si which using the difference of mole ratios of VTES to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0

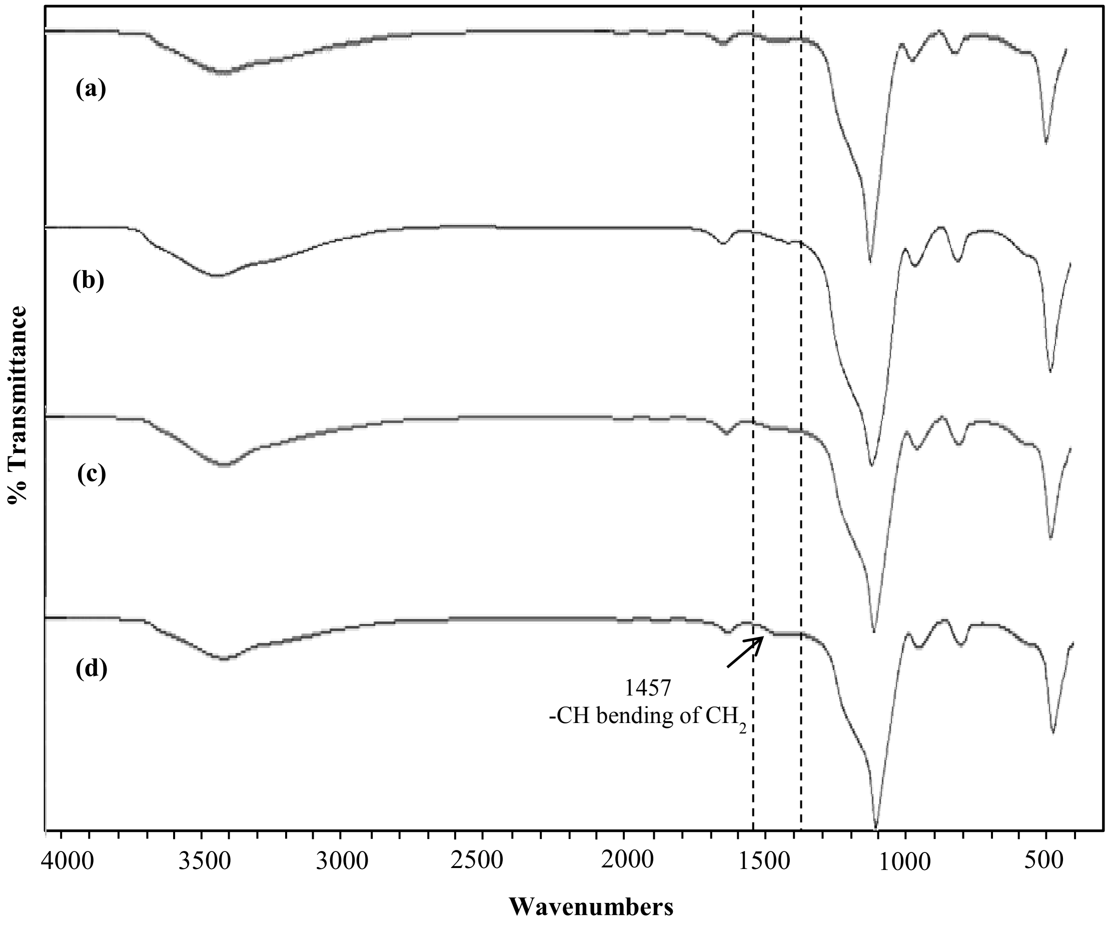


Figure 4.8 FTIR spectra of A-Si which using the difference of mole ratios of APTMS to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0

Table 4.4 The peak area of Si–OH groups (A.cm^{-1}) and contact angle of U-Si, M-Si, V-Si and A-Si particles which using the difference of mole ratios of modifier to TEOS: (a) 0.1, (b) 0.5, (c) 1.0 and (d) 2.0, respectively from FTIR spectra

Silica particles	**Mole ratios of modifier to TEOS**	**Peak area of Si–OH groups (A.cm^{-1})**	**contact angle (°)**
U-Si	-	3.60	could not determine
M-Si	0.1	0.90	140 ± 1.15
	0.5	0.84	144 ± 0.80
	1.0	0.70	147 ± 0.72
	2.0	0.33	148 ± 1.47
V-Si	0.1	1.35	141 ± 1.23
	0.5	0.93	145 ± 0.21
	1.0	0.80	148 ± 0.99
	2.0	0.70	148 ± 0.59
A-Si	0.1	1.47	67 ± 1.06
	0.5	1.40	71 ± 0.42
	1.0	1.30	75 ± 3.69
	2.0	1.22	77 ± 1.55

4.2 Properties of NR vulcanizates

4.2.1 Morphology

Figure 4.9 shows the TEM micrographs of NR vulcanizates with 10 phr of silica particles. Gray and black color in micrographs indicated NR matrix and silica particles, respectively.

The morphology of NR vulcanizates prepared by direct and indirect methods was compared. The dispersion of silica particles inside the NR matrix was significantly different. In the case of preparing by direct method, the silica particles were well dispersed with fine particles, and with a smaller particle size than that prepared by indirect method. The silica particle sizes prepared by direct and indirect method were in the range of 50-70 nm and 150-180 nm, respectively. This is due to the prepared silica filled NR vulcanizates by direct method generating silica particles inside the NR matrix. The generating of silica was conducted after the uniform distribution of TEOS solution in the matrix of NR latex, giving a fine distribution of silica in the NR latex. The NR matrix prevents the aggregation of silica and provides a reduced size for the silica particles [35].

However, the aggregation of silica particles prepared by direct method could form, although it was dispersed with very small particles size, but these particles were in close distribution so it may have caused aggregation. And the high surface area of silica particles prepared by direct method may have led to the aggregation of these silica particles, while the silica particles prepared by indirect method were distributed with proper distance.

When comparing among different types of silica particles, the aggregates of U-Si particles were clearly observed, while the M-Si, V-Si and A-Si were well dispersed in the NR matrix with some aggregation. This result indicated that the polarity of silica particles could be reduced by modification (according with the contact angle results), resulting in enhanced compatibility between silica particles and NR matrix.

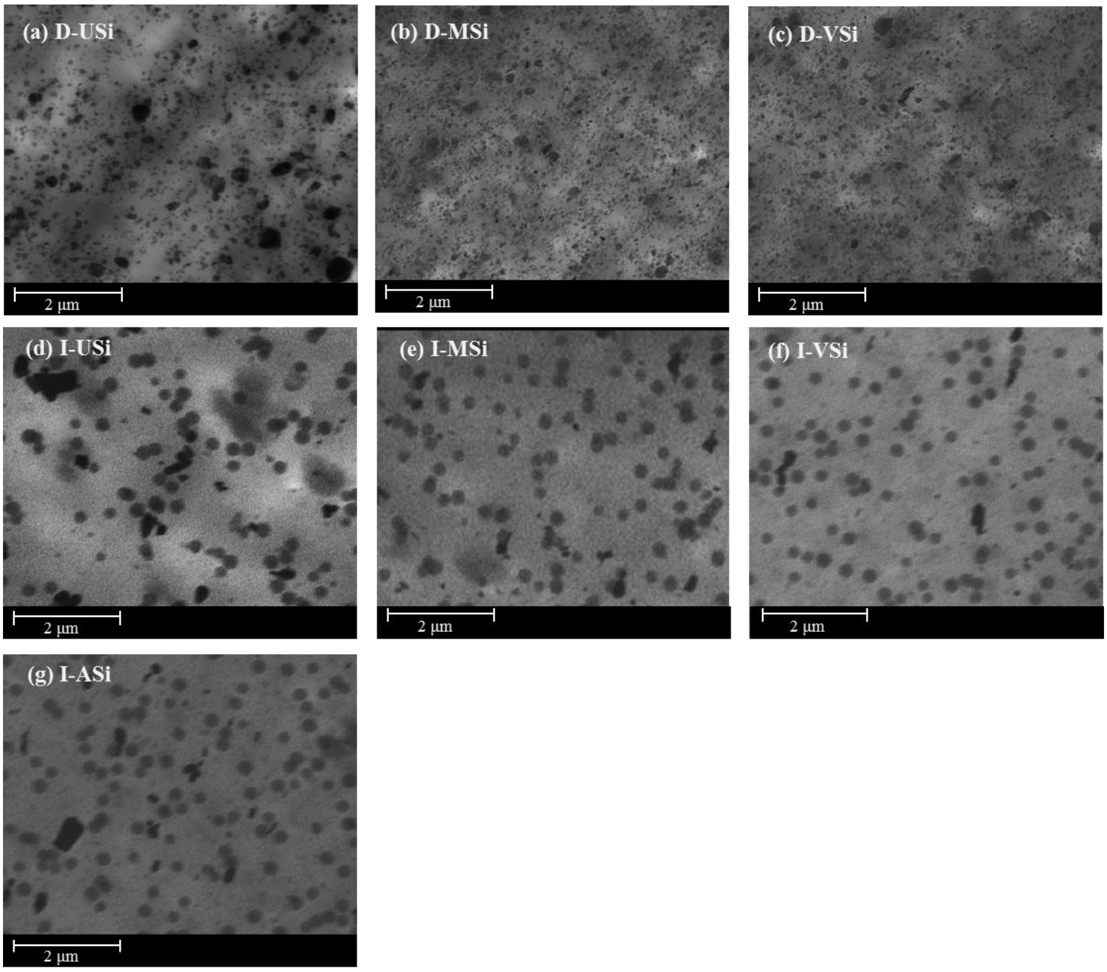


Figure 4.9 TEM micrographs of NR vulcanizates with silica content of 10 phr by direct method of (a) U-Si (b) M-Si and (c) V-Si and by indirect method of (d) U-Si (e) M-Si, (f) V-Si and (g) A-Si, respectively

4.2.2 Cure characteristics

The cure properties of NR vulcanizates without and with silica content of 10 phr are presented in Table 4.5.

The scorch times (t_{s2}) and curing times (t_{c90}) of U-Si filled NR vulcanizates were longer than those of unfilled NR vulcanizates and modified silica filled NR vulcanizates, respectively. It is because the surfaces of U-Si particles generally contained silanol groups, which are acidic and highly reactive. The silanol groups can react quickly with the curing agents, i.e., accelerator or activator, in which these agents can be trapped by the silanol groups on the silica surface. The vulcanization reaction is therefore somewhat retarded, leading to an increase in the t_{s2} and t_{c90} of NR vulcanizates [4, 11, 22].

After the silica surface was modified, the t_{s2} and t_{c90} of NR vulcanizates were shorter than that of those U-Si particles filled NR vulcanizates. This is due to silanol groups on the silica surface being decreased by substitution of modifier, relating with the FTIR results (Table 4.4). The quantitative analysis mode of FTIR spectra indicated that the amount of –OH groups on silica surface decreased with the modification and it decreased with the increase of the mole ratio of modifier to TEOS.

In addition, it is interesting to note that the t_{s2} and t_{c90} of NR vulcanizates prepared by indirect method showed longer values than those of NR vulcanizates prepared by direct method. Accordingly, the TEM results (Figure 4.9) show that silica particles filled NR vulcanizates obtained via direct or indirect methods showed a difference in surface properties. It is consistent with the report results by using the Atomic Force Microscopy (AFM) of Kohjiya et. al. [36], and shows that the silanol groups on the silica surface prepared by direct method were lower than those prepared by indirect method.

The delta torque (ΔM) of NR vulcanizates increases on loading with all types of silica particles. The U-Si particles filled NR vulcanizates exhibit higher ΔM values than that of unfilled NR vulcanizates. It can be explained that the addition of rigid filler leads to higher stiffness of the NR matrix and the effect of silica-silica network formation [30, 37].

The ΔM of all types of modified silica filled NR vulcanizates showed higher values than that of U-Si particles filled NR vulcanizates. This effect may be attributed to a higher degree of crosslinking compared to the NR composites containing U-Si particles, leading to more stiffness [30]. These explanations were confirmed with the results of the swelling ratio.

As seen in the swelling ratio result (Table 4.6), it is inversely proportional to the degree of crosslink. The swelling ratios of modified silica filled NR vulcanizates showed lower values than that of U-Si particles filled NR vulcanizates. It could be concluded that the crosslink density of NR was enhanced by modification of the surface of the silica.

Furthermore, the swelling ratios of silica filled NR vulcanizates via direct method gave lower values than those of silica filled NR vulcanizates via indirect methods. This result approved with the ΔM of NR vulcanizates via direct method, which exhibited higher values than that prepared by indirect method.

Interestingly, in the case of the A-Si filled NR vulcanizates, it showed the shortest t_{s2} and t_{c90}. The results prove that the A-Si can promote rubber vulcanization and accelerate the vulcanization rate. This is because the aminopropyl groups of APTMS can promote the agents and sulphur, leading to an activation of vulcanization. Furthermore, the ΔM of A-Si filled NR vulcanizates showed the highest values. These are attributed to the fact that A-Si can chemically react with both silica and rubber, improving filler–rubber interactions, therefore increasing the crosslinking density of composites [31].

Table 4.5 Cure properties of rubber vulcanizates

Cure characteristics	Direct method				Indirect method			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
T_{s2}^{a} (min)	2.42	2.56	2.36	2.27	2.73	2.40	2.33	1.67
T_{c90}^{b} (min)	3.73	3.86	3.58	3.49	4.74	3.89	3.44	3.02
M_{H}^{c} (lbf·in)	3.47	4.20	4.38	4.62	4.03	4.34	4.38	4.50
M_{L}^{d} (lbf·in)	0.16	0.21	0.20	0.23	0.18	0.20	0.20	0.20
ΔM^{e} (lbf·in)	3.31	3.99	4.18	4.39	3.85	4.14	4.18	4.30

[a] Scorch time, [b] Curing time at 150 °C, [c] Highest modulus of elasticity, [d] Lowest modulus of elasticity, [e] Delta torque ($M_H - M_L$)

4.2.3 Mechanical properties

Table 4.6 summarized the mechanical properties of NR composite materials. It can be seen that the moduli (M_{100}, M_{300} and M_{500}) and tensile strengths of NR vulcanizates increased significantly when using silica as reinforcing filler. The improvement may be explained by the reinforcement effect of silica particles [38].

It can also be observed that the moduli and tensile strengths of NR vulcanizates were obviously improved by the modification of silica surface particles when compared with U-Si particles. This means that the modified silica filled NR vulcanizates must require higher energy to stretch more than that of unmodified silica filled NR vulcanizates. This is due to the modified silica particles being well dispersed in the NR matrix, more than that of the U-Si particles. The well dispersed modified silica particles lead to giving a high efficiency of transfer loading which is applied from an external force, as well as stronger interfacial interaction between rubber and fillers, which allows an improvement in the mechanical properties of the NR vulcanizates.

In the case of A-Si, the previous results were shown the hydrophobicity of A-Si became increased when compared with U-Si. The increasing hydrophobicity of modified silica particles caused to the more interaction with rubber molecules, which would allow an improvement of mechanical properties of the composites. The elongation at break tended to decrease when the stiffness of the composite material increased. The hardness for all silica filled NR vulcanizates seemed to be constant, owing to the same silica content added in the NR matrix.

The tear strength and abrasion resistance also followed the same trend as that of the tensile strength. The tear strength and abrasion resistance of silica filled NR vulcanizates was higher than those of unfilled NR vulcanizates owing to the silica particles being able to interact preferentially with the NR phase, as shown by the higher reduction of volume loss in the NR vulcanizates [39]. After the silica surface was modified, more uniform distribution of modified silica particles in the NR matrix was obtained. It has been claimed that a vulcanizate with good filler dispersion exhibits better tear and wear resistance than that with poor filler dispersion [40-41]. Additionally, the functional groups of the modified silica particles are hydrocarbon molecules that are well compatible with silica particles and NR molecules. This causes a strong adhesion between the modified silica particles and the NR matrix.

The compression set of NR vulcanizates significantly decreased with the addition of the silica particles. Moreover, the combination of modified silica particles showed a further decrease than that with unmodified silica particles. This may be explained by the aggregation of the U-Si resulting in a low recovery of rubber chain segments [29]. The better dispersion of modified silica particles, the deformation and compression set tend to be decreased [42].

It is interesting to note that the mechanical properties of NR vulcanizates prepared by direct method tended to be higher than those of NR vulcanizates prepared by indirect method. This result correlates well with the difference in surface properties, based on TEM results. It has been explained in the previous section.

4.2.4 Thermal properties of rubber vulcanizates

The thermal degradation of NR vulcanizates without and with 10 phr of unmodified silica and modified silica particles by both direct and indirect methods are presented in Table 4.6 and the thermal degradation behavior are shown in Figure 4.10.

The initial decomposition temperature (T_{id}) and the temperature of maximum weight loss rate (T_{max}) of all silica particles filled NR vulcanizates were higher than that of unfilled NR vulcanizates. The incorporation of the silica nanoparticles into the NR matrix increased the thermal decomposition temperatures of NR composites, due to the silica particles, which effectively acted as physical barriers to prevent the transport of volatile decomposed products out of NR composites during thermal decomposition [43-44].

Interestingly, the thermal degradation (T_{id} and T_{max}) of modified silica filled NR vulcanizates increased when compared with U-Si filled NR vulcanizates. The improvement of the thermal stability of the prepared NR vulcanizates with modified silica particles can be based on the fact that these materials have inherently good thermal stability, and also due to the strong interaction/chemical bonding that exists between the modified silica particles and the NR matrix.

In addition, the NR vulcanizates prepared by both direct and indirect method showed a similar trend of thermal degradation behavior. The thermal degradation of NR vulcanizates prepared by direct method exhibited a slight increase when compared with the indirect method. This is due to the smaller size and well dispersed silica particles in the NR matrix, prepared by direct method, bringing a high specific surface area for heat transfer from an external source.

Table 4.6 Properties of NR vulcanizates

Properties	Direct method				Indirect method			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
M_{100}^{a} (MPa)	0.81 ± 0.03	0.99 ± 0.02	1.05 ± 0.04	1.11 ± 0.02	0.84 ± 0.02	0.88 ± 0.02	0.87 ± 0.02	0.93 ± 0.02
M_{300}^{a} (MPa)	1.03 ± 0.06	3.12 ± 0.09	3.13 ± 0.16	3.73 ± 0.09	2.23 ± 0.08	2.52 ± 0.10	2.36 ± 0.10	2.64 ± 0.08
M_{500}^{a} (MPa)	1.85 ± 0.10	10.85 ± 0.28	10.87 ± 0.89	12.80 ± 0.43	7.80 ± 0.63	8.50 ± 0.49	7.96 ± 0.34	9.56 ± 0.52
T_{B}^{b} (MPa)	17.42 ± 1.54	23.59 ± 2.01	24.59 ± 1.08	26.34 ± 1.00	23.50 ± 2.24	24.41 ± 1.06	24.15 ± 1.80	25.42 ± 0.61
E_{B}^{c} (%)	770.23 ± 27.13	662.20 ± 24.29	652.37 ± 11.12	651.43 ± 6.69	693.06 ± 16.04	688.07 ± 22.83	689.35 ± 16.97	679.00 ± 11.19
Hardness (Shore A)	34.00 ± 0.35	47.00 ± 0.42	46.00 ± 0.42	47.00 ± 1.20	44.00 ± 0.27	44.00 ± 0.27	45.00 ± 0.42	45.00 ± 0.27
Tear resistance (N/mm)	48.30 ± 1.10	83.66 ± 3.62	90.67 ± 4.29	91.28 ± 2.20	82.82 ± 2.23	88.56 ± 1.65	91.64 ± 2.60	90.66 ± 2.78
Volume loss (mm^3)	692.01 ± 10.26	216.11 ± 10.81	192.06 ± 8.75	209.18 ± 12.74	238.21 ± 11.11	222.10 ± 8.62	228.00 ± 10.47	225.10 ± 13.29
Compression set (%)	34.11 ± 1.64	22.91 ± 0.90	20.32 ± 0.69	20.41 ± 0.95	25.02 ± 1.12	20.10 ± 0.86	20.82 ± 1.20	20.42 ± 0.49
Swelling ratio	4.96 ± 0.22	3.34 ± 0.36	3.12 ± 0.37	3.01 ± 0.34	3.43 ± 0.34	3.14 ± 0.21	3.13 ± 0.40	2.87 ± 0.10
T_{id}^{d} (°C)	310	318	338	334	312	330	332	341
T_{max}^{e} (°C)	375	379	384	385	377	380	381	386
E' at 25 °C (MPa)	1.13	1.89	2.25	2.26	1.65	2.00	2.14	2.23
T_{g}^{g} (°C)	– 50.3	– 48.2	– 45.4	– 45.1	– 49.3	– 46.0	– 46.2	– 46.2

[a] Stress at 100, 300 and 500% elongation, [b] Tensile strength, [c] Elongation at break, [d] The initial decomposition temperature, [e] The temperature of maximum weight loss rate, [f] Storage modulus, [g] Glass transition temperature

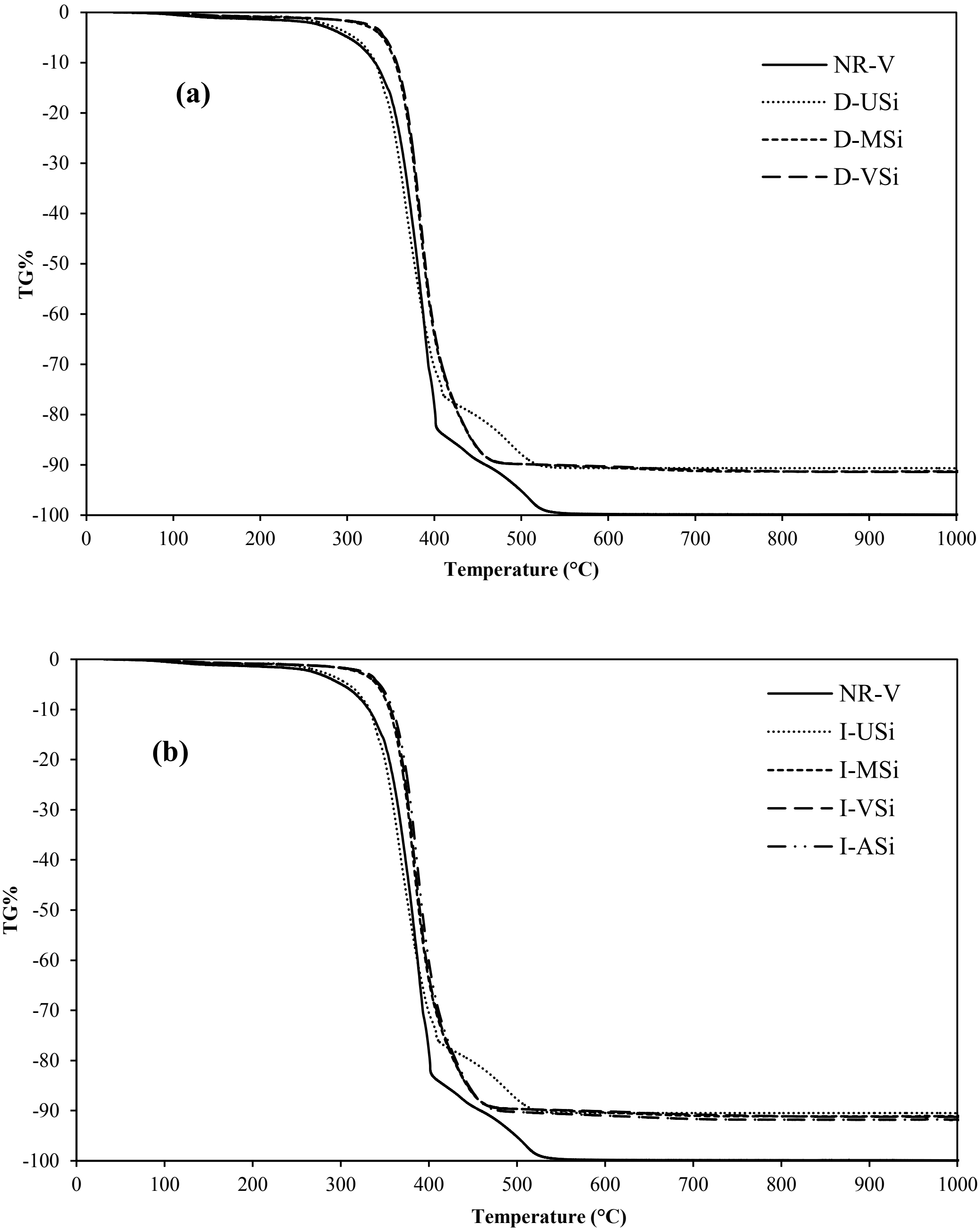


Figure 4.10 The thermal properties of NR vulcanizates with silica content of 10 phr by (a) direct method and (b) indirect method of unmodified silica and modified silica particle

4.2.5 Dynamic mechanical analysis

The dynamic mechanical behavior NR vulcanizates with prepared by direct and indirect method and summarized the dynamic mechanical properties are presented in Figure 4.11, 4.12 and Table 4.6, respectively. The effect of modified silica surface on dynamic mechanical properties of NR vulcanizates were investigates. The storage modulus (E') was determined as a function of temperature and it was provided also values of tanδ that related with loss modulus (E") by

$$\tan\delta = E''/ E'$$

E' and tanδ of NR vulcanizates showed temperature dependent dynamic behaviors with three distinct regions (Figure 4.11(a) and 4.12(a)), including glassy, transition and rubbery regions. In the glassy regions (-80 to -70 °C), E' of modified silica filled NR vulcanizates exhibited higher values than those of U-Si filled NR vulcanizates and unfilled NR vulcanizates, respectively. The effect of modified silica surface in the preceding sections, caused an increase in the efficacy of the curing reaction, leading to a decrease in the degree of swelling, and thus causing a higher crosslink density and higher E'.

In the transition region, the starting point in the falling of unfilled NR vulcanizates was lower than that of other filled NR vulcanizates. This is because the adding of rigid silica particles inside the NR matrix led to a hindering in the moving of rubber chains. Interestingly, the modified silica filled NR vulcanizates exhibited a starting point falling higher than that of U-Si. It could be explained by the high interaction between modified silica particles, which was more than that of the U-Si particles.

Considering E' at 25 °C, it was still in the same order of modified silica filled NR vulcanizates being higher than those of U-Si filled NR vulcanizates and unfilled NR vulcanizates, respectively.

In the glass transition temperature (T_g), estimated from the temperature at the maximum tanδ peak (Figure 4.11(b) and 4.12(b)) of both direct and indirect methods, samples were ranked in the order of: Modified silica filled NR vulcanizates > U-Si filled NR vulcanizates > and unfilled NR vulcanizates. The T_g of all types of silica filled NR vulcanizates were higher than that of unfilled NR vulcanizates, due to the silica particles having the ability to hinder the movement of NR chains and forming a pseudo-network. This caused difficult mobility for the rubber chains and thus a need for more energy. The T_g of modified silica filled NR vulcanizates tended to increase, when compared with the U-Si filled NR vulcanizates. This can be explained by the strong interaction of filler with the NR matrix [30].

Comparing E' at 25 °C of NR vulcanizates between the direct and indirect method, E' of NR vulcanizates prepared by direct method tended to be higher than those prepared by indirect method. This is due to the preparing by indirect method which tended to aggregate the silica particles more than that when prepared by direct method. The large aggregates of silica particles led to a weakening effect in the NR matrix, causing inferior reinforcement. The T_g of NR vulcanizates prepared by direct method were also higher than that prepared by indirect method. This is the cause of the aggregation of silica prepared by indirect method, bringing a large gap between the NR molecules and the filler, leading to easy mobility for the rubber molecules.

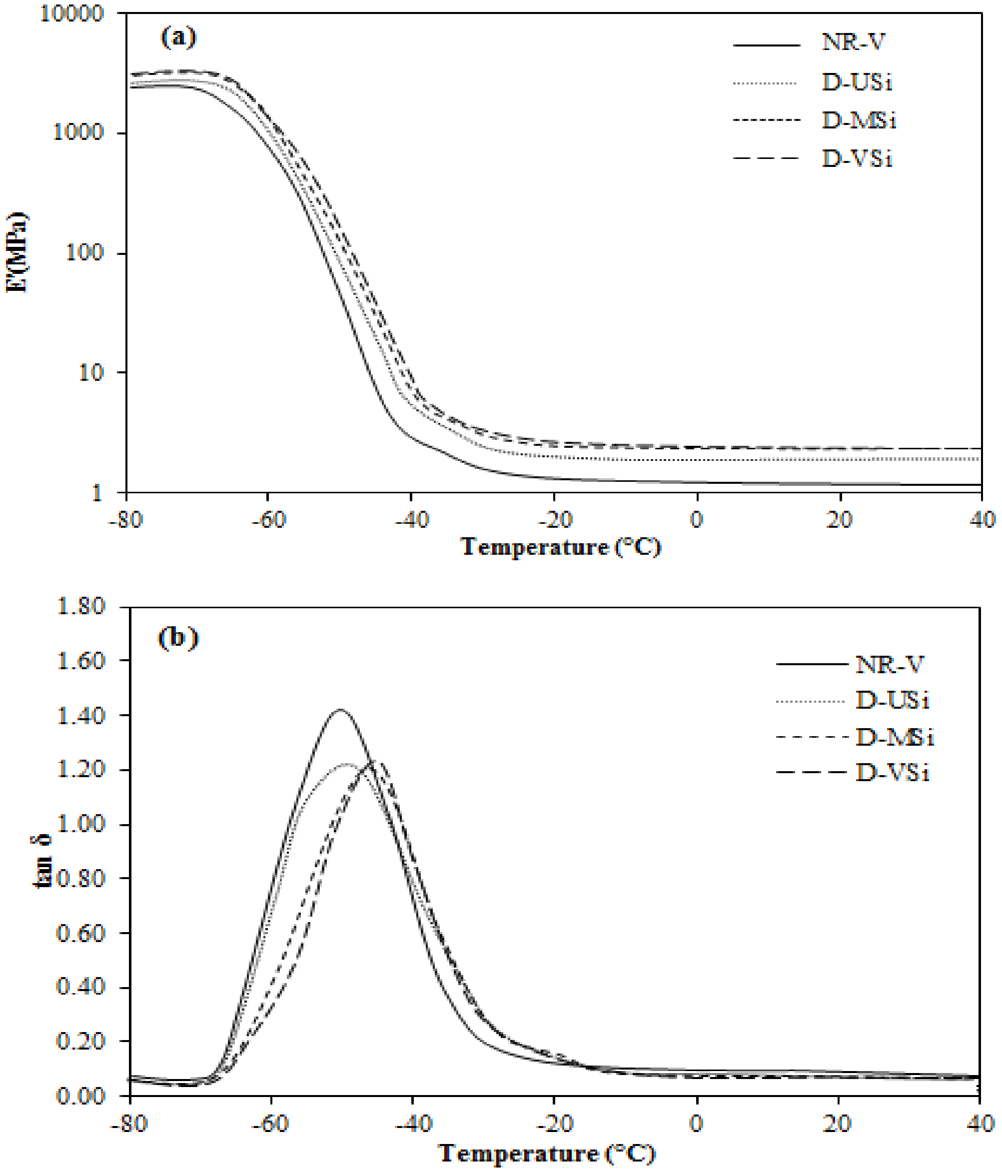


Figure 4.11 Dynamic mechanical properties of NR vulcanizates with silica content of 10 phr by direct method of unmodified silica and modified silica particles as described by (a) the storage modulus (E') and (b) tan δ

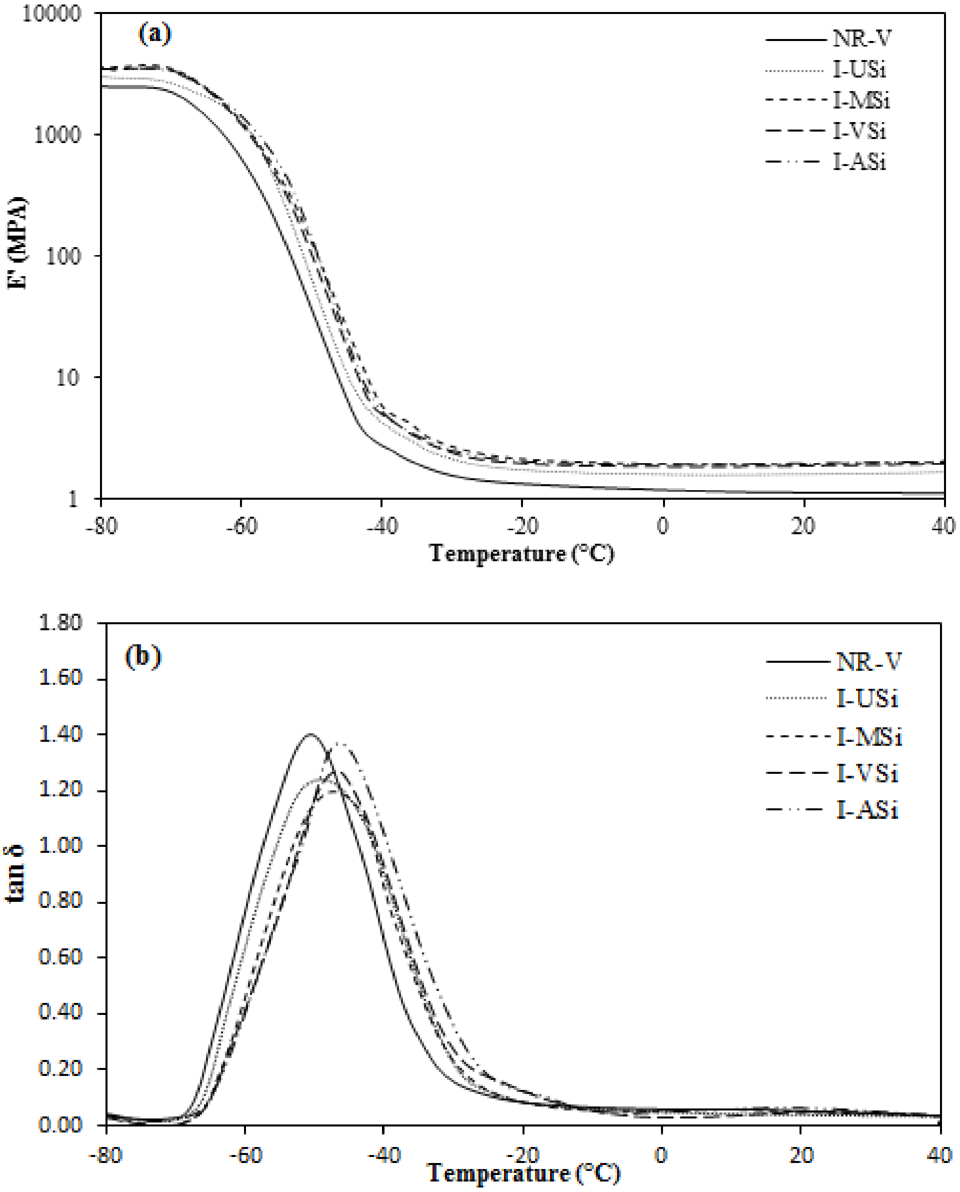


Figure 4.12 Dynamic mechanical properties of NR vulcanizates with silica content of 10 phr by indirect method of unmodified silica and modified silica particles as described by (a) the storage modulus (E') and (b) tan δ

CHAPTER V

CONCLUSION AND FUTURE DIRECTION

5.1 Conclusion

In this research, the NR compounds were prepared by using two methods, “direct method” and “indirect method. The advantage and disadvantage of different methods were discussed.

The preparation of silica filled NR matrix by direct method is easily compare to indirect method. This is because the silica particles were generated in NR matrix and their surface was modified in the same time. The well dispersion of in situ silica particles by direct method was obtained when compared with indirect method. It is due to the in situ silica particle size generated by direct method were smaller than those generated by indirect method. Moreover, the mechanical, thermal and dynamic mechanical properties of NR vulcanizates obtained by direct method were higher than those of NR vulcanizates obtained by indirect method. The properties of NR vulcanizates prepared by both methods were comparable, although the sizes of silica particles from indirect method were larger than those of prepared by direct method. In addition, it is interesting to note that the cure characteristic, mechanical, thermal and dynamic mechanical properties of modified silica filled NR vulcanizates via both direct and indirect methods were improved when compared with the unmodified silica filled NR vulcanizates. This is due to the modification of silica surface could improve the compatibility between silica particles and NR molecules since hydrophobicity of silica were increased after modification. Therefore, the modified silica were well dispersed in NR matrix and leading to enhance the efficiency of reinforcement.

5.2 Future Direction

5.2.1 Study the other type of modifier to modify on silica surface for improvement the some properties of NR.

5.2.1 Study the effect of mole ratio of modifier to TEOS on the properties of NR vulcanizates.

REFFERANCES

[1] Zafarmehrabian, R., Gangali, S. T., GHOREISHY, M. H. R. and Davallu, M. The effects of silica/carbon black ratio on the dynamic properties of the tread compounds in truck tires. E-Journal of Chemistry 9, 3 (2012): 1102-1112.

[2] Arun, K. J., Joseph francis, P. J. and Joseph, R. Mechanical properties of NR latex-nano silica composites. Optoelectronics and Advanced Materials-Rapid Communications 4, 10 (2010): 1520-1525.

[3] Choi, S. S. and Choi, S. J. Influence of silane coupling agent content on crosslink type and density of silica-filled natural rubber vulcanizates. Bulletin of the Korean Chemical Society 27, 9 (2006): 1473-1476.

[4] Sae-oui, P., Sirisinha, C., Hatthapanit, K. and Thepsuwan, U. Comparison of reinforcing efficiency between Si-69 and Si-264 in an efficient vulcanization system. Polymer Testing 24 (2005): 439–446.

[5] Tangpasuthadol, V., Intasiri, A., Nuntivanich, D., Niyompanich, N. and Kiatkamjornwong, S. Silica-reinforced natural rubber prepared by the sol-gel process of ethoxysilanes in rubber latex. Applied Polymer Science 109 (2008): 424-433.

[6] Zou, H., Wu, S. and Shen, J. Polymer/silica nanocomposites: preparation, characterization, properties, and applications. Chemical Reviews 108, 9 (2008): 3893-3957.

[7] Rahman, I. A. and Padavettan, V. Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites-a review. Hindawi Publishing Corporation Journal of Nanomaterials (2012).

[8] Dash, S., Mishra, S., Patel, S. and Mishra, B. K. Organically modified silica: synthesis and applications due to its surface interaction with organic molecules. Advances in Colloid and Interface Science 140 (2008): 77-94.

[9] Yang, J., Chen, J. and Song, J. Studies of the surface wettability and hydrothermal stability of methyl-modified silica films by FT-IR and Raman spectra. Vibrational Spectroscopy 50 (2009): 178-184.

[10] Xue, L., Li, J., Fu, J. and Han, Y. Super-hydrophobicity of silica nanoparticles modified with vinyl groups. Colloids and Surfaces A: Physicochemical and Engineering Aspects 338 (2009): 15–19.

[11] Malekzadeh, M., Nouri, H. and Farahani, M. Investigation on the influence of silane coupling agent structure on the properties of nano-silica filled rubber compound. Journal of Applied Chemical Researches 3, 12 (2010): 41-45.

[12] Sridee, J. Rheological properties of natural rubber latex. Master's Thesis, Department of Polymer Engineering, Faculty of Engineering, Suranaree University of Technology, 2006.

[13] Narkkun, T., Possibility of membrane preparation from natural rubber latex. Master's Thesis, Department of Polymer Science and Technology, Faculty of Science, Prince of Songkla University, 2009.

[14] Gent, A. N. Engineering with Rubber. New York: Hanser Publishers, 1992.

[15] Ciullo, P. A. Industrial minerals and their uses: a handbook and formulary. United States of America: Noyes Publication, 1996.

[16] Boonstra. B. B. Fillers: Carbon Black and Nonblack. Rubber Technology 1895: 51-86.

[17] Ciullo, P. A. and Hewitt, N. The rubber Formulary. New York: Noyes Publication/ William Andrew Publishing, 1999.

[18] Rothon, R. N. Particulate Fillers for Polymers. New York: Rapra Technology Limited, 2001.

[19] Vansant, E.F., Van Der Voort, P. and Vrancken, K.C. Characterization and chemical modification of the silica surface. Netherlands: Elsevier Science B. V., 1995.

[20] Hewitt, N. and Ciullo, P. Compounding precipitated silica in elastomers: theory and practice. New York: William Andrew Publishing, 1999.

[21] Maya, K.S. Studies on in situ precipitated silica filled rubber composites with special reference to NR, NBR and SBR. Doctoral dissertation, Department of Science and Rubber Technology, Faculty of Science and Technology, Cochin University of Science and Technology, 2007.

[22] Sae-oui, P., Sirisinha, C., Hatthapanit, K. and Thepsuwan, U. Comparison of reinforcing efficiency between Si-69 and Si-264 in a conventional vulcanization system. Polymer Testing 23 (2004): 871-879.

[23] Kortesuo, P. Sol-gel derived silica gel monoliths and microparticles as carrier in controlled drug delivery in tissue administration. Department of Pharmacy, Faculty of Science, University of Helsinki, 2001.

[24] Milea, C.A., Bogatu, C. and Duta, A. The influence of parameters in silica sol-gel process. Series I: Engineering Sciences 4, 53 (2011): 59-66.

[25] Ranjan, R. Surface modification of silica nanoparticles. Doctoral dissertation, University of Akron, 2008.

[26] Wu, Z., Xiang, H., Kim, T., Chun, M. S. and Lee, K. Surface properties of submicrometer silica spheres modified with aminopropyltriethoxysilane and phenyltriethoxysilane. Colloid and Interface Science 304 (2006): 119-124.

[27] Siramanont, J., Tangpasuthadol, V., Intasiri, A., Na-Ranong, N. and Kiatkamjornwong, S. Sol-Gel process of alkyltriethoxysilane in latex for alkylated silica formation in natural rubber, Polymer Engineering and Science 49 (2009): 1099-1106.

[28] Jeon, B. J., Hah, H. J. and Koo, S. M. Surface modification of silica particles with organosilanes through two-step (acid-base) process in aqueous solution, Ceramic Processing Research 3 (2002): 216-221.

[29] Chaichua, B., Prasassarakich, P. and Poompradub, S. In situ silica reinforcement of natural rubber by sol-gel process via rubber solution. Sol-Gel Science and Technology 2009.

[30] Chonkaew, W., Mingvanish, W., Kungliean, U., Rochanawipart, N. and Brostow, W. Vulcanization characteristics and dynamic mechanical behavior of natural rubber reinforced with silane modified silica. Nanoscience and Nanotechnology 11 (2011): 2018-2024.

[31] Xu, S. H., Gu, J., Luo, Y. F. and Jia, D. M. Effects of partial replacement of silica with surface modified nanocrystalline cellulose on properties of natural rubber nanocomposites. eXPRESS Polymer Letters 6 (2012): 14-25.

[32] Asem, A., Ahmed, M. and Waheeba, A. Adsorption/desorption behavior of acid orange 10 on magnetic silica modified with amine groups. Chemical Engineering Journal 150 (2009): 55–62.

[33] Donia, A. M., Atia, A. A., Daher, A.M., Desouky, O.A. and Elshehy, E.A. Selective separation of U (VI) from its solutions using amine modified silica gel produced from leached zircon. International Journal of Mineral Processing 2011.

[34] Despoina, D.A., Kostas, S.T., Nikolaos, K.L. and Kostas, A.M. Adsorption of Remazol Red 3BS from aqueous solutions using APTES and cyclodextrin-modified HMS-type mesoporous silicas. Colloids and Surfaces A: Physicochemical and Engineering Aspects 346 (2009): 83-90.

[35] Maya, K.S. and Rani, J. Preparation of in situ precipitated silica filled acrylonitrile butadiene rubber composites. Department of Polymer Science and Rubber Technology, Faculty of Science and Technology, Cochin University, 2007.

[36] Murakami, K., Lio, S., Tanahashi, T., Kohjiya, S., Kajiwara, K. and Ikeda, Y. Reinforcement of nr by silica generated in situ: comparison with carbon black stock. KGK Kautschuk Gummi Kunststoffe 54 (2001): 668-672.

[37] Fu, S. Y., Feng, X. Q., Lauke, B. and Mai, Y. W. Effects of particle size, particle/ matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. Composites: Part B 39 (2008): 933-961.

[38] Tangudom, P., Sombatsompop, N. and Thongsang, S. Cure characteristics and mechanical properties of rubbers filled with silica hybrid filler. The 4th Science Research Conference, Bangkok, Thailand, 12-13 March 2012.

[39] Arayapranee, W. Abrasion Resistance of Materials. Thailand: InTech, 2012.

[40] Prasertsri, S. and Rattanasom, N. Mechanical and damping properties of silica/ natural rubber composites prepared from latex system. Polymer Testing 30 (2011): 515-526.

[41] Buathong, S. Modification of silica surface by γ-ray induced admicellar polymerization of polyisoprene for improving natural rubber properties. Master's Thesis, Department of Chemical Engineering, Faculty of Engineering, King Mongkut's Institute of Technology North Bangkok, 2005.

[42] Maridass, B. and Gupta, B. R. Effect of carbon black on devulcanized ground rubber tire-natural rubber vulcanizates: cure characteristics and mechanical properties. Elastomers and Plastics 38 (2006): 211-229.

[43] Bikiaris, D. Can nanoparticles really enhance thermal stability of polymers? Part II: An overview on thermal decomposition of polycondensation polymers. Thermochimica Acta 523 (2011): 25-45.

[44] Ahmad, M. B., Gharayebi, Y., Salit, S., Hussein, Z., Ebrahimiasl, S. and Dehzangi, A. Preparation, characterization and thermal degradation of polyimide (4-aps/btda)/ SiO_2 composite films. International Journal of Molecular Sciences 13 (2012): 4860-4872.

APPINDICES

APPENDIX A

CALCULATION

A.1 Calculation of %yield of silica from TEOS

$$Si(OC_2H_5)_4 + 2H_2O \rightleftharpoons SiO_2 + 4C_2H_5OH$$

Percent yield = (actual yield / theoretical yield) × 100

Theoretical yield calculate from equation

1 mole of TEOS = 1 mole of SiO_2

Using TEOS 3 ml $= 3\ \text{ml} \times \frac{0.933\ \text{g/ml}}{208.33\ \text{g/mole}}$

= 0.01344 mole TEOS

∴ Theoretical yield = 0.01344 mole SiO_2

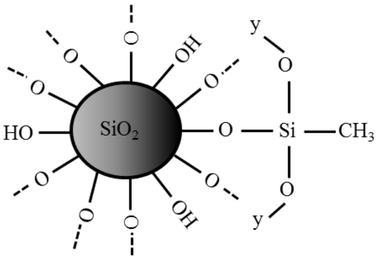
= 0.01344 mole × 60.08 g/mole

= 0.8075 g SiO_2

Actual yield at 30 °C, 12 h = 0.68 g SiO_2

∴ Percent yield = (0.68 g SiO_2 / 0.8075 g SiO_2) × 100 = 84.21%

A. 2 Calculation of organic group's coat on silica surface by CHN analysis



M-Si (y = H or Si)

From model, M-Si contain C 12 %wt, H 3 %wt

From CHN analysis, M-Si contain C 6.27 %wt, H 2.15 %wt

Basis on model, C = 6.27 %wt

$$H = \frac{6.27 \times 3\ \%wt}{12} = 1.57\ \%wt$$

$$C + H = 6.27 + 1.57 = 7.84\ \%wt$$

A. 3 Calculation of mole of organic group's coat on silica surface by TAG analysis

From TGA results, M-Si show methyl group's decomposition 6.7 %wt

MW of methyl group = 15 g/mole

$$\text{Mole of methyl groups' coat on silica surface} = \frac{6.7\ \text{g}}{15\ \text{g/mole}} = 0.45\ \%\ \text{mole}$$

APPENDIX B

Table B.1 CHN analysis of U-Si, M-Si, and A-Si particles, respectively

Silica particles	%C	%H	%N
U-Si	0.00	1.45	0.00
	0.00	1.50	0.00
	0.00	1.42	0.00
Average	0.00	1.46	0.00
SD	0.00	0.04	0.00
M-Si	6.23	2.15	0.00
	6.34	2.10	0.00
	6.24	2.20	0.00
Average	6.27	2.15	0.00
SD	0.06	0.05	0.00
V-Si	7.16	1.50	0.00
	7.21	1.45	0.00
	7.16	1.48	0.00
Average	7.18	1.48	0.00
SD	0.03	0.03	0.00
A-Si	2.98	2.08	1.22
	3.16	2.01	1.25
	3.09	2.07	1.25
Average	3.08	2.05	1.24
SD	0.09	0.04	0.02

Table B.2 Silica particle size (nm) determined by SEM (50 particles)

Silica particles	particle size (nm)				
U-Si	158	132	132	105	105
	145	132	118	132	132
	132	158	132	145	105
	145	158	132	145	118
	145	145	145	132	118
	132	118	132	145	118
	158	145	118	132	118
	184	118	118	118	132
	158	145	105	132	118
	145	132	118	132	132
Average	133				
SD	0.06				
M-Si	132	145	158	158	132
	158	158	145	132	158
	145	158	158	145	145
	158	184	145	145	158
	158	158	145	145	158
	145	132	184	132	145
	132	158	132	145	158
	184	171	132	158	158
	197	132	145	158	132
	171	145	158	132	158
Average	151				
SD	0.06				

Silica particles	particle size (nm)				
V-Si	211	158	158	158	132
	132	132	132	145	158
	158	158	132	158	145
	184	145	158	158	132
	184	158	158	132	145
	132	158	118	158	158
	132	158	132	145	158
	184	145	158	158	145
	158	158	145	158	145
	171	158	158	158	158
Average	152				
SD	0.06				
A-Si	158	132	158	197	158
	158	158	132	171	132
	145	158	158	145	145
	158	158	145	145	158
	158	184	158	132	171
	158	211	132	132	184
	145	132	118	184	171
	158	132	158	184	132
	132	158	171	158	158
	132	132	145	145	158
Average	154				
SD	0.07				

Table B.3 The contact angle (°) of M-Si, V-Si and A-Si particles

Silica particles	mole ratios of modifier to TEOS			
	0.1	0.5	1.0	2.0
M-Si	141	145	146	147
	138	144	146	147
	141	143	148	147
	140	145	147	150
	139	145	146	147
Average	140	144	147	148
SD	1.15	0.80	0.72	1.47
V-Si	141	145	149	148
	140	146	148	149
	139	145	149	149
	143	145	147	148
	141	146	147	148
Average	141	145	148	148
SD	1.23	0.21	0.99	0.59
A-Si	67	70	71	76
	66	71	79	77
	67	71	75	78
	69	71	73	79
	68	71	79	75
Average	67	71	75	77
SD	1.06	0.42	3.69	1.55

Table B.4 Effect of reaction time and temperature on % yield of U-Si particles

Temperature (°C)	Time (h)		
	12	24	48
30	85.45	98.14	99.38
	86.69	97.52	102.17
	78.95	99.07	98.76
	86.69	98.45	100.00
	83.59	97.83	98.14
Average	84.27	98.20	99.69
SD	0.10	0.02	0.05
40	86.00	99.69	99
	87.50	100.00	99.8
	85.40	100.31	100
	87.50	98.45	99.9
	86.50	97.83	99.7
Average	86.58	99.26	99.68
SD	0.03	0.03	0.01
50	89.5	100.31	99.25
	90.5	99.69	100.1
	92.6	98.76	98.5
	87.84	99.07	100
	89.65	100.00	99.65
Average	90.018	99.57	99.5
SD	0.06	0.02	0.02

Table B.5 100% modulus of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
100% Modulus (MPa)	0.83	0.97	1.06	1.12	0.83	0.86	0.85	0.93
	0.80	1.02	1.05	1.09	0.86	0.86	0.89	0.95
	0.84	1.00	1.10	1.12	0.85	0.89	0.86	0.91
	0.77	0.98	1.00	1.11	0.83	0.89	0.86	0.92
	0.80	0.99	1.03	1.09	0.81	0.91	0.87	0.95
Average	0.81	0.99	1.05	1.11	0.84	0.88	0.87	0.93
SD	0.03	0.02	0.04	0.02	0.02	0.02	0.02	0.02

Table B.6 300% modulus of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
300% Modulus (MPa)	1.05	3.01	3.17	3.81	2.25	2.36	2.35	2.65
	1.00	3.25	3.09	3.64	2.30	2.48	2.45	2.69
	1.12	3.14	3.37	3.81	2.30	2.56	2.41	2.55
	0.98	3.05	2.95	3.76	2.13	2.56	2.41	2.57
	1.00	3.13	3.07	3.63	2.18	2.63	2.20	2.74
Average	1.03	3.12	3.13	3.73	2.23	2.52	2.36	2.64
SD	0.06	0.09	0.16	0.09	0.08	0.10	0.10	0.08

Table B.7 500% modulus of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
500% Modulus (MPa)	1.90	10.51	11.20	13.13	7.05	7.65	7.66	9.49
	1.80	11.08	10.53	12.39	7.70	8.53	8.47	9.69
	1.98	11.00	12.22	13.25	7.64	8.72	8.11	9.07
	1.73	10.60	9.86	12.91	8.80	8.66	7.93	9.17
	1.83	11.08	10.53	12.30	7.80	8.92	7.64	10.37
Average	1.85	10.85	10.87	12.80	7.80	8.50	7.96	9.56
SD	0.10	0.28	0.89	0.43	0.63	0.49	0.34	0.52

Table B.8 Tensile strength of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
Tensile strength (MPa)	19.55	25.32	24.55	27.84	25.68	24.55	25.17	25.35
	16.05	24.72	24.86	25.36	25.78	22.63	24.17	25.23
	18.40	24.42	23.99	26.58	20.80	24.45	23.62	26.04
	17.10	20.26	26.22	26.45	21.82	25.16	21.49	24.54
	16.00	23.24	23.32	25.47	23.43	25.25	26.30	25.95
Average	17.42	23.59	24.59	26.34	23.50	24.41	24.15	25.42
SD	1.54	2.01	1.08	1.00	2.24	1.06	1.80	0.61

Table B.9 Elongation at break of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
Elongation at break (%)	786.89	681.47	640.40	660.00	696.96	720.00	674.06	679.61
	725.65	652.36	654.87	641.24	717.69	688.67	701.95	675.56
	763.07	669.17	642.13	651.27	674.02	687.77	686.77	697.25
	785.27	683.25	667.01	652.24	688.31	688.47	672.78	675.58
	790.27	624.77	657.44	652.42	688.31	655.45	711.21	667.01
Average	770.23	662.20	652.37	651.43	693.06	688.07	689.35	679.00
SD	27.13	24.29	11.12	6.69	16.04	22.83	16.97	11.19

Table B.10 Hardness of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
Hardness (Shore A)	34.50	47.00	46.50	45.00	43.50	44.50	44.50	45.50
	34.00	47.00	47.00	47.00	44.00	45.00	44.00	45.50
	34.00	46.50	47.00	47.50	43.50	45.00	43.50	45.00
	33.50	47.50	47.50	45.00	44.00	44.50	43.50	45.00
	34.00	47.50	47.50	47.00	44.00	45.00	44.00	45.00
Average	34.00	47.00	46.00	47.00	44.00	44.00	45.00	45.00
SD	0.35	0.42	0.42	1.20	0.27	0.27	0.42	0.27

Table B.11 Tear resistance of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
Tear resistance (N/mm)	48.10	78.90	88.70	92.40	82.20	87.00	91.90	89.70
	50.10	88.50	92.60	88.95	83.70	87.40	88.60	87.70
	47.10	84.50	96.80	91.20	83.70	89.80	89.50	95.20
	48.20	81.60	89.85	94.36	81.60	90.80	93.40	89.90
	48.00	84.80	85.40	89.50	86.20	87.80	94.80	90.80
Average	48.30	83.66	90.67	91.28	82.82	88.56	91.64	90.66
SD	1.10	3.62	4.29	2.20	2.23	1.65	2.60	2.78

Table B.12 Volume loss of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
Volume loss (mm^3)	692.97	206.90	186.50	212.30	228.60	213.40	220.90	245.70
	675.67	219.00	197.80	228.50	236.50	212.90	240.90	229.40
	698.56	218.60	192.60	208.00	226.90	231.70	237.90	219.20
	702.40	204.60	180.70	203.00	246.80	228.50	220.30	220.50
	690.46	231.45	202.70	194.12	252.25	224.00	220.00	210.70
Average	692.01	216.11	192.06	209.18	238.21	222.10	228.00	225.10
SD	10.26	10.81	8.75	12.74	11.11	8.62	10.47	13.29

Table B.13 Compression set (%) of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
Compression set (%)	36.70	21.93	21.08	21.73	26.60	21.33	20.77	20.37
	33.20	23.00	20.02	19.40	25.50	20.50	19.68	20.76
	33.50	24.35	19.80	19.86	25.00	19.10	22.50	21.05
	34.65	22.80	21.05	21.05	24.35	19.56	21.45	19.87
	32.50	22.46	19.65	20.00	23.67	20.02	19.70	20.04
Average	34.11	22.91	20.32	20.41	25.02	20.10	20.82	20.42
SD	1.64	0.90	0.69	0.95	1.12	0.86	1.20	0.49

Table B.14 Compression set (%) of NR vulcanizates

	Direct				Indirect			
	NR-V	D-USi	D-MSi	D-VSi	I-USi	I-MSi	I-VSi	I-ASi
Swelling ratio	5.11	3.54	3.54	2.64	3.66	2.94	3.28	2.76
	5.06	3.55	3.01	3.29	3.04	3.36	3.43	2.94
	4.71	2.92	2.83	3.12	3.58	3.13	2.68	2.91
Average	4.96	3.34	3.12	3.01	3.43	3.14	3.13	2.87
SD	0.22	0.36	0.37	0.34	0.34	0.21	0.40	0.10

VITAE

Miss Thawinan Theppradit was born on April 22, 1988 in Suratthani, Thailand. She received her Bachelor’s degree in Petrochemicals and Polymeric Material, from the Faculty of Engineering and Industrial Technology, Silpakorn University in 2009. She has pursued Master’s degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2010 and finished her study in 2012.

Presentation

2012 Preparation of in situ silica with multi-functional groups in natural rubber via sol-gel process, April 19-20, The Science Forum 2012, Faculty of Science, Chulalongkorn University, Bangkok, Thailand.

2012 Preparation of in-situ silica with multi-functional groups via sol-gel process for natural rubber reinforcement, December 5-8, International Conference on 10th Eco-Energy and Materials Science and Engineering Symposium 2012, Ubon ratchathani, Thailand.